

Engineering Hierarchically Nano-structured Self-standing Model and Gas Diffusion Copper Foam Electrodes via Dynamic Hydrogen Bubble Templating for Efficient Carbon Dioxide Reduction

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As you prepare your breakfast, think of others
(do not forget the pigeon's food).

As you conduct your wars, think of others
(do not forget those who seek peace).

As you pay your water bill, think of others
(those who are nursed by clouds).

As you return home, to your home, think of others
(do not forget the people of the camps).

As you sleep and count the stars, think of others
(those who have nowhere to sleep).

As you liberate yourself in metaphor, think of others
(those who have lost the right to speak).

As you think of others far away, think of yourself
(say: "If only I were a candle in the dark").

Mahmoud Darwish

To the created-from-love, my mother.

To the strong man, my father.

To my sister, with whom I become a child
again.

Abstract

Carbon dioxide reduction reaction (CO₂RR) on nano-structured Cu foams synthesized via the Dynamic Hydrogen Bubble Templating method (DHBT) has emerged as a promising strategy for storing the intermittently available renewable energy in the form of fuels or chemical feedstocks and for mitigating rising atmospheric CO₂ levels. In the DHBT method, electrochemically generated H₂ bubbles serve as dynamic negative templates during Cu electrodeposition, producing Cu foam architectures whose morphology can be efficiently tuned via the DHBT parameters. Specifically, key morphology descriptors, such as foam interconnectivity, pore diameter, pore density, foam thickness, electrochemically active surface area (ECSA), and mass density, can be precisely controlled via the synthesis conditions. Moreover, the local stirring caused by bubble formation and detachment alters the hydrodynamics of electrodeposition, producing surface nano-structures of different sizes and shapes that strongly promote electrocatalytic performance.

In this work, various DHBT parameters were systematically applied to prepare model Cu foams, followed by morphological characterization and CO₂RR performance evaluation in a conventional H-cell setup. The study was organized into four main series: (1) Current-time series, which probed the influence of the most fundamental DHBT parameters: the applied current density and deposition time; (2) Current mode series, in which the direct current (DC), pulsating current (PC), reversing current (RC), and alternating current (AC) modes were compared during DHBT; (3) Chemical effect series, in which the role of Cu²⁺ concentration, electrolyte pH, surfactants, and Cu-complexing agents was examined; and (4) Physical effect series, which evaluated the impact of physical parameters such as stirring, substrate orientation, bath temperature, and post-DHBT annealing. This systematic investigation of different DHBT parameters enabled the establishment of practical synthesis-morphology and morphology-activity relationships. Thereafter, a concise, time-efficient three-step protocol was developed to convert the most promising model Cu foams into gas diffusion electrodes (GDEs), which were subsequently evaluated for CO₂RR performance in a flow-cell configuration.

Generally, synthesis parameters that promoted H₂ evolution reaction (HER) during DHBT, as indicated by reduced electrodeposition Faradaic efficiencies, increased the density of H₂ nucleation sites and thereby produced a larger number of smaller bubble templates. This behavior produced compact Cu foam structures characterized by small pore diameters or the absence of an interconnected foam network, lower foam thickness, reduced ECSA, lower mass density, and finer surface nano-dendrites. Conversely, conditions that suppressed HER during DHBT exhibited the opposite behavior, producing more open foam architectures. A notable exception to this trend is the PC mode, where repeated interruptions of the cathodic signal substantially suppressed HER and produced mass-dense foams dominated by micro-to-nano agglomerates with reduced foam interconnectivity. Another exception concerns surface nano-particle morphology, where the PC and RC samples, as well as foams prepared in the presence of 3,5-diamino-1,2,4-triazole (DAT), developed surface nano-cauliflowers rather than nano-dendrites, indicating altered local hydrodynamic conditions under those DHBT conditions. Finally, stirring the DHBT bath had only a minor effect on the foam skeleton but resulted in a marked increase in surface nano-dendrite size, supporting the role of hydrodynamic conditions in shaping and sizing surface nano-structures.

It is widely accepted that Cu surfaces can optimize the binding energy of *CO intermediates during CO₂RR, promoting C-C coupling and enhancing C₂₊ product formation. Nevertheless, Cu catalysts face challenges such as their broad product distribution and limited operational stability, which

must be addressed to enable practical CO₂RR applications. In this study, three fundamental factors were found to control the CO₂RR activity of the model Cu foam samples: (1) Foam compactness: increased compactness was highly beneficial for C₂₊ activity, which was attributed to suppressed internal mass-transport limitations along the pore axis; (2) Surface nano-structures: smaller surface nano-dendrites improved C₂₊ performance at highly negative potentials compared to their larger counterparts. Additionally, samples exhibiting nano-cauliflowers showed superior selectivity toward C₂₊ products at highly negative potentials compared to those exhibiting nano-dendrites. When the nano-cauliflowers were combined with higher mass density, as observed for the PC samples, remarkable formate selectivity was obtained at less negative potentials; and (3) Chemical effects: Ex-situ X-Ray Photoelectron Spectroscopy (XPS) and Operando Surface-Enhanced Raman Spectroscopy (SERS) confirmed DAT incorporation into the DAT-modified samples and demonstrated that DAT stabilizes surface *CO intermediates, thereby facilitating C-C coupling, which is a key step for C₂₊ formation, and also promotes local alkalization that suppresses the parasitic HER. Cu foam GDEs reproduced the same activity trends observed for the model foams. The DAT-mediated GDEs and the GDEs prepared at 4 °C outperformed the other GDEs in C₂₊ activity, achieving total C₂₊ product Faradaic efficiencies of approximately 52% at -1.1 V vs. the reversible hydrogen electrode (RHE), which corresponds to total C₂₊ product partial current densities of about 104 mA cm⁻² at -2.5 V vs. RHE, and good operational stability demonstrated over 12 hours. In addition, bimetallic Ag-Cu foam GDEs were successfully synthesized using the same protocol and were found to enhance C₂₊ activity at a Cu:Ag ratio of 65.6, achieving total C₂₊ product Faradaic efficiencies of about 37% in the potential range from -1.5 to -2.3 V vs. RHE, along with total C₂₊ product partial current densities of approximately 76 mA cm⁻² at -2.3 V vs. RHE.

In conclusion, the DHBT method was demonstrated to be an effective, scalable, and fast method for the fabrication of numerous metallic structures with precisely controlled properties for many possible applications, with the possibility of integration within industrially relevant configurations. In addition, the product distribution of CO₂RR can be effectively steered by adjusting the DHBT conditions and applied potentials to favor specific products, such as C₂₊ products or formate. Follow-up work should include a focus on further optimizing the GDE protocol and upscaling the other promising model Cu foams that were not tested here at the GDE level. Moreover, integrating active machine learning with systematic experimental evaluation of CO₂RR performance of Cu foams can further accelerate discovery of active Cu foam structures and more effectively promote C₂₊ product activity.

Zusammenfassung

Die Kohlendioxid-Reduktionsreaktion (CO_2RR) auf nanostrukturierten Cu-Schäumen, die mittels der Dynamic Hydrogen Bubble Templating-Methode (DHBT) synthetisiert wurden, hat sich als vielversprechende Strategie zur Speicherung der intermittierend verfügbaren erneuerbaren Energie in Form von Brennstoffen oder chemischen Rohstoffen und zur Minderung des steigenden CO_2 -Gehalts in der Atmosphäre herausgestellt. Bei der DHBT-Methode dienen elektrochemisch erzeugte H_2 -Blasen als dynamische negative Template während der Cu-Elektroabscheidung, wodurch Cu-Schaumstrukturen entstehen, deren Morphologie über die DHBT-Parameter effizient eingestellt werden kann. Insbesondere können wichtige Morphologie-Deskriptoren wie die Vernetzung des Schaums, der Porendurchmesser, die Porendichte, die Schaumdicke, die elektrochemisch aktive Oberfläche (ECSA) und die Massendichte über die Synthesebedingungen präzise gesteuert werden. Darüber hinaus verändert die durch die Blasenbildung und -ablösung verursachte lokale Bewegung die Hydrodynamik der Elektrodeposition und erzeugt Oberflächen-Nanostrukturen mit unterschiedlichen Größen und Morphologien, die die elektrokatalytische Leistung stark fördern.

In dieser Arbeit wurden verschiedene DHBT-Parameter systematisch angewendet, um Modellhafte-Cu-Schäume herzustellen, gefolgt von der Charakterisierung der erhaltenen Proben hinsichtlich ihrer Morphologie und CO_2RR -Leistung in einer herkömmlichen H-Zellen-Anordnung. Die Studie gliederte sich in vier Hauptserien: (1) Strom-Zeit-Serie, in der der Einfluss der grundlegendsten DHBT-Parameter untersucht wurde: der angelegte Strom und die Abscheideszeit; (2) Strommodus-Serie, in der die Modi Gleichstrom (DC), pulsierender Strom (PC), Umkehrstrom (RC) und Wechselstrom (AC) während der DHBT verglichen wurden; (3) Eine Reihe zu chemischen Effekten, in der die Rolle der Cu^{2+} -Konzentration, des pH-Werts des Elektrolyten, von Tensiden und Cu-Komplexbildnern untersucht wurde; und (4) Eine Reihe zu physikalischen Effekten, in der die Auswirkungen physikalischer Parameter wie Rühren, Substratorientierung, Badtemperatur und Tempern nach dem DHBT bewertet wurden. Diese systematische Untersuchung verschiedener DHBT-Parameter ermöglichte die Ermittlung praktischer Beziehungen zwischen Synthese und Morphologie sowie zwischen Morphologie und Aktivität. Anschließend wurde ein prägnantes, zeitsparendes dreistufiges Protokoll entwickelt, um die vielversprechendsten Cu-Modellschäume in Gasdiffusionselektroden (GDEs) umzuwandeln, die anschließend in einer Durchflusszellenkonfiguration auf ihre CO_2RR -Leistung hin bewertet wurden.

Im Allgemeinen erhöhten Syntheseparameter, die die H_2 -Entwicklungsreaktion (HER) während der DHBT förderten, was sich in einer verringerten Faraday-Effizienz der Elektrodeposition zeigte, die Dichte der H_2 -Keimbildungsstellen und damit eine größere Anzahl kleinerer Blasen. Dieses Verhalten führte zu kompakten Cu-Schaumstrukturen, die sich durch kleine Porendurchmesser oder das Fehlen eines miteinander verbundenen Schaumnetzwerks, eine geringere Schaumdicke, eine verringerte ECSA, eine geringere Massendichte und feinere Oberflächen-Nano-Dendriten auszeichneten. Umgekehrt zeigen Bedingungen, die die HER während der DHBT unterdrücken, das gegenteilige Verhalten und erzeugen offenere Schaumstrukturen. Eine bemerkenswerte Ausnahme von diesem Trend ist der PC-Modus, bei dem wiederholte Unterbrechungen des kathodischen Signals die HER erheblich unterdrückten und massendichte Schäume erzeugten, die von Mikro- bis Nano-Agglomeraten mit reduzierter Schaumvernetzung dominiert wurden. Eine weitere Ausnahme betrifft die Morphologie der Oberflächen-Nanopartikel, bei der die PC- und RC-Proben sowie die in Gegenwart von 3,5-Diamino-1,2,4-triazol (DAT) hergestellten Schäume eher Oberflächen-Nanokohlköpfe als Nanodendriten entwickelten, was auf veränderte lokale hydrodynamische Bedingungen unter diesen DHBT-Bedingungen hindeutet. Schließlich hat das Rühren des DHBT-Bades nur einen

geringen Einfluss auf die Schaumstruktur, führt jedoch zu einer deutlichen Zunahme der Größe der Oberflächen-Nanodendriten, was die Rolle der hydrodynamischen Bedingungen bei der Bildung und Dimensionierung von Oberflächen-Nanostrukturen untermauert.

Es ist allgemein anerkannt, dass Cu-Oberflächen die Bindungsenergie von $^*\text{CO}$ -Zwischenprodukten während der CO_2RR optimieren, die C–C-Kopplung fördern und die Bildung von C_{2+} -Produkten verbessern können. Dennoch stehen Cu-Katalysatoren vor Herausforderungen wie ihrer breiten Produktverteilung und begrenzten Stabilität im Betrieb, die angegangen werden müssen, um praktische CO_2RR -Anwendungen zu ermöglichen. In dieser Studie wurden drei grundlegende Faktoren identifiziert, die die CO_2RR -Aktivität der Cu-Schaum-Modellproben steuern: (1) Schaumkompaktheit: Eine erhöhte Kompaktheit war für die C_{2+} -Aktivität sehr vorteilhaft, was auf die Unterdrückung interner Massentransportbeschränkungen entlang der Porenachse zurückgeführt wurde; (2) Oberflächen-Nanostrukturen: Kleinere Oberflächen-Nanodendriten verbesserten die C_{2+} -Leistung im Vergleich zu ihren größeren Gegenstücken bei negativeren Potentialen. Darüber hinaus zeigten Proben mit Nano-Cauliflowers im Vergleich zu denen mit Nano-Dendriten eine überlegene Selektivität gegenüber C_{2+} -Produkten. Wenn die Nano-Cauliflowers mit einer höheren Massendichte kombiniert wurden, wie dies bei den PC-Proben beobachtet wurde, wurde bei weniger negativen Potentialen eine bemerkenswerte Formiat-Selektivität erzielt; und (3) Chemische Effekte: Ex-situ-Röntgen-Photoelektronenspektroskopie (XPS) und Operando-Oberflächenverstärkte Raman-Spektroskopie (SERS) bestätigten die Einlagerung von DAT in die DAT-modifizierten Proben und zeigten, dass DAT Oberflächen- $^*\text{CO}$ -Zwischenprodukte stabilisiert und dadurch die C–C-Kopplung erleichtert, die ein wichtiger Schritt für die C_{2+} -Bildung ist, und außerdem eine lokale Alkalisierung fördert, die die parasitäre HER unterdrückt. Cu-Schaum-GDEs reproduzierten die gleichen Aktivitätstrends, die für die Modellschäume beobachtet wurden. Die DAT-basierten GDEs und die bei 4 °C hergestellten GDEs übertrafen die anderen GDEs in ihrer C_{2+} -Aktivität und erreichten eine Faraday-Effizienz des gesamten C_{2+} -Produkts von etwa 50% bei -1,1 V gegenüber der reversiblen Wasserstoffelektrode (RHE), was einer partiellen Stromdichte des gesamten C_{2+} -Produkts von etwa 104 mA cm^{-2} bei -2,5 V gegenüber RHE entspricht, und einer guten Betriebsstabilität über 12 Stunden. Darüber hinaus wurden bimetallische Ag-Cu-Schaum-GDEs unter Verwendung desselben Protokolls erfolgreich synthetisiert und es wurde festgestellt, dass sie die C_{2+} -Aktivität bei einem Cu:Ag von 65,6 erhöhten, wodurch eine Faraday-Effizienz des gesamten C_{2+} -Produkts von etwa 37% im Potentialbereich von -1,5 bis -2,3 V gegenüber RHE sowie eine partielle Stromdichte des gesamten C_{2+} -Produkts von etwa 76 mA cm^{-2} bei -2,3 V gegenüber RHE erreicht wurde.

Zusammenfassend lässt sich sagen, dass sich die DHBT-Methode als effektive, skalierbare und schnelle Methode zur Herstellung zahlreicher Metallstrukturen mit präzise kontrollierten Eigenschaften für viele mögliche Anwendungen erwiesen hat, mit der Möglichkeit der Integration in industriell relevante Konfigurationen. Außerdem kann die Produktverteilung von CO_2RR durch Anpassung der DHBT-Bedingungen und der angelegten Potentiale effektiv gesteuert werden, um bestimmte Produkte wie C_{2+} -Produkte oder Formiat zu begünstigen. Die Folgearbeiten sollten sich auf die weitere Optimierung des GDE-Protokolls und die Skalierung der anderen vielversprechenden Cu-Schäume konzentrieren, die hier nicht auf GDE-Ebene getestet wurden. Darüber hinaus kann die Integration von aktivem maschinellem Lernen mit einer systematischen experimentellen Bewertung der CO_2RR -Leistung auf Cu-Schäumen die Entdeckung weiter beschleunigen und die C_{2+} -Produktaktivität effektiver fördern.

List of abbreviations

AEM	Anion Exchange Membrane
ABS	Acrylonitrile Butadiene Styrene
AC	Alternating Current
ATP	Adenosine Triphosphate (ATP)
a.u.	Arbitrary Units
BPM	Bipolar Membrane
CEM	Cation Exchange Membrane
CE	Counter Electrode
CL	Catalytic Layer
CO ₂ RR	Carbon Dioxide Reduction Reaction
CTAB	Cetyltrimethylammonium Bromide
CPE	Constant Phase Element
CV	Cyclic Voltammogram
DAT	3,5-Diamino-1,2,4-Triazole
DFT	Density Functional Theory
DHBT	Dynamic Hydrogen Bubble Templating
ECSA	Electrochemically Active Surface Area
EDX	Energy-Dispersive X-Ray Spectroscopy
EXAFS	Extended X-Ray Absorption Fine Structure
FCC	Face-Centered Cubic
FE	Faradaic Efficiency
FE _{C₂+}	Total C ₂ ⁺ Faradaic Efficiencies
FID	Flame Ionization Detector
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer
GC	Gas Chromatograph
HPLC	High-Performance Liquid Chromatograph
HER	Hydrogen Evolution Reaction
IR	Infrared
j _{C₂+}	Total C ₂ ⁺ ECSA-Normalized Partial Current Densities
j _{C₂+} ^{Max}	Maximum Total C ₂ ⁺ ECSA-Normalized Partial Current Densities Exhibited by the Cu Foam Sample
j _{ECSA}	ECSA-Normalized Partial Current Density
j _{geo}	Geometric-Area-Normalized Partial Current Density
LGC	Liquid Gas Chromatograph
LSV	Linear Sweep Voltammogram
LHV	Lower Heating Value
MEA	Membrane Electrode Assemblies
MFC	Mass Flow Controller
NRR	Nitrogen Reduction Reaction
OCP	Open Circuit Potential
OER	Oxygen Evolution Reaction
PC	Pulsating Current
PCET	Proton-Coupled Electron Transfer
PFSA	Perfluorosulfonic Acid
PP	Polypropylene
PTFE	Polytetrafluoroethylene
RE	Reference Electrode
RHE	Reversible Hydrogen Electrode
RC	Reversing Current

RPM	Revolutions Per Minute
R _u	Uncompensated Resistance
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Spectroscopy
TCD	Thermal Conductivity Detector
TXRF	Total Reflection X-Ray Fluorescence
UV-VIS-NIR	Ultraviolet, Visible, and Near-Infrared Radiation
WE	Working Electrode
XANES	X-Ray Absorption Near Edge Spectroscopy
XAS	X-Ray Absorption Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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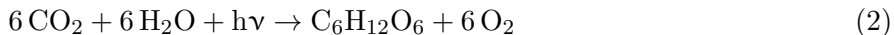
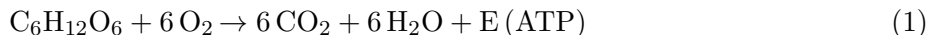
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1 Introduction

1.1 Climate Change and Renewable Energy Sources

Carbon dioxide (CO_2) is a linear triatomic molecule with the Lewis structure $\text{O}=\text{C}=\text{O}$. The central carbon atom is sp -hybridized, resulting in a bond angle of 180° and placing the molecule in the $D_{\infty h}$ point group, implying the presence of a center of inversion. CO_2 is the thermodynamically favored oxidation product of carbon and is kinetically inert under ambient conditions, with $\text{C}=\text{O}$ bond energy of 805 kJ mol^{-1} , which requires high energy to be reduced. Each $\text{C}=\text{O}$ bond is polarized because oxygen is more electronegative than carbon, but the two bond dipoles are equal in magnitude and opposite in direction, and thus, CO_2 has no permanent dipole moment. As a consequence, intermolecular interactions are dominated by weak London dispersion forces, which is consistent with CO_2 being a gas at standard temperature and pressure.^[1,2] CO_2 is generated by multiple natural processes, including cellular respiration, wildfires, and volcanic out-gassing. In cellular respiration, organic substrates such as glucose are oxidized to release energy stored as adenosine triphosphate (ATP), as presented by Equation 1. Conversely, during photosynthesis, the enzyme RuBisCO catalyzes the reduction of CO_2 into carbohydrates, e.g., glucose, thereby storing solar energy in chemical bonds, as presented in Equation 2.^[3,4]



CO_2 possesses three fundamental vibrational modes: (1) The symmetric stretch, in which both oxygen atoms move in phase along the molecular axis, resulting in no change in the net dipole moment; thus, this mode is IR inactive; (2) The asymmetric stretch, in which the oxygen atoms move out of phase producing a transient dipole, which is IR active and observed near 2349 cm^{-1} ; and (3) The doubly degenerate bending mode, consisting of two equivalent perpendicular “scissoring” motions that move the oxygen atoms out of linearity, and it is IR active and observed around 667 cm^{-1} . The three vibrational modes, as presented in Figure 1.^[5]

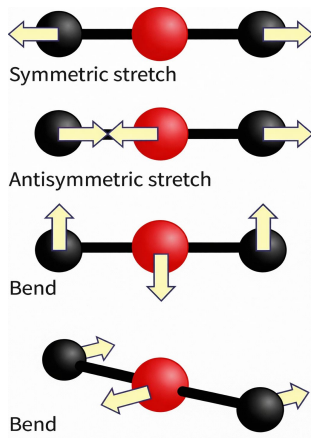
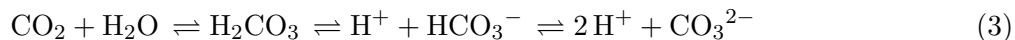


Figure 1: Vibrational modes of CO_2 molecule

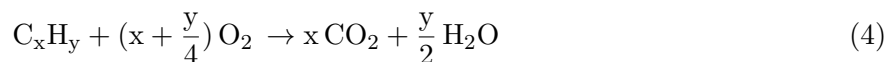
Moreover, CO_2 dissolves in water at ambient temperature and pressure, with a saturation concentration of $\approx 1.5 \text{ g L}^{-1}$ (reported for CO_2 dissolution in pure water at 25°C and 1 atm). About one out of 400 dissolved CO_2 molecules is hydrated to form carbonic acid (H_2CO_3). Carbonic acid is

a diprotic acid and dissociates in two sequential steps with respective pKa values of ≈ 6.35 and 10.33 , as presented by Equation 3. As a result, pure water equilibrated with ambient air contains measurable carbonic acid and buffers to a pH of approximately 5.6-5.8.^[6-11]



Due to these unique characteristics, CO_2 contributes substantially to the habitability of Earth. CO_2 is the principal inorganic carbon source for photosynthesis in terrestrial ecosystems. Through the Calvin cycle, CO_2 is converted into sugars and a wide range of organic molecules that support primary productivity and food chains. Additionally, CO_2 dissolves in the oceans and forms carbonic acid, which buffers ocean pH and supplies bicarbonate and carbonate ions, which are essential for marine calcifiers to precipitate calcium carbonate for their shells and skeletons.^[11] Importantly, CO_2 's capability to interact with IR photons renders it the most significant greenhouse gas in Earth's atmosphere, playing a crucial role in retaining thermal energy and maintaining Earth temperatures conducive to life. In the absence of CO_2 , the Earth's average temperature would fall below freezing. Specifically, Earth absorbs incoming solar radiation and re-emits it as thermal IR radiation in the range of $100\text{-}2500\text{ cm}^{-1}$, which includes CO_2 principal IR absorption bands. Therefore, CO_2 absorbs outgoing long-wave radiation in the lower atmosphere and re-emits it isotropically, including back toward the Earth's surface, thereby increasing Earth's effective insulation, preventing extreme temperature swings between day and night, and contributing to climate regulation.^[8-14] Nevertheless, anthropogenic activities, primarily fossil-fuel combustion for energy, transport, and industry, release large quantities of CO_2 into the atmosphere, as represented by Equation 4 and depicted schematically in Figure 2.^[8,14,15]

Atmospheric CO_2 measurements at the Mauna Loa Observatory represent the longest-running direct record of global CO_2 concentrations, initiated by C. David Keeling in March 1958. These data reveal a clear and sustained upward trend in atmospheric CO_2 , closely aligned with the post-World War II industrial expansion. Specifically, atmospheric CO_2 concentrations have risen markedly from approximately 315 ppm in the late 1950s/early 1960s to over 427 ppm in November 2025, driven primarily by fossil fuel combustion. This accumulation of CO_2 strengthens the greenhouse effect, trapping additional heat and contributing to an increase in global mean temperature of about 1.1°C relative to pre-industrial conditions. The rise in global temperature increases the frequency and intensity of extreme weather events (e.g., heatwaves, heavy precipitation, and droughts), melts polar ice sheets, and causes subsequent sea-level rise that threatens coastal infrastructure. Furthermore, excessive CO_2 absorption by oceans triggers intensified ocean acidification, compromising marine ecosystems by dissolving the calcium carbonate shells of organisms at the base of the food chain.^[8,16]



Despite their serious consequences, fossil fuels continue to supply the majority of the world's energy, with coal, natural gas, and petroleum together accounting for roughly 80% of global energy demand. This reliance reflects steady global population growth and expanding economies.^[17,18] According to the International Energy Agency, global energy consumption is projected to increase by about 70% by 2050.^[17] Given this rising demand and the negative environmental and public-health consequences of combusting fossil fuels, it is essential to develop effective clean energy alternatives to move toward a sustainable energy supply. While nuclear energy has remarkable potential as a low-carbon energy source, it raises political, environmental, and public-health concerns that must be carefully managed.^[19] On the contrary, renewable energy sources have continued to experience robust growth in 2025, providing a clean energy alternative with no or negligible CO_2 emissions, driven by

technological advancements, falling costs, and policy support in many regions.^[20–22] Consequently, there has been a growing global recognition of the importance of advancing and investing in renewable energy research. Global investment in the renewable energy sector in 2025 was estimated to be \$3.3 trillion, with estimated employment of about 5.7 million individuals, including the author of this thesis.^[23,24] To put the scale of this investment in perspective, it equals about 86% of China’s annual public budget.^[25]

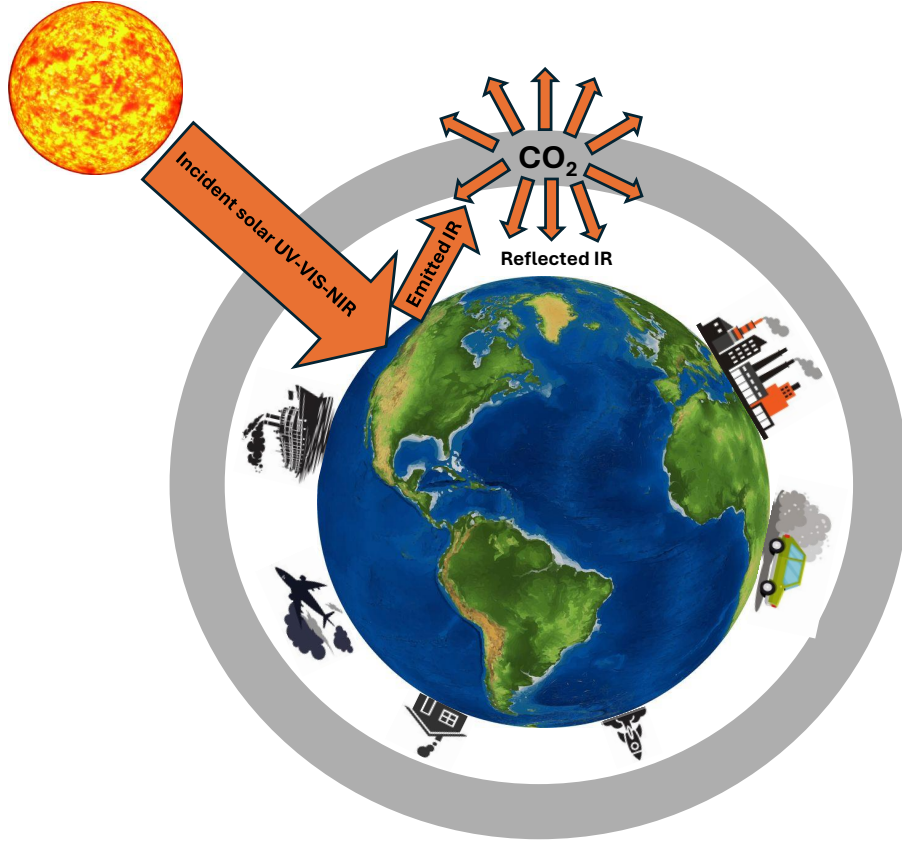


Figure 2: Schematic representation of global warming driven by anthropogenic CO₂ emissions

Although the majority of the world’s energy consumption still relies on non-renewable sources, a growing number of countries are adopting decisive measures to shift from fossil fuels to renewable energy. For instance, Germany is among the countries actively shifting from non-renewable energy to sustainable alternatives. Figure 3 is a pie chart illustrating the breakdown of energy sources used for electricity production in Germany in 2025, based on data from "Arbeitsgemeinschaft Energiebilanzen".^[26,27] Clearly, in 2025, Germany’s gross electricity generation was dominated by renewable energy sources, which accounted for 292 TWh or 57.3% of total output. The remaining share was supplied by conventional fuels; specifically, lignite contributed 75.2 TWh (14.8%), natural gas 84.9 TWh (16.7%), hard coal 29.7 TWh (5.8%), mineral oil 4.0 TWh (1.0%), and other sources 23.5 TWh (4.6%). Within the renewable energy segment, onshore wind represented the largest contributor at 110.1 TWh (21.6%), followed by solar photovoltaics with 89.5 TWh (17.6%), biomass with 42.7 TWh (8.4%), offshore wind with 26.3 TWh (5.2%), hydropower with 17.8 TWh (3.5%), and other renewable technologies with a contribution of 5.4 TWh (1.1%).^[27]

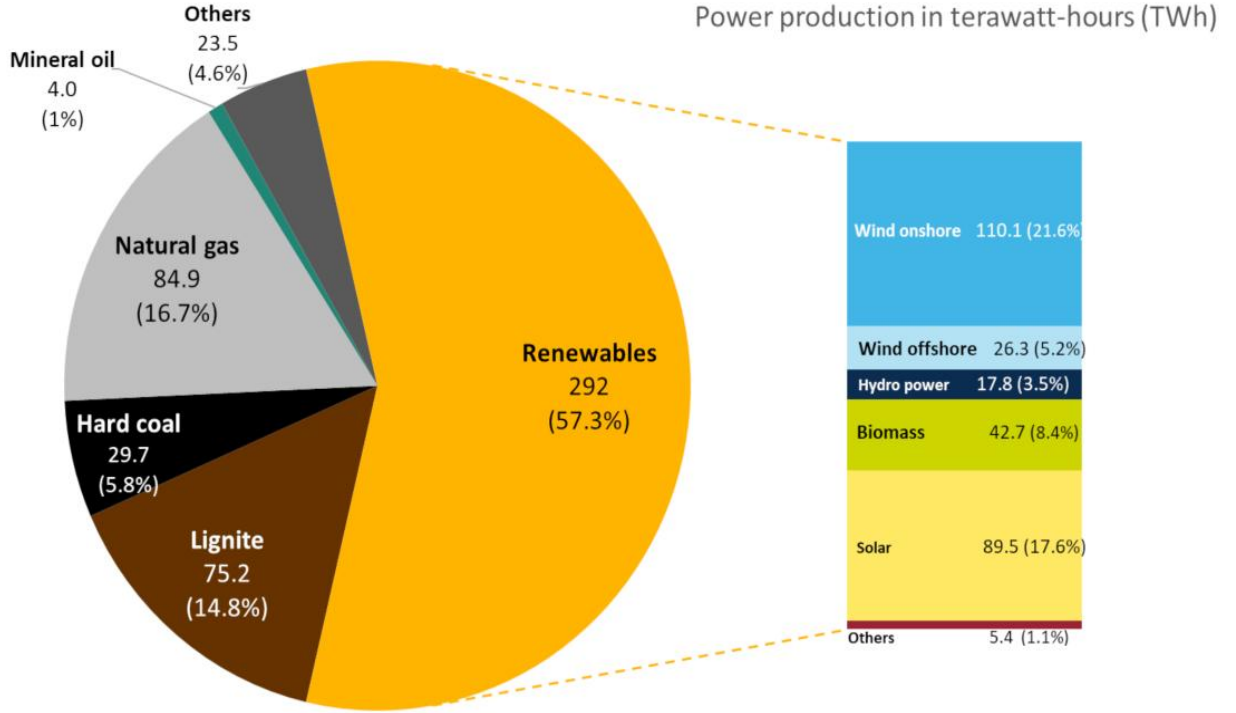
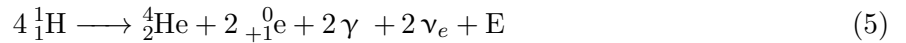


Figure 3: Composition of energy sources in Germany's gross electricity generation in 2025, obtained from references^[26,27]

Among renewable energy sources, hydropower and geothermal sources provide reliable low-carbon base-load power that helps stabilize the grid. However, their expansion is often constrained by site availability and high upfront capital costs. Biomass can also contribute dispatchable energy, but it can release particulate matter and NO_x species, e.g., NO, NO₂, and N₂O, that degrade local air quality and harm human health unless advanced controls are used.^[28] By contrast, solar- and wind-derived energy is currently the most effective pathway for rapid decarbonization. Solar and wind energy sources are relatively cost-effective, highly scalable, and widely available, but their variability requires storage, enhanced grid flexibility, and careful system planning to maintain reliability. In terms of land-use efficiency, solar energy sources exhibit an outperforming energy density of 5-10 W m⁻², in comparison to wind (1-2 W m⁻²), hydropower (0.1-1.0 W m⁻²), geothermal (2-10 W m⁻²), and biomass (≤ 0.8 W m⁻²) sources.^[29-31]

In this context, the Sun can be viewed as a natural nuclear reactor that generates enormous amounts of energy through nuclear fusion, primarily via the proton-proton chain. During this sequence, four protons combine to form a He-4 nucleus, along with the release of two positrons, two gamma-ray photons, and two neutrinos (Equation 5). This reaction involves a small decrease in mass, which is transformed into a large quantity of energy in accordance with Einstein's mass-energy equivalence relation, $E = mc^2$.^[32]



From this fusion process, several forms of energy propagate outward, but almost exclusively ultraviolet, visible, and near infrared (UV-VIS-NIR) radiation reach the Earth. Atmospheric absorption

removes a large portion of UV radiation, so sunlight at the Earth’s surface is dominated by VIS-NIR radiation, accounting for a solar energy flux of $1.73 \times 10^{17} \text{ W (J s}^{-1}\text{)}$ reaching the Earth’s surface.^[33] To illustrate the scale of this energy input, the energy received by the Earth from the Sun in just one second is sufficient to power the construction of around 70,000 replicas of Khufu’s Great Pyramid of Giza, based on estimates of the mechanical energy required for the original structure.^[34] Similarly, this same solar influx in one second could fuel approximately 1,500 round trips between the Earth and the Moon using a spacecraft like NASA’s Orion.^[35] Nevertheless, solar energy is inherently intermittent, meaning that generating solar electricity fluctuates with weather and daylight, producing rapid swings over minutes and hours, predictable daily cycles, and sometimes multi-day or seasonal lulls. These events can suppress solar energy output across different regions for several days in Germany and have driven recent price and reliability concerns in the winter.^[36–38]

To manage the minutes-to-hours energy gaps, battery-based storage systems provide fast frequency response and intraday smoothing. Specifically, grid-scale batteries are typically sized to deliver energy over minutes to a few hours and are optimized for rapid dispatch and frequency containment. To cover longer gaps, multi-day or seasonal solar energy storage must combine large-scale storage with dispatchable energy forms, quick response to demand, and stronger interconnections, such that surplus generation in one region can cover deficits in other regions. Relying solely on short-duration batteries risks leaving large energy drops during extended low-renewable periods. Effective integration of renewable energy into existing energy systems requires better forecasting, smarter inverter controls, flexible market designs, and coordinated planning across transmission zones so that reserves and flexible resources are available when weather patterns create correlated low output across wide areas.^[36–38] In this regard, the power-to-X strategy addresses the intermittency of renewable electricity generation by converting surplus electricity into storable energy carriers (e.g., H_2 and synthetic fuels), enabling large-scale storage and on-demand supply.^[36,39]

1.2 CO₂ Reduction Reaction as Power-to-X Approach

1.2.1 Power-to-X Technology

Power-to-X technology is based on converting surplus renewable electricity (the Power) into storable energy carriers or value-added chemical feedstocks (the X). Power-to-X pathways include electrochemical water splitting to produce H₂; electrochemical N₂ reduction (NRR) to synthesize ammonia; and electrochemical CO₂ reduction to produce chemicals or fuels. Power-to-X decouples energy production from end use, enabling surplus solar and wind energy to be stored for extended periods and to replace fossil feedstocks in industry. Thus, it can effectively address the intermittency of renewable energy sources and provide seasonal and long-duration storage that batteries cannot cost-effectively deliver at scale.^[39–43]

Power-to-X pathways provide a practical alternative for long duration energy storage because they can use relatively inexpensive tanks or underground caverns, making them a scalable complement to batteries for decarbonizing energy systems. For example, H₂ produced from water splitting can offer high volumetric energy density (about 187 kWh m⁻³), and geological salt caverns could store very large amounts of energy (up to approximately 1,680 TWh). In addition to bulk storage, H₂, as a gas, enables sector coupling, as it can be blended into gas grids or used across industrial and transport applications, increasing system flexibility.^[44]

1.2.2 Carbon Dioxide Products, Mechanisms, and Electrode Materials

Among power-to-X approaches, the electrochemical CO₂ reduction reaction (CO₂RR) stands out as a promising route for storing renewable electricity in the form of value-added products, such as CO, formic acid, ethanol, and ethylene, enabling a C-neutral industrial cycle while also mitigating rising atmospheric CO₂ levels. Although non-electrochemical methods for the utilization of CO₂ exist, including biochemical, photo-catalytic, and thermo-catalytic routes, which respectively use bacteria, photons, and heat to convert CO₂ into useful products; electrochemical CO₂RR has been reported in the literature as a particularly promising alternative. In addition to the general benefits of electrification, most notably the ability to couple electrolysis directly to renewable electricity, CO₂RR offers further advantages, such as the possibility of tuning product selectivity by adjusting the applied potential, performing the reaction under ambient temperature and pressure, easily scaling up the reaction (as reactor designs are modular), readily affording the procurers (CO₂ and H₂O molecules), and reusing the electrolyte and electrode to some extent, which lowers the costs and environmental impact of large scale CO₂RR applications. Figure 4 provides a schematic representation of a CO₂RR electrolyzer powered by renewable electricity sources, such as solar photovoltaics. The electrolyzer is integrated with CO₂ supply streams, either point sources, e.g., industrial flue gas, or direct air capture units, and converts CO₂ into value-added fuels and chemical feedstocks. Downstream product-separation units separate and purify gaseous and liquid products, yielding target compounds at the required purity for storage. Purified products are then transferred to dedicated tanks or other bulk storage systems for later use, enabling dispatch to meet large-scale or seasonal demand.^[45–50]

Nevertheless, CO₂RR faces several substantial challenges; specifically, producing C₂₊ products at industrially relevant rates and selectivities remains difficult. Also, large overpotentials are often required for activating the CO₂ molecule and forming the bent radical anion CO₂^{•-}, as this step is associated with a high energy barrier. Moreover, in conventional electrochemical setups

with aqueous electrolytes, the limited mass transport and low solubility of CO_2 lead to sluggish reaction rates and strong competition from the parasitic HER, which lowers the overall CO_2RR Faradaic efficiency (FE). Additionally, CO_2RR can produce a broad product spectrum, creating persistent challenges for selectivity control and for downstream product separation and purification^[51,52].

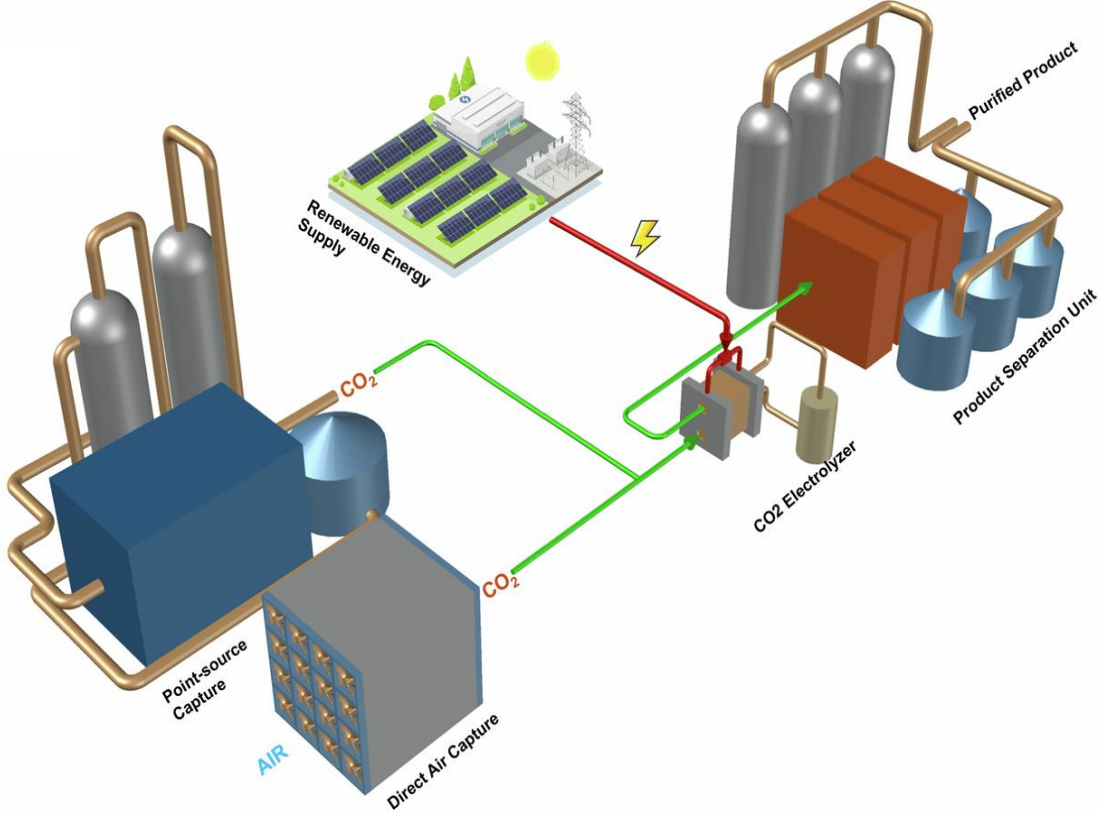
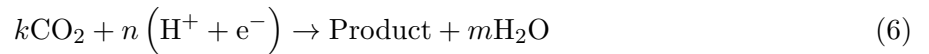


Figure 4: Schematic representation of a CO_2RR electrolyzer integrated with CO_2 sources, and powered by renewable electricity, obtained from reference^[45]

CO_2RR can be generally described by Equation (6), where CO_2 is electrochemically reduced at the cathode in the presence of protons to form reduced carbon species and water, while water oxidation takes place at the anode. The overall CO_2RR pathway comprises multiple elementary steps that involve the concerted transfer of electrons and protons and the formation of surface-bound intermediates, driving the electrocatalytic conversion of CO_2 into different products such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and propanol ($\text{C}_3\text{H}_7\text{OH}$). The literature reports about 18 distinct CO_2RR products, including higher-order oxygenates such as glyoxal and ethylene glycol, although these higher-order species are typically detected only at trace concentrations under most experimental conditions.^[45–50,52,53]



The formation of a specific CO_2RR product is governed by the number of electrons and protons transferred, denoted as n in Equation 6. For $n = 2$, the principal CO_2RR products are CO or formic

acid; $n = 6$ yields methanol; and $n = 8$ yields methane. A 12-electron reduction ($n = 12$) can produce C_2 products such as ethylene or ethanol, while a 14-electron pathway ($n = 14$) can form ethane (C_2H_6). C_3 products require a larger number of electron and proton transfers (e.g., $n = 18$ for propanol). Table 1 lists the half-cell reactions for the formation of selected CO_2RR products together with the associated standard reduction potentials in acidic, neutral, and basic media. The standard potentials for these products formation fall within a relatively narrow window of values. For example, in neutral media, the reported standard reduction potentials range approximately from -0.25 to 0.169 V vs. the reversible hydrogen electrode (RHE). This makes achieving high product selectivity based only on the applied potential particularly challenging. Since many CO_2RR pathways have large activation barriers and compete with the parasitic HER, selectivity is governed mainly by kinetic factors rather than by small differences in equilibrium potential.^[52,54] Therefore, the product distribution depends on the nature of the active sites, how surface intermediates are stabilized, the local pH at the electrode surface, and mass-transport conditions that control reactant and product fluxes.^[52,54] Although the equilibrium standard potential reflects the thermodynamic preferability of the reaction, it offers no insights into kinetics, which are influenced by the electrode catalytic properties. Additionally, a more positive standard reduction potential for a specific product means that the reduction of CO_2 to this product is thermodynamically easier, and vice versa. However, for the complete process, the cell’s overall potential, i.e., the difference between cathode and anode potentials, must be evaluated to assess the overall reaction ease. The coefficients k , n , and m from Equation 6 for different CO_2RR products are listed in Table 2, together with the minimum work required for the formation of one mole of each product. Minimum work represents the theoretical minimum energy input required to drive the reaction forward, derived from the Gibbs free energy change (ΔG) of the process. It quantifies the reversible electrical work needed per mole of product under standard conditions. The theoretical minimum work for each CO_2RR product can be calculated from Equation 7, where F is Faraday’s constant, and E_{cell}^o represents the cell’s overall potential, which can be obtained from Equation 8.^[52,54]

$$\Delta G = -nFE_{cell}^o \quad (7)$$

$$E_{cell}^o = E_{cathode}^o - E_{anode}^o \quad (8)$$

Among the products listed in Table 2, propanol requires the largest number of CO_2 molecules per mole of product ($k = 3$). In contrast, CO, formic acid, methanol, and methane each derive from a single CO_2 molecule ($k = 1$). Therefore, propanol formation results in a higher CO_2 emission reduction than the C_1 products. However, from an energy perspective, propanol is the most energy demanding product. Although propanol exhibits a more positive standard formation potential than CO, the minimum reversible work required for propanol formation under standard electrolysis conditions is significantly higher than that for CO, indicating that propanol synthesis is energetically less favorable than CO.^[52,54]

Table 1: Standard potentials of electrochemical CO₂ reduction into different products in different reaction media, obtained from reference [54]

Products	Acid		Neutral		Base	
	Equation	E (V) vs RHE	Equation	E (V) vs RHE	Equation	E (V) vs RHE
Hydrogen	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.828
Formic acid/ formate	$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$	-0.171	$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$	-0.250	$\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HCOO}^- + \text{OH}^-$	-0.639
Carbon mon- oxide	$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.104	$\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.106	$\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + 2\text{OH}^-$	-0.932
Methane	$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	0.169	$\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	0.169	$\text{CO}_2 + 6\text{H}_2\text{O} + 8e^- \rightarrow \text{CH}_4 + 8\text{OH}^-$	-0.659
Methanol	$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	0.016	$\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	0.016	$\text{CO}_2 + 5\text{H}_2\text{O} + 6e^- \rightarrow \text{CH}_3\text{OH} + 6\text{OH}^-$	-0.812
Ethylene	$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	0.085	$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	0.064	$2\text{CO}_2 + 8\text{H}_2\text{O} + 12e^- \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$	-0.743
Ethane	$2\text{CO}_2 + 14\text{H}^+ + 14e^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	0.144	$2\text{CO}_2 + 14\text{H}^+ + 14e^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	0.144	$2\text{CO}_2 + 10\text{H}_2\text{O} + 14e^- \rightarrow \text{C}_2\text{H}_6 + 14\text{OH}^-$	-0.685
Ethanol	$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}$	0.084	$2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O}$	0.084	$2\text{CO}_2 + 9\text{H}_2\text{O} + 12e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + 12\text{OH}^-$	-0.744
Acetic acid/ acetate	$2\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	0.098	$2\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	0.114	$2\text{CO}_2 + 5\text{H}_2\text{O} + 8e^- \rightarrow \text{CH}_3\text{COO}^- + 7\text{OH}^-$	-0.653
n-Propanol	$3\text{CO}_2 + 18\text{H}^+ + 18e^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 5\text{H}_2\text{O}$	0.095	$3\text{CO}_2 + 18\text{H}^+ + 18e^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 5\text{H}_2\text{O}$	0.104	$3\text{CO}_2 + 13\text{H}_2\text{O} + 18e^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 18\text{OH}^-$	-0.733

Table 2: Stoichiometric coefficients and minimum work for selected CO₂RR products, obtained from reference^[52]

Compound	k	n	m	Minimum work (kWh/mole of product)
CO (Carbon monoxide)	1	2	1	0.07
HCOOH (Formic acid)	1	2	0	0.08
CH ₃ OH (Methanol)	1	6	1	0.19
CH ₄ (Methane)	1	8	2	0.23
C ₂ H ₄ (Ethylene)	2	12	4	0.37
C ₂ H ₅ OH (Ethanol)	2	12	3	0.38
C ₃ H ₇ OH (Propanol)	3	18	5	0.55

Consequently, choosing an optimal target product requires balancing energy consumption against CO₂ utilization while also accounting for additional practical considerations, such as product energy density, market price, separation and purification energy, process complexity, and overall system efficiency^[52,55]. Figures 5-6 present the market price and lower heating values (LHVs) of different CO₂RR products. The LHV represents the amount of heat released when 1 kg of fuel is completely combusted and the water produced remains as vapor; therefore, the latent heat of condensation of that water is not counted in the energy content. Clearly, H₂, propanol, ethylene, and CO have the highest market prices among the listed CO₂RR products, with values roughly between \$1.2 and \$1.6 kg⁻¹. Ethane, formic acid, acetic acid, ethanol, and methanol have moderate market prices of approximately \$0.4 to \$0.6 kg⁻¹, while methane shows the lowest market price of around \$0.1 kg⁻¹. H₂ has the highest LHV (about 120 MJ kg⁻¹) which explains why water splitting is an attractive power-to-X strategy for replacing fossil fuels. However, producing H₂ by electrolysis does not directly consume atmospheric CO₂ or captured industrial CO₂ emissions.^[54,56]

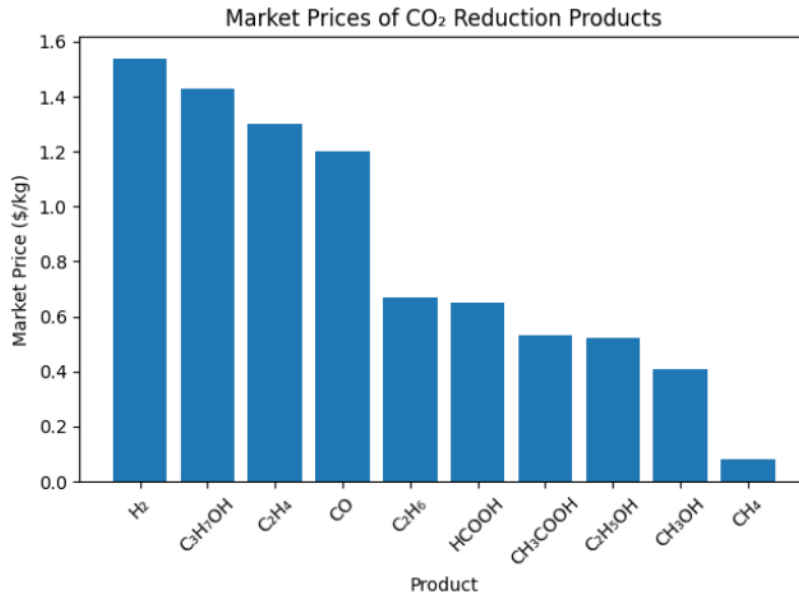


Figure 5: Estimated market prices for different CO₂RR products and the parasitic H₂, reproduced from reference^[54]

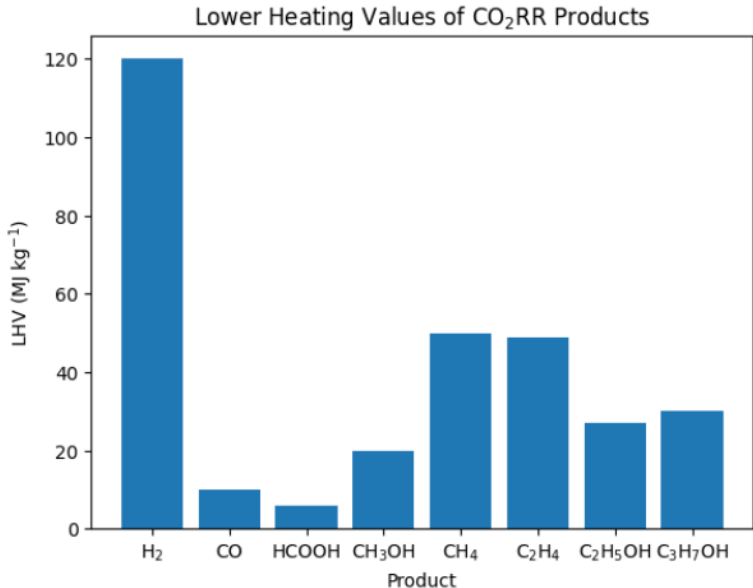


Figure 6: Lower heating values of different CO₂RR products and the parasitic H₂, reproduced from reference^[56]

By contrast, CO₂RR fixes CO₂ into chemical products and can therefore play a direct role in lowering net atmospheric CO₂ and enabling a C-neutral economy. Among CO₂RR-derived hydrocarbons and oxygenates, methane and ethylene have the highest LHVs values of about 50 MJ kg⁻¹, while methanol, ethanol, and propanol show somewhat lower but still substantial LHVs (from 20 to 30 MJ kg⁻¹). In contrast, CO and small oxygenates, such as formic acid, have remarkably lower energy content, with LSVs of less than 10 MJ kg⁻¹.^[56]

Figure 7 illustrates the possible mechanistic pathways of CO₂RR leading to the formation of different CO₂RR products. CO₂ is a very stable molecule, which makes its activation inherently challenging. In electrochemical CO₂RR, the generation of C₂₊ products requires considerably higher activation energy than the formation of C₁ products. This is mainly attributed to the increased complexity of the reaction pathways involved. Specifically, the formation of C₂₊ products proceeds via multiple C-C coupling steps, which raise the energy barriers and require effective stabilization of reaction intermediates on the electrocatalyst surface. For example, weak binding of *CO intermediates to the catalyst leads to rapid CO desorption, manifested as higher CO FEs and lower FEs for C₂₊ products. Moreover, highly controlled proton-coupled electron transfer (PCET) steps are essential for achieving the selective formation of a desired C₂₊ product, introducing further challenges to the reaction process. Consequently, CO₂RR catalyst design is crucial, not only for effectively stabilizing the surface intermediates but also for maintaining long-term activity and avoiding deactivation over time. As shown in Figure 7, the generally accepted initial step in the CO₂RR is a PCET to the linear CO₂ molecule at either the C or an O atom. This step produces the bent *COOH or *OCHO surface intermediates. A subsequent PCET step to the *OCHO intermediate leads to the formation of formic acid. The production of CO begins with the formation of the *COOH intermediate, followed by a PCET step to the hydroxyl group and the eventual release of CO. Other C₁ products, such as methanol and methane, are generated similarly through the initial formation of *CO, followed by successive PCET steps. Specifically, a PCET to the adsorbed *CO intermediate produces the *COH intermediate, which can undergo further PCET steps to form the methoxy intermediate (*OCH₃),

which is then reduced by an additional PCET to yield methanol (CH_3OH), or converted to methane (CH_4) through three successive PCET steps.^[51,57–59]

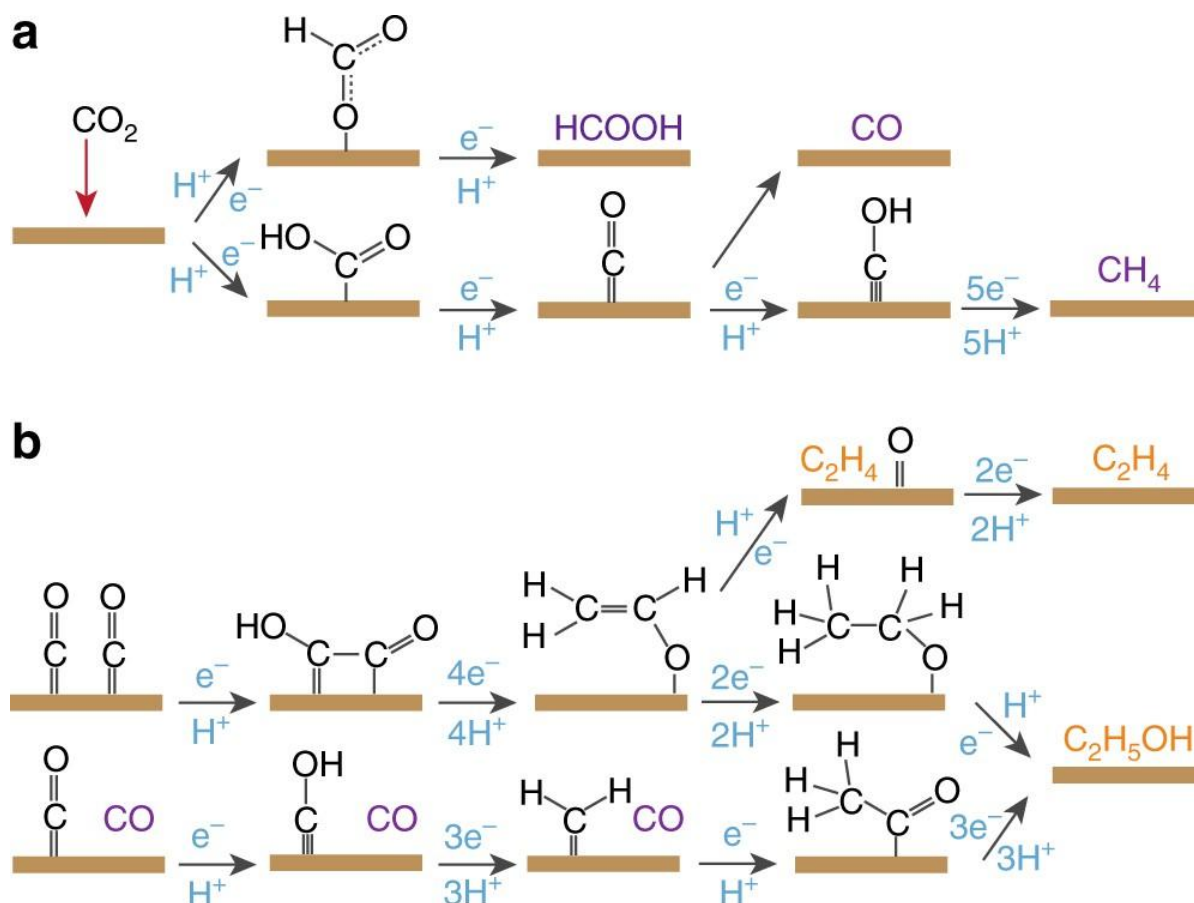


Figure 7: An overview of possible reaction pathways of CO_2 reduction into different products, obtained from reference^[59]

The reaction pathways leading to C_2 products are generally considered to be centered on the dimerization of two *CO intermediates and a subsequent PCET step, resulting in the $\text{*CO} - \text{*COH}$ intermediate. After four PCET steps, $\text{*CO} - \text{*COH}$ is converted into *OCHCH_2 , which can then be further transformed into ethylene by undergoing three successive PCET processes. Alternatively, the *OCHCH_2 intermediate can be reduced to form the $\text{*OCH}_2 - \text{CH}_3$ intermediate, which can be converted either to ethanol via a PCET step or to ethane via three PCET steps. Alternatively, surface-bound *CO can undergo a PCET step to form the *COH intermediate. Three additional PCET steps convert *COH to *CH_2 , which can react with a free CO molecule to form *COCH_3 . A further three PCET steps then convert *COCH_3 into ethanol.^[57–59]

The reduction of CO_2 to form longer-chain C_3 compounds is even more challenging. C_3 products are typically formed through intermolecular C-C coupling between an adsorbed C_2 intermediate and a neighboring C_1 intermediate, most commonly *CO , followed by subsequent PCET steps. For instance, the $\text{*OCH}_2\text{CH}_3$ intermediate can couple with an additional *CO molecule to form *CH(OH)CH(OH)CH_3 . This species can then undergo dehydration to form *C(OH)CHCH_3 , followed by three PCET steps to form 1-propanol.^[57,58]

These reaction pathways demonstrate that effective coupling between two C_1 species, or between a C_1 and a C_2 species, is crucial for C-C bond formation and the generation of a wide range of C_{2+} products. Engineering the catalyst to enhance the stabilization of the involved intermediates and promote C-C coupling is, therefore, a key strategy for increasing the rate of C_{2+} product formation, where the catalyst structural and electronic characteristics play an essential role in facilitating C_{2+} activity.^[57–59]

To evaluate CO_2RR performance for a given electrocatalyst, the following metrics are commonly used^[51,52]:

1. **Overpotential:** the difference between the onset potential for a given product and its standard formation potential. A good electrocatalyst exhibits low overpotentials for the targeted products.
2. **Partial current density:** the current density associated with the formation of a specific product, usually normalized to the electrode geometric area or the electrochemically active surface area (ECSA). Partial current density indicates the rate of the desired reaction and is used to calculate the FE of the specified CO_2RR product formation. This metric is also crucial for industrial applications, as it is directly correlated to production rates and operating costs.
3. **Product Faradaic efficiency:** the percentage of the total charge that is consumed to form a specific product, reflecting the electrocatalyst’s selectivity toward that specific product.
4. **Operational stability:** it describes the change (mostly loss) in CO_2RR FEs and partial current densities over time. This is a pivotal industrial metric, as it dictates lifecycle costs and helps mitigate expensive production downtime.

Different electrocatalysts have been explored for CO_2RR , including noble metals, non-noble metals, metal oxides, and bimetallic materials.^[60–63] In a pioneering study, Hori et al. demonstrated that copper (Cu) is unique among metals in catalyzing the electrochemical reduction of CO_2 to a wide range of hydrocarbons and oxygenates, notably ethylene and ethanol, thereby establishing that Cu stabilizes the $*CO$ intermediate and promotes C-C coupling under CO_2RR conditions.^[64] A systematic investigation by Hori and co-workers showed that product selectivity on Cu electrodes depends strongly on applied potential, surface morphology, and the local reaction environment.^[64] Subsequent work reported that up to 16 different hydrocarbon and oxygenate products can be obtained from CO_2RR on Cu electrodes at different potentials.^[53] Mechanistic studies have identified key elementary steps leading to C_{2+} products, such as the formation of $*CO$ and subsequent C-C coupling, which were detailed earlier. Building on these insights, Bagger et al. developed a classification diagram for different metals using density functional theory (DFT) calculations of two binding energies, ΔE_{CO*} and ΔE_{H*} , which quantify the affinity of metal surfaces for CO^* and H^* , and explain the obtained CO_2RR product distribution on different metals.^[65]

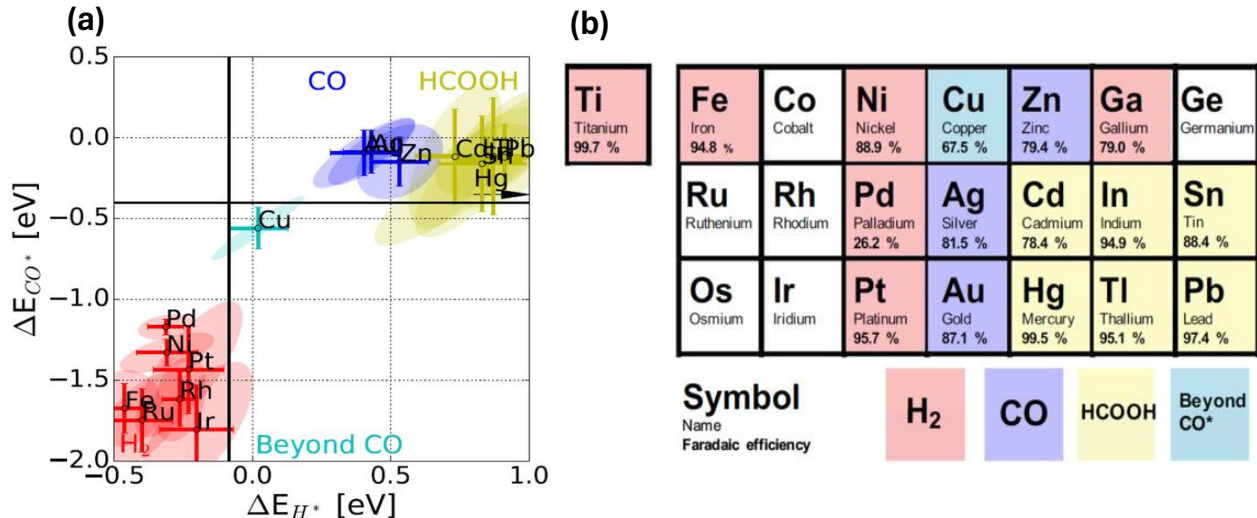


Figure 8: Classification of CO₂RR performance on different metals based on H* and CO* binding energies (a), and cropped periodic table indicating each metal’s dominant product and corresponding major-product Faradaic efficiency (b), obtained from reference^[65]

As presented in Figure 8, metals with strong binding of both CO and H (e.g., Fe, Ru, Ni, Pd, and Pt) fall in a region dominated by HER; metals with weak binding of both intermediates (e.g., In, Cd, Pb, and Hg) favor formate/HCOOH formation via the *OCHO pathway; metals with moderate CO binding but weak H binding (e.g., Au, Ag, and Zn) produce CO that desorbs readily; and Cu alone occupies the narrow “sweet-spot” region where CO binds strongly enough to enable C-C coupling (via *CO dimerization) while H binding is weak enough to suppress HER, thereby enabling multi-carbon (C₂₊) products. This classification is consistent with the Sabatier principle, which holds that intermediate(s) binding must be optimized to achieve optimal electrocatalytic performance.^[64,65] Despite these advantages, Cu exhibits several critical drawbacks that limit its practical deployment. First, Cu exhibits poor selectivity due to its broad product distribution; thus, achieving a high single product FE requires precise catalyst design and strict control of reaction conditions. Second, Cu displays surface instability and reconstruction under CO₂RR conditions, resulting in time-dependent changes in activity and selectivity. Third, the formation of C₂₊ products on Cu requires substantially higher overpotentials compared to, for example, the overpotentials for CO formation on Au and Ag. Fourth, scale-up remains challenging for Cu electrodes because maintaining the active Cu sites that promote C-C coupling over the large-area gas diffusion electrodes (GDEs) is difficult. This difficulty arises from the critical need to optimize the local micro-environment of the catalytic layer (CL) and flow cell conditions. Consequently, ongoing research aims to improve selectivity, activity, durability, and the scale-up of laboratory-scale C₂₊ performance of Cu-based catalysts.^[66–68]

The catalytic activity and selectivity of Cu electrodes are heavily influenced by structural parameters such as surface morphology, size effects, crystal orientation, and roughness. Smaller Cu nano-particles were reported to enhance selectivity for CO and C₂H₄ due to increased binding affinity for key intermediates like *COOH. Similarly, the dimensions and density of Cu nano-wires were tuned to modulate hydrocarbon production, with promoted C₂H₆ formation via the *CH₃CH₂O intermediate or via the dimerization of two *CH₃ species. Surface roughness also dictates product distribution, as high roughness was reported to favor CO, formate, and H₂ production, yielding only trace amounts of C₂H₄, C₂H₆, and C₃H₆. Finally, crystal facet orientation remains a decisive factor, with Cu(100) promoting C₂H₄ production and Cu(111) favoring CH₄ formation.^[52]

As shown in Figure 8, the noble metals Au and Ag are remarkably active towards CO formation. However, their high cost limits their widespread use in catalytic processes.^[69] Au is substantially active for the electrochemical reduction of CO₂ into CO, and nano-structuring Au can further improve its performance and result in very small overpotentials.^[70] For example, Au nano-particles with an 8 nm diameter were reported to deliver a CO FE of 90% at -0.67 V vs. RHE.^[71] Ag was proposed as an alternative to Au because it is more cost-effective and can offer higher selectivity than bulk Au surfaces.^[52] Nevertheless, Ag typically requires a larger overpotential due to the substantial activation energy required for the formation of *COOH intermediate. For instance, Hatsukade et al. observed a CO FE of about 90% in the potential range from -1.0 to -1.2 V vs. RHE.^[72] The elevated overpotentials typically required on Ag electrodes compared to Au counterparts can be substantially decreased by employing nano-structured Ag with low-coordinate sites, which enhance CO₂ activation and reduce the energy barrier for *COOH formation.^[52,73,74] For example, Hoffmann et al. obtained excellent CO FEs of above 95% from Ag foams adorned with surface nano-dendrites synthesized via the Dynamic Hydrogen Bubble Templating method (DHBT) at low potentials of -0.6 V vs. RHE.^[74] A correlation between the crystal structure of the Ag electrodes and CO selectivity was also performed, where higher activity was obtained from the Ag(110) facet compared to Ag(111) and Ag(100) facets.^[52]

As a non-noble metal, Zn also showed good selectivity for CO, with the advantages of earth abundance and low cost. While bulk Zn typically exhibits low current density and large overpotentials for CO formation, nano-structured Zn foam electrodes achieved a CO FE of above 55% at an overpotential of -0.5 V vs. RHE, demonstrating that tailored Zn morphologies can substantially improve activity and selectivity^[75].

Metal oxides have also emerged as promising CO₂RR electrocatalysts because they can enhance the adsorption of CO₂ precursors and stabilize key CO₂RR intermediates on the catalyst surface, thereby suppressing HER, promoting C-C coupling, and improving C₂₊ product selectivity. For instance, Liu et al. achieved a C₂₊ FE of 77% at a high current density of 514 mA cm⁻² using Cu₂O multi-shell catalysts^[76]. Cu₂O-based catalysts were also reported to provide good activity toward other CO₂RR products. For example, Li and Kanan reported FEs of 40% for CO and 33% for HCOOH at -0.5 V vs RHE at Cu₂O-based electrodes, which were attributed to the stabilization of the CO₂⁻ intermediate and high density of grain boundaries.^[77] Beyond Cu oxides, oxide-derived Au nano-catalysts displayed 96% FE for CO at a low overpotential of 0.24 V, attributed to the high density of grain boundaries. Ag₂O exhibited high CO selectivity (about 80% FE) at an overpotential of 0.49 V vs. RHE due to the stabilization of the *COOH intermediate. Also, ZnO-derived electrodes demonstrated excellent CO activity and operational stability, maintaining a CO FE greater than 90% for over 18 hours of electrolysis at an applied current density of 200 mA cm⁻².^[52]

Bimetallic catalysts were also reported to enhance CO₂RR performance by tuning the electronic structure of host materials to optimize intermediate binding strengths. Cu-based bimetallics are the most extensively researched. For example, Cu-In electrocatalysts were prepared for CO production, reporting a FE of 90% at an overpotential of 0.39 V. Increasing the Zn content in a series of Cu-Zn binary catalysts was shown to enhance selectivity toward ethanol, with a FE of 29% at -1.05 V vs. RHE obtained from the Cu₄Zn sample. Additionally, a Cu-Zr catalyst, denoted as ZrO₂/Cu-Cu₂O, with a Cu:Zr molar ratio of 7:1, reached a 62.5% FE for ethylene with a corresponding partial current density of 24 mA cm⁻² at an applied potential of -1.28 V vs RHE. Additionally, the as-prepared Pb single-atom-alloyed Cu catalysts demonstrated near-unity selectivity for formic acid

with excellent stability, allowing for industrial-scale production.^[52] Interestingly, in a remarkable work, Cu-Al binary alloys identified through an active machine-learning workflow guided by DFT calculations exhibited outstanding ethylene activity, achieving a FE exceeding 80%, compared with approximately 66% for pure Cu at -1.5 V vs. RHE. Computational analysis indicated that Cu-Al alloys provide a diversity of surface active sites and orientations with near-optimal CO binding energies, which promote both efficient and selective CO₂ reduction toward C₂₊ products. In situ X-ray absorption spectroscopy (XAS) further showed that the incorporation of Al modifies the Cu coordination environment in a way that facilitates C-C dimerization. These results underscore the value of combining computation and machine learning with experimental studies to accelerate the experimental discovery of multi-metallic electrocatalysts that overcome the limitations of single-metal systems.^[78]

1.2.3 Carbon Dioxide Reduction Cells

CO₂RR cells are operated in either batch or flow configurations. The most common batch setup is the H-cell, which is simple and primarily used for small-scale studies. Flow reactors are better suited for scale-up and improved mass transport. Typical flow electrolyzers include: (1) basic flow cells, (2) polymer electrolyte membrane (PEM) reactors, and (3) microfluidic reactors.^[52] In this study, PEM refers to polymer electrolyte membrane to avoid confusion with proton exchange membrane. The H-cell configuration represents the most fundamental type of electrochemical reactor employed for laboratory-scale investigations of CO₂RR electrodes. In a typical H-cell setup, the working electrode (WE) and reference electrode (RE) are positioned in the cathodic compartment, whereas the counter electrode (CE) is placed in the anodic compartment. These two compartments are generally connected by a circular channel and separated by an ion-exchange membrane, which serves to prevent the oxidation of reduced products during operation and gives rise to the characteristic H-shaped geometry of the cell (Figure 9). The WE in an H-cell can be self-supporting samples, e.g., metal foams, or powder catalysts deposited onto conductive substrates, e.g., glassy carbon or carbon paper. During electrolysis, CO₂ gas is continuously introduced into the cathodic compartment through a capillary tube or glass frit, and the output flow is subsequently directed to an online gas chromatograph (GC) for the analysis of gaseous products. As a result, the gas flow rate must be carefully regulated, typically using a mass flow controller (MFC) installed at either the inlet or the outlet of the electrochemical cell. To enable accurate determination of FEs, the cathodic compartment must be fully gas-tight. In addition, liquid products are commonly analyzed after electrolysis using techniques such as proton nuclear magnetic resonance spectroscopy, liquid-gas chromatography (LGC), and/or high-performance liquid chromatography (HPLC). The H-cell is simple to assemble, cost-effective, and well suited for small-scale electrolysis. It enables rapid, time-efficient screening of CO₂RR electrocatalysts and often yields reproducible results because it has relatively few operating parameters. However, H-cells suffer from several important drawbacks. They are strongly limited by mass transport, exhibit higher cell resistance, and typically deliver low CO₂ conversion rates and low current densities. In addition, dissolved metal contaminants in the electrolyte can more readily poison the catalyst in H-cell experiments than in continuous flow configurations.^[52,79]

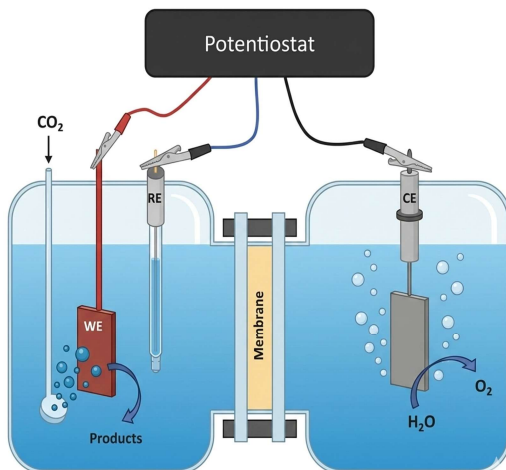


Figure 9: Schematic representation of a CO₂RR H-cell electrolyzer, obtained from reference [52]

The limitations of the H-cell setup are mitigated in flow-cell configurations. Flow cells are designed to enhance CO₂ transport to the catalyst active sites by continuously delivering CO₂ directly to the catalyst active sites and removing products, which reduces mass-transport limitations and enables higher current densities. Flow reactors also offer improved control over local reaction conditions, e.g., local pH and reactant abundance, and facilitate scale-up and continuous operation. In contrast to typical H-cells, flow cells can be operated with or without an RE; in some setups, two REs are used to monitor the potential of both half-cells independently. [52,79] The so-called basic flow reactor is the simplest flow cell architecture and serves as the foundation for more advanced designs. It typically comprises three separate streams: a CO₂ gas feed stream, a catholyte stream, and an anolyte stream, with the gas stream controlled by an MFC and the liquid streams circulated by pumps to maintain constant flows, as presented in Figure 10. The cathode and anode compartments are separated by an ion-exchange membrane to limit product crossover. In the cathode compartment, a GDE is placed between the CO₂ chamber and the catholyte chamber. A porous electrode in the anode compartment functions as the CE. Two distinct modes are used to supply CO₂ to the GDE CL:

1. **Flow-by mode (flow-adjacent mode):** CO₂ flows alongside the GDE and reaches the catalyst by diffusion through the gas diffusion layer (GDL). This arrangement is simple and reduces the risk of electrolyte intrusion into the GDL; however, it can produce concentration gradients of CO₂ and reaction products near the catalyst, which limits mass transport at high current densities.
2. **Flow-through mode (forced convection mode):** gas input is driven through the GDE, with both diffusion and convection processes delivering CO₂ to the catalyst. This reduces concentration gradients at the reaction interface and can support higher local reactant fluxes; nevertheless, it often generates gas bubbles in the catholyte and promotes salt crystallization inside the GDL.

Because flow-through operation can cause salt deposition and flooding of the GDL over time, the flow-by mode is frequently preferred for long-term CO₂ electrolysis, despite its diffusion limitations. The optimal choice depends on the targeted current density, product, and durability requirements. [52]

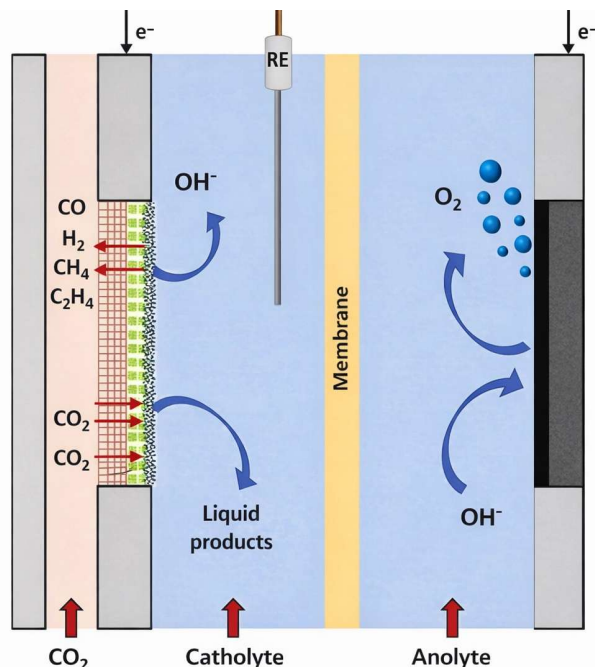


Figure 10: Schematic representation of a CO₂RR basic flow electrolyzer, obtained from reference^[52]

PEM electrolyzers (Figure 11) are among the most widely studied flow reactors for CO₂ reduction. In these cells, a polymer ion-exchange membrane separates the anode and cathode compartments, allowing selective ion transport while limiting product crossover. In PEM electrolyzers, both the anode and cathode are GDEs, with a stack configuration of GDE/membrane/GDE that creates a compact "zero-gap" architecture in which the CL is in direct contact with the membrane, with no separation between the electrode and membrane via the liquid electrolyte. Due to the stacked configuration of the PEM electrolyzers, they are also often called membrane-electrode assemblies (MEA).^[45,52]

Similar to the basic flow reactor, CO₂ is fed directly to the GDE in the PEM cells, enabling high current densities, efficient mass transport, and low ohmic losses. These features render PEM reactors attractive for industrial-scale CO₂ electrolysis. The ion exchange membrane can be a cation exchange membrane (CEM), an anion exchange membrane (AEM), or a bipolar membrane (BPM), depending on the desired ion transport and local pH. Each electrode assembly typically comprises three elements: the GDE, a current collector, and a flow plate. The flow plate serves as an engineered interface that delivers CO₂ uniformly to the GDE and removes produced water and CO₂RR products. The zero-gap arrangement of PEM electrolyzers reduces cell resistance and minimizes ohmic losses compared with basic flow cells that use thicker liquid layers. PEM-type CO₂RR reactors are relatively straightforward to scale and pressurize, benefiting from the established PEM water-electrolyzer engineering and exhibiting a lower risk of catalyst poisoning from dissolved electrolyte impurities.^[45,52]

Despite the significant progress in PEM systems, several fundamental challenges remain, especially those related to membrane transport, durability, and long-term operational stability. Limited ion transport through the membrane can create local pH gradients at the electrode-membrane interface, which often shifts selectivity toward the HER rather than the desired CO₂RR. Moreover, membrane drying under low humidity or high current density can reduce ion conductivity and lead to a gradual

increase in cell resistance. Polymer membranes are also costly and can degrade during extended operation due to chemical and radical attack, which lowers ion conductivity and the overall system performance. AEMs can improve CO_2RR selectivity in some cases, but they face stability challenges under strongly alkaline conditions, where degradation of the polymer backbone or functional groups may occur over time. Beyond membrane limitations, GDEs used in PEM configurations are prone to flooding. Specifically, the accumulation of liquid water inside the porous structure can occur, blocking CO_2 transport pathways and limiting CO_2 access to the catalyst. This issue is particularly problematic when water is produced as a reaction byproduct, leading to reduced reaction efficiency and degraded long-term performance.^[45,52]

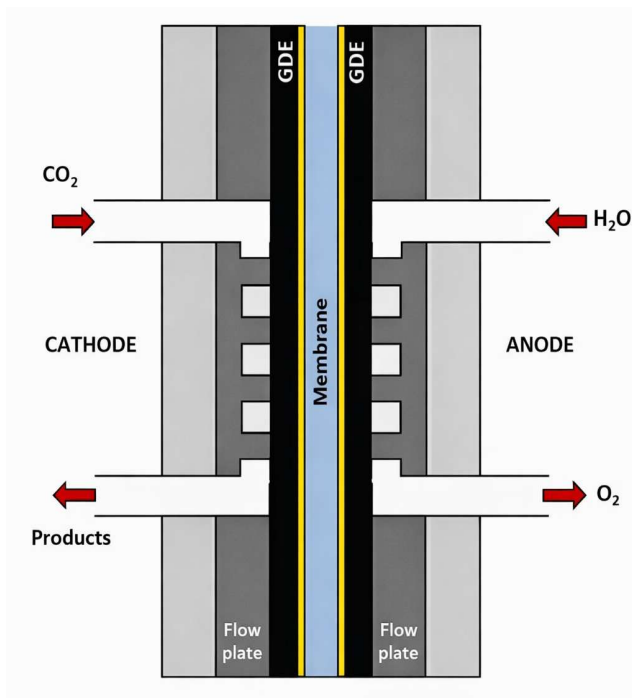


Figure 11: Schematic representation of a CO_2RR polymer electrolyte membrane electrolyzer, obtained from reference^[52]

In addition to membrane-based systems, membraneless flow cells, namely microfluidic reactors, emerged as an alternative in which no physical barrier separates the anode and cathode. In these systems, the separation of oxidation and reduction products relies primarily on the diffusion behavior of the liquid electrolyte rather than on a membrane (Figure 12). A typical microfluidic electrolyzer consists of two GDEs facing each other with a very thin liquid electrolyte layer (less than 1 mm) flowing in a laminar regime between them. In microfluidic reactors, a micro RE placed in the electrolyte channel is commonly used to measure the individual potentials of the cathode and anode. Because the electrolyte flow is controllable, the water balance can be managed to avoid cathode flooding or anode drying. Compared with conventional PEM cells, membraneless microfluidic designs can achieve high power densities in small-scale devices by eliminating mass-transport and pH imbalance issues, as well as reducing ohmic losses due to membrane removal. They also allow fast catalyst screening under varied conditions and avoid the expense of membrane materials. Nevertheless, the absence of a membrane may result in ineffective product separation in some cases, increasing the risk of product crossover, which can lower energy efficiency and productivity. Moreover,

microfluidic flow cells suffer from limitations in flow-channel dimensions required to maintain laminar flow conditions.^[45,52]

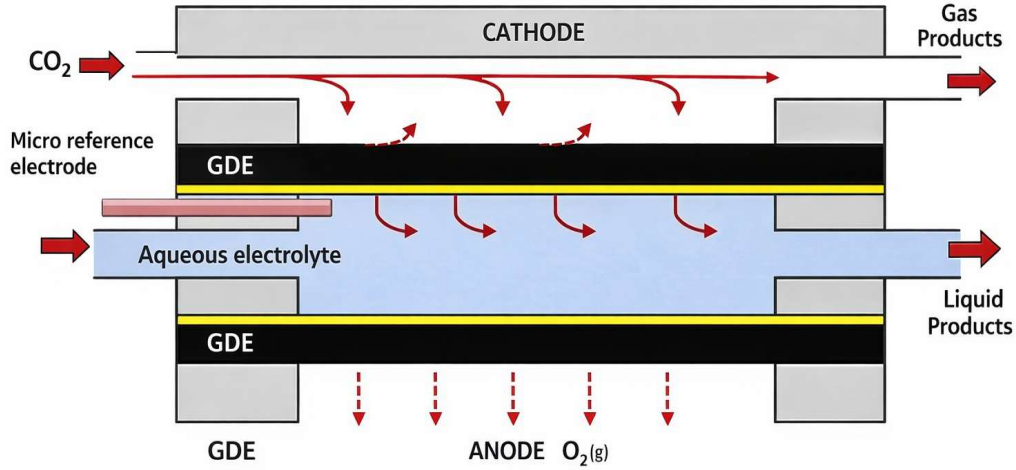


Figure 12: Schematic representation of a CO₂RR microfluidic electrolyzer, obtained from reference^[52]

Despite their advantages, flow-cell systems face several challenges, most notably the need to balance high current densities with high product selectivity and long operational stability. Strategies to increase current density, such as raising the CO₂ flow rate or reducing the electrolyte volume, may inadvertently promote competing side reactions, particularly HER, thereby decreasing selectivity toward desired CO₂ reduction products. Furthermore, the selection and design of membrane and GDL materials strongly influence ion transport and mass-transfer behavior in these systems.^[45,52]

1.3 Metal Foams via Dynamic Hydrogen Bubble Templating for Carbon Dioxide Reduction

1.3.1 Dynamic Hydrogen Bubble Templating

Nano-structured porous metals play a central role in electrocatalysis, where the porous framework functions as a catalytically active yet dimensionally stable electrode that lowers activation barriers for the transformation of reactants and intermediates and improves overall device performance.^[80] A typical electrocatalytic reaction can be described in five steps (Figure 13): (1) transport of reactants from the bulk electrolyte to the electrode surface, (2) adsorption of reactants to the electrode surface, (3) interfacial charge transfer between the electrode and both reactants and intermediates, (4) desorption of products from the surface, and (5) their diffusion into the bulk electrolyte.^[81] Mass transport (steps 1 and 5) can be controlled through device and catalyst design. For example, highly porous GDEs implemented in flow cell configurations enable technically relevant current densities and conversion rates by mitigating the mass-transport limitations often associated with planar electrodes, as detailed earlier.^[80,82–87] Surface processes (steps 2-4) are governed by the nature, density, and spatial distribution of active sites. Generally, porous nano-structures demonstrate enhanced activity due to their abundance of active sites and surface defects, which induce confinement effects and tune adsorption and charge transfer properties.^[81]

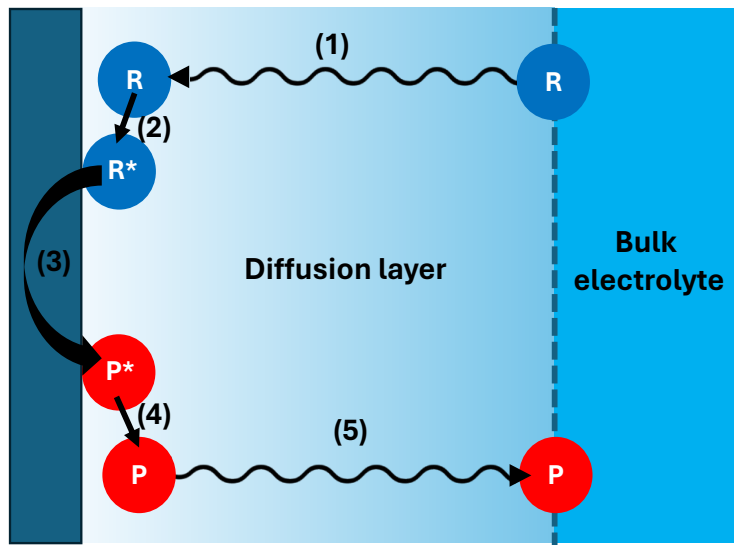


Figure 13: Illustration of the steps of an electrochemical process, starting with reactants (R) diffusion from bulk electrolyte to electrode surface, adsorption of reactants on the electrode surface, charge transfer between the electrode and adsorbed species, desorption of products (P) from the electrode surface, and diffusion of products from the electrode surface to the bulk electrolyte

Following the IUPAC nomenclature, porous materials can be classified by pore size as micro-porous (< 2 nm), meso-porous (2-50 nm), and macro-porous (> 50 nm).^[81,88] A material is defined as hierarchical when it contains two or more of these pore size regimes, and a porous material is often referred to as a foam when a large fraction of its volume is occupied by gas-filled pores or dispersed bubbles.^[88] Numerous fabrication routes for metal foams have been reported, including selective dissolution, templating, combustion synthesis, and sol-gel methods. These approaches

are frequently multi-step, complicated, and can be limited by precursor availability, the need for elevated temperatures or pressures, working under inert atmospheres, and/or additional purification steps.^[89–96] By contrast, the DHBT technique offers a more recent, single-step, versatile, and scalable route to hierarchical self-standing metal foams without requiring external organic or inorganic templates or extensive post-processing steps.^[89,97]

Specifically, electrodeposition is typically performed within the electrochemical stability window of the solvent to avoid solvent decomposition. During aqueous electrodeposition of both noble and base metals (e.g., Cu, Ag, Au, Pt, Zn, Co, Fe, Ni), the parasitic HER commonly occurs and can reduce electrodeposition FE and compromise deposit integrity.^[89,97] The DHBT method deliberately exploits this phenomenon by applying large cathodic overpotentials or high current densities, such that electrochemically generated H_2 bubbles serve as dynamic, self-removing templates, producing macro-, meso-, and micro-porous morphologies. Moreover, bubble nucleation and growth, which are controlled by DHBT parameters, induce local stirring and modify the hydrodynamics at the electrode surface, promoting the formation of self-supporting nano-structures within the foam walls and eliminating the need for binders or additional fixation of metallic nano-particles.^[89,97,98] Figure 14 shows a possible schematic representation of the DHBT fabrication of a Cu foam sample. It illustrates the sequential stages of the process: simultaneous nucleation of H_2 bubbles and Cu agglomerates, followed by bubble growth and coalescence that produce a dynamic negative templating effect for Cu deposition, ultimately yielding a porous Cu foam structure.

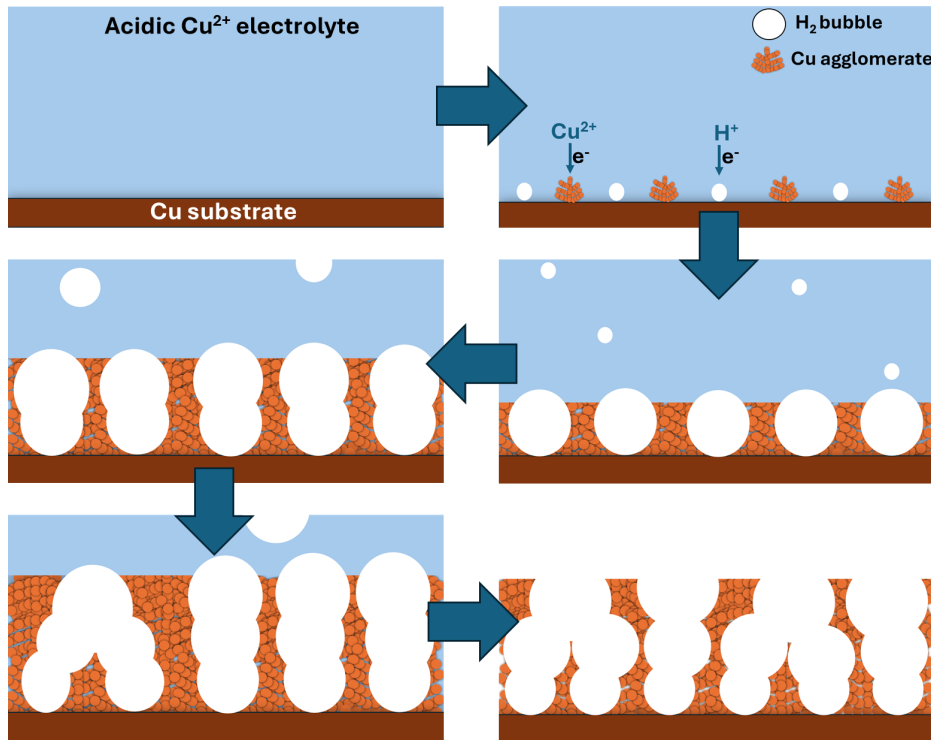


Figure 14: Schematic representation of the different stages of a Cu foam synthesis via the DHBT method

1.3.2 DHBT-Derived Metal Foams for Carbon Dioxide Reduction

The DHBT-derived foams were found to be promising electrodes for CO₂RR. Klingan et al. investigated CO₂RR on Cu foam samples synthesized via DHBT.^[96] Quasi in situ X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) were performed on Cu foam samples after surface reduction via cyclic voltammetry (CV) in the potential range from 0 to -1.2 V vs. RHE and subsequent freezing in N₂. These frozen samples exhibited a mixture of metallic Cu and Cu₂O, with Cu₂O content ranging from 15 to 45%. This oxide fraction was attributed either to the presence of a stable Cu₂O component or to partial oxidation during air exposure before freezing or prior to the XAS measurements. To probe the oxidation state of the freshly deposited Cu foams, XAS measurements were performed on a Cu foam sample immediately after electrodeposition, at the open circuit potential (OCP), -0.20 V, and -0.95 V vs. RHE, with each potential maintained for 30 minutes. This sample exhibited a Cu-O distance of 1.95 Å, attributed to Cu²⁺, as well as three Cu-Cu distances of 2.51, 3.58, and 4.41 Å. After electrolysis at both -0.2 and -0.95 V vs. RHE, the sample was fully reduced to metallic Cu. Electrolysis at -0.95 V vs. RHE for only 9 minutes also produced complete reduction, demonstrating that reduction to the metallic state can occur rapidly under these conditions. Local alkalization at the Cu foam surface under CO₂RR conditions was determined using operando surface-enhanced Raman spectroscopy (SERS). As the pH increases, the HCO₃⁻/CO₃²⁻ equilibrium shifts toward CO₃²⁻, resulting in a decrease in the 1015 and 1363 cm⁻¹ signals (associated with HCO₃⁻) and an increase in the 1065 cm⁻¹ signal (associated with CO₃²⁻). Reference HCO₃⁻/CO₃²⁻ solutions with adjusted pH values were used to calibrate the SERS response and determine the local pH exhibited by the Cu foam samples in comparison to a flat Cu foil. At applied potentials of -0.6 and -0.7 V vs. RHE, the Cu foam samples exhibited high local pH values of about 9 and 10, respectively, whereas the flat Cu foil showed lower local pH values of about 7.8 and 9.5 at the same potentials. This pronounced local alkalization suppresses the parasitic HER and enhances CO₂RR activity. This accounts for the promising CO₂RR performance exhibited by the Cu foams. Specifically, Cu foams exhibited a CO FE of 37% (at -0.6 V vs. RHE), formate FE of 34% (at -0.6 V vs. RHE), and ethylene FE of 19% (at -0.95 V vs. RHE), while the flat Cu foil exhibited negligible FEs for these products.

Kottakkat et al. synthesized a series of bimetallic AgCu foams via the DHBT method.^[95] The addition of Ag⁺ to the DHBT bath produced pronounced changes in the obtained foam morphology. Specifically, the surface nano-dendrites of the AgCu foams were noticeably smoother and shorter than those of the pure Cu foam. The pore diameters of the bimetallic AgCu foams were larger than those of both the pure Ag and pure Cu foams, which suggests increased ECSAs for the AgCu samples relative to the mono-metallic foams. Quantitatively, the roughness factors followed the order: pure Ag < pure Cu < AgCu-10 < AgCu-50, where AgCu-10 and AgCu-50 denote bimetallic foams prepared at Ag⁺ concentrations of 10 and 50 mM, respectively. Total reflection X-ray fluorescence (TXRF) analysis indicated that Ag⁺ concentrations of 10 and 50 mM in the DHBT bath yielded Ag weight percentages of approximately 11% and 33%, respectively, independent of the electrodeposition durations (5-20 s). Electrodeposition FEs of the investigated AgCu samples were below 10%, with the remaining Faradaic charge consumed by H₂ template formation. EXAFS analysis of the AgCu-50 sample indicated that the coordination number of neighboring Cu atoms decreased by roughly a factor of four with respect to the pure Cu foam, consistent with a less ordered Cu metal phase compared to bulk Cu foil. Chromatographic analysis of CO₂RR products showed that AgCu-50 and AgCu-10 achieved CO FEs comparable to that of pure Ag foam (about 50%), whereas the pure Cu foam exhibited a lower CO FE of approximately 20%, at -0.6 V vs. RHE. At the same potential, the AgCu-50 and AgCu-10 samples produced CO partial current

densities of about 2.2 and 0.7 mA cm⁻², respectively, while the pure Ag and pure Cu foams showed negligible CO partial current densities. These results indicate that incorporating Ag into the Cu foams is an effective strategy to achieve promising CO activity at less negative potentials with better cost-efficiency compared to pure Ag foams. Operational stability tests were performed at -0.6 V vs. RHE, the potential at which the bimetallic samples showed promising CO activity, for 5 hours. The AgCu-50 sample demonstrated stable performance, maintaining a CO FE of approximately 60% throughout the experiment, corresponding to a CO partial current density of about 2.5 mA cm⁻².

Hoffmann et al. synthesized a series of Ag foam samples using the DHBT method.^[74] Two cathodic current densities were applied during DHBT: 0.5 and 2 A cm⁻². At 0.5 A cm⁻², deposition times of 40, 60, and 80 s were used, while at 2 A cm⁻², deposition times of 10, 15, and 20 s were applied. Samples produced at 0.5 A cm⁻² were denoted as low current density (lcd) samples, and those produced at 2 A cm⁻² were referred to as high current density (hcd) samples. The major CO₂RR products observed for the Ag foams and the Ag foil substrate were CO and HCOOH, in addition to the parasitic H₂ evolution. The Ag foams reached partial current densities of up to about 15 mA cm⁻² for CO at -1.0 V vs. RHE, 19 mA cm⁻² for H₂ at -1.3 V vs. RHE, and 2 mA cm⁻² for HCOOH at -1.3 V vs. RHE, while the Ag foil exhibited negligible partial current densities for these products. CO FEs of around 70% at -0.6 V vs. RHE were obtained from Ag foams, which increased with more negative potentials to reach a maximum in the potential range from -0.7 to -1.0 V vs. RHE with values of $\approx 90\%$ for the (2Acm⁻² 20s) sample and $\approx 85\%$ for the (0.5Acm⁻² 80s) counterpart. Generally, increasing the DHBT current density at a constant electrodeposition charge produced compact Ag foams with lower deposition FEs, smaller ECSAs, and smaller pore sizes. This higher compactness correlated with improved C₁ product performance for the investigated Ag foams.

Yang et al. investigated the dynamics and reformation of Cu oxides on both the Cu foam surface and bulk, using operando SERS and operando XAS under CO₂RR conditions.^[99] Time-resolved measurements revealed that surface oxides are reduced on the order of seconds, whereas subsurface (bulk) oxides undergo reduction on the order of minutes. Therefore, a rapid reduction of surface Cu oxides takes place and kinetically traps subsurface Cu oxides. This subsurface Cu oxide species were found to facilitate *CO adsorption, promote C-C coupling, and enhance C₂₊ product formation. This accounts for the improved CO₂RR performance of the Cu foams; specifically, the Cu foams exhibited enhanced C₂₊ activity compared with Cu foil, with respective total C₂₊ FEs of 36% and 7% at -0.9 V vs. RHE.

1.4 Gas Diffusion Electrodes for Carbon Dioxide Reduction

GDEs play a crucial role in addressing mass-transport limitations in CO_2 reduction systems and have become a key component in the development of highly efficient CO_2RR technologies. GDE-based systems facilitate improved mass transport by supplying gaseous CO_2 directly to the reaction interface, thereby enabling higher current densities and enhanced reaction efficiencies. The superior performance of GDE-based systems is largely attributed to the structural design of the electrodes, which typically consist of three distinct layers: (1) the macro-porous layer that supplies reactant gas from the GDE backside, (2) the micro-porous layer that stabilizes the local gas-liquid distribution, and (3) the CL, which is often treated with an ionomer to impart hydrophobicity and inhibit flooding. The phase formed at the GDE, comprising the CL, gaseous CO_2 , and liquid electrolyte, is often described as a three-phase boundary; however, this is debated in the literature, and some authors treat it instead as a two-phase boundary between the electrolyte, in which CO_2 is dissolved, and the CL. The GDE multilayer architecture (Figure 15) allows efficient diffusion of gaseous CO_2 through the electrode and ensures CO_2 effective transport to the catalyst surface, thereby promoting rapid reaction kinetics. [45,100–104]

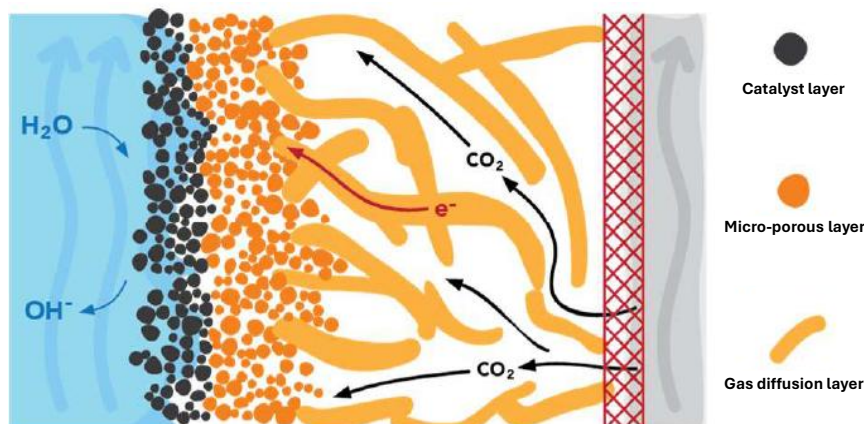


Figure 15: Schematic representation of a gas diffusion electrode setup for electrochemical CO_2 reduction, obtained from reference [105]

GDEs are typically integrated into flow cells, supporting the scalability and process intensification required for industrial applications. By accelerating the delivery of gaseous reactants directly to the catalyst-electrolyte interface, GDEs overcome the low solubility and sluggish diffusion of CO_2 , enabling substantially higher current densities compared to conventional H-cell electrolysis. Despite these advantages, GDEs face several key challenges that limit long-term CO_2 electrolysis performance. These include flooding, where the electrolyte intrudes into GDE pores and blocks gas pathways; (bi)carbonate salt precipitation, which blocks pores; local pH gradients, which alter product selectivity; mechanical and chemical degradation of catalyst and ionomer layers; and increased cell complexity, requiring careful membrane selection, sealing, and electrolyte management. The reliable deployment of GDEs, therefore, demands targeted engineering of the electrolyte and membrane, precise control of hydrophobicity and pore architecture in the micro-porous layer, and optimization of the catalyst micro-environment (ionomer content, local buffering, and wettability) to stabilize mass transport and selectivity. [45,100–104]

Among the aforementioned drawbacks of GDE configurations, the precipitation of (bi)carbonate

salts is a particularly severe challenge, and it becomes more pronounced at high current densities. Specifically, the strong local alkalization at the cathode, driven by OH^- generation from both parasitic HER and CO_2RR , shifts the equilibrium between dissolved CO_2 and bicarbonate/carbonate salts towards the formation of the salts. This shift reduces the concentration of free CO_2 at the catalyst surface and can produce supersaturated bicarbonate and carbonate phases that precipitate inside the CL or form dense surface films. Such salt deposits block active sites, impede gas and ion transport, alter local mass transport, and ultimately degrade CO_2RR activity and selectivity.^[45,100–104]

Common strategies reported in the literature for mitigating GDE disadvantages include optimizing electrolyte composition and bulk pH (for example, by using buffered electrolytes); controlling local alkalization through cell design, flow management, and pulsed operation; enhancing mass transport to avoid local supersaturation; and engineering the electrode micro-environment and hydrophobicity, for example, by tuning the GDL pore structure and ionomer content to discourage salt nucleation and adhesion. Combining these approaches has been shown to extend stable operation and preserve selectivity in many GDE systems.^[45,100–104]

In an interesting study^[106], Cu-based GDEs were synthesized by the co-electrodeposition of Cu and poly-N-(6-aminohexyl)acrylamide onto a carbon-fiber GDL, yielding GDEs that exhibited markedly enhanced C_2H_4 activity, with C_2H_4 FE of $87 \pm 3\%$ at -0.47 V vs. RHE, obtained in 10 M KOH electrolyte in a flow reactor with two distinct cathodic and anodic compartments, separated by an anion-exchange membrane. Figure 16 presents a schematic representation of the co-electrodeposition process and the SEM image of the resulting Cu foam agglomerates. Additionally, the figure shows the N 1s X-ray photoelectron spectroscopy (XPS) results of the obtained GDEs, demonstrating the presence of surface C-NH_2 and N-C=O species, and confirming amine incorporation into the metallic deposits.

The authors attributed the enhanced C_2+ activity of the synthesized GDEs to two effects of the surface amino species, namely the stabilization of the $^*\text{CO}$ intermediates and an increase in local pH at the catalyst surface. SERS-derived pH values, obtained from the CO_3^{2-} and HCO_3^- relative peak intensities, indicated surface pHs of about 10.6 and 9.7 for the amine-modified and pure Cu GDEs at -0.47 V vs. RHE, respectively.

Despite the high C_2H_4 activity of the amine-modified GDEs, stability tests revealed a decline in performance after approximately 3 hours of operation. The authors attributed this loss to the corrosion of the carbon-fiber GDL, which reduced the electrode hydrophobicity and promoted HER over time. They proposed that replacing the carbon-fiber support with a polymer-based GDL could mitigate corrosion and preserve hydrophobicity, thereby improving operational stability.^[106]

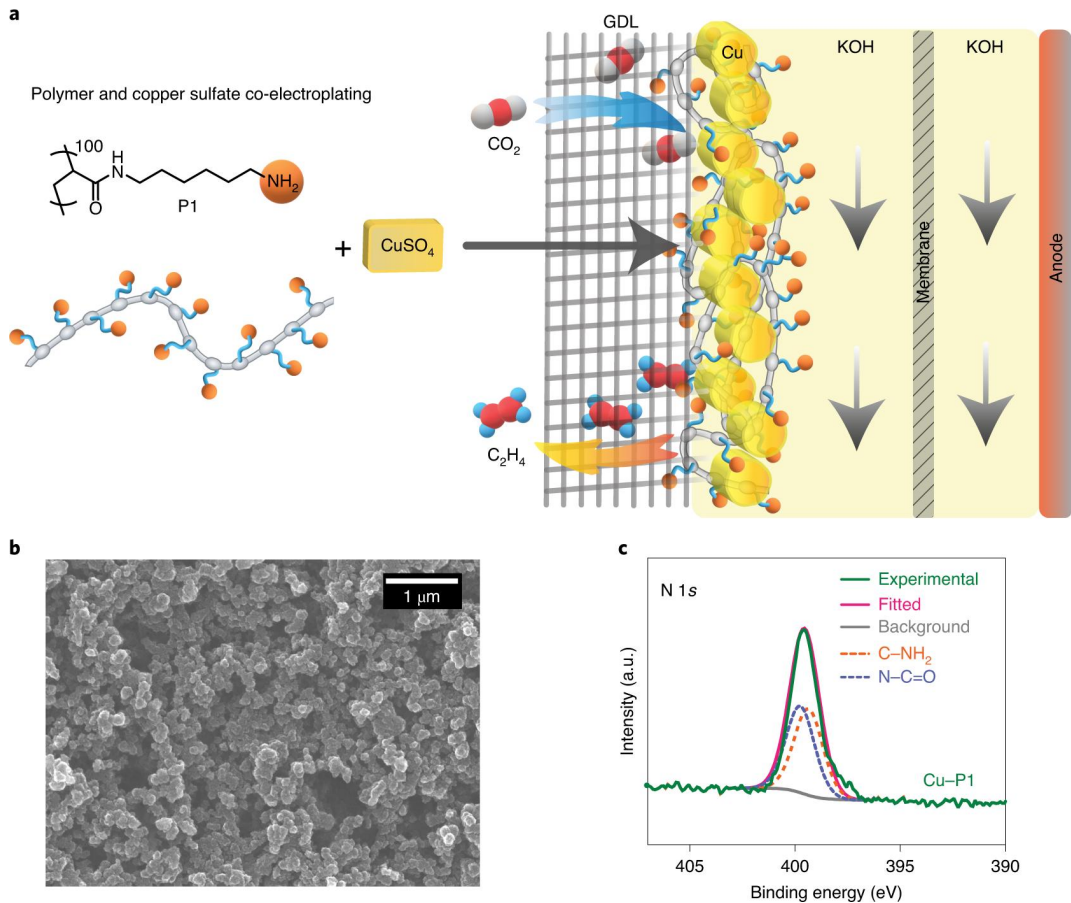


Figure 16: Schematic representation of the amine-modified Cu GDE synthesis (a), the SEM image of the resulting Cu agglomerates (b), and the XPS N 1s spectra of the resulting Cu GDEs (c), obtained from reference^[106]

In another study, a simple and efficient route for the synthesis of amine-modified Cu nano-wire GDEs was reported.^[107] The method suppresses Cu nucleation during electrodeposition by incorporating the additive 3,5-diamino-1,2,4-triazole (DAT), resulting in the formation of Cu nano-wire deposits on a carbon-paper GDL. The degree of nucleation inhibition was controlled by the electrolyte pH and the applied current density, allowing effective tuning of the deposited morphology. The CO₂RR performance of the DAT-modified Cu GDEs was evaluated in a flow reactor with separate cathodic and anodic compartments divided by an anion-exchange membrane, as reported in a previous study.^[108] The Cu nano-wire GDEs exhibited FEs of approximately 35% for ethylene and 25% for ethanol, with corresponding partial current densities of about 100 and 70 mA cm⁻² at -0.70 V vs. RHE. Moreover, the synthesized Cu nano-wire GDEs demonstrated good operational stability, retaining their catalytic activity over continuous operation for at least 8 hours.

In a remarkable work, bimetallic Ag-Cu nano-wires were deposited on a carbon-paper GDL in the presence of DAT.^[109] Specifically, a mixed electrolyte containing Cu²⁺, Ag⁺, and DAT was employed for the co-electrodeposition, yielding Cu-Ag nano-wires with an excellent C₂⁺ product activity. Specifically, at -0.70 V vs. RHE and a total current density of 300 mA cm⁻², the reported FEs were ≈75% for C₂H₄ and ≈25% for ethanol, measured in a flow-cell configuration with separate cathode and anode compartments divided by an anion-exchange membrane, which was reported in

a previous study.^[108] EXAFS measurements indicated that in the Ag-Cu polycrystalline samples electrodeposited in the absence of DAT, Cu and Ag atoms are completely phase-segregated, whereas in the Ag-Cu wire samples prepared with DAT, the two metals are distributed in a much more homogeneous manner. Insights from in situ SERS combined with electrochemical analysis suggest that the exceptional selectivity toward C_{2+} products arises from a synergistic effect between the enhanced stabilization of a Cu_2O surface overlayer and the optimized availability of the *CO reaction intermediate, which is promoted by the incorporation of Ag into the Cu matrix.

A straightforward and time-efficient DHBT synthesis of Ag foam GDEs was developed by Hoffmann et al.^[82] In their procedure, a PTFE (polytetrafluoroethylene) / PP (polypropylene) bipolymeric porous fabric was first sputter-coated with a 120 Å layer of Ag and then used as the substrate for pulsed DHBT electrodeposition. After deposition, the porous Ag foams were infiltrated with a perfluorosulfonic acid (PFSA) ionomer to impart hydrophobicity to the GDE. By tuning the deposition parameters, most notably the pulse-to-pause ratio, the authors increased the mass of deposited catalyst while simultaneously lowering the operational overpotential for electrochemical CO_2 reduction to CO. CO_2RR measurements were performed in a flow cell configuration with distinct cathodic and anodic compartments separated by an anion exchange membrane. The Ag foam GDEs exhibited an outstanding CO FE of approximately 100% at an applied current density of 10 mA cm^{-2} , which remained high at more elevated current densities, decreasing to about 75% at 500 mA cm^{-2} . Operational stability tests at a total current density of 200 mA cm^{-2} showed excellent durability, where the CO FE was near 100% initially and decreased only to about 90% after 100 hours of continuous electrolysis.

In light of the GDE literature discussed above, it can be concluded that amine-based additives result in a remarkable enhancement in C_{2+} product selectivity during CO_2RR , making it a promising candidate as an additive during DHBT. While some studies attributed the enhanced C_{2+} selectivity of amine-mediated Cu GDE to the incorporation of amino species into the GDE surface, which can stabilize reaction intermediates and increase local alkalization, other works attributed the effect to the nucleation inhibition caused by DAT during Cu electrodeposition. Specifically, DAT alters the deposition pathways and yields distinct nano-structures with different shapes, defect densities, and active sites, which in turn produce different catalytic activities.^[106,107]

This gap highlights the need for systematic studies to clarify how amine additives influence C_{2+} product formation. Additionally, the simple three-step protocol used to prepare Ag foam GDEs (sputter coating, pulsed DHBT deposition, and ionomer infiltration) represents an attractive starting point for adapting the method to Cu foam GDE synthesis, given the reported combination of high activity, excellent operational stability, and the relative ease of fabrication. Transforming the approach to Cu will require careful optimization of deposition parameters, ionomer type and loading, and support materials to avoid GDE degradation and preserve hydrophobicity, as well as systematic testing of product distribution and long-term stability at high current densities. Pursuing this direction could yield Cu foam GDEs that combine enhanced C_{2+} selectivity with practical durability and scalable manufacture.

1.5 Motivation & Objectives

The rational design of nano-structured hierarchical Cu architectures for various applications, such as energy conversion and storage, sensing, and catalysis, remains a major challenge. Conventional approaches typically rely on complex multi-step templating methods that require sacrificial organic or inorganic templates and their post-synthesis removal, which complicates scale-up and reproducibility.^[89–94] By contrast, the DHBT method offers a time-efficient, single-step electrodeposition route to produce nano-structured Cu foams with tunable morphology and porosity, avoiding the need for sacrificial templates and extensive post-synthesis processing. As reviewed in the previous sections, prior studies on DHBT-derived Cu foams have largely focused on the dynamics of Cu_xO species under reaction conditions and on identifying surface intermediates, and have typically performed the DHBT using the direct current (DC) at selected times and currents. Although these investigations have provided valuable mechanistic insights, they have not established a detailed correlation between the DHBT synthesis parameters and both the resulting Cu foam morphologies and CO_2RR product distributions. Moreover, various DHBT parameters, such as current modes, electrolyte composition, temperature, substrate orientation, and post-deposition annealing, have not been systematically explored, despite their potentially significant impact on foam morphology and CO_2RR performance. Moreover, a clear correlation between Cu foam morphology descriptors, such as the shape and size of surface nano-structures, ECSA, pore diameter, and foam thickness, with the corresponding CO_2RR performance, particularly C_{2+} selectivity and activity, has not been established. Although amino-based additives, such as DAT, have been investigated for the synthesis of nano-structured Cu samples, they have not been studied for Cu foam synthesis via the DHBT method, and the mechanistic reasons for their positive influence on C_{2+} product formation have not been thoroughly elucidated. To the best of our knowledge, no DHBT-based synthesis route for Cu foam GDEs has been reported, despite the potential of the DHBT technique to offer a fast, scalable, and reproducible approach for fabricating highly active, nano-structured Cu foam GDEs. Consequently, these uncovered topics reveal substantial research gaps, whose systematic investigation promises to yield valuable structural, mechanistic, and performance-related insights. Additionally, the broad product spectrum and limited operational stability remain persistent challenges for Cu electrodes. Addressing these issues requires targeted strategies to enhance C-C coupling, suppress competing H_2 evolution, and improve long-term durability under device-relevant operating conditions.

Therefore, this PhD project is structured to achieve three main interrelated objectives. The **first objective** is to systematically investigate the influence of a broad set of DHBT parameters on the morphology of model Cu foams prepared on Cu foil substrates with a 1 cm^2 geometric area. The synthesis variables are grouped into four series: (1) a current-time series that probes the basic DC deposition parameters; (2) a current-mode series in which the DC, pulsating current (PC), reversing current (RC), and alternating current (AC) modes are compared; (3) a chemical effect series that shows the impact of the DHBT bath composition, including Cu^{2+} concentration, pH, surfactants, and complexing agents; and (4) a physical effect series in which physical parameters, such as stirring, substrate orientation, bath temperature, and post-synthesis annealing, are investigated. For each condition, the resulting foams are characterized comprehensively in terms of foam interconnectivity, pore diameter and density, foam thickness, ECSA, surface nano-features, mass density, and Cu deposition FE. This systematic mapping enables the establishment of practical synthesis-morphology correlations that form the foundation for rational electrode design.

The **second objective** is to evaluate the synthesized model Cu foams as electro-catalysts for CO_2RR in a conventional H-cell configuration to enable rapid screening and direct comparison of product

distributions and C_{2+} selectivity across the sample sets. Electrochemical performance testing is performed in parallel with operando SERS measurements to correlate product distributions with the potential-dependent evolution of adsorbed intermediates, surface Cu oxidation states, and local alkalization. This allows identifying which morphological features and surface structures promote *CO adsorption, C-C coupling, and enhanced C_{2+} formation.

The **third objective** is to develop a simple, time-efficient, three-step protocol to convert the most promising model foams into Cu foam GDEs and to evaluate these GDEs in a flow-cell configuration that mitigates mass-transport limitations of CO_2 and enables operation at higher current densities compared to the conventional H-cell setup. This objective includes upscaling selected model foams into GDE architectures, measuring intrinsic activity and selectivity under more industrially-relevant conditions, and testing operational stability over 12 hours to assess suitability for long-term applications. In addition, the feasibility of bimetallic Ag-Cu DHBT synthesis of GDEs is explored, with a preliminary screening of Ag:Cu ratios to identify composition windows that may enhance C_{2+} activity and guide subsequent optimization.

Consequently, this work provides a coherent pathway from controlled DHBT synthesis to mechanistic understanding and device translation. It delivers practical synthesis-morphology rules, identifies DHBT conditions that maximize C_{2+} selectivity, and establishes straightforward fabrication routes for nano-structured Cu GDEs that are compatible with scalable, industrially relevant configurations. Together, these outcomes aim to accelerate the development of selective, durable nano-structured Cu-based electrodes for CO_2RR and related energy conversion applications that can be operated at technically-relevant current densities.

2 Experimental Part

2.1 DHBT Synthesis of Model Cu Foams

2.1.1 Standard DHBT Procedure

Cu sheets (0.1 mm thickness, Goodfellow GmbH, 99.999% purity) were cut into 1 cm × 2 cm foil pieces. Each foil was polished with 0.7 μm diamond paste, ultrasonicated sequentially in ethanol and Milli-Q water, and etched in a 10 vol% nitric acid solution (Fisher Chemical GmbH, 65%). The active area for DHBT on each Cu foil was defined as 1 cm × 1 cm using Kapton tape, and then the foils were weighed. All solutions in this work were prepared in Milli-Q water. Unless otherwise mentioned, the standard DHBT protocol described below was applied for Cu foams synthesis.

The DHBT electrolyte was a mixture of CuSO₄ (0.2 M) (Sigma-Aldrich, 99.995% purity) and H₂SO₄ (1.5 M) (Carl Roth, 95-98%), resulting in a calculated pH of approximately -0.5. Electrodeposition was performed in an open single-compartment cell using a two-electrode configuration. The cell was filled with 20 mL of the DHBT electrolyte. A polished Pt foil (1 cm × 2 cm) served as the CE, while the prepared Cu foil acted as the WE. Both electrodes were placed vertically in the cell with a separation of about 0.3-0.5 cm, as presented in Figure 17-a and -b. The DHBT deposition was performed from a quiescent solution at room temperature using a Gamry 3000 reference potentiostat. Immediately after deposition, each Cu foam sample was removed from the bath, rinsed with Milli-Q water, dried under a N₂ stream, and weighed. Figure 17-c depicts a Cu foil before DHBT and a Cu foam sample after DHBT.

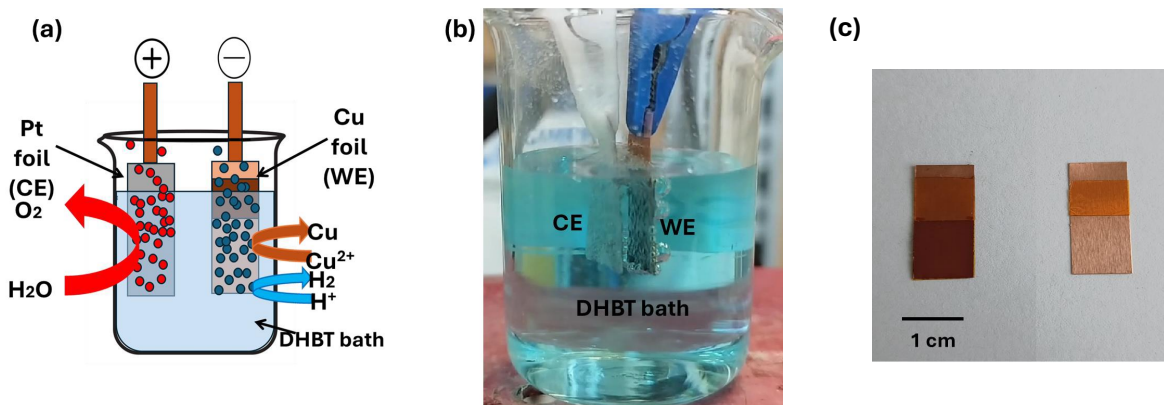


Figure 17: Schematic representation of the model DHBT setup (a), digital photo of the DHBT cell used for model Cu foams synthesis (b), and digital photo of a dry model Cu foam sample after DHBT (left) and the Cu foil substrate before DHBT (right) (c)

Various DHBT parameters were investigated and grouped into four categories: (1) current-time series, (2) current mode series, (3) physical effect series, and (4) chemical effect series. The synthesis procedures for the samples of each series are described below and summarized in Table 3.

2.1.2 Current-Time Series

Six Cu foam samples were prepared using the standard DHBT procedure discussed above. Electrodeposition was performed under the following combinations of continuous cathodic DC density

and time: 1 A cm⁻² for 10 s, 1 A cm⁻² for 20 s, 1 A cm⁻² for 30 s, 2 A cm⁻² for 5 s, 2 A cm⁻² for 10 s, and 2 A cm⁻² for 15 s.

2.1.3 Current Mode Series

Five Cu foam samples were electrodeposited in the PC mode using five different pulse/pause time pairs of (1 ms/10 ms), (5 ms/10 ms), (20 ms/10 ms), (20 ms/40 ms), and (20 ms/200 ms). A cathodic DC density of 1 A cm⁻² was applied during each pulse time. The total cathodic charge density for every sample was fixed at 20 C cm⁻² by varying the number of pulse-pause cycles. For the five samples, the numbers of pulse-pause cycles were 20,000; 4000; 1000; 1000; and 1000, respectively. For the RC DHBT, cathodic and anodic pulse durations were fixed at 20 ms and 10 ms, correspondingly. Also, the number of cathodic-anodic pulse cycles was fixed at 1000 for all RC Samples. Three pairs of cathodic/anodic pulse current densities of (1.05 A cm⁻²/0.1 A cm⁻²), (1.15 A cm⁻²/0.3 A cm⁻²), and (1.3 A cm⁻²/0.6 A cm⁻²) were employed, with a fixed total charge density of 20 C cm⁻².

For the AC DHBT, a cathodic DC offset of 1 A cm⁻² was applied, and the deposition time was fixed at 20 s. Five different AC amplitude/frequency combinations of (1.2 A cm⁻²/0.5 Hz), (1.5 A cm⁻²/0.5 Hz), (2 A cm⁻²/0.5 Hz), (1.5 A cm⁻²/1000 Hz), and (1.5 A cm⁻²/5000 Hz) were tested, with the total charge density maintained at 20 C cm⁻² for all AC samples.

PC, RC, and AC samples were compared to a reference sample electrodeposited at a continuous cathodic DC density of 1 A cm⁻² for 20 s, with a total charge density of 20 C cm⁻².

A detailed explanation of the rationale for selecting the specified parameters for each current mode, along with schematic illustration of each mode, is provided in Section 3.2.

2.1.4 Physical DHBT Effect Series

Several physical alterations to the standard DHBT procedure were made individually, with all samples electrodeposited at a continuous cathodic DC density of 1 A cm⁻² for 20 s. The individual modifications were as follows:

- (a) A sample was electrodeposited with the DHBT bath stirred at 1350 revolutions per minute (rpm) using a magnetic stirrer.
- (b) Two samples were prepared at 5 °C and 60 °C using ice and heated water baths to evaluate the effect of DHBT bath temperature.
- (c) A custom cell was designed to align the WE and CE horizontally. In this cell, electrical connections were made collaterally with Al tape strips surrounded by insulating Kapton tape, leaving exposed ends for connection between the electrodes and potentiostat leads. The strips were routed through side apertures in the cell wall and bent upward. Then, a hydrophobic parafilm thick layer was secured over the connectors with screws to prevent leakage. No leakage was observed during operation. Figure 18 shows the horizontal DHBT cell design and the electrode connectors.
- (d) Post-DHBT annealing was performed in air under two conditions: 300 °C for 15 minutes and 150 °C for 30 minutes. After cooling to room temperature, the samples were reweighed to determine mass changes resulting from annealing.

A reference sample for this series was prepared at a continuous cathodic DC density of 1 A cm⁻² for 20 s, without any modifications to the standard DHBT procedure.

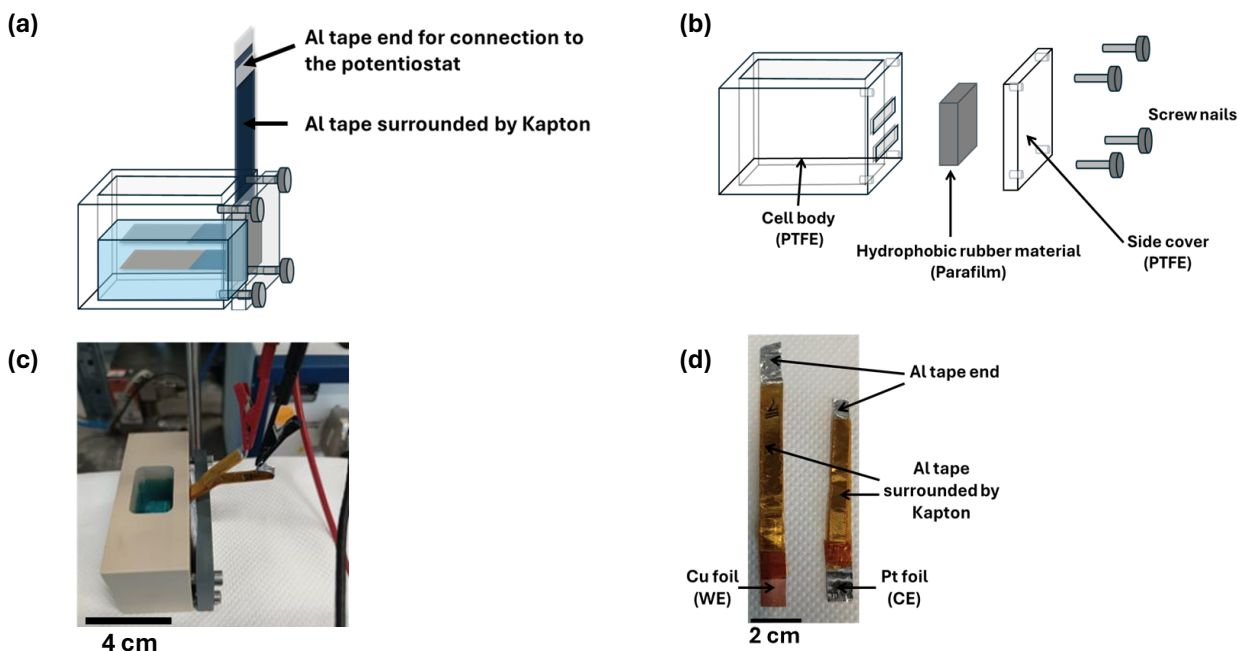


Figure 18: Schematic illustration of the experimental setup (a), individual cell components (b), a digital photo of the assembled cell (c), and a digital photo of the CE and WE (d) of the horizontal DHBT

2.1.5 Chemical DHBT Effect Series

In this series, the electrolyte composition was varied from that used in the standard DHBT procedure, with all samples electrodeposited at a constant cathodic DC density of 1 A cm^{-2} for 20 s. A reference Cu foam was prepared under the same current density and time using the electrolyte from the standard DHBT procedure. Each modification below was introduced individually:

(a) Changes to CuSO_4 concentration:

- (i) CuSO_4 (0.05 M) and H_2SO_4 (1.5 M) ($\text{pH} \approx -0.5$).
- (ii) CuSO_4 (0.1 M) and H_2SO_4 (1.5 M) ($\text{pH} \approx -0.5$).

(b) Change to H_2SO_4 concentration:

- (i) CuSO_4 (0.2 M) and H_2SO_4 (0.15 M) ($\text{pH} \approx 0.5$).

(c) Adding surfactants:

- (i) CuSO_4 (0.2 M), H_2SO_4 (1.5 M), and SDS (0.25 mM) ($\text{pH} \approx -0.5$).
- (ii) CuSO_4 (0.2 M), H_2SO_4 (1.5 M), and CTAB (0.25 mM) ($\text{pH} \approx -0.5$).

(d) Adding a complexing agent with and without pH increasing:

- (i) CuSO_4 (0.2 M), H_2SO_4 (1.5 M), and DAT (1.5 mM) ($\text{pH} \approx -0.5$).
- (ii) CuSO_4 (0.2 M), H_2SO_4 (1.5 M), and DAT (4 mM) ($\text{pH} \approx -0.5$).
- (iii) CuSO_4 (0.2 M), H_2SO_4 (0.15 M), and DAT (4 mM) ($\text{pH} \approx 0.5$).

Table 3: Summary of the synthesized Cu foam samples, each with the corresponding DHBT parameters, where i_{DC} , i_{pulse} , i_{anodic} , and $i_{cathodic}$ denote the applied current density in the DC-DHBT, pulse current density in the PC-DHBT, anodic pulse current density in the RC-DHBT, and cathodic pulse current density in the RC-DHBT, while t_{DC} , t_{pulse} , t_{pause} , t_{anodic} , and $t_{cathodic}$ represent the DC-DHBT time, PC-DHBT pulse time, PC-DHBT pause time, RC-DHBT anodic pulse time, and RC-DHBT cathodic pulse time. N_{cycles} represents the number of applied cycles for the PC, RC, and AC modes

Sample	Current and time parameters	Additional changes
1Acm ⁻² 10s	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 10 \text{ s}$	None
1Acm ⁻² 20s = DC = Ref	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	None
1Acm ⁻² 30s	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 30 \text{ s}$	None
2Acm ⁻² 5s	DC, $i_{DC} = 2 \text{ A cm}^{-2}$, $t_{DC} = 5 \text{ s}$	None
2Acm ⁻² 10s	DC, $i_{DC} = 2 \text{ A cm}^{-2}$, $t_{DC} = 10 \text{ s}$	None
2Acm ⁻² 15s	DC, $i_{DC} = 2 \text{ A cm}^{-2}$, $t_{DC} = 15 \text{ s}$	None
PC1:10	PC, $i_{pulse} = 1 \text{ A cm}^{-2}$, $t_{pulse} = 1 \text{ ms}$, $t_{pause} = 10 \text{ ms}$, $N_{cycles} = 20,000$	None
PC5:10	PC, $i_{pulse} = 1 \text{ A cm}^{-2}$, $t_{pulse} = 5 \text{ ms}$, $t_{pause} = 10 \text{ ms}$, $N_{cycles} = 4000$	None
PC20:10	PC, $i_{pulse} = 1 \text{ A cm}^{-2}$, $t_{pulse} = 20 \text{ ms}$, $t_{pause} = 10 \text{ ms}$, $N_{cycles} = 1000$	None
PC20:40	PC, $i_{pulse} = 1 \text{ A cm}^{-2}$, $t_{pulse} = 20 \text{ ms}$, $t_{pause} = 40 \text{ ms}$, $N_{cycles} = 1000$	None
PC20:200	PC, $i_{pulse} = 1 \text{ A cm}^{-2}$, $t_{pulse} = 20 \text{ ms}$, $t_{pause} = 200 \text{ ms}$, $N_{cycles} = 1000$	None
RC1mC	RC, $i_{cathodic} = 1.05 \text{ A cm}^{-2}$, $i_{anodic} = 0.1 \text{ A cm}^{-2}$, $t_{cathodic} = 20 \text{ ms}$, $t_{anodic} = 10 \text{ ms}$, $N_{cycles} = 1000$	None
RC3mC	RC, $i_{cathodic} = 1.15 \text{ A cm}^{-2}$, $i_{anodic} = 0.3 \text{ A cm}^{-2}$, $t_{cathodic} = 20 \text{ ms}$, $t_{anodic} = 10 \text{ ms}$, $N_{cycles} = 1000$	None
RC6mC	RC, $i_{cathodic} = 1.3 \text{ A cm}^{-2}$, $i_{anodic} = 0.6 \text{ A cm}^{-2}$, $t_{cathodic} = 20 \text{ ms}$, $t_{anodic} = 10 \text{ ms}$, $N_{cycles} = 1000$	None
AC0.5Hz	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 1.2 A cm^{-2} , frequency = 0.5 Hz , $N_{cycles} = 10$	None
AC1.2A	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 1.5 A cm^{-2} , frequency = 0.5 Hz , $N_{cycles} = 10$	None
AC0.5Hz	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 2 A cm^{-2} , frequency = 0.5 Hz , $N_{cycles} = 10$	None
AC0.5Hz	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 1.5 A cm^{-2} , frequency = 1000 Hz , $N_{cycles} = 20,000$	None
AC100Hz	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 1.5 A cm^{-2} , frequency = 5000 Hz , $N_{cycles} = 100,000$	None
AC500Hz	AC, $i_{DC,offset} = 1 \text{ A cm}^{-2}$, amplitude = 1.5 A cm^{-2} , frequency = 5000 Hz , $N_{cycles} = 100,000$	None
1.5A	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	Stirred at 1350 rpm
Horizontal	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	Horizontal WE-CE orientation
5°C	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	DHBT bath temperature = 5°C
60°C	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	DHBT bath temperature = 60°C
An ^{150°C}	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	Annealing at 150°C for 30 minutes in air
An ^{30min}	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	Annealing at 300°C for 15 minutes in air
An ^{15min}	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[SDS] = 0.25 mM
SDS	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[CTAB] = 0.25 mM
CTAB	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[DAT] = 1.5 mM
DAT1.5mM	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[DAT] = 4 mM
DAT4mM	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[DAT] = 4 mM , pH = 0.5
DAT ^{pH0.5}	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[Cu ²⁺] = 0.1 M
0.1 M Cu ²⁺	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	[Cu ²⁺] = 0.05 M
0.05 M Cu ²⁺	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	pH = 0.5
pH 0.5	DC, $i_{DC} = 1 \text{ A cm}^{-2}$, $t_{DC} = 20 \text{ s}$	

2.2 DHBT Synthesis of Cu Foam Gas Diffusion Electrodes

A simple three-step protocol for the synthesis of Cu foam GDEs was developed, as presented in Figure 19, to convert several model Cu foam samples into Cu foam GDEs that operate under more industrially relevant conditions.

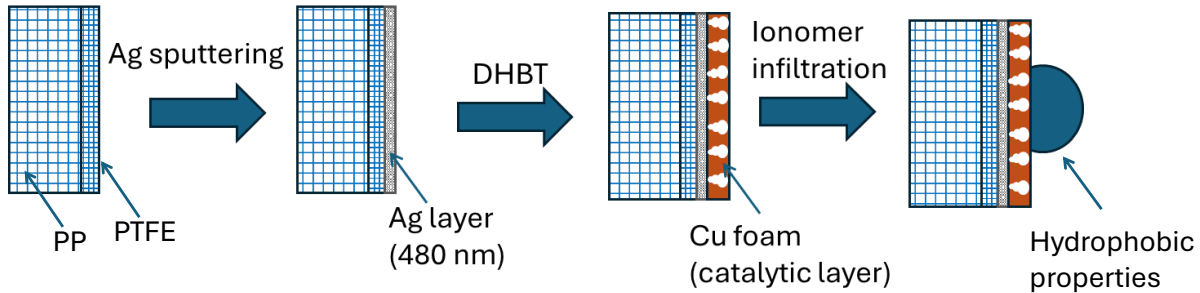


Figure 19: Schematic representation of DHBT-based synthesis of Cu foam GDEs

Sheets of PTFE/PP bilayer fabric (20 cm x 25 cm, 0.2 micron, Sterlitech) were cut into 3 cm x 4 cm pieces and sputter-coated on the PTFE side with a 480 nm Ag layer at a target current of 25 mA using a VAC COAT Desk sputter-coater to impart electrical conductivity. Then, the coated substrates were weighed and mounted in a custom 3D-printed acrylonitrile butadiene styrene (ABS) holder, consisting of a front window with an integrated top electrical contact and a solid back cover. The Ag-coated fabric was clamped between the two holder parts using four insulating screws at the holder corners, and was oriented such that the sputtered PTFE side faced the open window, exposing an active area of 3 x 2.5 cm for DHBT, while the PP side rested against the back solid part. This assembly served as the WE (Figure 20a and d). The CE consisted of a sacrificial Cu mesh (50 mesh size, 0.23 mm wire diameter, Alfa Aesar) placed in a holder that comprised two ABS windows and four insulating corner screws (Figure 20b and e). Unless specified otherwise, the Cu foam synthesis procedure was as follows: DHBT was carried out at room temperature in a quiescent electrolyte comprising 0.2 M CuSO₄ and 1.5 M H₂SO₄, using a Gamry 3000 reference potentiostat equipped with a Gamry reference 30k booster. During DHBT, the PC mode was applied with a cathodic pulse current density of 0.67 A cm⁻², a pulse duration of 20 ms, and a pause duration of 40 ms, for 2250 pulse-pause cycles, yielding a total electrodeposition charge density of 30 C cm⁻². The sample synthesized using this standard GDE synthesis procedure was referred to as PC_{30C cm⁻²}. Figure 20c and f present the DHBT setup for the Cu foam GDE synthesis and the resulting Cu foam sample, respectively.

In addition to this standard procedure, the following changes were conducted individually:

- To compare the PC and DC modes on the morphology and activity of the resulting Cu foam GDEs, a sample was electrodeposited at a continuous cathodic direct current density of 0.67 A cm⁻² for 45 s and was abbreviated as DC_{30C cm⁻²}.
- To study the effect of DHBT charge density on the GDEs performance, additional GDEs were synthesized at cathodic charge densities of 60 and 90 C cm⁻² by applying 4500 and 6750 pulse-pause cycles, respectively, alongside the reference sample deposited at 30 C cm⁻² and 2250 pulse-pause cycles. The two additional samples were abbreviated as PC_{60C cm⁻²} and PC_{90C cm⁻²}.

(c) Two kinds of additives were studied: DAT and Ag_2SO_4 ($\geq 99.5\%$, Honeywell Fluka), with four different electrolyte modifications performed individually as follows:

- (i) 0.2 M CuSO_4 , 1.5 M H_2SO_4 , and 4 mM DAT ($\text{pH} \approx -0.5$)
- (ii) 0.2 M CuSO_4 , 1.5 M H_2SO_4 , and 1 mM Ag_2SO_4 ($\text{pH} \approx -0.5$).
- (iii) 0.2 M CuSO_4 , 1.5 M H_2SO_4 , and 2 mM Ag_2SO_4 ($\text{pH} \approx -0.5$)
- (iv) 0.2 M CuSO_4 , 1.5 M H_2SO_4 , and 4 mM Ag_2SO_4 ($\text{pH} \approx -0.5$)

The Ag-mediated GDEs were labeled according to the Ag^+ concentration in the DHBT bath of each sample as $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$, $\text{PC}_{30\text{C cm}^{-2}}^{4\text{mM Ag}^+}$, and $\text{PC}_{30\text{C cm}^{-2}}^{8\text{mM Ag}^+}$, and the DAT-mediated sample as $\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$.

(d) To evaluate the effect of DHBT bath cooling, a sample was electrodeposited at 4 °C using an ice bath and was denoted as $\text{PC}_{30\text{C cm}^{-2}}^{4^\circ\text{C}}$.

After the DHBT, the Cu foam GDE was immediately removed from the bath and rinsed sequentially with Milli-Q water, a 0.1 M KHCO_3 solution to neutralize any residual acid in the foam pores, and a final Milli-Q water rinse. The GDE was left to dry completely and then weighed. The ionomer solution used for the hydrophobic treatment was prepared by mixing 15 mg of PFSA (800 EW, 3 MTM) with 10 mL of a 95:5 (v/v) 1-propanol/water solution and stirring the mixture for 24 hours using a magnetic stirrer. Then, each geometric 1 cm² of the Cu foam GDE surface was drop-cast with 5 μL of the ionomer solution, and then the GDE was left to dry for a period of 24 hours before any measurements.

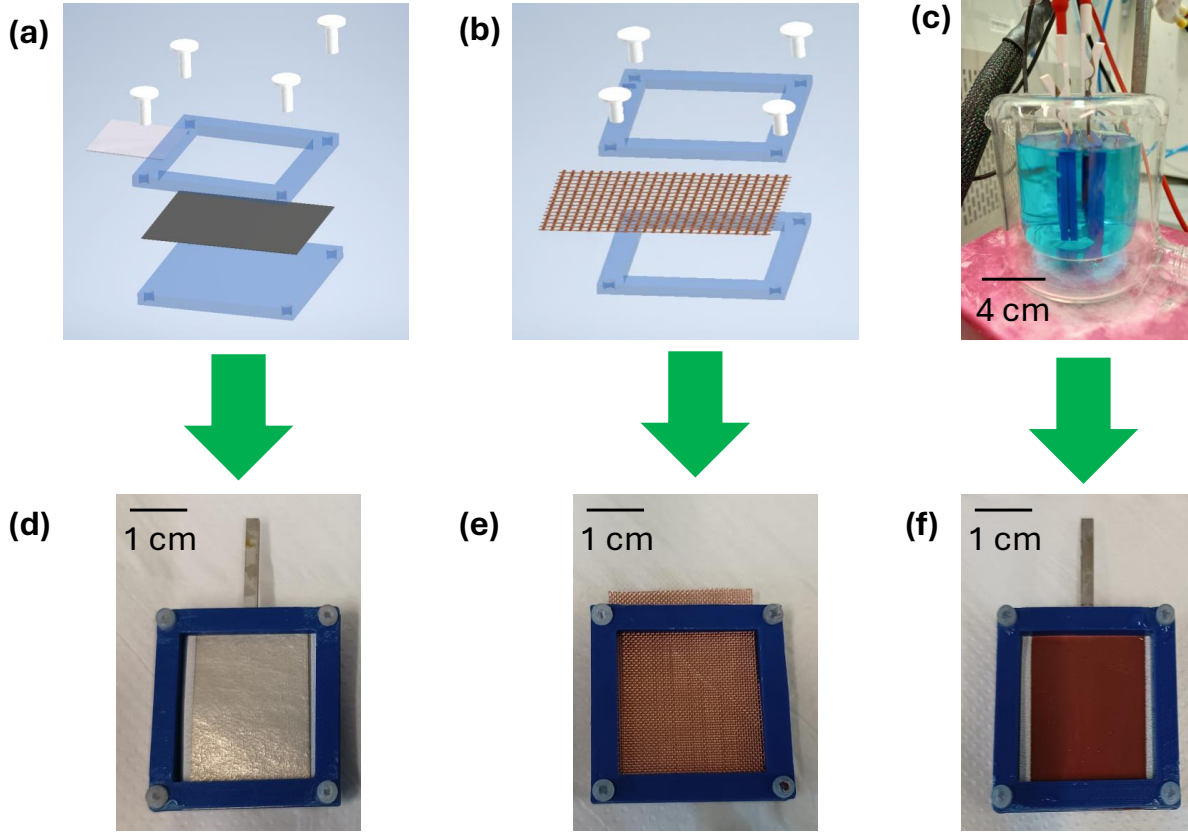


Figure 20: Schematic representations of the 3D-printed WE (a) and CE (b) holders with the respective digital photos of the electrodes mounted in their holders (d and e), a digital photo of the DHBT configuration (c), and a digital photo of a Cu foam GDE after DHBT (f)

2.3 Cu Foam Morphological Characterization

2.3.1 Gravimetric Analysis

A Kern ABT 220-5DM balance with a 0.01 mg resolution was used to weigh the Cu foil (the substrate for model Cu foams), Ag-sputtered PTFE fabric (the substrate for Cu foam GDEs) before DHBT, and the dry Cu foam samples after DHBT. The mass of the deposited Cu foam was calculated by subtracting the initial substrate mass from the final mass measured after DHBT. The FE for the electrodeposition ($FE_{Deposition}$) was determined using Equation 9, where F is Faraday's constant, Q is the total charge passed during DHBT, $m_{Deposited}$ is the electrodeposited mass, M is the atomic mass of Cu, and n is the number of electrons required to deposit one Cu atom.

$$FE_{Deposition} = \frac{m_{Deposited} \cdot n \cdot F}{Q \cdot M} \cdot 100\% \quad (9)$$

2.3.2 X-Ray Analysis of Cu Foam Samples

XRD patterns of the Cu foams were recorded on a Rigaku SmartLab diffractometer with a rotating Cu anode (wavelength = 1.54 Å) operated at 45 kV/200 mA, using a HyPix-3000 2D detector. Measurements were taken at 2θ values from 10 to 100 °, with a step size of 0.02 °, at a fixed incident angle of 0.35 °, and a scan rate of 8 ° min⁻¹. The XRD data were processed in Origin

software. Instrumental broadening was evaluated using the XRD pattern of a LaB₆ standard, and Equation 10 was used to correct the measured broadening ($\beta_{measured}$) for instrumental contributions ($\beta_{instrumental}$), yielding the corrected broadening ($\beta_{corrected}$). Subsequently, the Williamson-Hall plots were constructed for the model Cu foam samples based on Equation 11, where θ is the Bragg angle, K is the shape factor (typically 0.9), L is the crystallite size, λ is the X-ray wavelength, and ϵ is the micro-strain in the crystal lattice.^[110]

$$\beta_{corrected}^2 = \beta_{measured}^2 - \beta_{instrumental}^2 \quad (10)$$

$$\cos(\theta) \cdot \beta_{corrected} = \frac{K \cdot \lambda}{L} + 4\epsilon \cdot \sin(\theta) \quad (11)$$

XPS measurements were carried out at room temperature under ultrahigh vacuum (approximately 10^{-7} Pa) using a SPECS PHOIBOS 100 spectrometer with an Al K α X-ray source (1486.74 eV). High-resolution spectra were collected with a step size of 0.10 eV, while survey spectra were recorded with a step size of 0.80 eV, and the dwell time was 0.05 s per step. Prior to measurements, Cu foam samples were additionally washed to remove any unbound additives or residual H₂SO₄ that might be trapped in the pores. Specifically, the samples were rinsed in 0.1 M KHCO₃ for at least 5 minutes to neutralize any trapped acid, rinsed in Milli-Q water for at least 5 minutes, and dried under a N₂ stream. Survey and high-resolution spectra were normalized, baseline-corrected, and processed with Shirley background subtraction using Fityk software.

2.3.3 Scanning Electron Microscopy Imaging and Elemental Analysis

SEM images were acquired using the in-lens and secondary electron detectors of a Zeiss Ultra Plus scanning electron microscope (Carl Zeiss) equipped with a high-resolution field-emission gun at an acceleration voltage of 3.00 kV. Elemental analysis was conducted with a Bruker XFlash 6-100 energy-dispersive X-ray spectroscopy (EDX) detector at an acceleration voltage of 5.00 keV.

2.3.4 Contact Angle Measurements

To evaluate the hydrophobic properties of Cu foam GDEs, the contact angle was measured using a DataPhysics optical contact angle device. A 10 μ L droplet of Milli-Q water was dispensed onto the Cu foam GDE and then contact angle images were taken. The recorded images were subsequently analyzed using SCA 20 software to extract contact angle values.

2.4 Electrochemical Characterization of Cu Foam Samples

2.4.1 Electrochemical Characterization of Model Cu Foams in H-Cell Configuration

ECSA and CO₂RR chronoamperometric measurements (combined with online chromatographic analysis) were performed at room temperature in a custom gas-tight two-compartment glass H-cell assembled with three electrodes (Figure 21). The WE and RE shared the same compartment, while the CE was placed in the other compartment. The two compartments were separated by a Selemion anion exchange membrane (AGC Chemicals Europe), and each was filled with 45 mL of the electrolyte solution. The electrolyte consisted of 0.1 M KHCO₃ (>99.7%, Carl Roth) saturated with CO₂ (99.995%, Air Liquide), resulting in a pH of 6.8. A Cu foam (geometric area 1 cm²) served as the WE, a Pt mesh (mesh size 80, 2.5 cm $\times$ 3.5 cm, ALS) as the CE, and a commercial Ag/AgCl electrode (ALS) as the RE. All reported potentials were iR-corrected and referenced to RHE. Electrochemical control was provided by a Gamry Reference 3000 potentiostat, and CO₂

flow was regulated with a calibrated MFC (Bronkhorst). Before measurements, both catholyte and anolyte were purged with CO_2 for at least 10 minutes at a flow rate of 20 mL min^{-1} to ensure saturation. To convert unstable surface Cu oxide species to metallic Cu, the samples were activated by cyclic voltammetry. Specifically, the potential was cycled between -0.05 and -1.05 V at 100 mV s^{-1} for up to 20 CVs until stable current responses were obtained, with the catholyte stirred at approximately 1350 rpm. Then, the ECSA was measured under a CO_2 flow rate of 5 mL min^{-1} with no catholyte stirring. Two independent electrochemical methods were used for ECSA estimation, namely CV- and electrochemical impedance spectroscopy (EIS)-based methods.

In the CV-based method, CVs were recorded between 0.15 and 0.35 V (a window free of Faradaic currents) at scan rates from 10 to 100 mV s^{-1} . The sum of the charging and discharging currents (Δi) was plotted vs. scan rate (ν). The double-layer capacitance (C_{DL}) of the Cu foam was obtained as half the slope of that plot according to Equation 12. ECSA was then calculated using Equation 13, where C_{Ref} is the double-layer capacitance of a flat Cu surface with 1 cm^2 geometric area. C_{Ref} was determined from a polished and cleaned 1 cm^2 Cu foil by extracting the double-layer capacitance from the plot of the summed charging and discharging currents, using the extracted value as the reference capacitance.

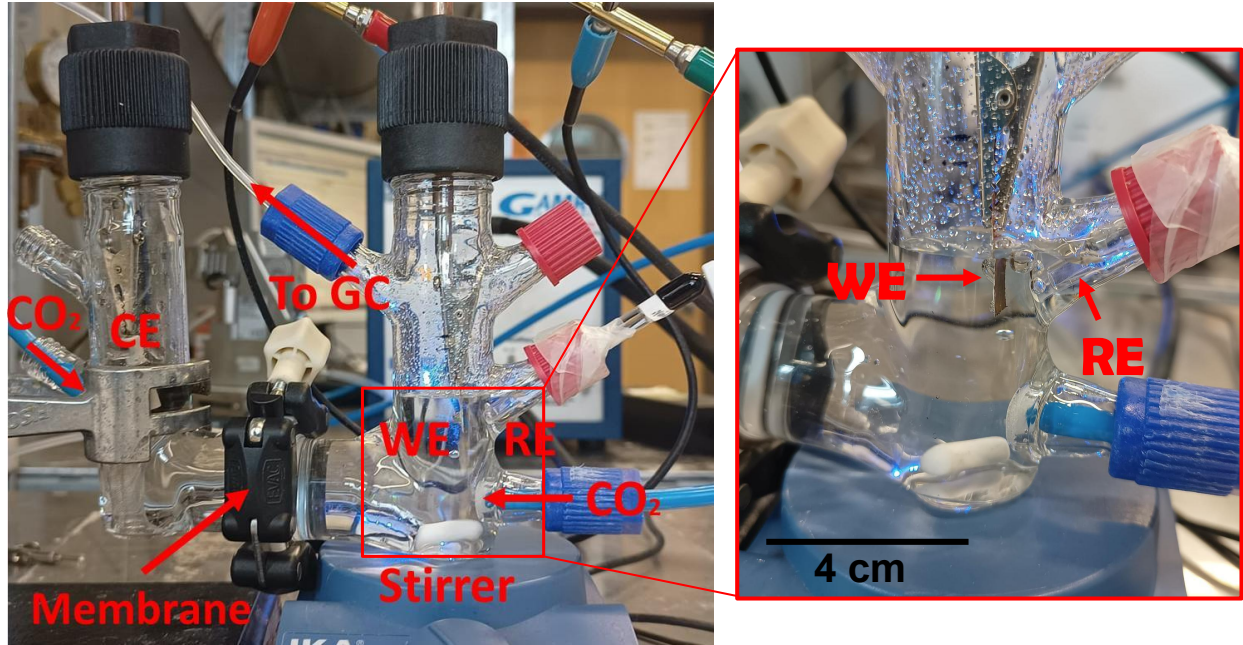


Figure 21: Digital photographs of the H-cell setup used for electrochemical measurements of the model Cu foam samples

In the EIS-based method, electrochemical impedance spectra were recorded at a non-Faradaic potential of 0.25 V with a 5 mV perturbation across a frequency range of 10 kHz to 0.5 Hz . The spectra were fitted in Aftermath software to an equivalent circuit consisting of the uncompensated solution resistance (R_u) in series with two constant phase elements (CPEs), as illustrated in Figure 22a. The high-frequency CPE was attributed to double-layer charging of the readily accessible outer surface and larger pores, while the low-frequency CPE represented full electrode charging.^[111–113]

$$C_{DL} = \frac{1}{2} \cdot \frac{d(\Delta i)}{d(\nu)} \quad (12)$$

$$ECSA = \frac{C_{DL}}{C_{Ref}} \quad (13)$$

The double-layer capacitance (C_{DL}) of the Cu foam was derived from the low-frequency CPE and inserted into Equation 13 to compute the ECSA. C_{Ref} for the EIS-based procedure was determined from the EIS data of a polished and cleaned Cu foil with a geometric area of 1 cm² acquired under identical conditions as the Cu foam samples. These spectra were modeled with a simplified equivalent circuit consisting of R_u in series with a single CPE (Figure 22b), and the fitted double-layer capacitance was taken as C_{Ref} .^[111–113]

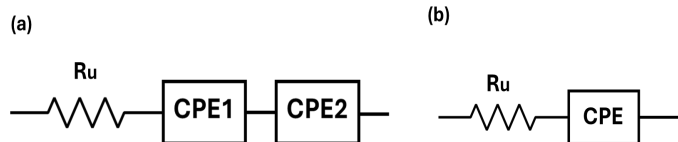


Figure 22: Equivalent circuit models used to fit the EIS data of the Cu foam sample (a) and Cu foil substrate (b)

After ECSA measurements, chronoamperometric CO₂RR experiments were conducted for one hour at applied potentials of -0.60, -0.75, -0.85, -0.95, or -1.05 V under a continuous CO₂ flow rate of 20 mL min⁻¹ and magnetic stirring at approximately 1350 rpm to improve CO₂ transport to the electrode. The cathode compartment headspace was routed directly to the 10-port valve of the online GC (Shimadzu GC-2014), which introduced the sample into serial HayeSep Q and HayeSep R columns, with high-purity Ar (Grade 5.0) used as the carrier gas. This enabled online detection and quantification of gaseous CO₂RR products every 15 minutes. The online GC was equipped with a thermal conductivity detector (TCD) for H₂ detection and a methanizer with a flame ionization detector (FID) for CO₂, CO, and hydrocarbons detection. The online GC was calibrated with a standard gas mixture (Riessner-Gase) containing H₂ (0.508 mol%), CO (0.05 mol%), CH₄ (0.051 mol%), C₂H₄ (0.051 mol%), C₂H₆ (0.00254 mol%), and CO₂ (rest).

After electrolysis, a catholyte sample was collected and analyzed for liquid products by an HPLC (LC-2010, Shimadzu) and a LGC (Nexis GC-2030, Shimadzu). The HPLC and LGC were calibrated for the expected analytes. For HPLC calibration, mixed standard solutions of formic acid ($\geq 99.7\%$, Sigma-Aldrich) and acetic acid ($\geq 99.99\%$, Sigma-Aldrich), both at concentrations of 0.04 - 2.00 mM, were used. For LGC calibration, mixed standard solutions of methanol ($\geq 99.9\%$, Merck) 0.13 - 5.08 mM; ethanol ($\geq 99.9\%$, Merck) 0.07 - 2.45 mM; acetone ($\geq 99.5\%$, Sigma-Aldrich) 0.06 - 2.49 mM; 1-propanol ($\geq 99.5\%$, Merck) 0.04 - 1.70 mM; 2-propanol ($\geq 99.9\%$, Sigma-Aldrich) 0.04 - 1.69 mM; allyl alcohol ($\geq 99\%$, Sigma-Aldrich) 0.05 - 1.87 mM; propionaldehyde ($\geq 98\%$, Sigma-Aldrich) 0.04 - 1.53 mM; and acetaldehyde ($\geq 99.5\%$, Sigma-Aldrich) 0.03 - 1.04 mM were used. All calibration curves exhibited good linearity across their ranges. Figure 23 depicts examples of the chromatograms of the standard mixtures injected into the online GC, LGC, and HPLC.

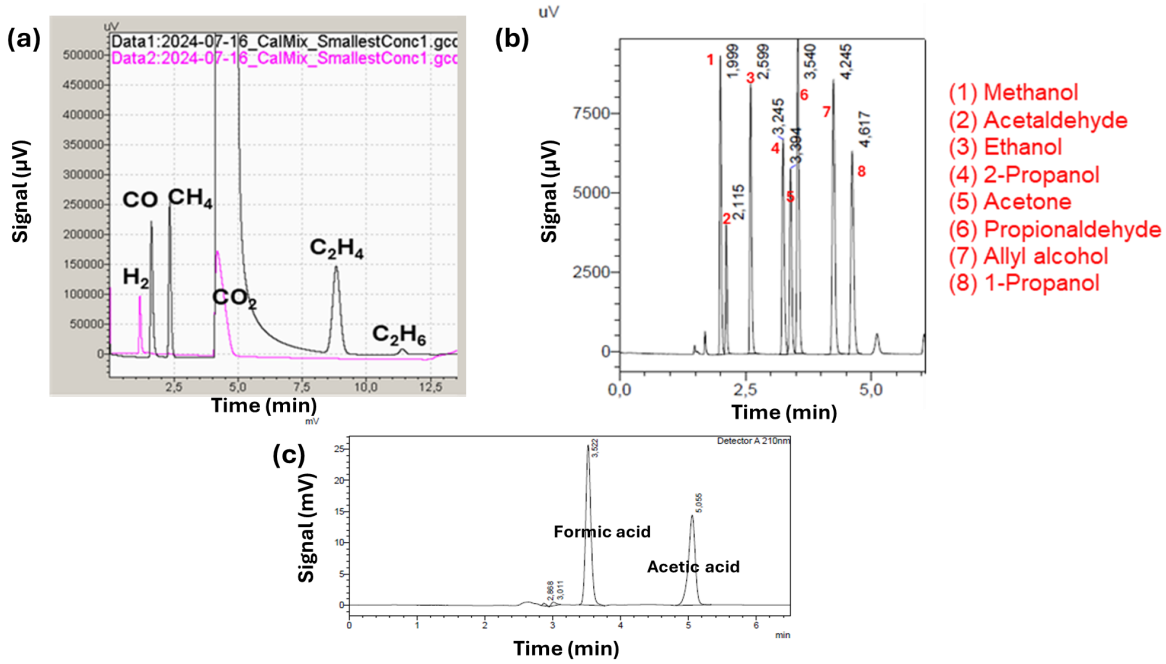


Figure 23: Chromatograms from the online GC (a), LGC (b), and HPLC (c), each illustrating the CO₂RR products for which the respective instrument is calibrated

FEs for each CO₂RR product (FE_i) were obtained by dividing the product partial current density (j_i) by the total measured current density (I_t) according to Equation 14. Partial current densities for gaseous and liquid products were calculated using Equations 15 and 16, respectively, with the following variables: gas product mole fraction (x_i), number of electrons transferred (z_i), applied molar flow rate (n'), liquid product concentration (c_i), catholyte volume (V_c), and electrolysis time (t). The applied molar flow rate n' was calculated from the ideal gas law using pressure (P), applied volumetric gas flow rate (V'), the general gas constant (R), and absolute temperature (T).

$$FE_i = \frac{j_i}{I_t} \cdot 100 \quad (14)$$

$$j_i = x_i \cdot z_i \cdot F \cdot n' \quad (15)$$

$$j_i = \frac{c_i \cdot z_i \cdot F \cdot V_c}{t} \quad (16)$$

$$n' = \frac{P \cdot V'}{R \cdot T} \quad (17)$$

2.4.2 Electrochemical Characterization of Cu Foam Gas Diffusion Electrodes in Flow Cell Configuration

Electrochemical characterization of Cu foam GDEs was carried out in the flow cell setup shown in Figures 24 - 25. The cell comprised cathode and anode compartments separated by a Selemion AEM. A dual-channel peristaltic pump (Shenzhen Pump YZ1515x) provided independent circulation of the catholyte and anolyte between their reservoirs and respective compartments. Each of the catholyte and anolyte reservoirs was filled with 250 mL of 1 M KHCO₃. The cathode contained

distinct gas and electrolyte chambers, with the Cu foam GDE positioned between them, such that the CL faced the electrolyte chamber and the PP macro-porous layer faced the CO₂ chamber. CO₂ was continuously supplied using a calibrated MFC to both the gas chamber and anolyte reservoir. A backpressure controller (BPC, Bronkhorst) maintained 30 mbar at the CO₂ chamber outlet, and the BPC outlet stream was routed into the catholyte gas-tight reservoir headspace, from which the gas stream could be directed through a three-port valve either to the online GC or a bubble flow meter to monitor the flow rate of the gas stream carrying the unreacted CO₂ plus CO₂RR gaseous products. In all GDE experiments, the CE was a Pt mesh (mesh 80, 2.5 cm × 3.5 cm, ALS), the RE was a HydroFlex RHE (Gaskatel GmbH, Germany), and the WE was the Cu foam GDE. Unless stated otherwise, CO₂ flow rate was 20 mL min⁻¹, and the flow rate of the electrolyte was 50 mL min⁻¹.

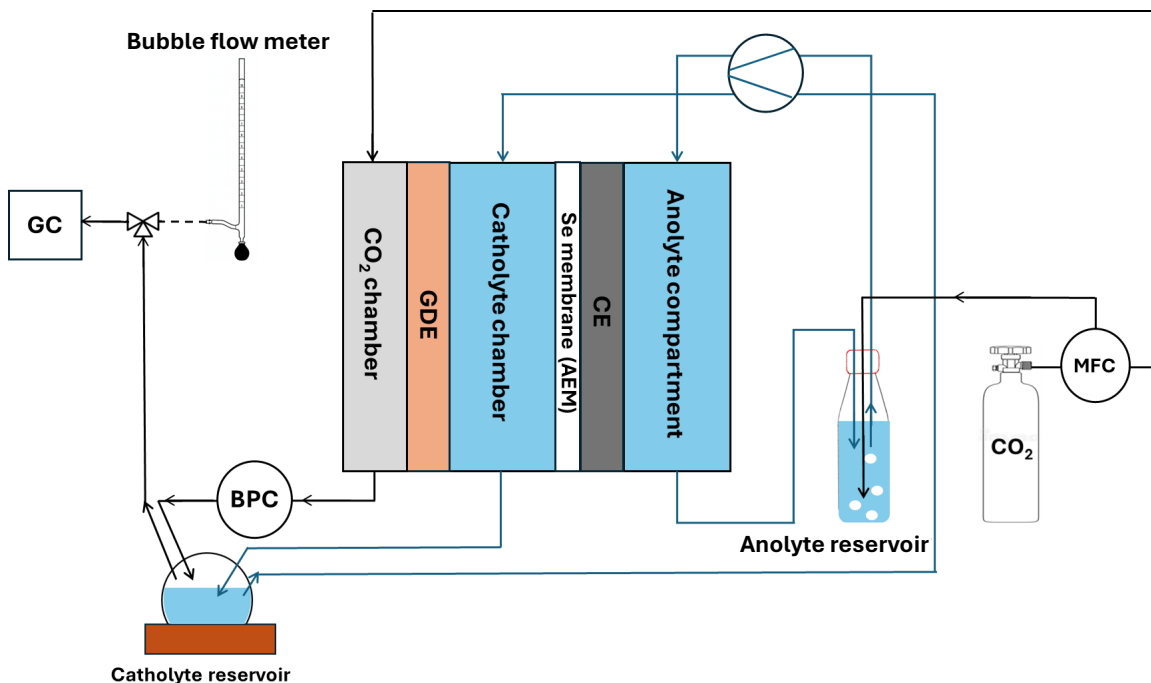


Figure 24: Schematic representation of the Cu foam GDE electrochemical measurements configuration

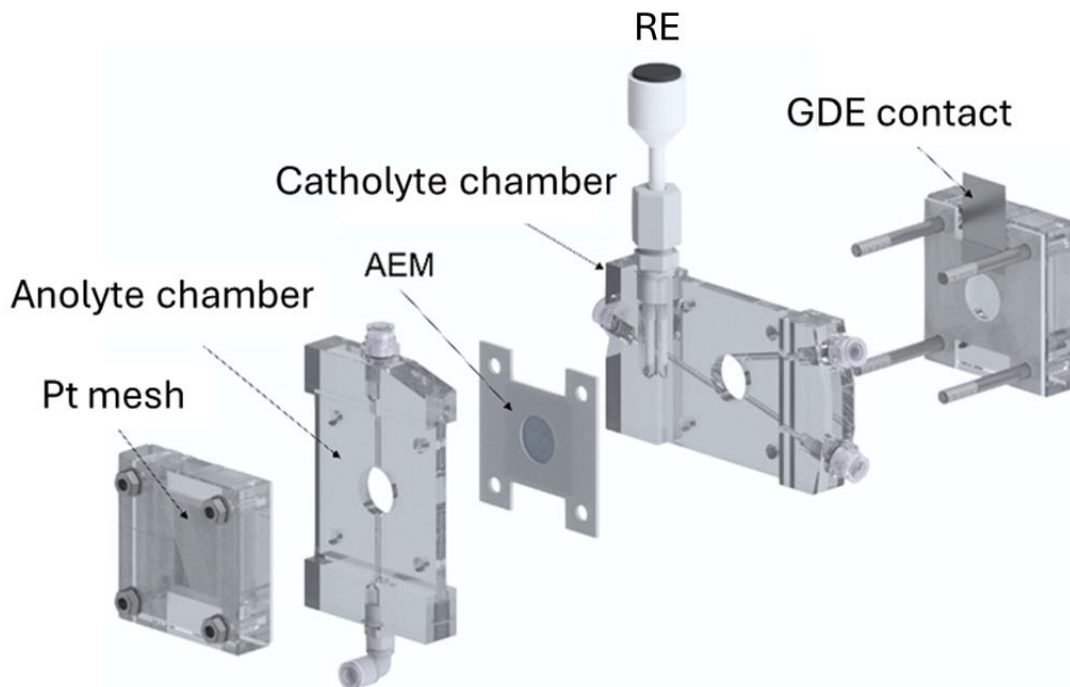


Figure 25: Illustration of the different parts of the GDE flow cell, obtained from reference^[82]

The electrochemical measurements of the Cu foam GDEs started with collecting CVs from -0.05 to -1.05 V at a scan rate of 100 mV s^{-1} , repeated for up to 20 cycles until reproducible currents were obtained to reduce unstable surface oxides. Then, for ECSA determination, CO_2 flow rate was reduced to 5 mL min^{-1} , and the pump was paused to minimize mechanical interference with the charging and discharging of the GDE double-layer. ECSA CVs were then collected in the potential range between 0.15 and 0.35 V at scan rates from 10 to 100 mV s^{-1} , and ECSA was calculated using Equations 12 and 13, as for model Cu foam samples. After ECSA measurements, CO_2 flow and electrolyte circulation were returned to 20 mL min^{-1} and 50 mL min^{-1} , respectively, and chronopotentiometric CO_2 electrolysis was performed at cathodic current densities of 50, 100, 150, and 200 mA cm^{-2} , each for 1.5 hours, with online GC injections performed every 15 minutes.

For the GDE samples, online GC calibration was extended to cover a broader range of gas product mole fractions. Specifically, two standard gas mixtures (Riessner-Gase, Germany) were used to calibrate the online GC for expected gas products in the following ranges: H_2 (0.999 - 14.964 mol%), CO (0.114 - 2.003 mol%), CH_4 (0.105 - 1.997 mol%), C_2H_4 (0.105 - 2.017 mol%), and C_2H_6 (0.00511 - 0.0513 mol%). The resulting calibration curves exhibited excellent linearity across the specified ranges.

After electrolysis, a catholyte sample was collected for the analysis of liquid products using HPLC and LGC. Equations 14-17 were used to calculate the FE_i of CO_2RR products. In contrast to the model Cu foam FE_i calculations, V' for the GDEs represents the actual flow rate of the gas injected into the GC, as measured by the bubble flow meter, to account for the significant change in the gas flow rate due to the intense electrolysis taking place at high current densities.

2.5 Operando CO₂RR Measurements

2.5.1 Potential-Dependent Operando Surface-Enhanced Raman Spectroscopy

Potential-dependent operando SERS experiments were conducted by Prof. Holger Dau's group using a commercial Raman flow cell (Shanghai Chuxi Industrial Co.), as shown in Figure 26. A CO₂-saturated 0.1 M KHCO₃ solution served as the electrolyte and was continuously circulated between the cell and an external reservoir via a peristaltic pump operated at a flow rate of 20 mL min⁻¹.

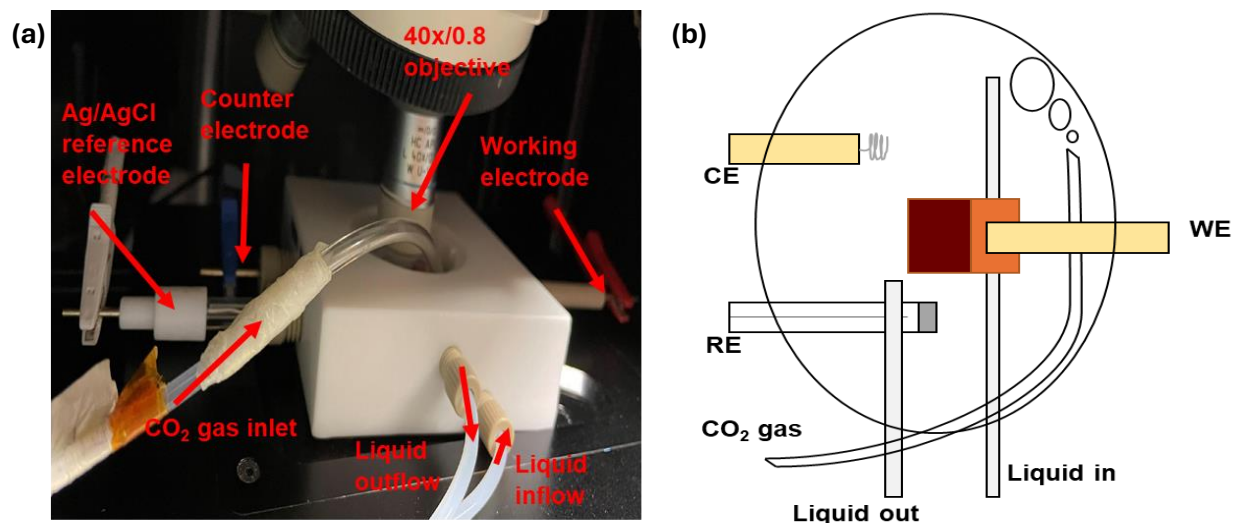


Figure 26: A digital photograph (a) and top-view schematic representation (b) of the cell used for potential-dependent operando surface-enhanced Raman spectroscopy experiments

Simultaneously, CO₂ gas was supplied at a flow rate of 20 mL min⁻¹ using a calibrated MFC. A model Cu foam sample was used as the WE, a standard Ag/AgCl electrode as the RE, and a Pt coil as the CE. SERS measurements were performed using a 40x/0.8 water-immersive objective and a 633 nm He-Ne laser. Prior to each measurement, the laser source was calibrated using a Si plate and operated at low intensity (1.3 mW) in streamline mode to minimize sample heating. Spectral acquisition covered two regions: 106-1967 cm⁻¹ and 1926-3384 cm⁻¹, taking a total time of 30 s. The potential-dependent SERS series was recorded during successive chronoamperometric experiments, each lasting 2 minutes, beginning at the OCP and progressing through the potential range from 0 to -0.9 V. At each applied potential, spectra were acquired at 30 s and 60 s after the onset of the chronoamperometric run. For the measurements conducted in a K₂HPO₄/KH₂PO₄ buffer solution of pH 6.8 (denoted as KPi solution), the same experimental setup and parameters were used, except that the electrolyte was an N₂-saturated 0.1 M KPi solution. Spectra were processed using Renishaw WiRE software by applying a baseline correction with a polynomial of order 7-11, followed by smoothing using a fourth-order polynomial with averaging over every 25 points. Subsequently, normalization was performed according to the method described in reference^[114], whereby the baseline-corrected and smoothed spectra were normalized to the baseline average intensity. Reference spectra were collected from a concentrated DAT solution (1.981 g DAT in 20 mL of Milli-Q water) and from Cu-DAT precipitate (prepared by mixing 99 mg DAT into 20 mL of 50 mM CuSO₄ solution). For the DAT solution measurement, the laser power was 1.3 mW, and the acquisition time was 30 s. For the Cu-DAT precipitate measurement, the laser power was 5.6 mW, and the

acquisition time was 80 s. To improve the signal-to-noise ratio, the spectra were taken 3 times and averaged.

2.5.2 Local Alkalization Raman Spectroscopy Measurements

Local alkalization was measured using the method developed by Klingan et al.^[96] The experimental configuration for the local alkalization studies matched that described in Section 2.5.1, except that a 473 nm blue laser with 5.6 mW power was used to minimize the excitation of surface-adsorbed species, and each spectrum was acquired for 80 s. A Teflon film protected the water-immersion objective, and a droplet of water was placed between the film and the objective to prevent abrupt refractive-index changes. To relate Raman features to the local pH, a series of KHCO_3 solutions with different pH values was measured. The spectra of these solutions (Figure 27a) display peaks at 1015 and 1363 cm^{-1} (for HCO_3^-) and at 1065 cm^{-1} (for CO_3^{2-}). A calibration curve was derived from the intensities of these three peaks, as shown in Figure 27b, correlating the ratio y , calculated from Equation 18, and the solution pH values. This correlation resulted in a sinusoidal regression relation, which is described by Equation 19.

$$y = \frac{I(\text{CO}_3^{2-})}{I(\text{HCO}_3^-) + I(\text{CO}_3^{2-})} = \frac{I(1065\text{cm}^{-1})}{I(1015\text{cm}^{-1}) + I(1065\text{cm}^{-1}) + I(1363\text{cm}^{-1})} \quad (18)$$

$$y = 0.92567 - \frac{0.78476}{1 + 10^{pH-9.89282}} \quad (19)$$

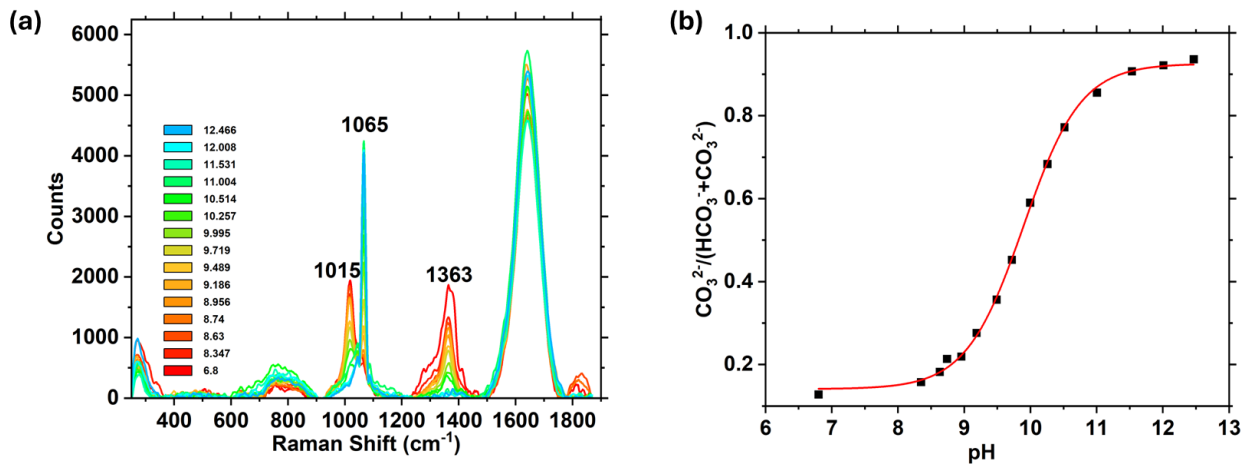


Figure 27: Surface-enhanced Raman spectra of KHCO_3 solutions with pH values ranging from 6.8 to 12.466 collected using a 473 nm laser at a power of 5.6 mW and an acquisition time of 80 s (a), and the corresponding local alkalization calibration curve (b)

Before local alkalization measurement experiments, 10 CVs were collected at 100 mV s^{-1} in the potential range of -0.05 to -1.05 V to reduce surface unstable oxides. Sequentially, a chronopotentiometric scan was conducted at -5 mA cm^{-2} for one hour. During chronopotentiometry, the laser was focused either on the deposited Cu material at the foam bridge or at the bottom of a macro-pore void, and spectra in the range 248-1869 cm^{-1} were recorded continuously. Data analysis proceeded by calculating the intensity ratio y and then determining the local pH using Equation 19.

2.6 Statistical Information

Gravimetric measurements (deposited Cu mass and deposition FE) are presented as the mean of 15-20 independent replicates, with error bars indicating the standard deviation.

ECSA values for the model Cu foams are reported as the mean of 3-6 independent determinations, with error bars indicating the standard deviation.

For each DHBT condition, 2-4 independent SEM datasets were acquired. Surface pores in the SEM images were annotated using Apeer.com online tools and subsequently processed with a Python script based on the scikit-image library to remove pores touching the image edges and compute individual pore areas and equivalent diameters. From the annotated images, we typically extracted several hundred to a few thousand equivalent pore diameter values per DHBT condition. These equivalent diameter values were used to construct the pore-diameter distributions. The number of equivalent pore diameters contributing to each distribution is shown in the corresponding figure. The mean pore diameter is given as the expected value of the distribution, and the error bars represent the standard error. The analysis workflow is illustrated in Figure 28.

Foam thickness is reported as the mean of six measurements taken at different positions on each sample, with the associated uncertainty expressed as the standard deviation.

Two outliers were identified in the correlation between foam thickness and mean pore diameter. This correlation was evaluated both including and excluding these outliers, and the handling of outliers is described in Section 3.6 and indicated in Figure 107.

CO₂RR FEs and partial current densities are reported as the mean of 2-4 independent measurements for each sample at each specified potential, and the error bar denotes the standard deviation.

The Cu foam GDE results represent initial successful attempts to adapt model Cu foams to GDE architectures.

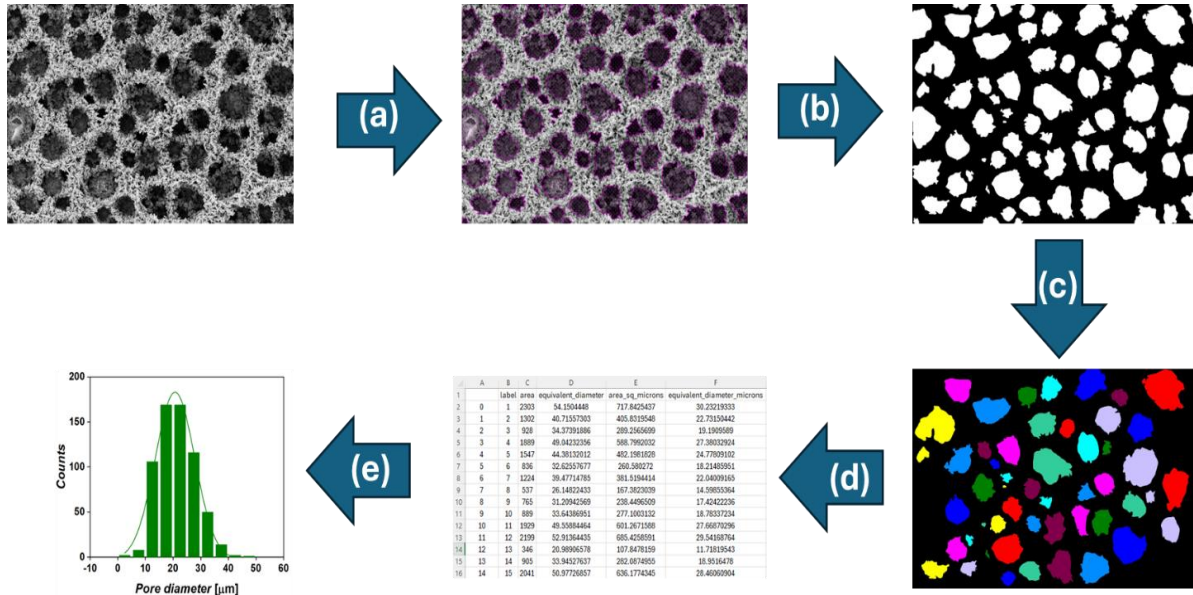


Figure 28: Steps of pore diameter analysis: annotation of the original images (a); extraction of annotated pixels (b); exclusion of edge-touching pores (c); calculation of pore area and diameter (d); and plotting the final pore diameter distribution (e)

3 Results & Discussion

3.1 Current-Time Series

The influence of the two primary DHBT parameters, deposition current density and deposition time, was investigated by preparing Cu foams under different current densities and durations, followed by morphological and CO₂RR performance characterization. Two cathodic DHBT direct current densities, 1 A cm⁻² and 2 A cm⁻², were applied. For the 1 A cm⁻² condition, electrodeposition times of 10, 20, and 30 s were used, while for the 2 A cm⁻² condition, the durations were 5, 10, and 15 s. Fixing the current density while varying the deposition times isolated the effect of DHBT duration and enabled the visualization of successive DHBT stages. Each sample produced at 1 A cm⁻² was paired with a counterpart produced at 2 A cm⁻² that received the same total charge density, thereby excluding the effect of deposition charge density while comparing the effect of current density.

Interconnected foam networks were observed throughout the entire current-time series, as illustrated in Figure 29, confirming that the applied cathodic bias effectively sustained both H₂ evolution and Cu deposition at considerable rates. Top-view SEM images at 200× magnification show a gradual increase in surface pore diameters as the DHBT time is extended. This trend indicates that longer DHBT durations promote H₂ bubble coalescence, producing a hierarchical pore architecture with smaller cavities adjacent to the substrate and larger cavities toward the electrolyte. Raising the DHBT current density produced foams with higher pore densities and smaller pore diameters, as seen when comparing SEM images of samples with equal total charge, e.g., (1Acm⁻² 10s) vs. (2Acm⁻² 5s), and (1Acm⁻² 20s) vs. (2Acm⁻² 10s). This behavior suggests that higher currents favor more HER nucleation sites on the substrate, whereas at lower currents, H₂ evolution is more strongly influenced by the initially present surface defects. All six Cu foams displayed surface nano-dendrites of varying sizes, as observed in the 3000x magnification SEM images. At a fixed current density, longer DHBT times produced larger nano-dendrites on the top surface. Conversely, increasing the DHBT current density resulted in smaller nano-dendrite features. Pore diameter distributions were extracted from SEM images to determine the mean pore diameter. Moreover, cross-sectional SEM images were used to measure foam thickness (Figure 30). Details on the pore diameter and foam thickness analysis, together with the associated statistical information, are described in Section 2.6.

A positive relationship between pore diameter and nano-dendrite size can be made, indicating an enhanced electrolyte stirring at the electrode interface when larger H₂ bubbles form. Specifically, larger bubbles, produced at a lower current density or longer deposition times, increase mass transport of Cu²⁺ ions from the bulk electrolyte to the electrode surface, decreasing the diffusion layer thickness and raising the limiting current density. An increased limiting current density reduces the overpotential for Cu electrodeposition^[115], which in turn favors the growth of larger nano-dendrites. In contrast, smaller bubbles, obtained at a higher current densities or shorter deposition durations, exhibit a weaker stirring effect, lowering the limiting current density for Cu electrodeposition, and consequently resulting in smaller nano-dendrites. Experimental support for this hypothesis is provided in Section 3.4, where external mass convection was introduced during DHBT. The sample (2Acm⁻² 5s) exhibited the smallest mean pore diameter ($9.4 \pm 0.1 \mu\text{m}$), the highest pore density ($\approx 3541 \text{ pore mm}^{-2}$), and the lowest foam thickness ($23.0 \pm 1.5 \mu\text{m}$). Conversely, the sample (1Acm⁻² 30s) showed the largest mean pore diameter ($36.7 \pm 0.5 \mu\text{m}$), the lowest pore density ($\approx 346 \text{ pore mm}^{-2}$), and the greatest foam thickness ($62.0 \pm 4.7 \mu\text{m}$).

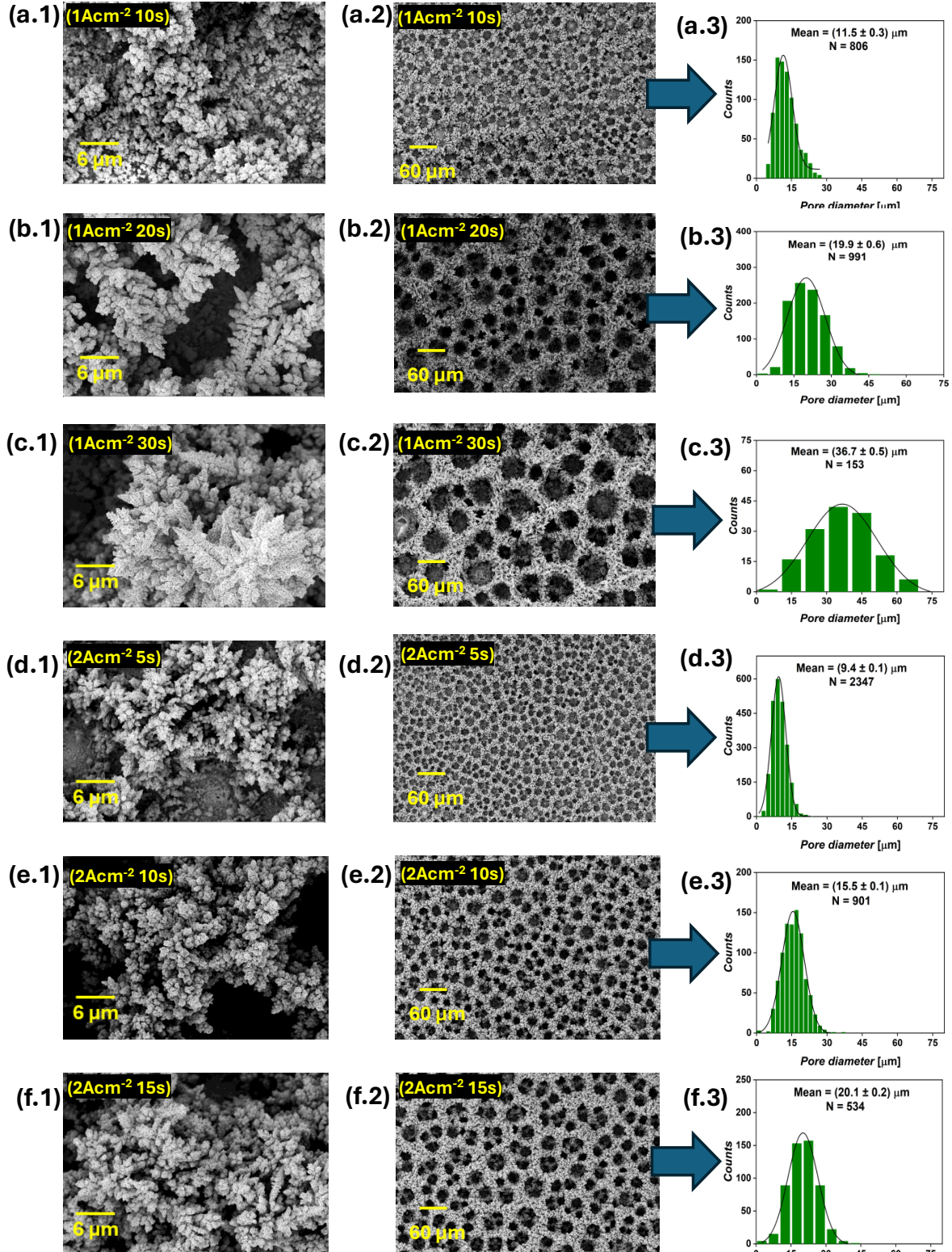


Figure 29: Top-view SEM images of the current-time DHBT series, presenting the surface nanostructures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the (1Acm⁻² 10s) (a), (1Acm⁻² 20s) (b), (1Acm⁻² 30s) (c), (2Acm⁻² 5s) (d), (2Acm⁻² 10s) (e), and (2Acm⁻² 15s) (f), where N denotes the number of pores from which the pore diameter distribution was obtained

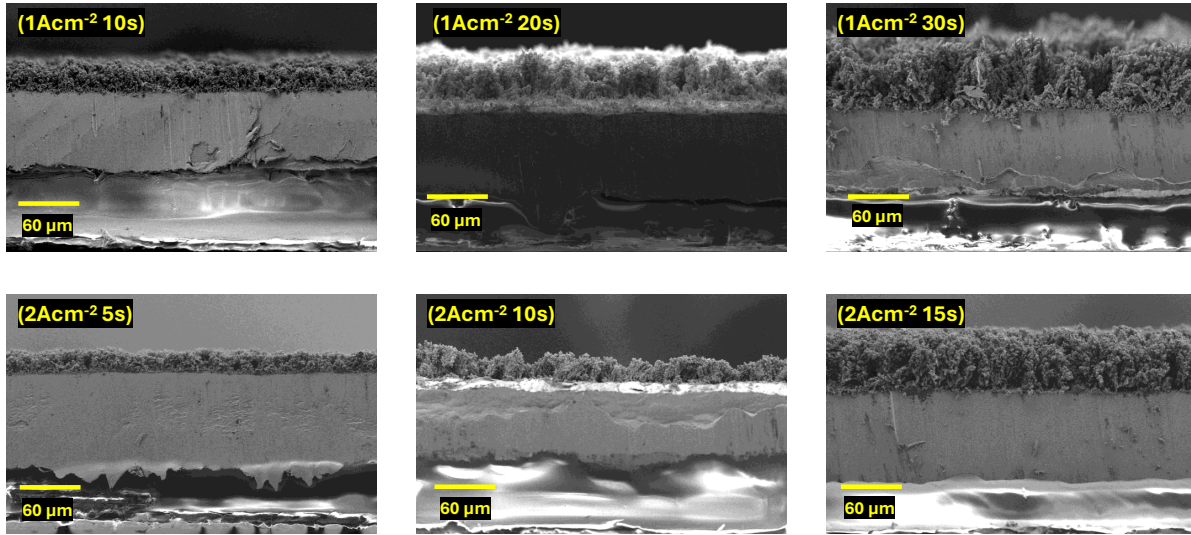


Figure 30: Examples of the cross-sectional SEM images of the current-time series

In this work, samples similar to the (2Acm^{-2} 5s) and (1Acm^{-2} 30s) foams are referred to respectively as "compact structures" and "open structures". Figure 31a presents the gravimetric analysis and the deposition FEs of the current-time series. At fixed DHBT current densities (1 A cm^{-2} or 2 A cm^{-2}), extending the DHBT duration produced a steady rise in the mass density of electrodeposited Cu. For example, at 1 A cm^{-2} , the Cu mass densities for the samples (1Acm^{-2} 10s), (1Acm^{-2} 20s) and (1Acm^{-2} 30s) were 1.5 ± 0.1 , 3.1 ± 0.3 , and $4.8 \pm 0.2\text{ mg cm}^{-2}$, respectively, consistent with the increased DHBT charge over time. These values correspond to FEs of $46 \pm 2\%$, $48 \pm 4\%$, and $49 \pm 2\%$, indicating that DHBT duration strongly affects the deposited Cu mass density while leading only to a modest impact on electrodeposition FEs. From an engineering standpoint, higher FEs for metal deposition are desirable. By contrast, raising the DHBT current density from 1 A cm^{-2} to 2 A cm^{-2} led to lower Cu mass densities of 1.2 ± 0.1 , 2.4 ± 0.2 , and $3.8 \pm 0.2\text{ mg cm}^{-2}$ for the (2Acm^{-2} 5s), (2Acm^{-2} 10s), and (2Acm^{-2} 15s) samples, with deposition FEs of $36 \pm 4\%$, $37 \pm 3\%$, and $39 \pm 2\%$, correspondingly.

These gravimetric observations, together with the SEM results, suggest that higher current densities increase the number of H_2 nucleation sites and the amount of released H_2 during DHBT, which reduces the FEs for Cu deposition. The ECSA values of the Cu foam samples reported in this work were obtained from the double-layer capacitance C_{DL} extracted using CV and EIS measurements at non-Faradaic potentials, as explained in detail in Section 2.4.1. All ECSA results were normalized to the geometric area of the Cu foam samples and reported in the unit of $\text{cm}^2_{\text{ECSA}}\text{ cm}_{\text{geo}}^{-2}$. Figure 31b represents the ECSA values of the current-time series. Examples of the CV and EIS results used for ECSA estimation in this work are shown in Figures 32 and 33, respectively. Clearly, the charging and discharging currents of the Cu foam double-layer capacitance increased with the scan rate, and the plot of their summation vs. scan rate was linear. Additionally, EIS experimental data were well fitted to the proposed equivalent circuit models.

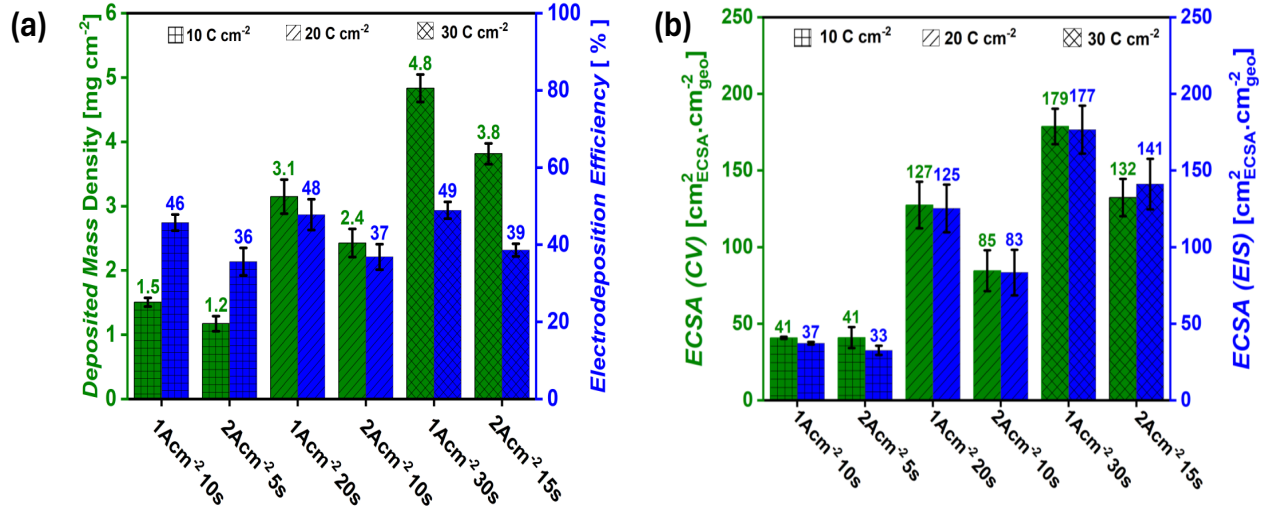


Figure 31: Gravimetric analysis (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis) of the current-time series

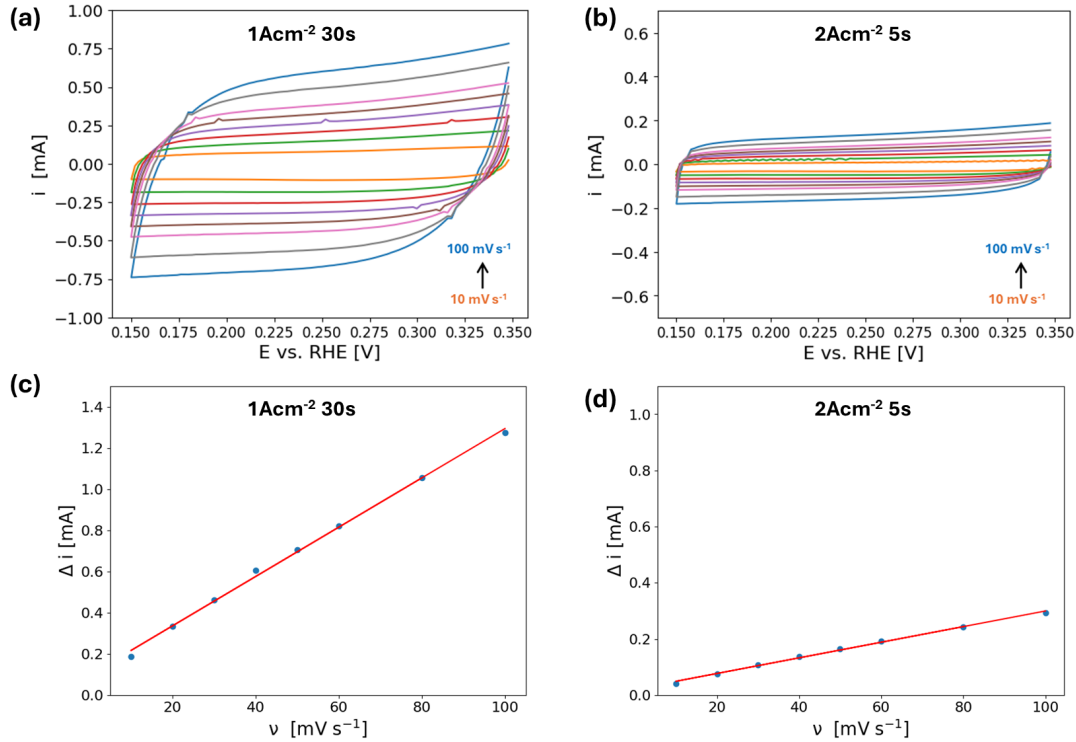


Figure 32: Examples of the CV curves (a and b) and the extracted plots of the summation of charging and discharging currents vs. scan rate (c and d) used for ECSA determination of the samples (1Acm⁻² 30s) and (2Acm⁻² 5s), correspondingly. Refer to Section 2.6 for the statistical analysis of the ECSA calculations

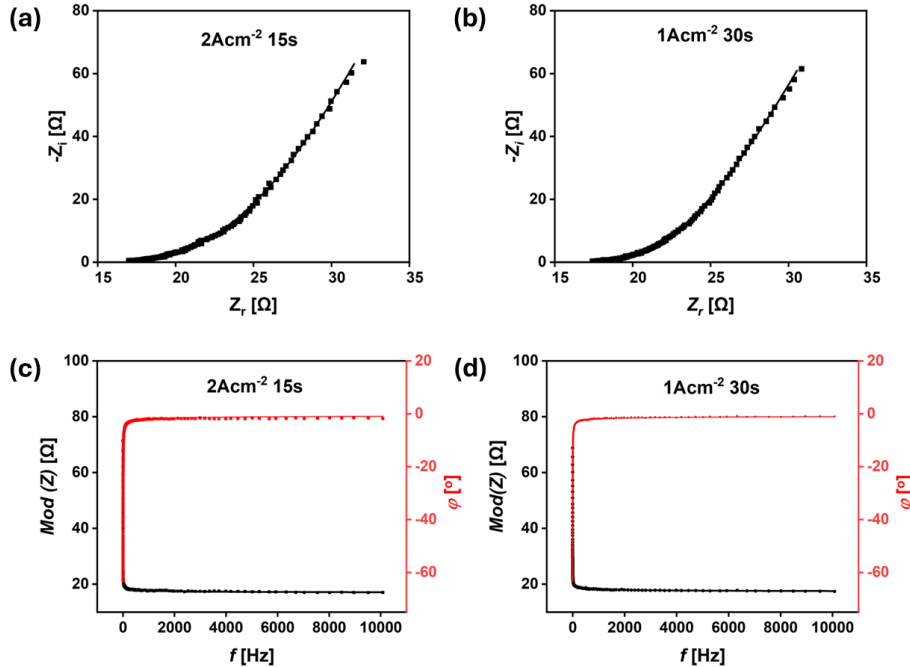


Figure 33: Examples of fitted EIS results used for ECSA determination represented as Nyquist plots (a and b) and Bode plots (c and d) for (2Acm^{-2} 15s) and (1Acm^{-2} 30s) samples, respectively. Experimental data are shown as scattered points, while the corresponding fitted curves are depicted as solid lines. Refer to Section 2.6 for the statistical analysis of the ECSA calculations

For all Cu foam samples, both CV- and EIS-based ECSA values agreed closely. Therefore, only the CV-based ECSA values were mentioned in the text. In line with SEM and gravimetric observations, raising the DHBT current density while keeping the total electrodeposition charge density constant reduced the ECSA. For example, at a DHBT charge density of 20 C cm^{-2} , increasing the applied current density from 1 A cm^{-2} to 2 A cm^{-2} decreased the ECSA from 127 ± 15 to $85 \pm 13\text{ cm}^2_{\text{ECSA}}\text{ cm}_{\text{geo}}^{-2}$. Conversely, prolonging the DHBT duration led to an increase in the ECSA. For instance, at 1 A cm^{-2} , the ECSA rose from 41 ± 1 to $179 \pm 12\text{ cm}^2_{\text{ECSA}}\text{ cm}_{\text{geo}}^{-2}$ when the deposition time was extended from 10 to 30 s.

The results of the current-time series are consistent with earlier studies, showing that longer DHBT times yield more open foam morphologies, while raising the DHBT current densities increases the number of H_2 bubble nucleation sites, which in turn raises pore density.^[89] Thus, it is possible to produce hierarchical architectures merely by tuning the DHBT current density or time. This feature renders the DHBT an ideal and versatile method for different applications. For instance, open Cu foams, with their high conductivity and relatively large surface area, are particularly useful as current collectors in batteries and supercapacitors.^[116] In a previous study, DHBT-synthesized compact Ag foams exhibited superior electrocatalytic activity towards the reduction of CO_2 into CO .^[74] Similarly, compact Cu foams reported in the current-time series can be good candidates for CO_2 conversion to C_{2+} products. To support this hypothesis, the CO_2RR performance of the current-time series was evaluated in an H-cell configuration, with online analysis of CO_2RR gaseous products and post-electrolysis analysis of CO_2RR liquid products, as detailed in Section 2.4.1.

Figure 34 shows CO_2RR FEs obtained from the current-time series. The major CO_2RR products

were formate, CO, ethylene, ethanol, 1-propanol, and the parasitic H_2 . Additionally, negligible FEs of methanol, ethane, allyl alcohol, acetaldehyde, acetone, and propionaldehyde were detected. Formate and CO FEs were dominant at less negative potentials (-0.6 to -0.85 V) and became negligible at more negative potentials (-0.95 to -1.05 V). For example, the sample (2Acm^{-2} 5s) exhibited respective formate and CO FEs of $48 \pm 7\%$ and $25 \pm 4\%$ at -0.6 V, which decreased to $3 \pm 1\%$ and $1 \pm 0\%$ at -1.05 V. Similarly, the sample (2Acm^{-2} 15s) showed a comparable trend, with formate FE declining from $50 \pm 5\%$ to $2 \pm 0\%$, and CO FE dropping from $18 \pm 2\%$ to 0% when the applied potential was shifted from -0.6 to -1.05 V. Methane displayed considerable FEs only at the most negative potential tested (-1.05 V), and the maximum CH_4 FE in this series was $9 \pm 3\%$ obtained from the sample (1Acm^{-2} 20s) at -1.05 V. H_2 FEs were relatively low in the potential range between -0.6 and -0.85 V and increased markedly in the range from -0.95 to -1.05 V. For instance, the sample (1Acm^{-2} 30s) exhibited H_2 FE of $19 \pm 2\%$ at -0.6 V and $79 \pm 3\%$ at -1.05 V. C_{2+} product FEs were lower at -0.6 V, increased to a maximum at -0.95 V, rendering -0.95 V a key potential for the current-time series, and then decreased at -1.05 V. For example, the (2Acm^{-2} 5s) sample showed ethylene and ethanol FEs of 0% and 0% at -0.6 V, which rose to $21 \pm 1\%$ and $9 \pm 0\%$ at -0.95 V and then decreased slightly to $18 \pm 2\%$ and $8 \pm 1\%$ at -1.05 V, respectively. Although some samples exhibited appreciable ethanol and 1-propanol FEs of up to $\approx 8\%$ in the potential range between -0.6 and -0.85 V, the corresponding partial current densities at these potentials were negligible, reflecting no significant enhancement in activity towards these products, as will be detailed later. Clearly, shorter DHBT durations suppress parasitic H_2 evolution of the resulting Cu foams during CO_2RR at -0.95 V. At 1Acm^{-2} , reducing the DHBT duration from 30 s to 10 s lowered the H_2 FEs of the obtained samples from $73 \pm 2\%$ to $34 \pm 1\%$ at -0.95 V. At 2Acm^{-2} , shortening the DHBT time from 15 s to 5 s reduced the H_2 FE at -0.95 V from $56 \pm 3\%$ to $30 \pm 2\%$. Consequently, longer DHBT times disfavor C_{2+} formation at -0.95 V. For example, the (1Acm^{-2} 30s) sample produced ethylene, ethanol and 1-propanol FEs of $5 \pm 0\%$, $5 \pm 0\%$ and $3 \pm 0\%$, whereas the (1Acm^{-2} 10s) counterpart produced $12 \pm 2\%$, $8 \pm 0\%$ and $8 \pm 1\%$ for the same products, respectively. Similarly, the (2Acm^{-2} 15s) and (2Acm^{-2} 5s) exhibited respective FEs of $10 \pm 0\%$ and $21 \pm 1\%$ for ethylene, $6 \pm 1\%$ and $9 \pm 0\%$ for ethanol, and $5 \pm 1\%$ and $9 \pm 1\%$ for 1-propanol at -0.95 V. Moreover, higher DHBT current densities favor C_{2+} products formation at -0.95 V. For example, the (1Acm^{-2} 10s) sample yielded ethylene, ethanol and 1-propanol FEs of $12 \pm 2\%$, $8 \pm 0\%$ and $8 \pm 1\%$, while the (2Acm^{-2} 5s) counterpart displayed $21 \pm 1\%$, $9 \pm 0\%$ and $9 \pm 1\%$ for the same products at -0.95 V, respectively. The slight deviations of the total measured FEs from 100% at some potentials for certain samples can be attributed to minor fluctuations in the gas flow rate from the applied 20 mL min^{-1} due to CO_2RR and to small cumulative experimental errors in estimating the amounts of individual CO_2RR products.

The observed trends for C_1 products are consistent with the reported mechanistic pathways for these products, detailed in Section 1.2.2. Specifically, the conversion of CO_2 to formate (HCOO^-) and to CO on Cu electrodes takes place via two-electron processes that typically proceed via PCET. Formate formation proceeds via an O-bound carboxyl intermediate ($^*\text{OCHO}$), and CO formation via a C-bound carboxyl intermediate ($^*\text{COOH}$). These pathways have relatively low activation barriers and therefore dominate at less negative potentials (the range from -0.6 to -0.85 V observed here), where surface coverages of spectator species such as $^*\text{H}$ and $^*\text{CO}$ remain low, and the desorption of formate and CO is facile.^[117–119] Methane formation requires a multi-PCET sequence involving stepwise hydrogenation of surface-bound $^*\text{CO}$ to $^*\text{CHO}$, $^*\text{CH}_2\text{O}$, $^*\text{CH}_3\text{O}$, and finally $^*\text{CH}_4$. This route has substantially higher energy barriers and therefore becomes appreciable only at larger overpotentials (observed here at -1.05 V).^[117–119] C_{2+} products arise from more complex multi-PCET sequences that require the generation of surface-bound $^*\text{CO}$, C-C Coupling (e.g., formation of $^*\text{OCCO}$), and subsequent hydrogenation steps to form intermediates such as $^*\text{OCHCHO}$ or $^*\text{COHCHO}$, before final

conversion to ethylene, ethanol, and higher alcohols. These steps require higher overpotentials (here -0.95 to -1.05 V) and sufficient local *CO coverage to enable C-C coupling.^[117–119] At increasingly negative potentials, both CO₂RR and H₂ formation become thermodynamically accessible, but HER typically exhibits faster kinetics because it is a simpler two-electron process. As a result, HER competes more effectively at high overpotentials (e.g., -0.95 and -1.05 V), especially when local CO₂ is depleted. In conventional configurations, such as the H-cell used here, the low solubility (only about 34 mM in aqueous electrolyte) and diffusivity of CO₂ become rate-limiting. This effect is elevated in deep or tortuous pores, where additional internal diffusion limitations along the pore axis reduce the effective CO₂ concentration even further and shift selectivity toward the more readily H₂ evolution at high current densities.^[120,121] By contrast, GDE setups supply gaseous CO₂ directly to the catalytic layer through the macro- and micro-porous layers, resulting in substantially shorter diffusion layer thicknesses.^[122,123]

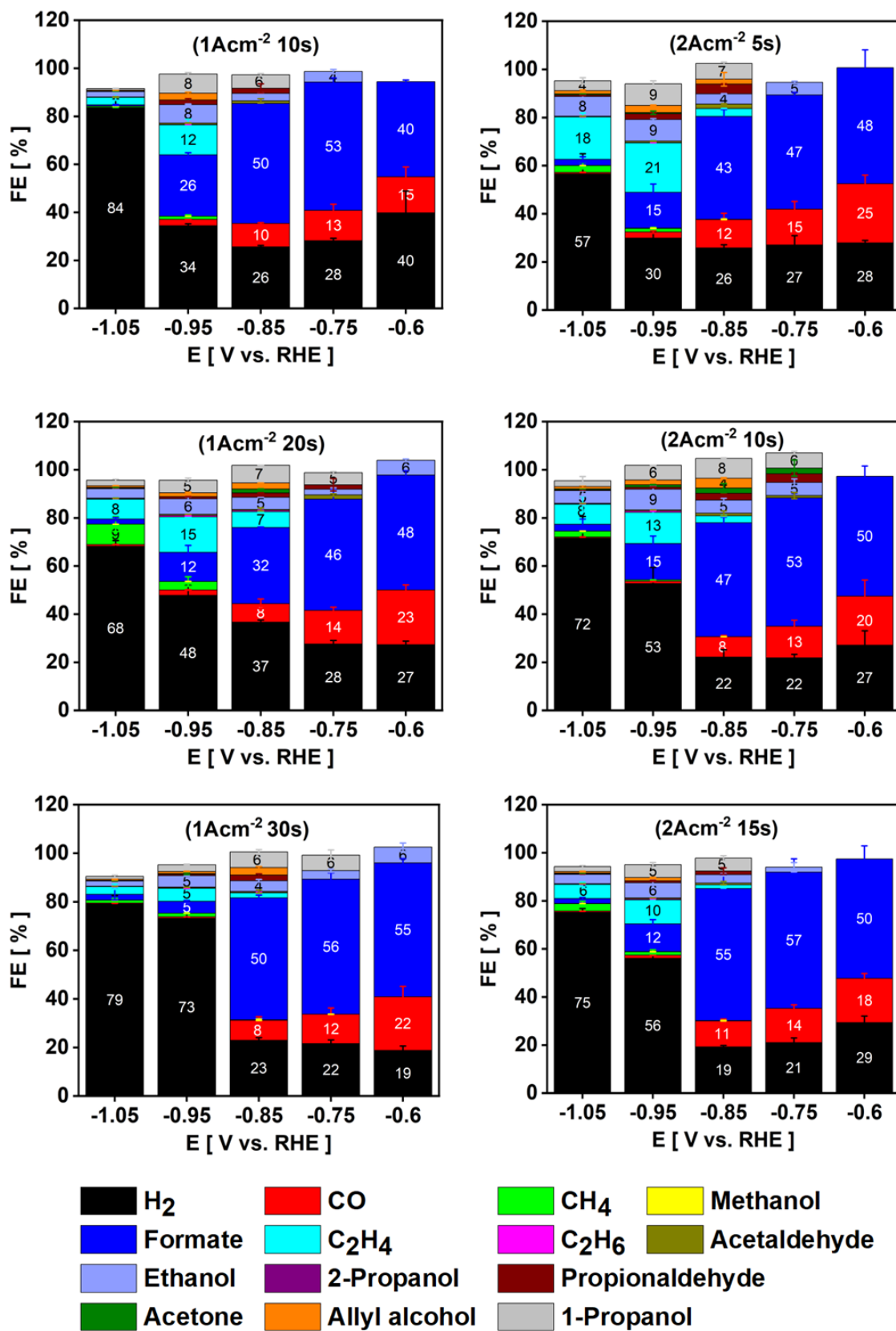


Figure 34: Faradaic efficiencies of CO₂RR products of the current-times series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Figure 35 presents geometric-area-normalized partial current densities (j_{geo}) for C_1 products. Methanol exhibited negligible j_{geo} values for the six samples. CO showed small partial current densities, peaking at -0.85 V with j_{geo} of $\approx 0.5 \text{ mA cm}_{\text{geo}}^{-2}$. Methane partial current densities were negligible between -0.6 and -0.95 V and increased at -1.05 V, with the highest j_{geo} of $6.0 \pm 2.1 \text{ mA cm}_{\text{geo}}^{-2}$ observed from the (1 A cm^{-2} 20s) sample. Formate j_{geo} followed a volcano-like trend that peaked either at -0.95 V for the samples (1 A cm^{-2} 10s), (1 A cm^{-2} 20s), (2 A cm^{-2} 5s), and (2 A cm^{-2} 10s) with corresponding peak j_{geo} of 3.3 ± 0.1 , 3.7 ± 0.3 , 2.5 ± 0.6 , and $2.8 \pm 0.5 \text{ mA cm}_{\text{geo}}^{-2}$, or at -0.85 V for the samples (1 A cm^{-2} 30s) and (2 A cm^{-2} 15s) with respective j_{geo} of 3.9 ± 0.3 and $3.7 \pm 0.2 \text{ mA cm}_{\text{geo}}^{-2}$.

Figure 36 shows geometric-area-normalized partial current densities for C_{2+} products. Ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol displayed negligible partial current densities. In contrast, ethylene, ethanol, and 1-propanol exhibited significant geometric partial current densities only between -0.95 and -1.05 V. The highest j_{geo} was observed from the (2 A cm^{-2} 5s) and (1 A cm^{-2} 20s) samples. Specifically, the two samples exhibited respective ethylene j_{geo} of 7.7 ± 0.9 and $5.8 \pm 0.4 \text{ mA cm}_{\text{geo}}^{-2}$, ethanol j_{geo} values of 3.6 ± 0.4 and $2.8 \pm 0.1 \text{ mA cm}_{\text{geo}}^{-2}$, and 1-propanol j_{geo} values of 1.8 ± 0.6 and $1.6 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$ at -1.05 V. Clearly, no direct correlation can be made between the DHBT parameters and the geometric-area-normalized partial current densities. Therefore, it was necessary to normalize the partial current densities to the ECSA values to provide insights into the intrinsic activities of Cu foam samples.^[124]

Figure 37 shows ECSA-normalized partial current densities (j_{ECSA}) of C_1 products for the current-time series. The formate peak was found to increase as the DHBT time of the produced sample decreased. For example, at 1 A cm^{-2} , formate j_{ECSA} at -0.95 V rose from 9 ± 0 to $79 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$ when the DHBT duration decreased from 30 s to 10 s. Analogously, at 2 A cm^{-2} , formate j_{ECSA} values increased from 25 ± 1 to $60 \pm 15 \mu\text{A cm}_{\text{ECSA}}^{-2}$ at -0.95 V when the DHBT time was shortened from 15 to 5 s. CO and methanol ECSA-normalized partial current densities followed similar trends to their geometric counterparts, with CO peaking at -0.85 V, with low peak values in the range of $\approx 5\text{-}10 \text{ mA cm}_{\text{ECSA}}^{-2}$, while methanol exhibited negligible j_{ECSA} . High methane j_{ECSA} values were only obtained at -1.05 V, with the highest values of 31 ± 14 and $48 \pm 17 \mu\text{A cm}_{\text{ECSA}}^{-2}$ observed from the (2 A cm^{-2} 5s) and (1 A cm^{-2} 20s) samples, respectively.

Figure 38 presents ECSA-normalized partial current densities of C_{2+} products for the current-time series. As for geometric-area normalization, allyl alcohol, acetone, propionaldehyde, acetaldehyde, and ethane showed negligible partial current densities. Additionally, ethylene, ethanol, and 1-propanol displayed appreciable j_{ECSA} values only between -0.95 and -1.05 V. Lower DHBT times favored higher C_{2+} j_{ECSA} . At 1 A cm^{-2} , ethylene, ethanol, and 1-propanol j_{ECSA} values increased from 12 ± 2 , 8 ± 0 , and $4 \pm 1 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for 30 s) to 56 ± 19 , 39 ± 18 , and $11 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for 10 s), at -1.05 V, correspondingly. Similarly, at 2 A cm^{-2} , j_{ECSA} of 27 ± 3 and $187 \pm 21 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethylene); 18 ± 2 and $87 \pm 10 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethanol); and 10 ± 2 and $43 \pm 14 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for 1-propanol) were obtained, corresponding to DHBT durations of 15 and 5 s.

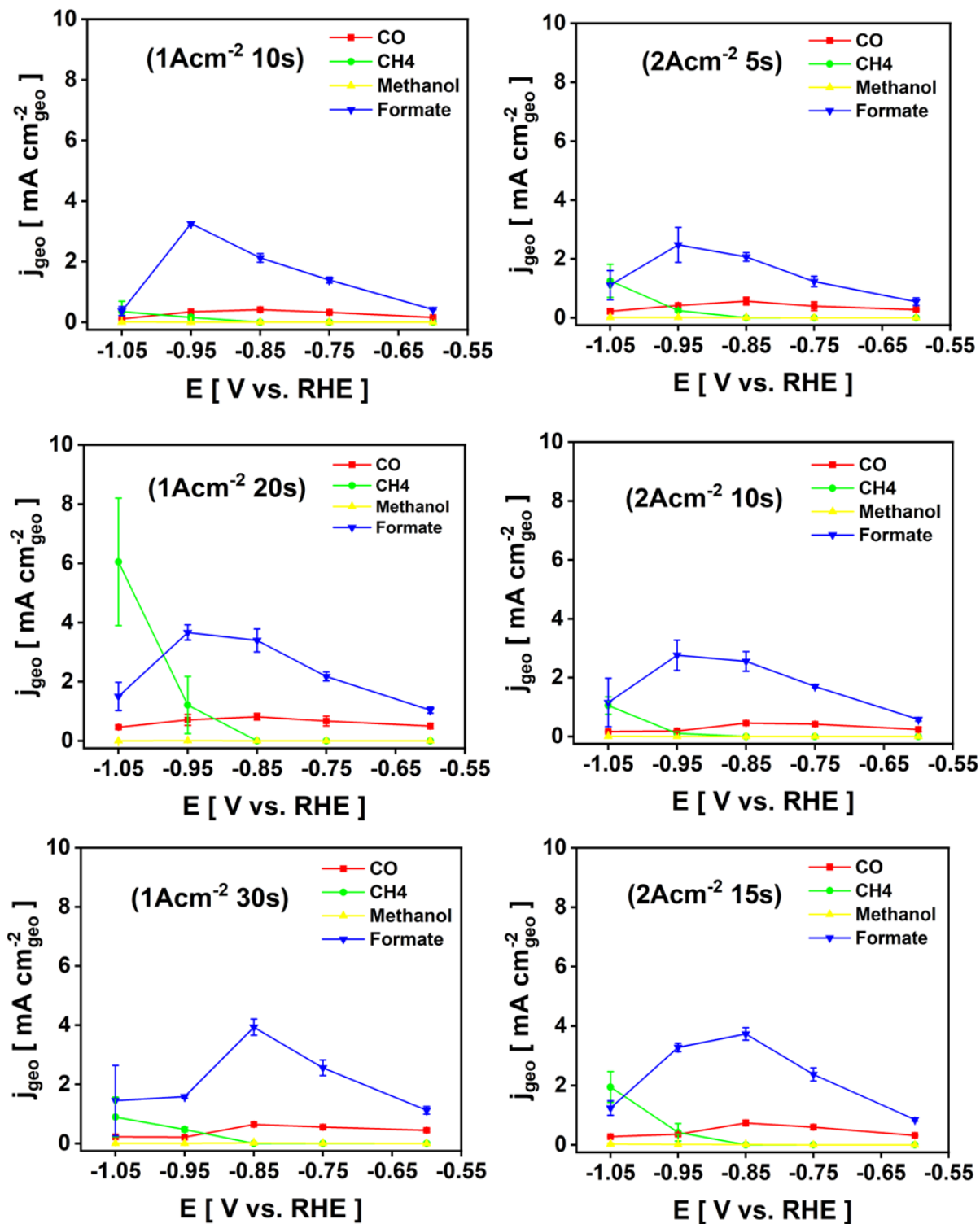


Figure 35: CO_2RR partial current densities of C_1 products of the current-times series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

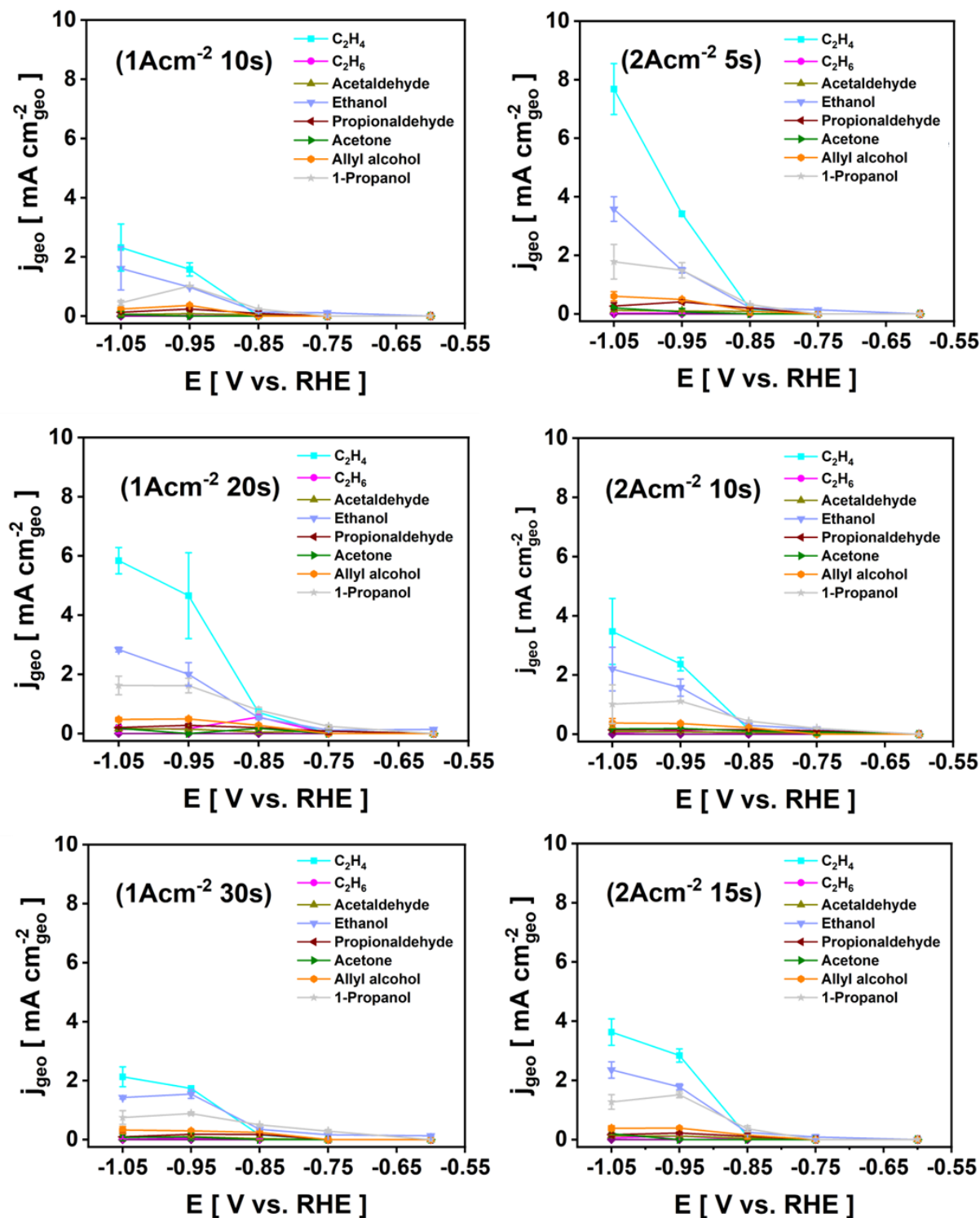


Figure 36: CO_2RR partial current densities of C_2^+ products of the current-times series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

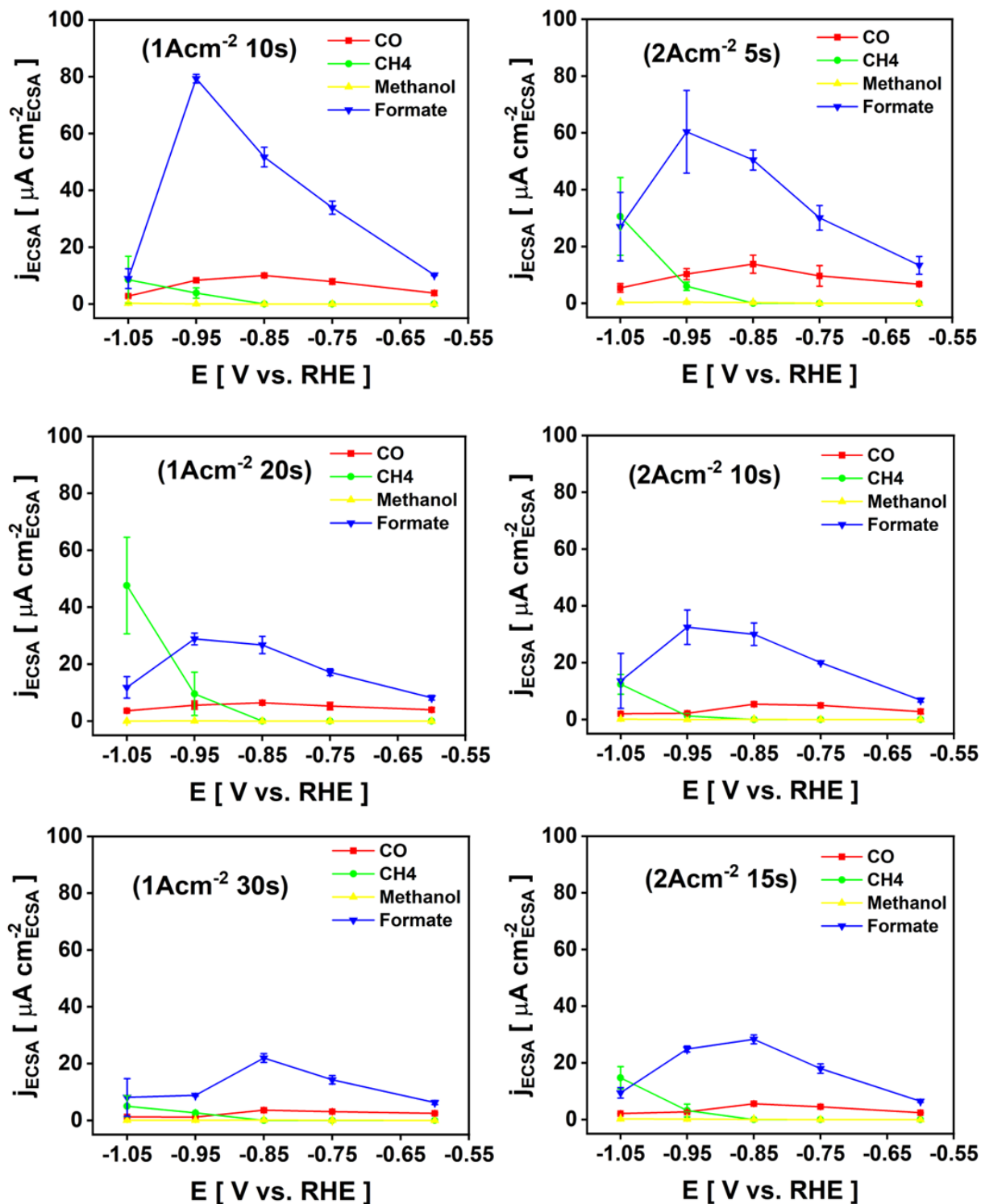


Figure 37: CO₂RR partial current densities of C_1 products of the current-times series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

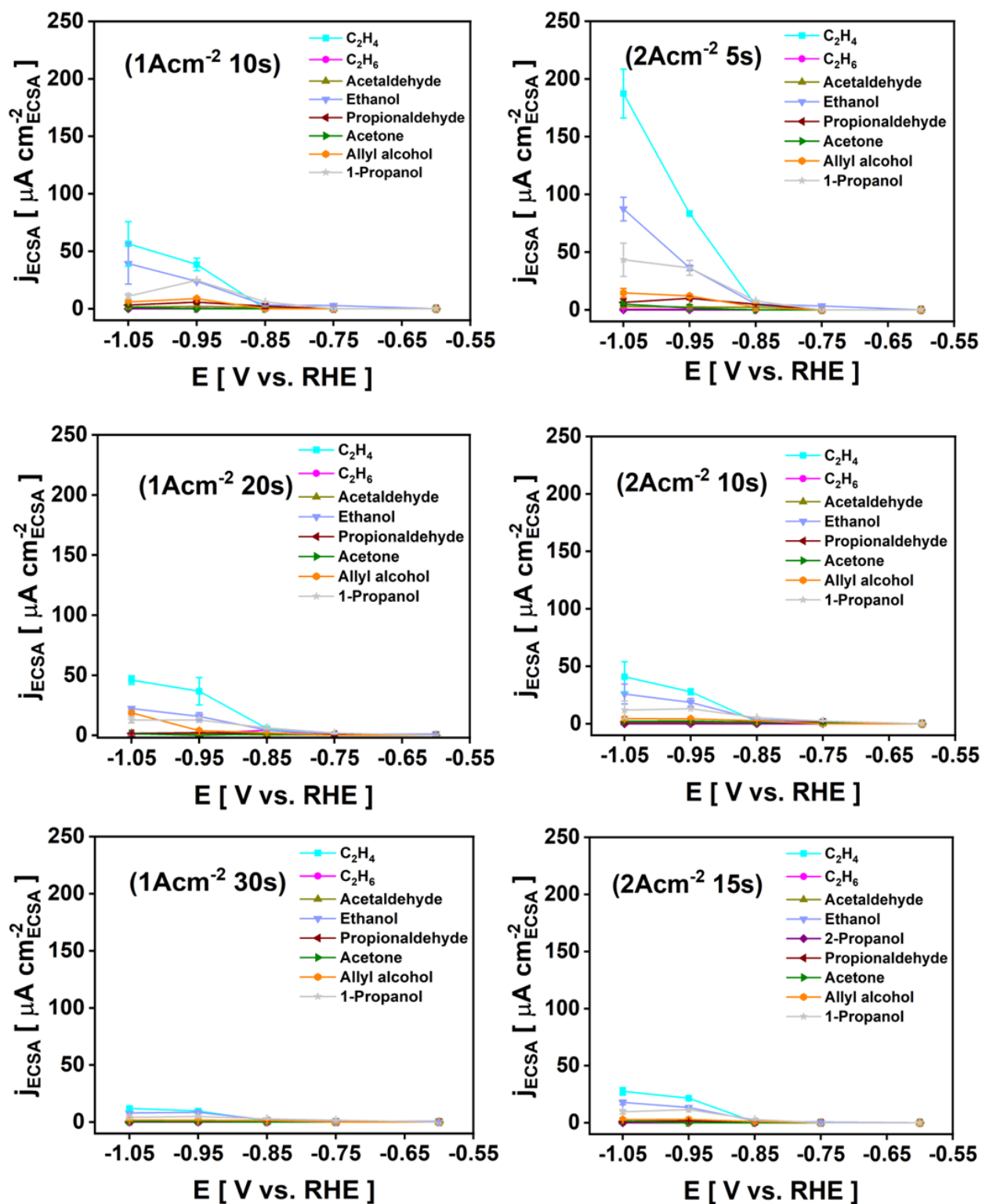


Figure 38: CO_2RR partial current densities of C_2^+ products of the current-times series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

Figure 39 presents a comparison between the current-time series samples with respect to the total C_{2+} product FEs ($FE_{C_{2+}}$) and the total C_{2+} product ECSA-normalized partial current densities ($j_{C_{2+}}$). Clearly, the potential range between -0.95 and -1.05 V is significant because only within this range did the samples display considerable C_{2+} partial current densities. Moreover, lowering DHBT time and increasing DHBT current densities were found to favor C_{2+} selectivity. Specifically, at -0.95 V, the three samples ($2Acm^{-2}$ 5s), ($2Acm^{-2}$ 10s), and ($2Acm^{-2}$ 15s) exhibited $FE_{C_{2+}}$ of 45 ± 4 , 32 ± 3 , and $25\pm3\%$, corresponding to j_{ECSA} values of 183 ± 17 , 70 ± 7 , and $53\pm4 \mu A cm_{ECSA}^{-2}$, while the three samples ($1Acm^{-2}$ 10s), ($1Acm^{-2}$ 20s), and ($1Acm^{-2}$ 30s) displayed $FE_{C_{2+}}$ of 34 ± 4 , 30 ± 2 , and $15\pm1\%$, corresponding to j_{ECSA} values of 104 ± 9 , 74 ± 18 , and $27\pm2 \mu A cm_{ECSA}^{-2}$. Increasing DHBT current densities evidently increased total C_{2+} product $j_{C_{2+}}$ at -1.05 V, with values of 118 ± 44 and $347\pm54 \mu A cm_{ECSA}^{-2}$ observed from the ($1Acm^{-2}$ 10s) and ($2Acm^{-2}$ 5s) samples, respectively.

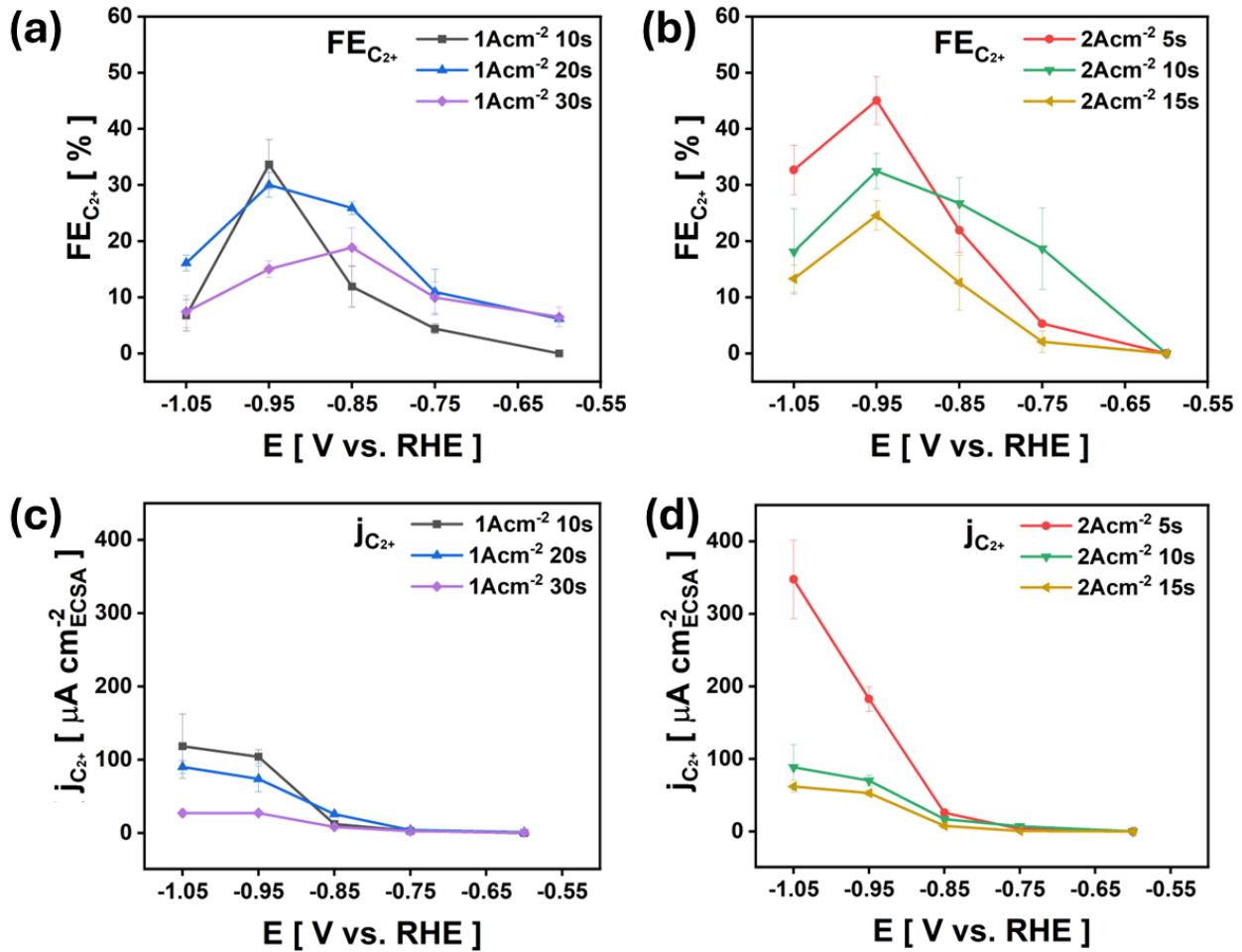


Figure 39: Comparison of the total Faradaic efficiencies and ECSA-normalized partial current densities of C_{2+} products of the current-time series samples electrodeposited at a current density of $1 A cm^{-2}$ (a and c) and $2 A cm^{-2}$ (b and d), respectively

CO_2RR results of the current-time series reveal that compact Cu foam samples are more active towards C_{2+} product formation, with the sample ($2Acm^{-2}$ 5s) being the most active sample, while the counterpart ($1Acm^{-2}$ 30s) was the least active sample in this series. Similarly, Ag foams synthesized

by the DHBT method at higher current densities exhibited superior CO activity compared with foams prepared at lower current densities during CO₂RR.^[74] This observation underscores the presence of internal mass-transport limitations along the pore axis. Specifically, it is plausible that highly open foams with larger pores and greater thickness experience internal CO₂ mass-transport limitations along the pore axis, producing additional concentration polarization between the external catalyst surface and the pore interiors, in addition to the expected concentration polarization between the bulk electrolyte and the electrode surface. At high current densities, the effective CO₂ concentration inside deep or tortuous pores drops, shifting the reaction toward the readily available water reduction in CO₂-depleted regions.^[125] Figure 40 presents the chronoamperometric curves of the (1Acm⁻² 20s) sample at different applied potentials, showing the dramatic increase in the measured current densities when the applied potential was shifted from -0.95 to -1.05 V.

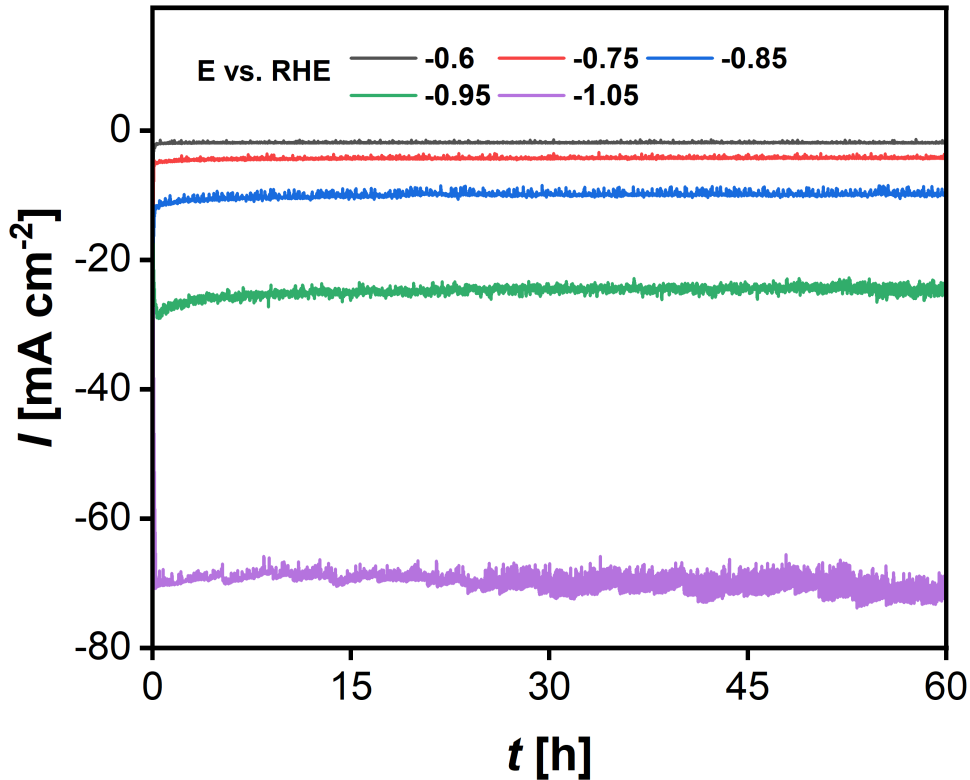


Figure 40: Chronoamperometric curves of the (1Acm⁻² 20s) sample, recorded for one hour over the potential range between -0.6 and -1.05 V

In brief, the current-time series demonstrated that increasing the DHBT current density while reducing the DHBT time effectively enhances C₂₊ product activity. This finding suggests that internal mass-transport limitations of CO₂ along the pore axis exist and are more pronounced for open foam samples synthesized at longer DHBT times and lower applied current densities.

3.2 Current mode series

Four different current regimes for Cu electrodeposition were reported in the literature: direct,^[96] pulsating,^[126] reversing,^[127,128] and alternating current,^[129] and were applied in this study for synthesizing Cu foams via the DHBT method. As illustrated in Figure 41, a continuous DC signal is applied for a defined time (t_{DC}) in the DC mode. Conversely, in the PC-DHBT mode, cathodic pulses of duration t_{pulse} separated by pause intervals of duration t_{pause} , both on the millisecond timescale, were applied and repeated for a specific number of cycles. In the RC mode, pulses alternate between the anodic and cathodic directions with respective durations of t_{anodic} and $t_{cathodic}$, while keeping the net cathodic charge density significantly larger to ensure overall deposition. The total RC charge can be effectively adjusted by varying the anodic and cathodic current densities (i_{anodic} and $i_{cathodic}$). The anodic charge density delivered in a single anodic pulse is denoted as $\Delta C = t_{anodic} i_{anodic}$. For a direct comparison between PC and RC regimes in this study, identical pulse timing (i.e., $t_{pulse} = t_{cathodic}$ and $t_{pause} = t_{anodic}$) and the same number of cycles were used for RC samples and one of the PC samples, as detailed later in this section. Moreover, an extra cathodic current density ($\Delta i_{cathodic}$) with respect to the PC pulse current density (i_{pulse}) was added to cancel the anodic charge density (ΔC) out, and maintain the total charge density of both RC and PC foams constant, i.e., $i_{cathodic} = i_{pulse} + \Delta i_{cathodic}$. In the AC mode, an alternating waveform is superimposed on a DC offset. In this mode, the principal parameters are the AC frequency and amplitude. Prior work has shown that to produce AC-derived morphologies that differ substantially from those obtained under a pure DC mode, the AC amplitude must exceed the DC offset.^[129] Because the positive and negative half-cycles of the AC component cancel each other out over a full period, the net applied charge density is effectively given by the product of the DC density offset and the deposition time. A schematic representation of the concept of this DHBT series is provided in Figure 42, showing the four different current modes used as cathodic bias during the DHBT.

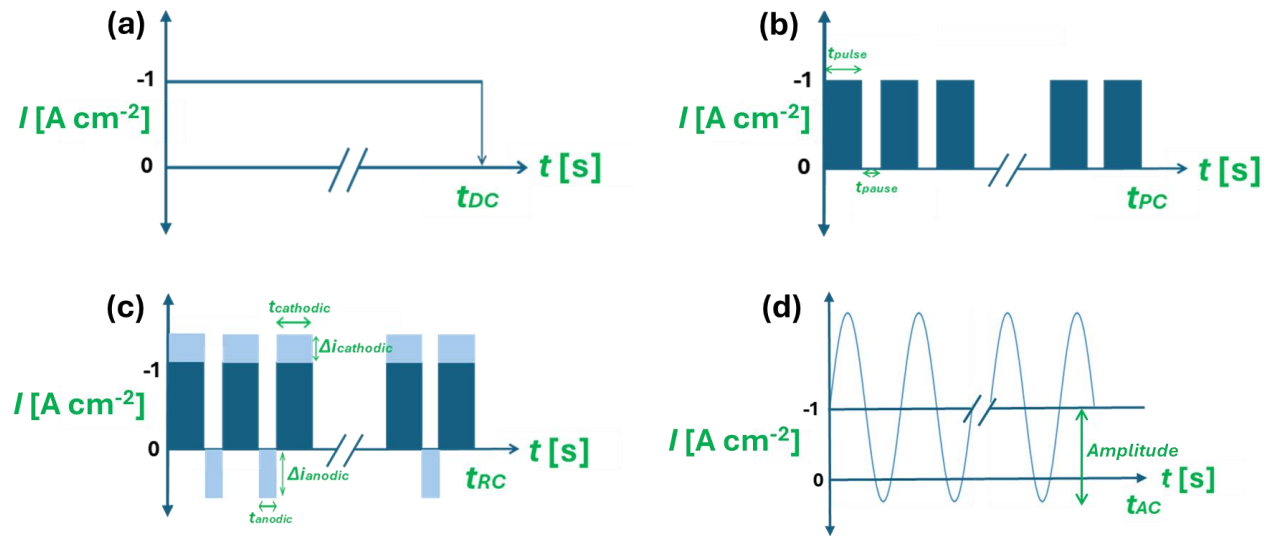


Figure 41: Illustration of the DC (a), PC (b), RC (c), and AC (d) DHBT modes, where t_{DC} , t_{PC} , t_{RC} , and t_{AC} are the total times of the DC, PC, RC, and AC electrodeposition, t_{pulse} , t_{pause} , $t_{cathodic}$, and t_{anodic} are the PC pulse, PC pause, RC cathodic pulse, and RC anodic pulse times, $\Delta i_{cathodic}$ and Δi_{anodic} are the additional current densities in the cathodic and anodic directions in case of the RC mode compared to the PC mode, correspondingly

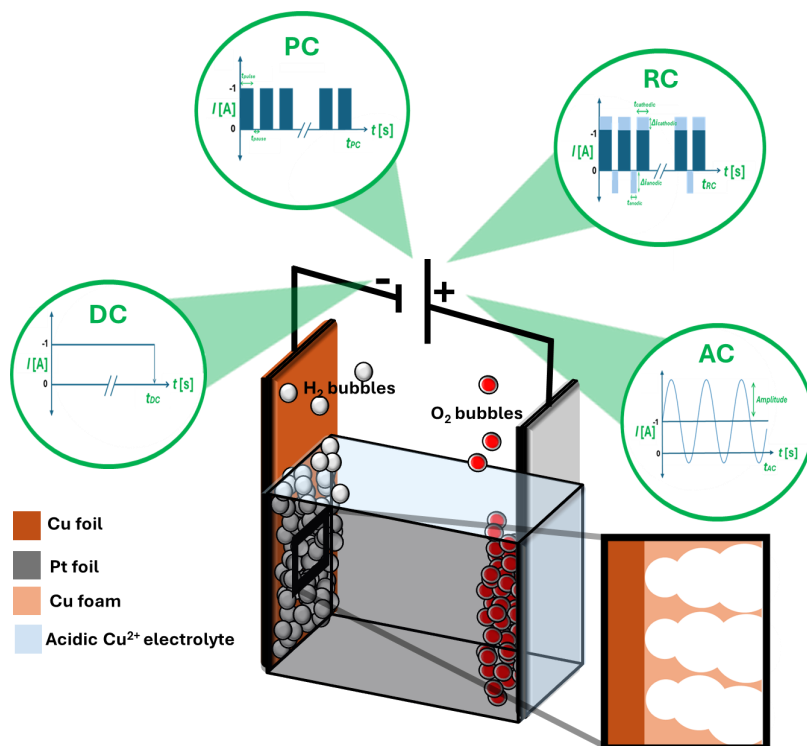


Figure 42: Schematic representation of the concept of the current mode series, where four different current regimes: direct, pulsating, reversing, and alternating current modes, were used for the DHBT

3.2.1 Pulsating Current Modes

Five PC samples were prepared using a fixed pulse current density of 1 A cm^{-2} and a total cathodic charge density of 20 C cm^{-2} , while varying the pulse and pause durations. In a constant pause time series (pause time fixed at 10 ms), three pulse durations of 1, 5, and 20 ms were tested individually. In a constant pulse time series (pulse fixed at 20 ms), three pause intervals of 10, 40, and 200 ms were examined separately. The sample produced with a 20 ms pulse and a 10 ms pause is common in both series. These conditions enabled independent assessment of pulse and pause durations on morphology, yielding three distinct pulse-to-pause ratios: 0.1, 0.5, and 2. The five PC samples were labeled by their pulse and pause values as $\text{PC}_{1:10}$, $\text{PC}_{5:10}$, $\text{PC}_{20:10}$, $\text{PC}_{20:40}$, and $\text{PC}_{20:200}$. They correspond to pulse/pause cycle counts of 20,000; 4000; 1000; 1000; and 1000, and to average current densities I_{avg}^{PC} of 0.09, 0.33, 0.67, 0.33, and 0.09 A cm^{-2} , calculated using Equation 20.^[126] Figure 43 summarizes the pulse time, pause time, and pulse-to-pause ratio of each sample of the PC series.

$$I_{avg}^{PC} = \frac{i_{pulse}}{1 + \frac{t_{pause}}{t_{pulse}}} \quad (20)$$

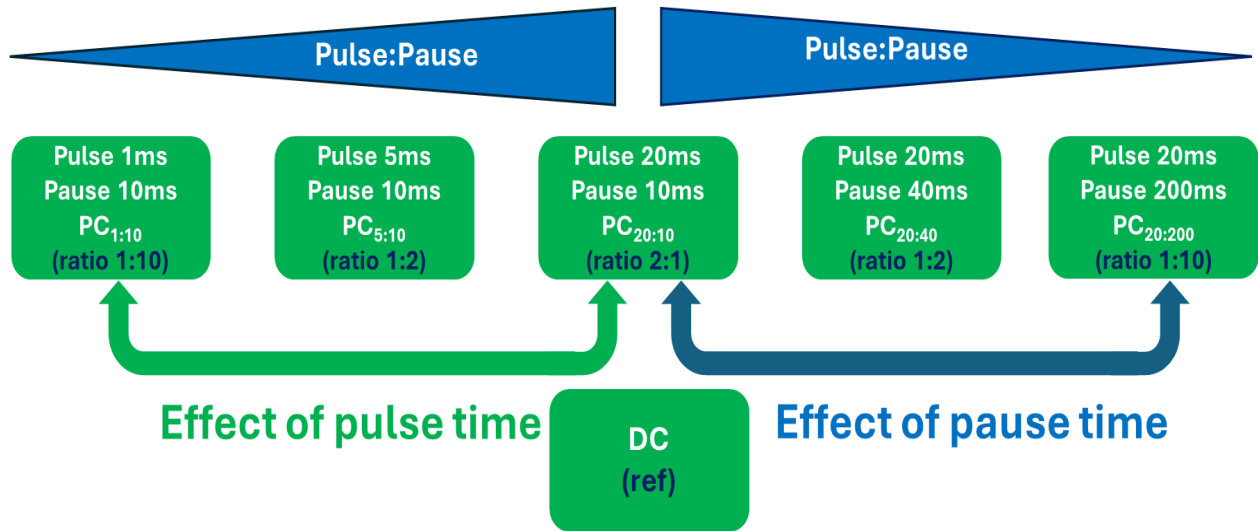


Figure 43: Illustration of the samples of the PC series, showing the pulse time, pause time, and pulse-to-pause ratio for each sample

SEM results of the five PC samples and DC reference are shown in Figure 44-45. Among the PC samples, only $\text{PC}_{20:10}$, with a pulse-to-pause ratio of 2, developed an interconnected foam structure, with a smaller average pore diameter ($17.4 \pm 0.4 \mu\text{m}$) with respect to the DC reference ($19.9 \pm 0.6 \mu\text{m}$). At a pulse-to-pause ratio of 0.5 ($\text{PC}_{5:10}$ and $\text{PC}_{20:40}$), the deposits exhibited isolated foam islands with dish-shaped craters and lacked uniform interconnectivity. Samples prepared at a pulse-to-pause ratio of 0.1 ($\text{PC}_{1:10}$ and $\text{PC}_{20:200}$) showed no foam structures entirely, and instead exhibited Cu agglomerates only. Foam thickness across the PC series followed a volcano-like trend for $\text{PC}_{1:10}$, $\text{PC}_{5:10}$, $\text{PC}_{20:10}$, $\text{PC}_{20:40}$, and $\text{PC}_{20:200}$, with measured thicknesses of 19.7 ± 3.7 , 23.8 ± 5.3 , 46.2 ± 5.2 , 25.7 ± 3.5 , and $19.0 \pm 1.6 \mu\text{m}$, respectively. All PC foams were markedly thinner than the DC reference, which displayed a thickness of $50.6 \pm 5.3 \mu\text{m}$. At higher magnification, the surface nano-structures of

the DC and PC samples differed significantly. Specifically, the DC sample displayed nano-dendrites, whereas the PC samples showed cauliflower-like nano-structures. The gravimetric analysis of the DC and PC samples is presented in Figure 46a. The Cu mass densities for PC_{1:10}, PC_{5:10}, PC_{20:10}, PC_{20:40}, and PC_{20:200} were 4.7 ± 0.1 , 3.8 ± 0.2 , 3.4 ± 0.1 , 3.6 ± 0.1 , and 4.4 ± 0.1 mg cm⁻², corresponding to FEs of 72 ± 2 , 58 ± 2 , 51 ± 2 , 55 ± 1 , and $67 \pm 2\%$, respectively. These values were higher than those of the DC reference, which exhibited a deposited mass density of 3.1 ± 0.3 mg cm⁻² and a deposition FE of $48 \pm 4\%$. The PC results indicate that introducing current pauses during DHBT suppresses H₂ bubbles formation and coalescence. The inhibited H₂ bubbles growth in the PC mode is demonstrated by the increased FE for Cu deposition, reflecting reduced FE for H₂ evolution, and accounting for the smaller pore diameter in the PC_{20:10} sample, absence of interconnected foam structures in the other PC samples, elevated electrodeposited Cu mass densities, and reduced thicknesses of the PC samples. This hindrance of H₂ bubble coalescence is more pronounced at lower pulse-to-pause ratios.

The ECSA results of the PC series, as well as the DC counterpart, are presented in Figure 46b. The PC series displayed a volcano-like trend in their ECSA results. Increasing the pulse-to-pause ratio from 0.1 (for PC_{1:10}) to 2 (for PC_{20:10}) raised the ECSA from 39 ± 2 to 56 ± 6 cm²_{ECSA} cm⁻²_{geo}, while extending the pause to 200 ms at a constant 10 ms pulse (for PC_{20:200}) reduced the ECSA to 28 ± 3 cm²_{ECSA} cm⁻²_{geo}. Clearly, all the PC samples exhibited substantially lower ECSA values than the DC reference, which displayed an ECSA of 127 ± 15 cm²_{ECSA} cm⁻²_{geo}.

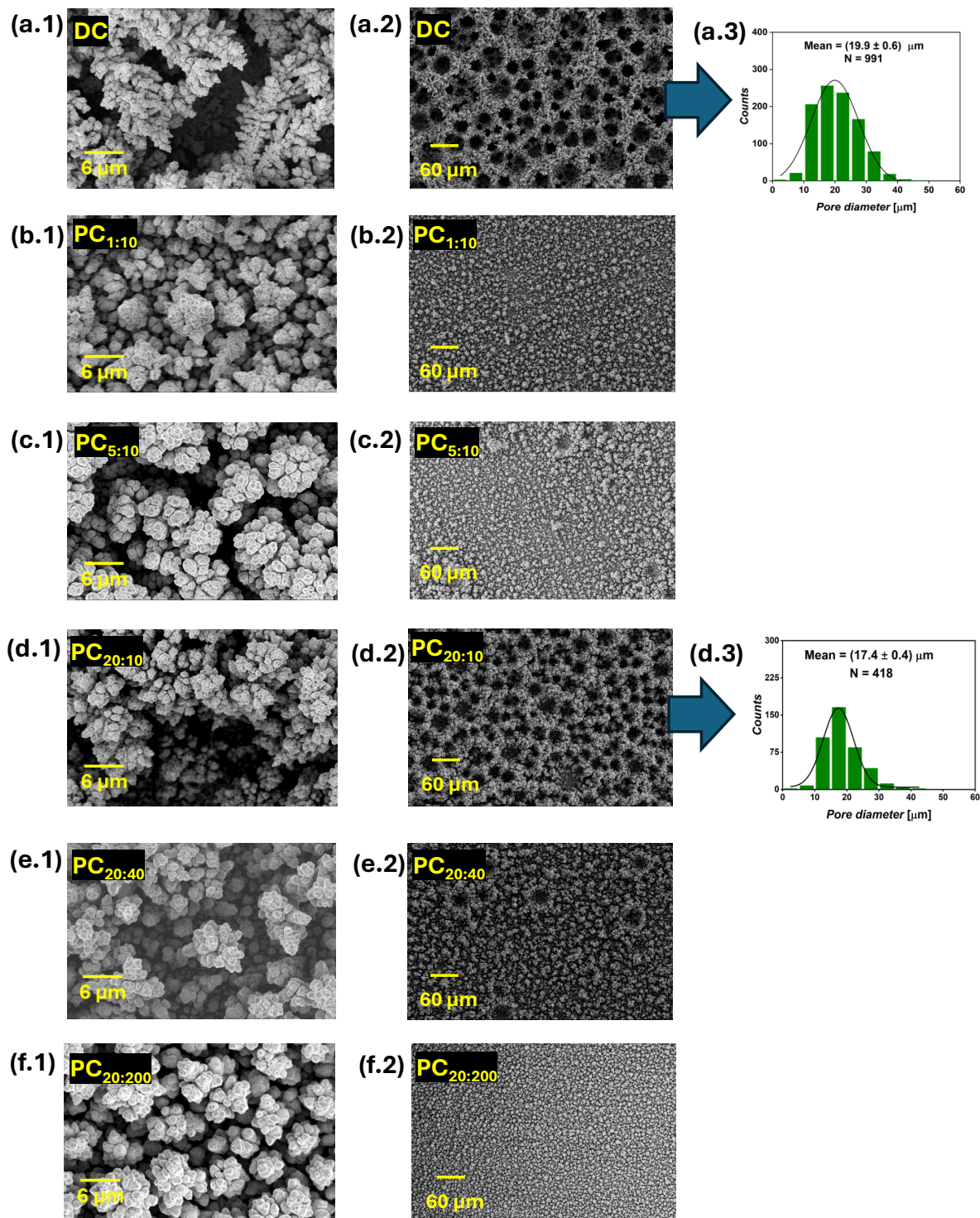


Figure 44: Top-view SEM images of Cu foam samples, presenting the surface nano-structures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the DC reference (a), PC_{1:10} (b), PC_{5:10} (c), PC_{20:10} (d), PC_{20:40} (e), and PC_{20:200} (f), where N is the number of pores from which the pore diameter distribution was obtained. For the samples without a displayed pore diameter distribution, there were insufficient pore counts to generate a reliable distribution

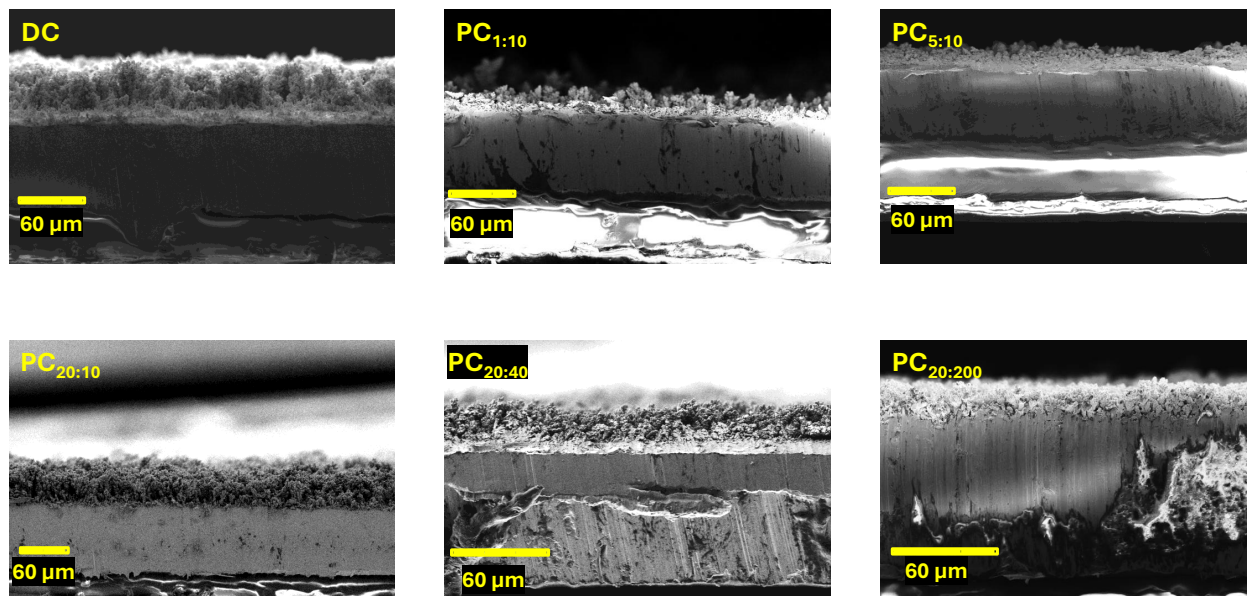


Figure 45: Examples of the cross-sectional SEM images of the pulsating current samples, each collected at an appropriate magnification

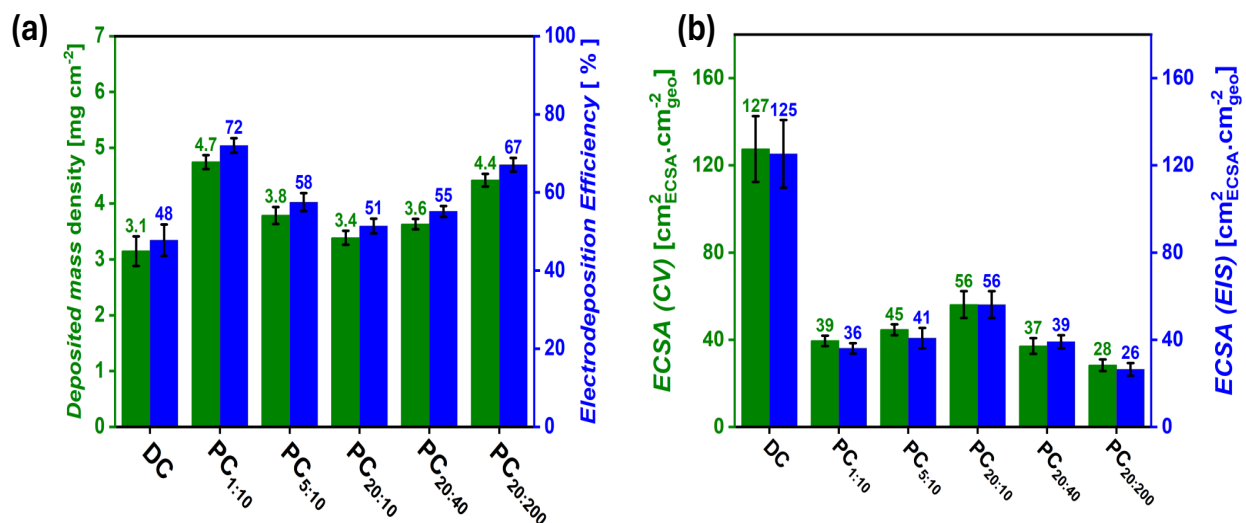


Figure 46: Gravimetric analysis of the pulsating current series (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis)

The combination of high mass density, dominant micro-to-nano porosity, and distinct surface nanostructures in the PC samples may lead to markedly different performance of Cu foams across various applications, including electrocatalysis, sensing, and fuel cells. In this work, CO₂RR performance of model PC samples was investigated in an H-cell configuration, while CO₂RR performance of PC-derived Cu foam GDEs was tested in a flow cell configuration, as detailed in Section 3.7. Figure 47 presents CO₂RR FEs of the model PC samples. Major products were formate, CO, ethylene, ethanol, 1-propanol, methane, and the parasitic H₂. Negligible FEs of allyl alcohol, acetone, propionaldehyde,

acetaldehyde, ethane, and methanol were obtained. Compared to the DC reference, PC samples exhibit substantially lower H_2 FEs across the applied potential range. For instance, at -0.85 V , the DC sample showed H_2 FE of $37 \pm 1\%$ compared to $14 \pm 1\%$ obtained from the $\text{PC}_{1:10}$ sample. The DC sample showed a gradual increase in H_2 FE with more negative applied potentials, rising from $27 \pm 1\%$ at -0.6 V to $68 \pm 2\%$ at -1.05 V . In contrast, PC samples displayed a V-shaped H_2 FE trend, where H_2 FE decreased when more negative potentials than -0.6 V were applied to reach a minimum near -0.85 V and then increased again at more negative potentials to record a maximum at -1.05 V . For example, the $\text{PC}_{1:10}$ sample showed H_2 FE of $30 \pm 1\%$ at -0.6 V , $14 \pm 1\%$ at -0.85 V , and $51 \pm 3\%$ at -1.05 V . Within the potential range from -0.6 to -0.85 V , both PC and DC samples exhibited their highest CO and formate FEs, which declined remarkably at more negative potentials. The PC samples showed superior selectivity toward formate $\approx 65\text{-}80\%$, while the DC reference displayed formate FEs below 50% . For instance, at -0.85 V , the $\text{PC}_{1:10}$ sample showed a formate FE of $79 \pm 4\%$, whereas the DC counterpart exhibited a much lower formate FE of $32 \pm 0\%$. Conversely, the DC sample showed higher CO FEs than the PC samples. For instance, at -0.6 V , the DC and $\text{PC}_{1:10}$ foams exhibited CO FEs of $23 \pm 2\%$ and $6 \pm 1\%$, respectively. All samples (PC and DC) produced considerable amounts of methane only at -1.05 V , with values of approximately $6\text{-}9\%$.

C_{2+} product FEs emerged at less negative potentials for the DC sample with respect to the PC counterparts. Specifically, the DC sample showed corresponding ethylene, ethanol, and 1-propanol FEs of $7 \pm 0\%$, $5 \pm 0\%$, and $7 \pm 0\%$ at -0.85 V , whereas the PC samples required more negative potentials to display significant C_{2+} FEs; however, the corresponding C_{2+} product partial current densities for the DC sample at -0.85 V were negligible, as will be detailed later, and they do not indicate an enhanced C_{2+} activity for the DC mode. Conversely, at -1.05 V , the PC samples prepared at low pulse-to-pause ratios (0.1 and 0.5) showed superior C_{2+} selectivity compared to the DC reference. For example, $\text{PC}_{1:10}$ and $\text{PC}_{5:10}$ exhibited higher FEs for ethylene, ethanol, and 1-propanol than the DC sample at the same potential. Specifically, the two samples exhibited respective FEs of 14 ± 1 and $17 \pm 1\%$ (for ethylene), 6 ± 0 and $7 \pm 0\%$ (for ethanol), and 3 ± 0 and $4 \pm 0\%$ (for 1-propanol), compared to FEs of 8 ± 1 , 4 ± 0 , and $2 \pm 0\%$ obtained from the DC reference at -1.05 V , correspondingly. At a pulse-to-pause ratio of 2 (i.e., the $\text{PC}_{20:10}$ sample), respective ethylene, ethanol, and 1-propanol FEs of 8 ± 1 , 4 ± 1 , and $2 \pm 0\%$ were observed at -1.05 V , which are comparable to the values obtained from the DC sample. Moreover, at the same pulse-to-pause ratios, samples with longer pause times were found to be more beneficial for C_{2+} activity. For instance, the two samples $\text{PC}_{20:40}$ and $\text{PC}_{5:10}$ showed respective FEs of 20 ± 0 and $17 \pm 1\%$ (for ethylene), 10 ± 0 and $7 \pm 0\%$ (for ethanol), and 5 ± 0 and $4 \pm 0\%$ (for 1-propanol) at -1.05 V . These findings demonstrate that the PC mode at low pulse-to-pause ratios favors C_{2+} product formation and a further enhancement in C_{2+} activity, at the same pulse-to-pause ratio, can be obtained by extending pause times.

Again, the observed FE trends for CO_2RR products are consistent with the previously reported mechanisms for these products, as discussed in detail earlier for the current-time series. Briefly, CO and formate are formed via simple two-electron PCET steps associated with lower energy barriers, explaining the dominance of these products at less negative potentials, while methane formation requires a multi-PCET sequence involving the stepwise hydrogenation of surface species, which needs higher energy, accounting for the emergence of methane considerably at -1.05 V . C_{2+} products require high local $\ast\text{CO}$ coverage, C-C coupling (e.g., $\ast\text{OCCO}$ formation), and further hydrogenation steps, accounting for their onset at more negative potentials, where H_2 evolution competes intensively.^[117–119]

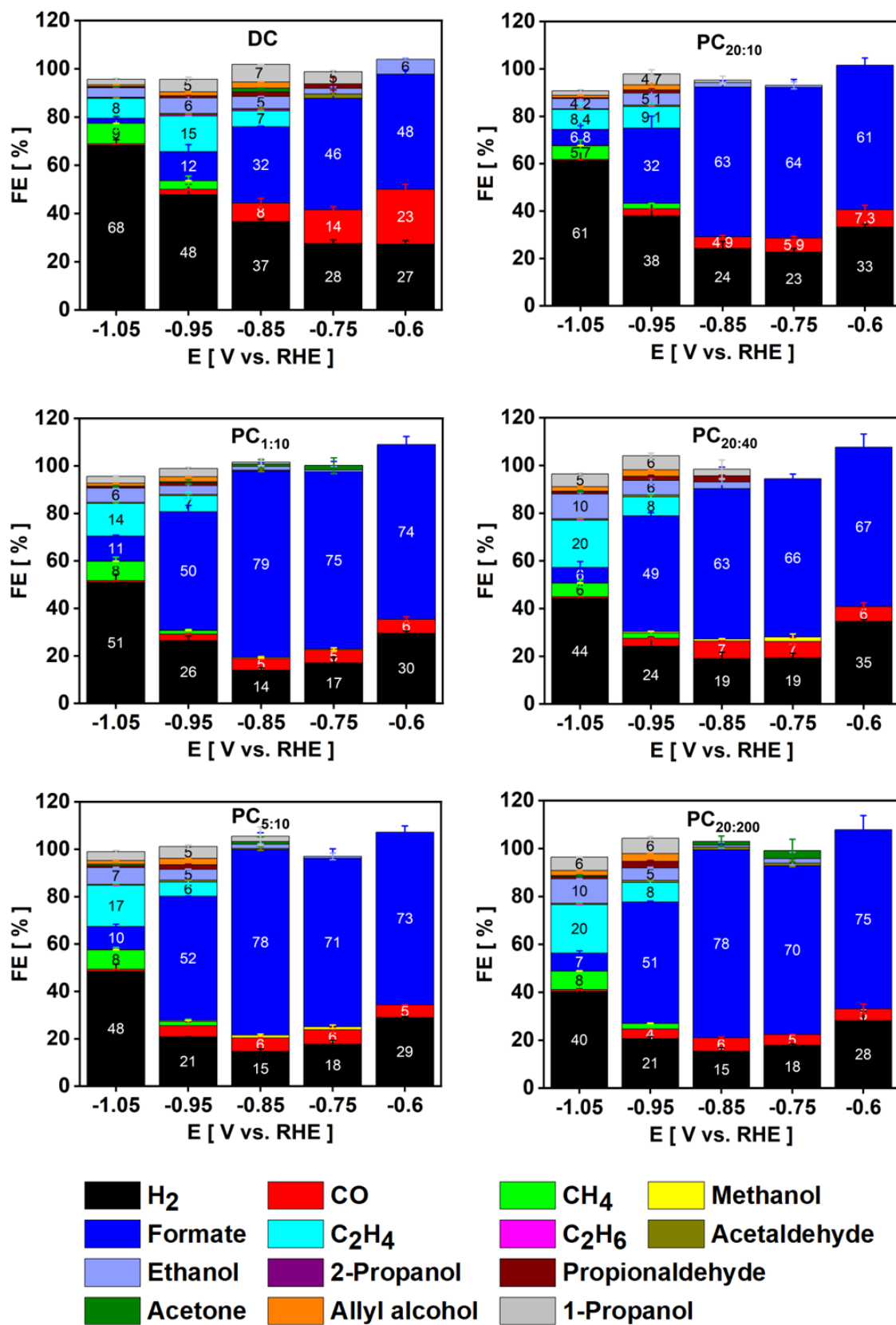


Figure 47: Faradaic efficiencies of CO₂RR products of the pulsating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Figure 48 depicts the geometric-area-normalized partial current densities of C_1 products of the PC series. Clearly, methanol exhibited negligible j_{geo} values across the applied potential range, while CO j_{geo} peaked in the range between -0.85 and -0.95 V, with low values of less than $1 \text{ mA cm}_{\text{geo}}^{-2}$. Methane j_{geo} was significant only at -1.05 V, with the highest j_{geo} of $6.0 \pm 2.2 \text{ mA cm}_{\text{geo}}^{-2}$ observed from the DC sample. Conversely, formate j_{geo} was dominant across the applied potential range, with a volcano-like trend peaking at -0.95 V. At -0.95 V, the samples PC_{1:10}, PC_{5:10}, PC_{20:10}, PC_{20:40}, and PC_{20:200} showed formate geometric partial current densities of 5.8 ± 0.1 , 4.8 ± 0.3 , 4.4 ± 0.5 , 5.3 ± 0.3 , and $4.6 \pm 0.2 \text{ mA cm}_{\text{geo}}^{-2}$, outperforming the DC reference, which displayed a peak value of $3.7 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$.

Geometric-area-normalized partial current densities of C_{2+} products of the PC series are presented in Figure 49. Negligible j_{geo} values were obtained for ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol. Ethylene, ethanol, and 1-propanol showed appreciable j_{geo} only between -0.95 and -1.05 V. At -0.95 V, the DC sample showed superior j_{geo} values for ethylene, ethanol, and 1-propanol of 4.7 ± 1.5 , 2.0 ± 0.4 , and $1.6 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$, respectively, while the PC samples exhibited corresponding values of less than 1.4, 0.7, and $0.7 \text{ mA cm}_{\text{geo}}^{-2}$ for the three products. At -1.05 V, different behaviors were observed, with no clear correlation between the PC-DHBT parameters and j_{geo} values. On the one hand, the samples PC_{20:40} and PC_{20:200} displayed j_{geo} of 7.3 ± 1.7 and 5.2 ± 0.6 (for ethylene); 3.9 ± 1 and 2.6 ± 0.2 (for ethanol); and 1.9 ± 0.3 and $1.4 \pm 0.1 \text{ mA cm}_{\text{geo}}^{-2}$ (for 1-propanol) at -1.05 V, which were higher than the respective values of the DC counterpart at the same potential: 5.8 ± 0.4 , 2.8 ± 0.1 , $1.6 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$. On the other hand, the three samples PC_{1:10}, PC_{5:10}, and PC_{20:10} displayed j_{geo} of 4.2 ± 0.6 , 4.8 ± 0.1 , and $2.8 \pm 0.9 \text{ mA cm}_{\text{geo}}^{-2}$ (for ethylene); 1.8 ± 0.2 , 2.0 ± 0.0 , and $1.5 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$ (for ethanol); and 0.9 ± 0.1 , 1.0 ± 0.1 , and $0.7 \pm 0.2 \text{ mA cm}_{\text{geo}}^{-2}$ (for 1-propanol) at -1.05 V, which were lower than the corresponding values obtained from the DC reference foam. The absence of a clear correlation between synthesis parameters and activity for the PC samples mainly stems from differences in ECSA; therefore, it was essential to normalize current densities to ECSA.

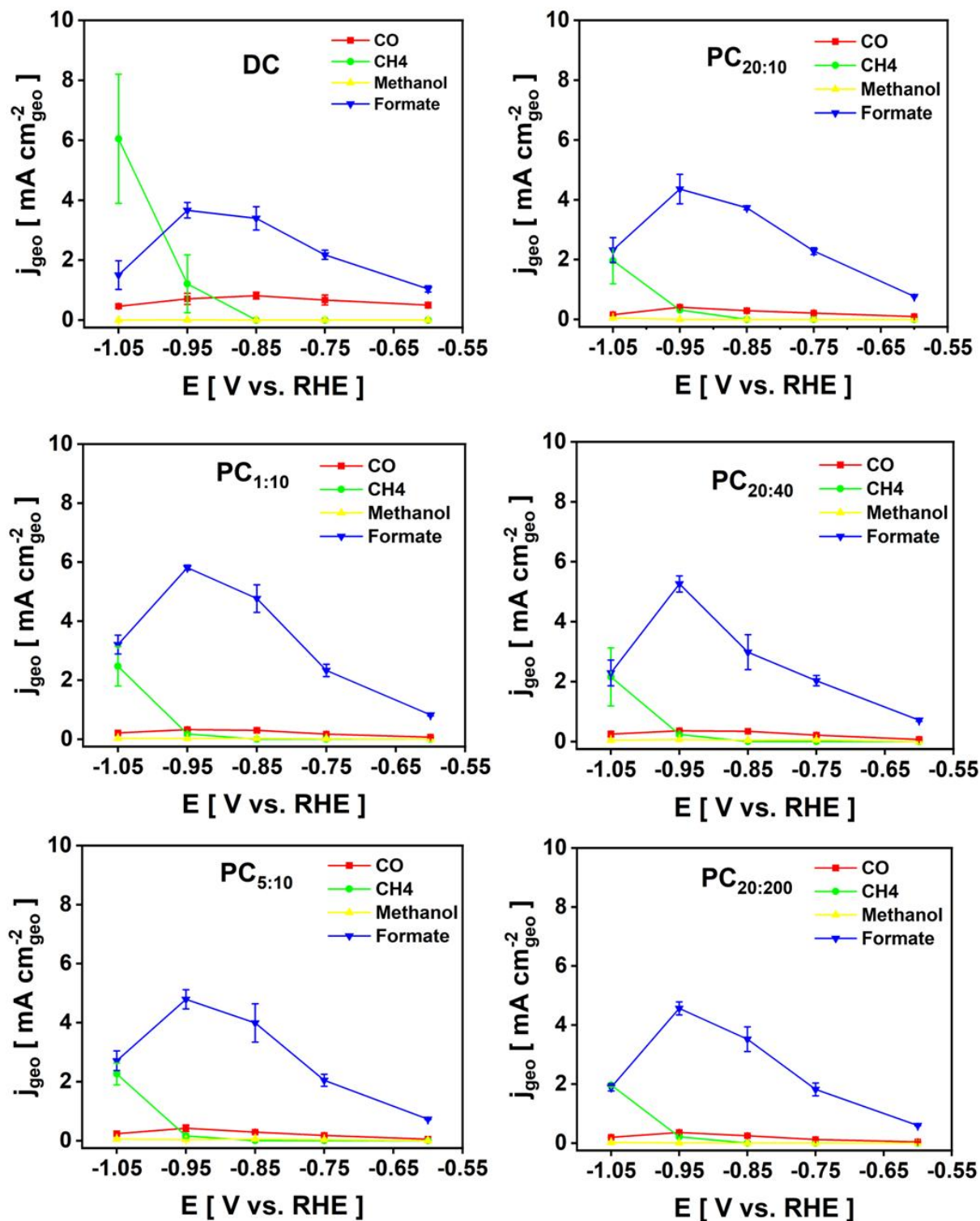


Figure 48: CO_2RR partial current densities of C_1 products of the pulsating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric surface area**

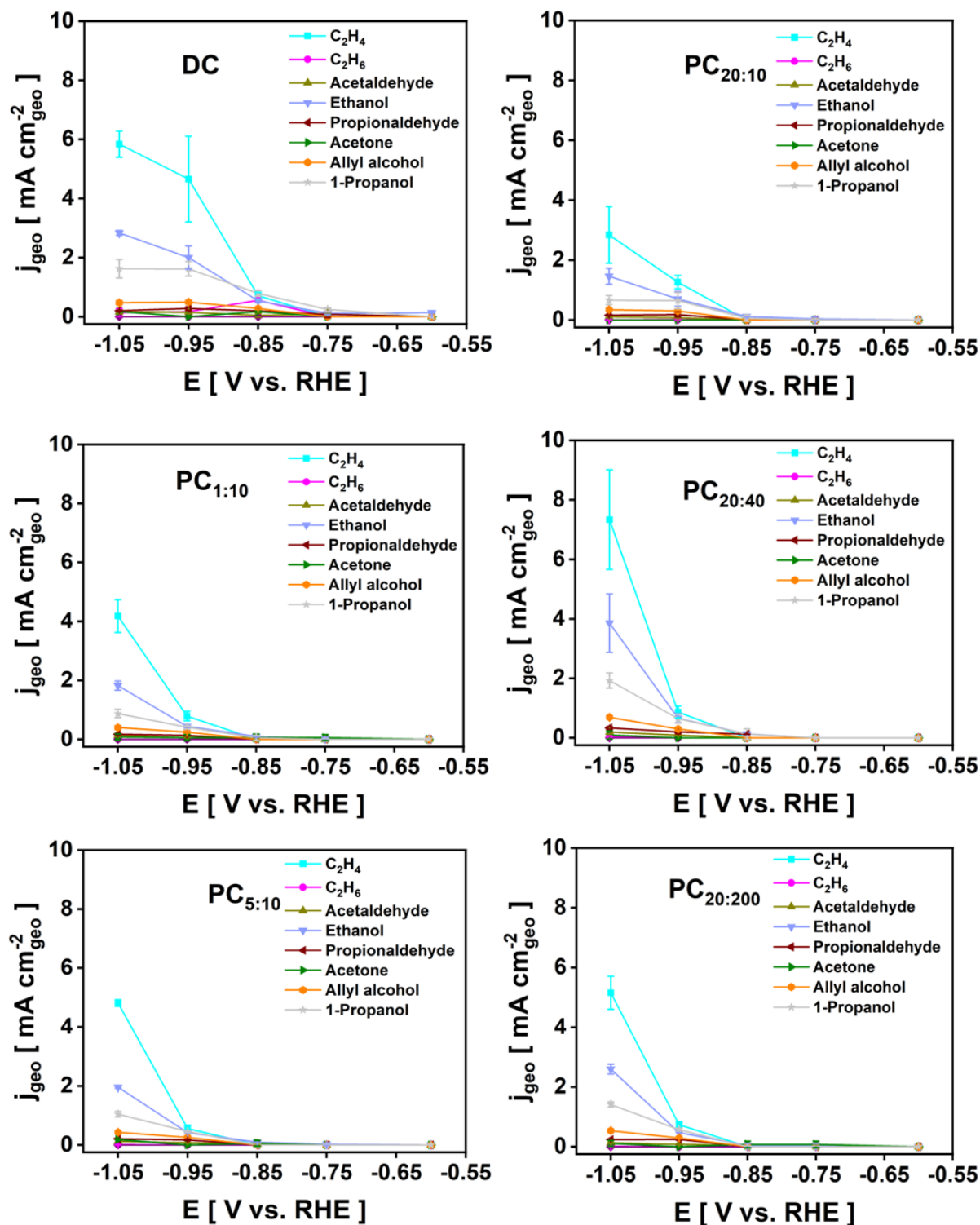


Figure 49: CO_2RR partial current densities of C_2^+ products of the pulsating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric surface area**

Normalizing the partial current densities of C_1 products to the ECSA (Figure 50) provided insights into the intrinsic C_1 activity of the PC samples. Again, methanol and CO showed low partial current densities in the applied potential range, and the highest methane j_{ECSA} across the PC series was $70 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$ obtained from the PC_{20:200} sample, outperforming the DC reference, which exhibited j_{ECSA} of $48 \pm 17 \mu\text{A cm}_{\text{ECSA}}^{-2}$, at -1.05 V. Importantly, formate j_{ECSA} peak values at -0.95 V decreased with increasing the pulse-to-pause ratio. For example, the three samples PC_{1:10}, PC_{5:10}, and PC_{20:10} showed formate j_{ECSA} peak values of 149 ± 2 , 106 ± 7 , and $78 \pm 9 \mu\text{A cm}_{\text{ECSA}}^{-2}$, respectively. Moreover, at the same pulse-to-pause ratios, longer pause durations were even more beneficial for formate activity. For example, formate j_{ECSA} peak values of 163 ± 8 and $149 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$ were obtained from the samples PC_{20:200} and PC_{1:10}, correspondingly. These values were dramatically higher than those of the DC reference, which exhibited a formate j_{ECSA} peak of $29 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$. This demonstrates that the PC mode produces Cu foams with greater intrinsic activity toward formate production compared to the DC regime, and that lower pulse-to-pause ratios, with extended pause durations, are more beneficial for formate activity.

For C_{2+} products, ECSA-normalized partial current densities are provided in Figure 51. The products ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol displayed negligible j_{ECSA} , while the products ethylene, ethanol, and 1-propanol showed considerable j_{ECSA} values only in the potential range between -0.95 and -1.05 V. In contrast to j_{geo} , j_{ECSA} afforded a perfect synthesis-activity relationship for C_{2+} products. Clearly, the PC mode, accompanied by lower pulse-to-pause ratios of 0.1 and 0.5, markedly promoted ethylene, ethanol, and 1-propanol formation at -1.05 V. Specifically, the samples DC, PC_{1:10}, PC_{20:10}, and PC_{20:200} showed corresponding j_{ECSA} values of 46 ± 4 , 107 ± 14 , 51 ± 17 , and $184 \pm 20 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethylene), 22 ± 1 , 47 ± 4 , 26 ± 5 , and $93 \pm 6 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethanol), and 13 ± 2 , 22 ± 4 , 12 ± 3 , and $50 \pm 3 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for 1-propanol) at -1.05 V. Evidently, at the same pulse-to-pause ratios, longer pause durations favored greater C_{2+} products j_{ECSA} , as can be seen, for example, by comparing the activities of the PC_{1:10} and PC_{20:200} samples. The promoted C_{2+} product j_{ECSA} values at -1.05 V agree with the more quenched H_2 FEs observed from the PC samples at this potential, in particular at low pulse-to-pause ratios, compared to the DC reference. These findings confirm the importance of ECSA-normalized partial current densities as essential descriptors of CO₂RR intrinsic activity of the Cu foam samples. In other words, if the two samples DC and PC_{20:40}, for example, possess the same ECSA, the latter will outperform the former in terms of absolute C_{2+} products partial current densities. Additionally, the high C_{2+} intrinsic activity of the PC samples at high potentials, where H_2 strongly competes, renders the PC samples excellent candidates for the transformation of model Cu foams into GDEs, as GDEs normally operate at high potentials and current densities.

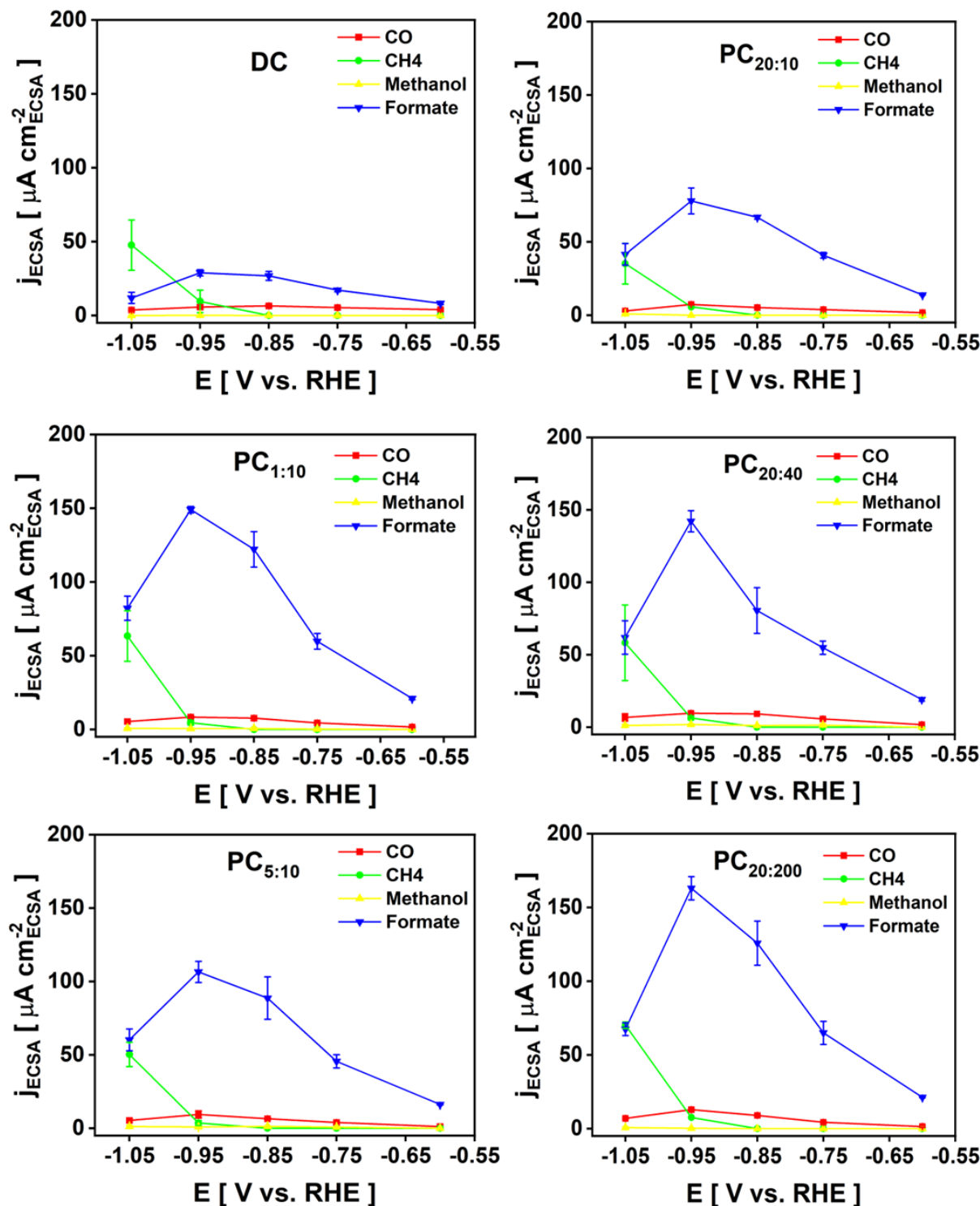


Figure 50: CO_2RR partial current densities of C_1 products of the pulsating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

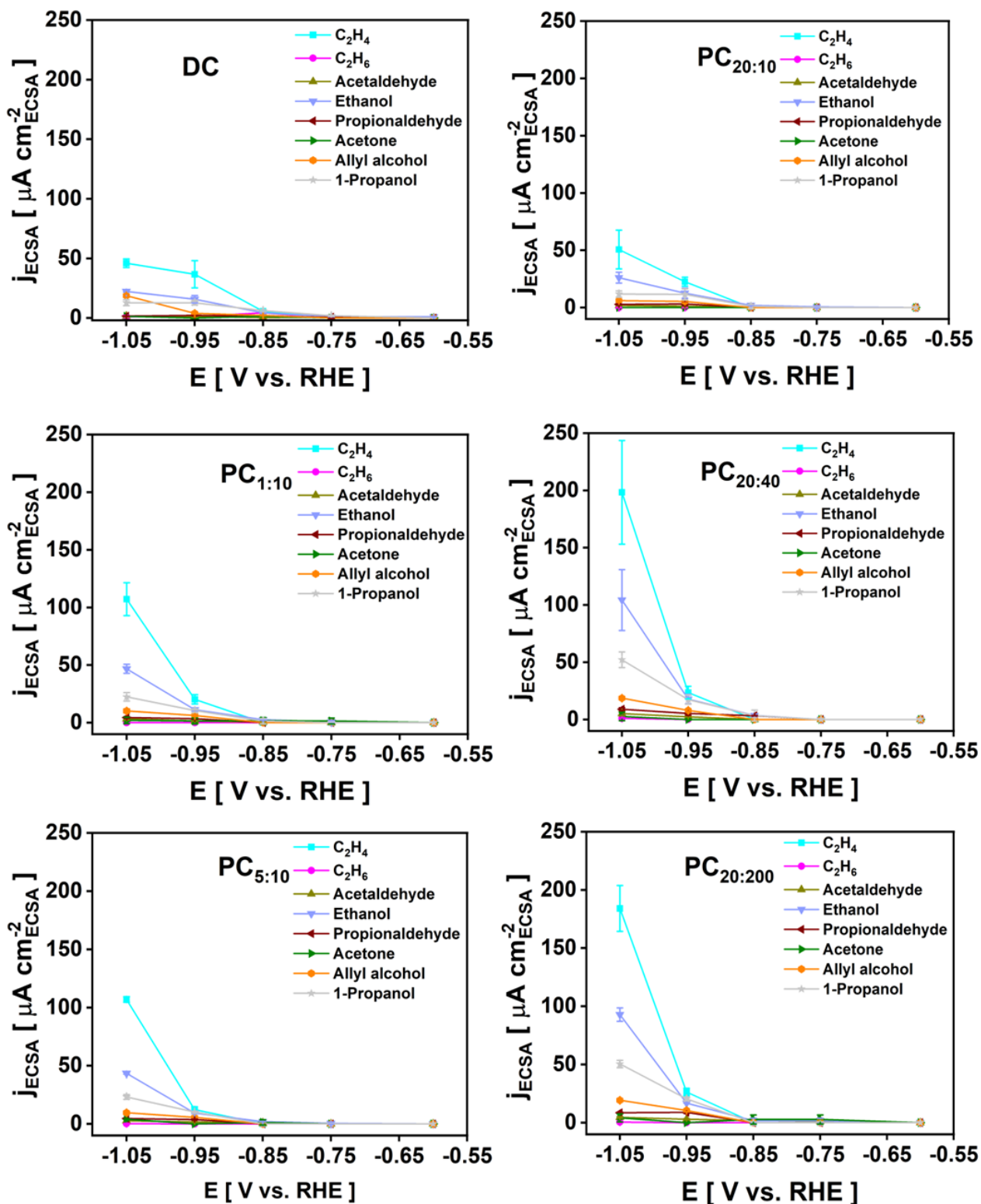


Figure 51: CO_2RR partial current densities of C_2^+ products of the pulsating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

Figure 52 presents the total C_{2+} product FEs and total C_{2+} product ECSA-normalized partial current densities of the PC series. In the potential range from -0.6 to -0.85 V, $FE_{C_{2+}}$ was higher for the DC sample than for the PC counterparts; however, these FEs correspond to negligible $j_{C_{2+}}$ values. At -0.95 V, the samples $PC_{20:40}$ and $PC_{20:200}$ showed total C_{2+} product FEs of 25 ± 5 and 27 ± 2 %, which are close to that of the DC reference (30 ± 2 %). The samples $PC_{1:10}$, $PC_{5:10}$, and $PC_{20:10}$ exhibited lower $FE_{C_{2+}}$ values of 18 ± 4 , 21 ± 2 , and 23 ± 6 % than the DC reference at -0.95 V. All the samples (PC and DC) showed comparable $j_{C_{2+}}$ at -0.95 V of around $60 \mu A cm_{ECSA}^{-2}$, reflecting no intrinsic activity difference at this potential. At -1.05 V, the PC samples exhibited an increase in $FE_{C_{2+}}$ as the pulse-to-pause ratio decreased from 2 to 0.1, with values of 16 ± 4 , 25 ± 2 , and 32 ± 2 %, corresponding to the samples $PC_{20:10}$, $PC_{5:10}$, and $PC_{1:10}$. Extending the pause time while maintaining low pulse-to-pause ratios of 0.1 and 0.5 resulted in a further enhancement of $FE_{C_{2+}}$ at -1.05 V, with values of 39 ± 2 and 40 ± 2 % for the samples $PC_{20:40}$ and $PC_{20:200}$, respectively. The two samples $PC_{20:40}$ and $PC_{20:200}$, with extended pause times, exhibited the highest $j_{C_{2+}}$ of 391 ± 87 , $364 \pm 35 \mu A cm_{ECSA}^{-2}$ at -1.05 V, respectively. The two samples $PC_{1:10}$ and $PC_{5:10}$, with lower pause times, exhibited lower total C_{2+} product j_{ECSA} values of 199 ± 32 , and $195 \pm 7 \mu A cm_{ECSA}^{-2}$ at -1.05 V, with respect to the counterparts prepared at longer pause times and the same pulse-to-pause ratios. The sample $PC_{20:10}$ together with the DC reference displayed the lowest total C_{2+} j_{ECSA} values of about $100 \mu A cm_{ECSA}^{-2}$.

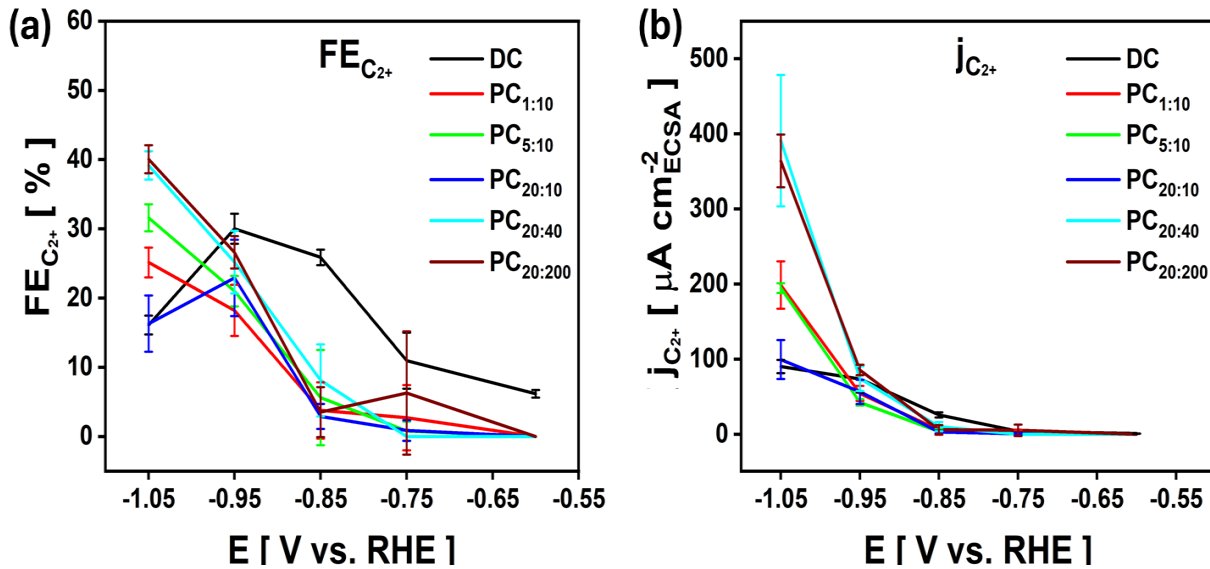


Figure 52: Comparison of the total Faradaic efficiencies (a) and ECSA-normalized partial current densities (b) of C_{2+} products for the pulsating current series

To conclude, the PC mode was shown to yield superior formate production across the potential range from -0.6 to -0.85 V, with FEs of up to ≈ 80 %. Other works achieved this high formate selectivity from bimetallic hazardous samples, e.g., Zn-In catalysts, at more negative applied potentials (-1.2 V vs. RHE) via more complicated synthesis routes.^[130] The herein reported DHBT method provides an alternative, single-step, simple route for accessing such high formate activity at remarkably less negative applied potentials. Moreover, at -1.05 V, the more compact PC samples obtained at low pulse-to-pause ratios displayed a superior intrinsic C_{2+} activity relative to the DC reference. These findings further indicate that, besides the expected CO_2 mass-transport limitation from the bulk electrolyte to the Cu foam surface, an additional concentration polarization exists between the foam

surface and the pore interior. This internal mass-transport limitation predominates in thicker, more open Cu foams, leading to a drop in CO_2 concentration in the pore interior, particularly at high potentials and current densities, and thereby increasing the contribution from the more readily available HER.^[125] This assumption perfectly agrees with the PC results, where the most open samples with interconnected foam architecture and higher thicknesses (DC and $\text{PC}_{20:10}$) displayed a suppressed C_{2+} product activity at -1.05 V. Conversely, the more compact PC samples (obtained at pulse-to-pause ratios of 0.1 and 0.5), lacking honeycomb-like morphology, exhibited higher C_{2+} product selectivity at the same potentials. Moreover, among these active PC samples, those produced with longer pause times of 40 and 200 ms had lower ECSA values than those produced with a 10 ms pause. For instance, ECSA values of 39 ± 2 and $28 \pm 3 \text{ cm}_{\text{ECSA}}^{-2} \text{ cm}_{\text{geo}}^{-2}$ were obtained from the samples $\text{PC}_{1:10}$ and $\text{PC}_{20:200}$, respectively. This indicates that longer pause times lead to slightly more compact foam structures, which, in turn, experience less internal CO_2 mass-transport limitation, thereby promoting C_{2+} activity in these samples. Additionally, the distinctive surface nano-structures of the PC samples cannot be overlooked while discussing their promising CO_2RR activity. It is widely accepted that nano-particle morphology critically influences electrocatalytic behavior. Particles with different shapes exhibit distinct crystal facets, edges, and corners, each characterized by a specific arrangement of under-coordinated atoms. These diverse atomic environments modify reactant adsorption and intermediate stabilization, generate varied distributions of active sites (steps, kinks, terraces), and substantially affect electrocatalytic performance.^[131] Accordingly, our results tentatively indicate that the nano-cauliflowers formed on the PC samples may be more favorable for C_{2+} product formation than the nano-dendrites found on the DC samples. It might be argued that this difference in the shape of surface nano-particles cannot account for the performance of the PC samples alone, since the overall foam skeleton appears to play a critical role. However, evidence was provided in Section 3.4 demonstrating that at a comparable foam skeleton, different surface nano-particles resulted in different CO_2RR performance.

3.2.2 Reversing Current Modes

For all RC samples, the cathodic and anodic pulse times were fixed at 20 ms and 10 ms, respectively, while the total cathodic charge density was maintained at 20 C cm^{-2} . The RC pulse separation mirrored that of the $\text{PC}_{20:10}$ sample, allowing direct comparison between the RC and PC modes. Three RC Cu foams were prepared by varying the anodic charge per pulse (ΔC) to 1, 3, and 6 mC cm^{-2} , which corresponded to anodic current densities of 0.1, 0.3, and 0.6 A cm^{-2} . To maintain the net cathodic charge density fixed at 20 C cm^{-2} , the cathodic pulse current densities were adjusted to 1.05, 1.15, and 1.3 A cm^{-2} , respectively, compensating for the anodic contribution. The average current density during DHBT for the three RC foams, $I_{\text{avg}}^{\text{RC}}$, and for the reference $\text{PC}_{20:10}$ sample was 0.67 A cm^{-2} , calculated from Equation 21, in which the absolute values of both cathodic and anodic current densities are to be substituted.^[128]

$$I_{\text{avg}}^{\text{RC}} = \frac{i_{\text{cathodic}} t_{\text{cathodic}} - i_{\text{anodic}} t_{\text{anodic}}}{t_{\text{cathodic}} + t_{\text{anodic}}} \quad (21)$$

Top-view SEM images of the RC foams, as well as both DC and $\text{PC}_{20:10}$ references, are presented in Figure 53, with cross-sectional images presented in Figure 54. The RC mode markedly affected both pore diameter and foam thickness. Compared with the $\text{PC}_{20:10}$ sample, which exhibited a mean pore diameter of $17.4 \pm 0.4 \text{ }\mu\text{m}$, the RC foams showed a gradual decrease in pore size to 15.7 ± 0.2 , 15.0 ± 0.1 , and $13.1 \pm 0.1 \text{ }\mu\text{m}$ for $\Delta C = 1, 3$, and 6 mC cm^{-2} , respectively. Foam thickness followed the same trend, decreasing from $46.2 \pm 5.2 \text{ }\mu\text{m}$ in $\text{PC}_{20:10}$ to 39.1 ± 2.1 , 29.4 ± 9.1 , and $24.8 \pm 5.3 \text{ }\mu\text{m}$ in $\text{RC}_{1\text{mC}}$, $\text{RC}_{3\text{mC}}$, and $\text{RC}_{6\text{mC}}$ samples, correspondingly. The $\text{RC}_{6\text{mC}}$ sample also displayed a higher pore density ($\approx 936 \text{ pore mm}^{-2}$) than $\text{PC}_{20:10}$ ($\approx 631 \text{ pore mm}^{-2}$). At the nanoscale, RC foams preserved the cauliflower-like nano-structures obtained from $\text{PC}_{20:10}$, which remained distinct from the nano-dendritic structures observed in the DC sample. A modest decline in both the deposited Cu mass density and deposition FE from $3.4 \pm 0.1 \text{ mg cm}^{-2}$ and $51 \pm 2\%$ for $\text{PC}_{20:10}$ to $3.1 \pm 0.1 \text{ mg cm}^{-2}$ and $47 \pm 1\%$ for $\text{RC}_{6\text{mC}}$ was obtained, with increasing ΔC from 0 to 6 mC cm^{-2} , as presented in Figure 55a. These findings might indicate that reversing the WE charge direction periodically during DHBT suppressed H_2 evolution more efficiently. Under identical pulse separation, the RC mode produced higher pore densities, smaller pore diameters, and decreased foam thicknesses, yielding more compact Cu foam structures.

The differences in surface nano-structures observed in both the PC and RC samples relative to the DC reference can be explained by changes in hydrodynamic conditions at the cathode surface during DHBT. While continuous, uninterrupted DHBT favors the growth of nano-dendrites, whose size depends on a bubble-induced stirring effect, sudden periodic interruptions of the cathodic signal, either by pauses or by anodic pulses, enable partial relaxation of the diffusion-layer thickness toward bulk conditions. This relaxation reduces the diffusion-layer thickness, increases the limiting current density, and lowers the overpotential, thereby promoting the rapid growth of Cu agglomerates. However, due to the periodic interruption of the cathodic signal, these nano-structures cannot extend axially into dendrites and instead form curled nano-cauliflowers.

The ECSA results of the RC series and the $\text{PC}_{20:10}$ reference are provided in Figure 55b. A gradual decline in the ECSA with increasing ΔC value from 0 mC cm^{-2} (for $\text{PC}_{20:10}$) to 6 mC cm^{-2} (for $\text{RC}_{6\text{mC}}$) was observed, with corresponding ECSA values 56 ± 6 and $37 \pm 1 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$. The ECSA results are consistent with the increased foam compactness observed with higher ΔC values, as shown by SEM images.

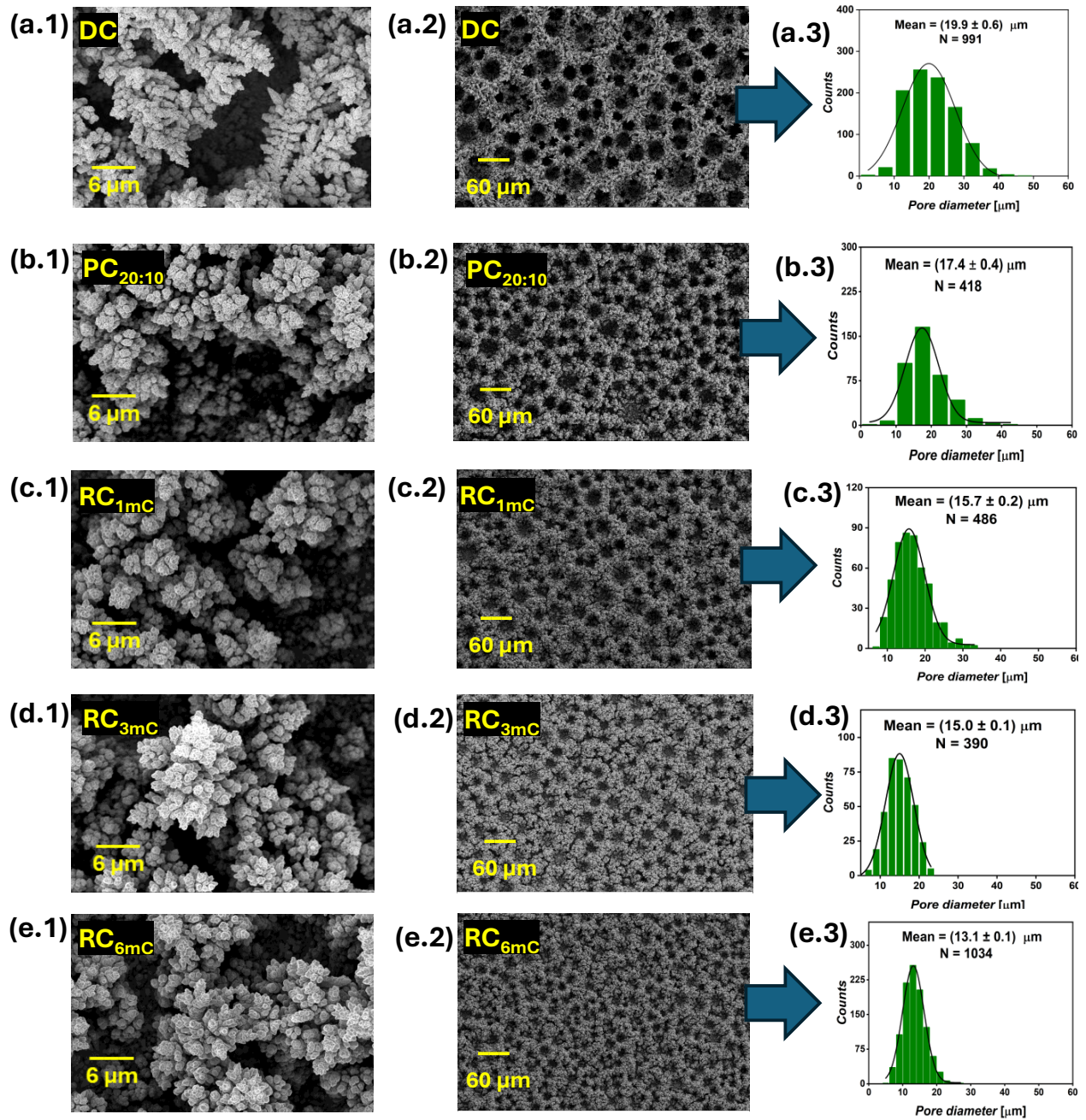


Figure 53: Top-view SEM images of Cu foam samples presenting the surface nano-structures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the DC reference (a), PC_{20:10} (b), RC_{1mC} (c), RC_{3mC} (d), and RC_{6mC} (e), where N is the number of pores from which the pore diameter distribution was obtained

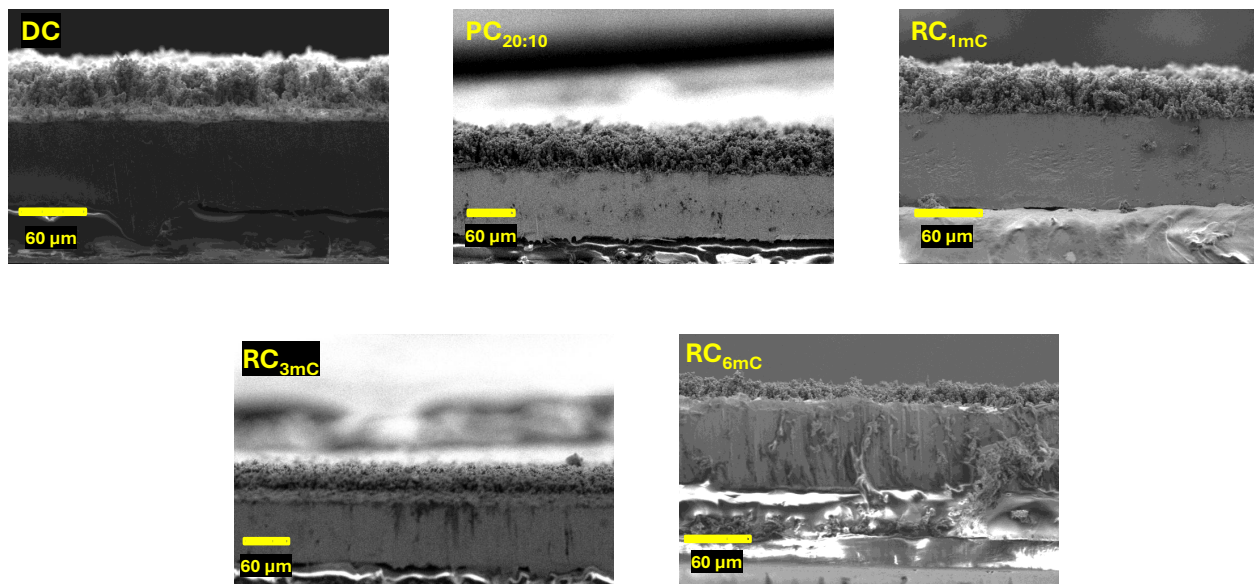


Figure 54: Examples of the cross-sectional SEM images of the RC samples, each collected at an appropriate magnification

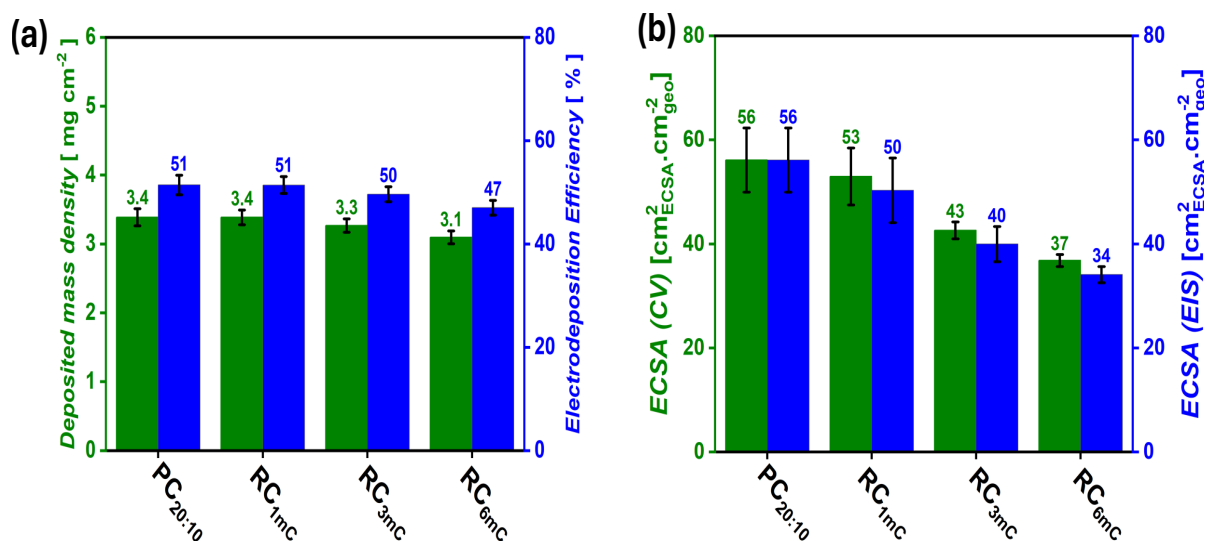


Figure 55: Gravimetric analysis (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis) of the reversing current series

Figure 56 presents the FEs of CO_2RR products obtained from the RC series. The major products across the RC samples were formate, CO, ethylene, ethanol, 1-propanol, methane, and H_2 , with trace amounts of allyl alcohol, acetone, propionaldehyde, acetaldehyde, and methanol. Overall, the RC samples showed substantially lower H_2 FEs than the PC_{20:10} and DC reference samples over the investigated potential range. For instance, at -0.85 V, the RC_{6mC} and DC samples showed respective H_2 FEs of 17 ± 1 and 37 ± 1 %. For the DC sample, H_2 FE increased progressively with more negative

applied potentials. In contrast, the PC_{20:10} and RC samples exhibited a V-shaped behavior, in which H₂ FE decreased with more negative applied potentials until a minimum at -0.85 V, then rose again at more negative potentials to record a maximum at -1.05 V across the applied potential range. For example, RC_{3mC} exhibited H₂ FEs of 31±2% at -0.6 V, decreasing to 18±1% at -0.85 V, and increasing again to reach 51±1% at -1.05 V, while the DC sample showed H₂ FE of 27±1% at -0.6 V, rising progressively to 68±2% at -1.05 V. Between -0.6 and -0.85 V, all samples (RC, PC_{20:10}, and DC) displayed the highest FEs for CO and formate, which declined markedly at more negative potentials in the range from -0.95 to -1.05 V. While formate FEs observed from the PC_{20:10} and RC samples were remarkably higher than those of the DC reference in the potential range from -0.6 to -0.85 V, the DC sample exhibited higher CO FEs in the same potential range. For instance, at -0.85 V, the RC_{1mC} sample showed a formate FE of 71 ± 5%, whereas the DC sample exhibited a formate FE of 32 ± 0%. Conversely, at -0.6 V, the DC sample displayed a higher CO FE than the RC_{1mC} and PC_{20:10} samples with respective FE values of 23 ± 2%, 9 ± 1%, and 7 ± 2%. All samples (RC, PC_{20:10}, and DC) produced considerable amounts of methane only at -1.05 V, with methane FEs of approximately 5-12%. C₂₊ products appeared at less negative potentials for the DC sample than for the RC and PC_{20:10} samples. Specifically, the PC_{20:10} and RC samples showed negligible FEs for ethylene, ethanol, and 1-propanol at -0.85 V, whereas the DC sample exhibited higher C₂₊ FEs of 7 ± 0%, 5 ± 0%, and 7 ± 0% for ethylene, ethanol, and 1-propanol. Nevertheless, the corresponding partial current densities for C₂₊ products obtained from the DC samples were negligible at -0.85 V, reflecting no enhancement in C₂₊ activity for the DC sample, as detailed later. At -1.05 V, the RC samples demonstrated substantially higher C₂₊ selectivity than the DC and PC_{20:10} references. For example, the DC, PC_{20:10}, and RC_{6mC} samples exhibited corresponding ethylene FEs of 8 ± 1%, 8 ± 3%, and 20 ± 1%; ethanol FEs of 4 ± 0%, 4 ± 1%, and 10 ± 1%; and 1-propanol FEs of 2 ± 0%, 2 ± 0%, and 6 ± 1% at -1.05 V. These results indicate that the RC mode favors C₂₊ product selectivity at more negative potentials compared with the PC (at the same pulse separation) and DC reference modes.

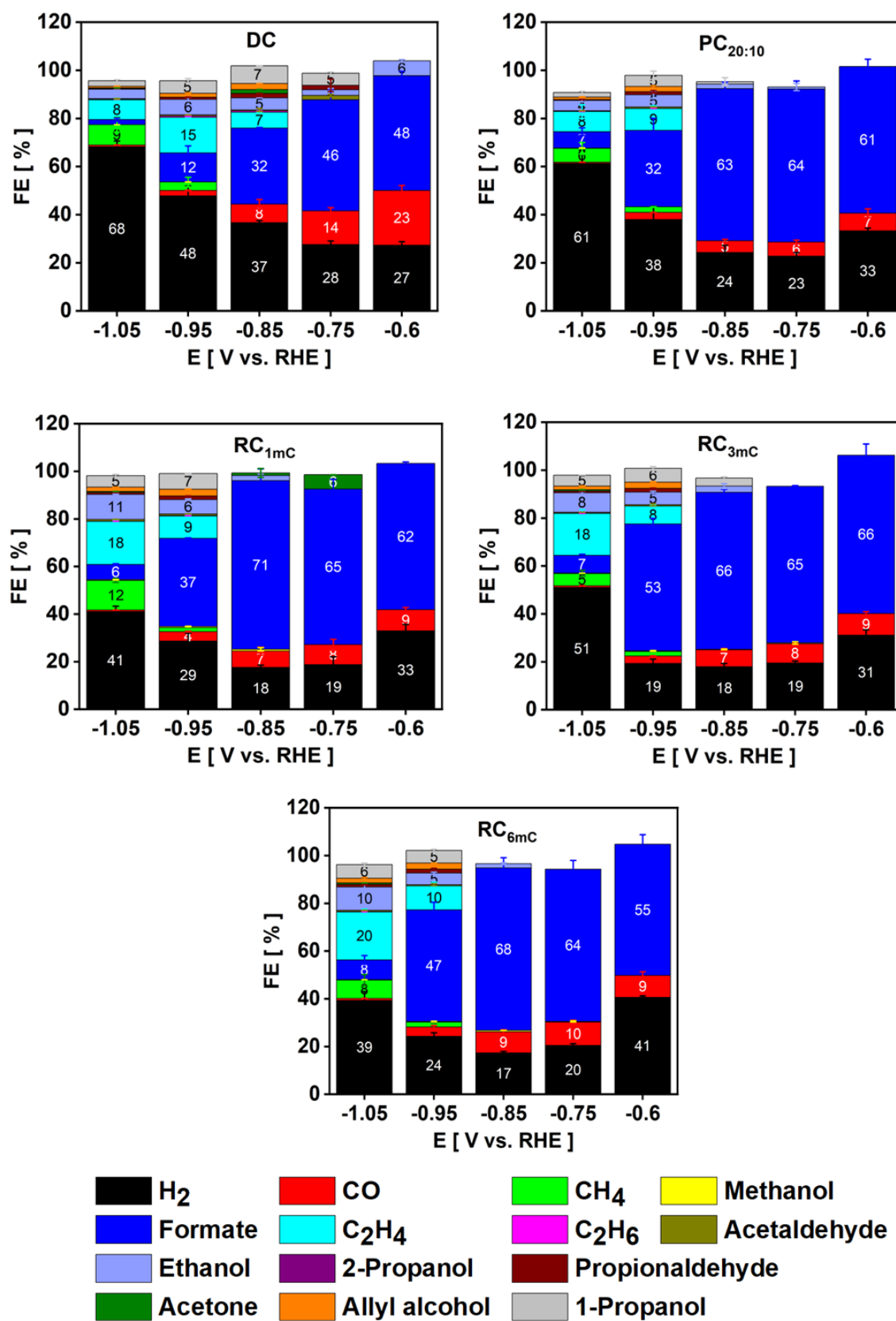


Figure 56: Faradaic efficiencies of CO₂RR products of the reversing current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Geometric-area-normalized partial current densities of CO₂RR C₁ products obtained from the RC series are provided in Figure 57. The RC and reference samples exhibited negligible j_{geo} values for methanol and low j_{geo} values for CO, peaking at -0.85 or -0.95 V, with peak values of less than 1 mA cm_{geo}⁻². Methane displayed significant j_{geo} values only at -1.05 V, with values of about 2-6 mA cm_{geo}⁻². Formate was the most dominant C₁ product across the applied potential range for both RC and reference samples, showing a volcano-like trend with a maximum at -0.95 V. For example, the DC, PC_{20:10}, and RC_{3mC} samples exhibited formate j_{geo} values of 3.7 ± 0.3 , 4.4 ± 0.5 , and 5.9 ± 0.1 mA cm_{geo}⁻² at -0.95 V, respectively, indicating a formate activity order of RC > PC > DC, which will be further supported by ECSA-normalized partial current densities.

Figure 58 presents geometric-area-normalized partial current densities for C₂₊ products of the RC series. Ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol exhibited negligible j_{geo} across the applied potential range. Ethylene, ethanol, and 1-propanol displayed significant j_{geo} only between -0.95 and -1.05 V. At -0.95 V, the DC sample outperformed the PC_{20:10} and RC counterparts in j_{geo} for ethylene, ethanol, and 1-propanol, with values of 4.7 ± 1.5 , 1.3 ± 0.2 , and 1.2 ± 0.1 mA cm_{geo}⁻² (ethylene), 2.0 ± 0.4 , 0.7 ± 0.2 , and 0.8 ± 0.0 mA cm_{geo}⁻² (ethanol), and 1.6 ± 0.2 , 0.6 ± 0.3 , and 0.8 ± 0.1 mA cm_{geo}⁻² (1-propanol) for DC, PC_{20:10}, and RC_{1mC}, respectively. By contrast, at -1.05 V, the three current modes behaved differently, and no clear correlation between the DHBT parameter ΔC and the C₂₊ geometric partial current densities was observed. For example, j_{geo} values for the DC, PC_{20:10}, and RC_{1mC} samples were 5.8 ± 0.4 , 2.8 ± 0.9 , 7.9 ± 0.2 mA cm_{geo}⁻² (for ethylene); 2.8 ± 0.1 , 1.5 ± 0.3 , 4.6 ± 0.4 mA cm_{geo}⁻² (for ethanol); 1-propanol 1.6 ± 0.3 , 0.7 ± 0.2 , 2.1 ± 0.3 mA cm_{geo}⁻² (for 1-propanol), correspondingly.

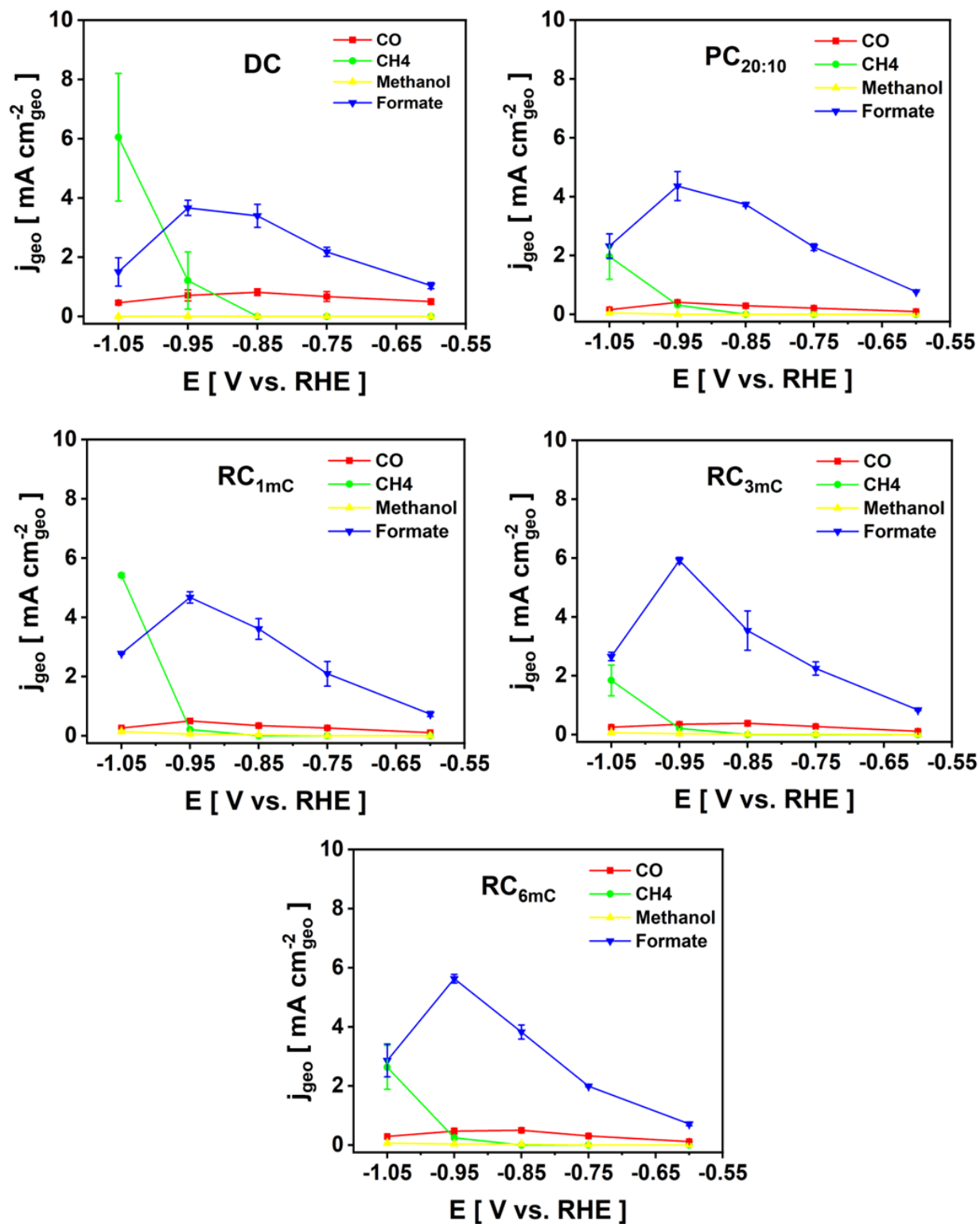


Figure 57: CO_2RR partial current densities of C_1 products of the reversing current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

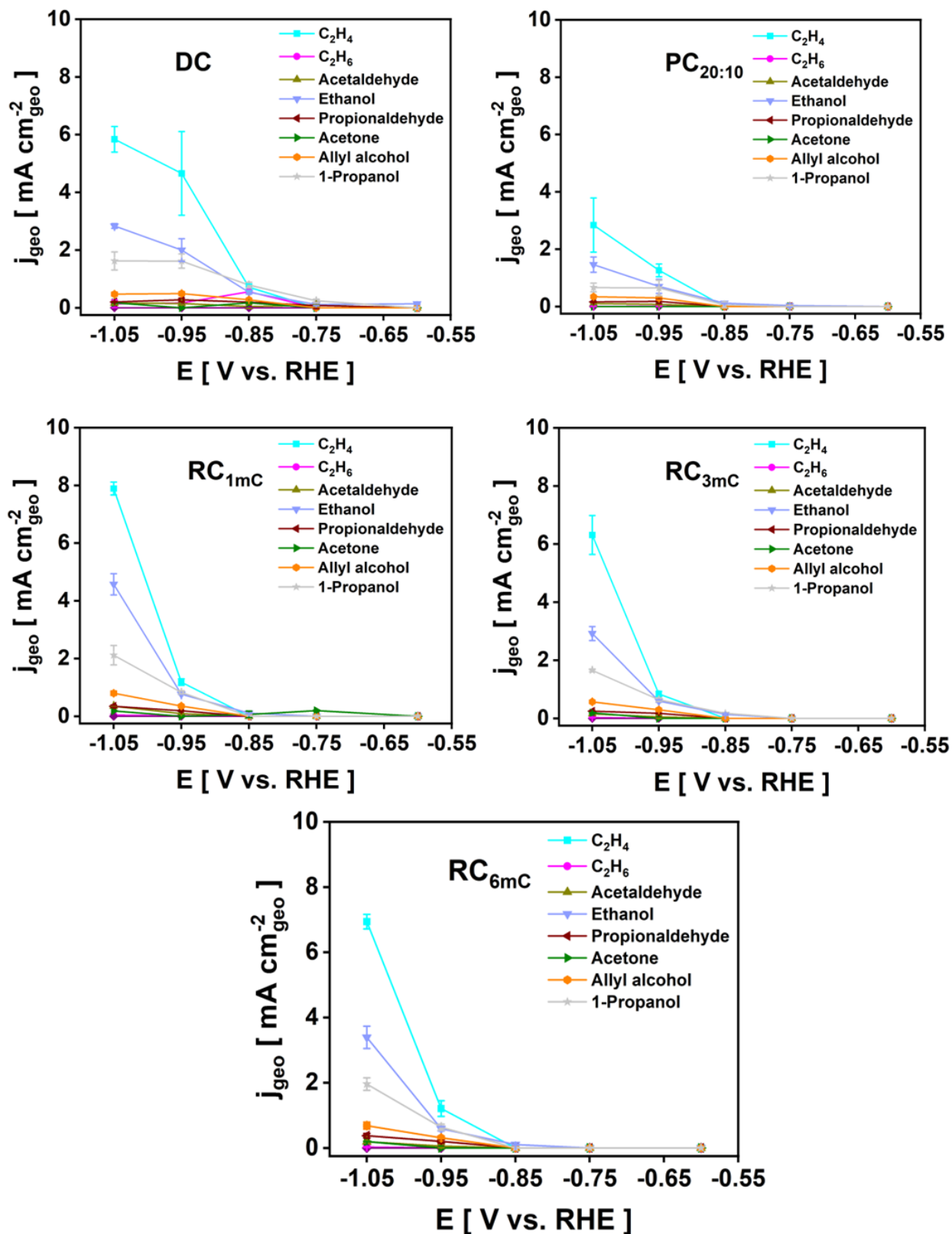


Figure 58: CO_2RR partial current densities of C_2^+ products of the reversing current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

Because of the large differences in ECSA between DC, PC_{20:10}, and RC samples, geometric-area-normalized partial current densities do not reliably reflect the intrinsic activity. Therefore, ECSA normalization of partial current densities is required to decouple surface area effects from intrinsic catalytic performance. ECSA-normalized partial current densities of C₁ products for the RC series are presented in Figure 59. Again, the partial current densities of methanol and CO remained negligible across the studied potential range when normalized to ECSA. Methane showed appreciable j_{ECSA} values of around $\approx 50\text{--}100 \mu\text{A cm}_{\text{ECSA}}^{-2}$ only at -1.05 V. Formate j_{ECSA} values were dominant across the applied potential range, with a maximum at -0.95 V. The maximum formate j_{ECSA} showed the order of $\text{DC} < \text{PC}_{20:10} < \text{RC}_{1\text{mC}} < \text{RC}_{3\text{mC}} < \text{RC}_{6\text{mC}}$, with corresponding values of 29 ± 2 , 78 ± 9 , 88 ± 4 , 138 ± 2 , and $152 \pm 4 \mu\text{A cm}_{\text{ECSA}}^{-2}$. These results, which showed a perfect synthesis-activity relationship, indicate that the RC mode intrinsically enhances formate activity relative to DC and PC under the investigated conditions, and that increasing ΔC further boosts formate activity. The results also underscore once again the importance of ECSA normalization when comparing CO₂RR activities across samples with significant differences in surface area.

Figure 60 shows the ECSA-normalized partial current densities for C₂₊ products of the RC series. Repeatedly, ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol exhibited negligible j_{ECSA} across the applied potential range, while ethylene, ethanol, and 1-propanol showed significant j_{ECSA} values only between -0.95 and -1.05 V. Unlike the geometric partial current densities, which did not reveal a clear correlation between DHBT conditions and C₂₊ performance, the ECSA-normalized partial current densities showed that RC samples outperform both DC and PC_{20:10} counterparts in C₂₊ intrinsic activity, with activity increasing with ΔC (particularly for ethylene). For instance, the DC, RC_{1mC}, and RC_{6mC} samples exhibited j_{ECSA} values of 46 ± 4 , 149 ± 4 , and $188 \pm 6 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethylene); 22 ± 1 , 86 ± 7 , and $92 \pm 9 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for ethanol); and 13 ± 2 , 40 ± 6 , and $53 \pm 5 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (for 1-propanol) at -1.05 V, respectively. These trends align with the stronger suppression of H₂ formation observed for RC samples at -1.05 V.

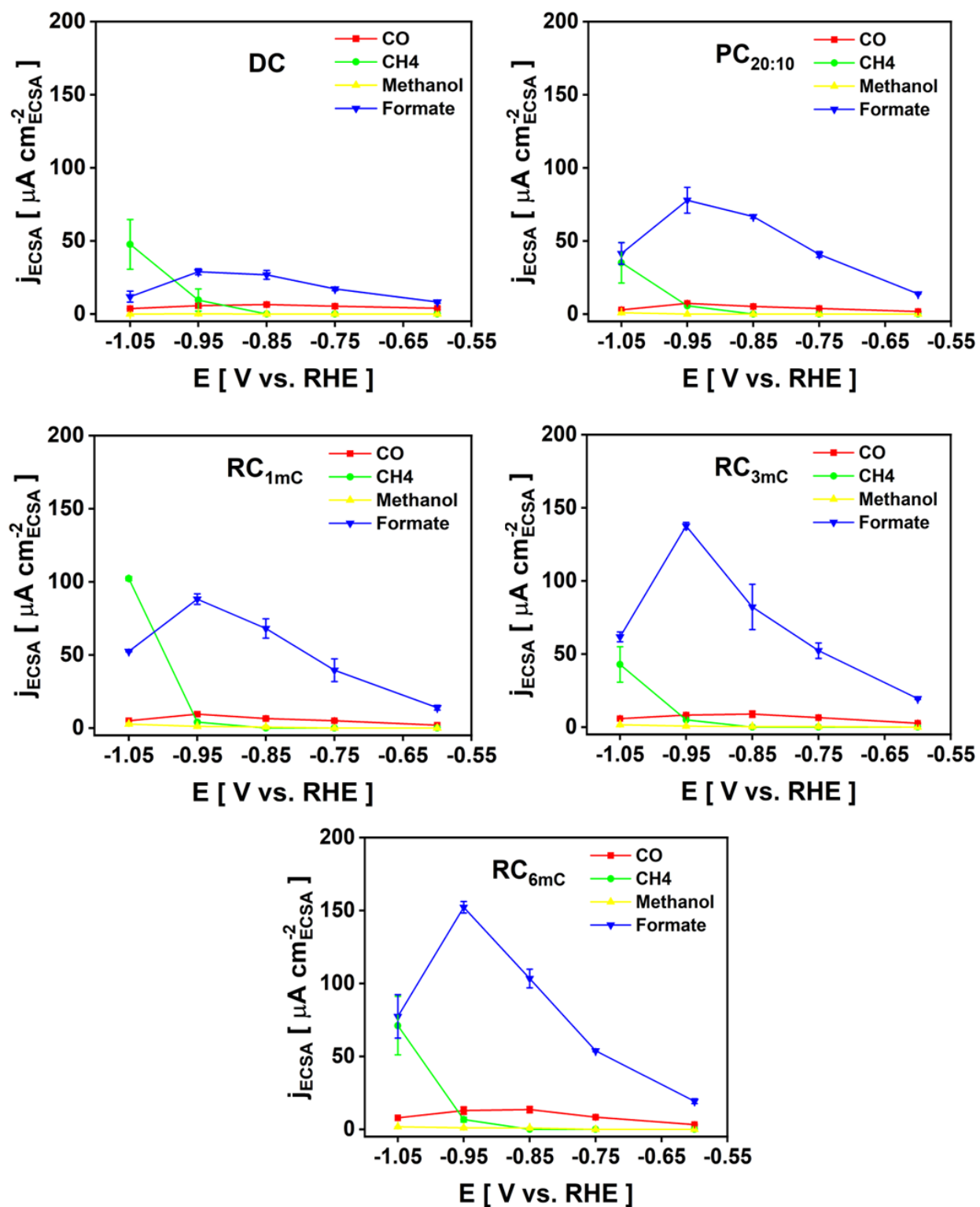


Figure 59: CO₂RR partial current densities of C_1 products of the reversing current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

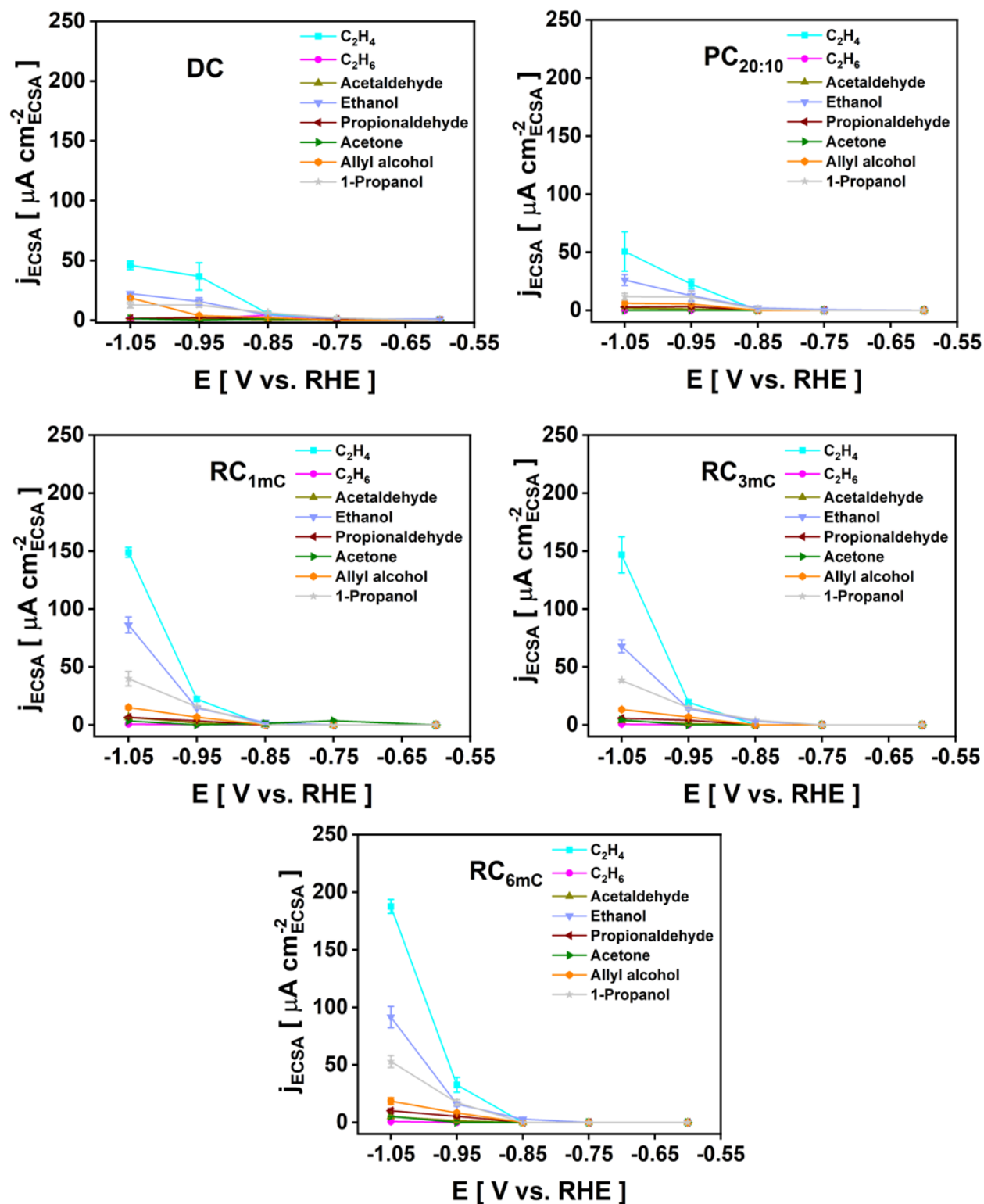


Figure 60: CO_2RR partial current densities of C_2^+ products of the reversing current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

Figure 61 compares the total C_{2+} product FEs and total C_{2+} product ECSA-normalized partial current densities for the RC series. From -0.6 to -0.85 V, the DC sample showed a higher $FE_{C_{2+}}$ than both $PC_{20:10}$ and RC samples; however, the corresponding $j_{C_{2+}}$ values were nearly negligible in this range, so total C_{2+} product FEs alone are not a reliable indicator of good C_{2+} intrinsic activity for the DC sample. At -0.95 V, all samples exhibited almost similar $j_{C_{2+}}$ values of around $65 \mu A cm_{ECSA}^{-2}$, with corresponding $FE_{C_{2+}}$ ranging between 23 and 30%. At -1.05 V, the RC samples showed a pronounced increase in both $FE_{C_{2+}}$ and $j_{C_{2+}}$ compared to the DC and $PC_{20:10}$ references. For example, the DC sample displayed an $FE_{C_{2+}}$ of $16 \pm 1\%$ and a $j_{C_{2+}}$ of $90 \pm 9 \mu A cm_{ECSA}^{-2}$, whereas the RC_{6mC} reached corresponding values of $40 \pm 4\%$ and $372 \pm 27 \mu A cm_{ECSA}^{-2}$.

Overall, besides the remarkable CO_2RR performance obtained from the PC-DHBT, the RC-DHBT demonstrated an additional dramatic enhancement of CO_2RR performance at the same pulse separation, with more effectively quenched H_2 FEs, promoting C_{2+} product activity in terms of FEs and j_{ECSA} values at -1.05 V, and preserving formate activity in the potential range between -0.6 and -0.85 V. Additionally, the activity of the RC foams can be improved by increasing the ΔC parameter. The hypothesis that the CO_2RR performance of the Cu foams is limited by CO_2 concentration polarization between the foam surface and pore bottom, which is in turn determined by the foam architecture, persists for the RC series. As the foam compactness increased with increasing ΔC , which is indicated by the decreased pore diameter, enhanced pore density, decreased foam thickness, and reduced ECSA, the C_{2+} activity increased, and H_2 FEs decreased, with respect to the more open $PC_{20:10}$ and DC references, which exhibited significantly lower performance. This confirms again that CO_2 concentration polarization between the pore top and bottom is strictly controlled by the sample compactness or openness.^[125]

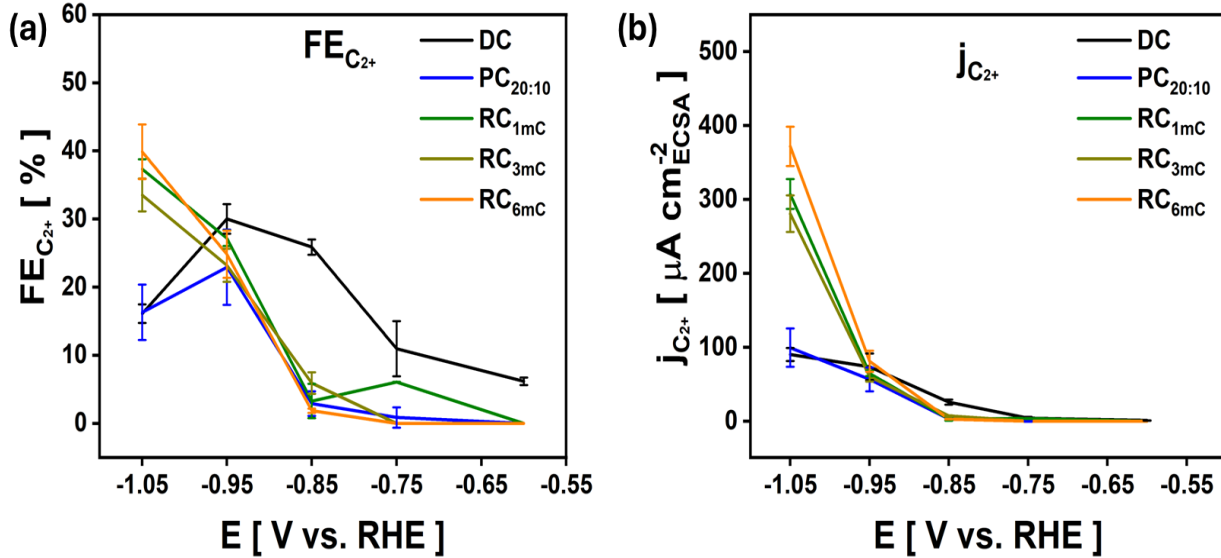


Figure 61: Comparison of the total Faradaic efficiencies (a) and total ECSA-normalized partial current densities (b) of C_{2+} products for the samples of the reversing current series

3.2.3 Alternating Current Modes

The effect of conducting DHBT with an AC waveform superimposed on a DC offset was examined systematically. Previous studies indicated that to produce AC-derived morphologies that differ significantly from those formed under a pure DC regime, the AC amplitude must exceed the DC offset^[129]. Guided by this criterion, five distinct AC-DHBT conditions were investigated. In all experiments, a cathodic DC density of 1 A cm^{-2} was applied for 20 s, with the total charge density maintained constant at 20 C cm^{-2} . The AC-derived foams were referenced against a Cu foam prepared under a continuous cathodic pure DC density of 1 A cm^{-2} for 20 s. Five AC foams were fabricated and abbreviated by their AC frequency and amplitude values as $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{1000\text{Hz}}$, and $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$, corresponding to applied cycles of 10; 10; 10; 20,000; and 100,000. SEM characterization of the AC foams is shown in Figure 62 and 63. Low-magnification SEM images reveal that all AC samples possessed honeycomb-like architectures. At a fixed frequency of 0.5 Hz, increasing the AC amplitude resulted in larger average pore diameters of 11.3 ± 0.3 , 12.1 ± 0.3 , and $14.5 \pm 0.4 \text{ }\mu\text{m}$ for $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$, and $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$, respectively. Fixing the AC amplitude at 1.5 A cm^{-2} and raising the frequency from 0.5 to 5000 Hz increased the mean pore diameter from 12.1 ± 0.3 to $20.4 \pm 0.5 \text{ }\mu\text{m}$. Measured thicknesses were 47.3 ± 3.8 , 37.4 ± 2.0 , 43.0 ± 3.1 , 40.7 ± 5.5 , and $44.0 \pm 4.1 \text{ }\mu\text{m}$ for $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{1000\text{Hz}}$, and $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$, respectively. The DC reference exhibited a mean pore diameter of $19.9 \pm 0.6 \text{ }\mu\text{m}$ and a thickness of $50.6 \pm 5.3 \text{ }\mu\text{m}$. Moreover, the AC foams, except $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$, showed higher pore densities than the DC reference. For instance, $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$ exhibited a pore density of $\approx 1379 \text{ pore mm}^{-2}$ vs. $\approx 748 \text{ pore mm}^{-2}$ for the DC foam. Foams formed at 0.5 and 1000 Hz displayed fine surface nano-dendrites, while the $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$ sample developed larger, more branched nano-dendrites. The different morphology of the $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$, relative to the other AC foams, was attributed to a greater fraction of the cathodic signal at 5000 Hz being consumed by capacitive processes during synthesis, as will be discussed later in more detail.

Gravimetric results and electrodeposition FEs are presented in Figure 64a. The samples $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$, and $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$ exhibited almost similar deposited Cu mass densities of 2.5 ± 0.2 , 2.5 ± 0.1 , and $2.4 \pm 0.1 \text{ mg cm}^{-2}$, corresponding to deposition FEs of $38 \pm 3\%$, $38 \pm 2\%$, and $37 \pm 1\%$, respectively. By contrast, $\text{AC}_{1.5\text{A}}^{1000\text{Hz}}$, $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$, and the DC sample showed higher mass densities of 3.0 ± 0.2 , 3.1 ± 0.2 , and $3.1 \pm 0.3 \text{ mg cm}^{-2}$ with FEs of $45 \pm 3\%$, $47 \pm 3\%$, and $48 \pm 4\%$, correspondingly. All AC samples exhibited lower ECSA values of around $75 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ than the DC reference, which displayed an ECSA of $127 \pm 15 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$, as shown in 64b. Within the low-to-moderate frequency range of 0.5-1000 Hz, the large cathodic amplitudes reached during the negative half-cycles effectively reproduce the influence of high DC densities observed in the current-time series, promoting compact deposits with smaller pores and higher pore density. Moreover, during AC-DHBT, part of the applied charge is consumed by charging and discharging the electrode double-layer capacitance,^[132] which attenuates the effective cathodic current density. This attenuation mimics the effect of lowering DHBT currents in DC-DHBT, producing larger pores and reducing pore densities. Because capacitive contributions grow with increasing AC amplitude or frequency, they can account for the progressive increase in pore size and the accompanying decrease in pore density observed at higher AC frequencies or amplitudes. Interestingly, developing cauliflower-like surface nano-structures appears to require abrupt, periodic drops in cathodic current (as in the PC and RC modes), whereas the relatively smoother cathodic-anodic transitions in AC-DHBT generate hydrodynamic conditions similar to DC-DHBT and favor nano-dendrite formation.

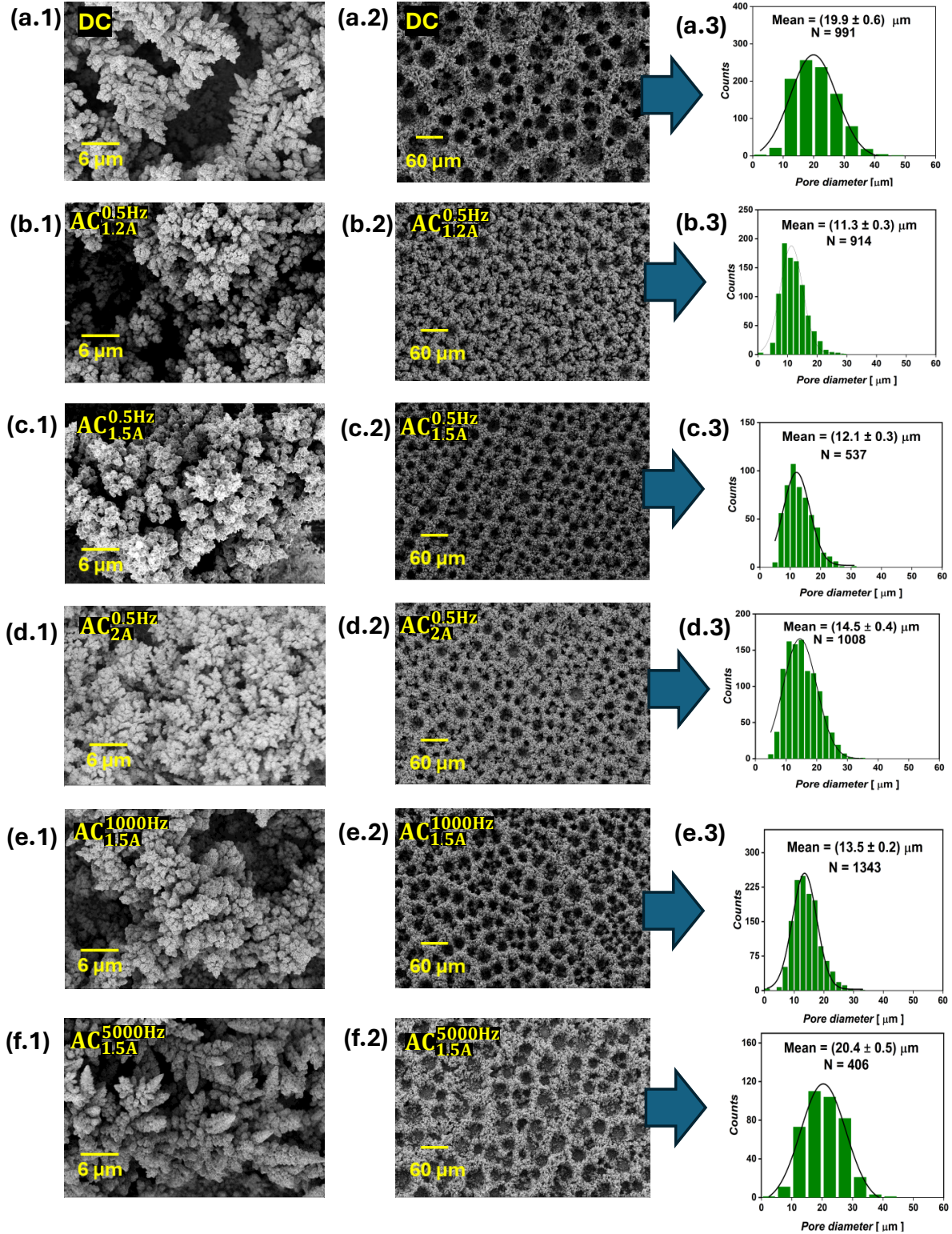


Figure 62: Top-view SEM images of Cu foam samples presenting the surface nano-structures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the DC reference sample (a), $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$ (b), $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$ (c), $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$ (d), $\text{AC}_{1.5\text{A}}^{1000\text{Hz}}$ (e), and $\text{AC}_{1.5\text{A}}^{5000\text{Hz}}$ (f), where N is the number of pores from which the pore diameter distribution was obtained

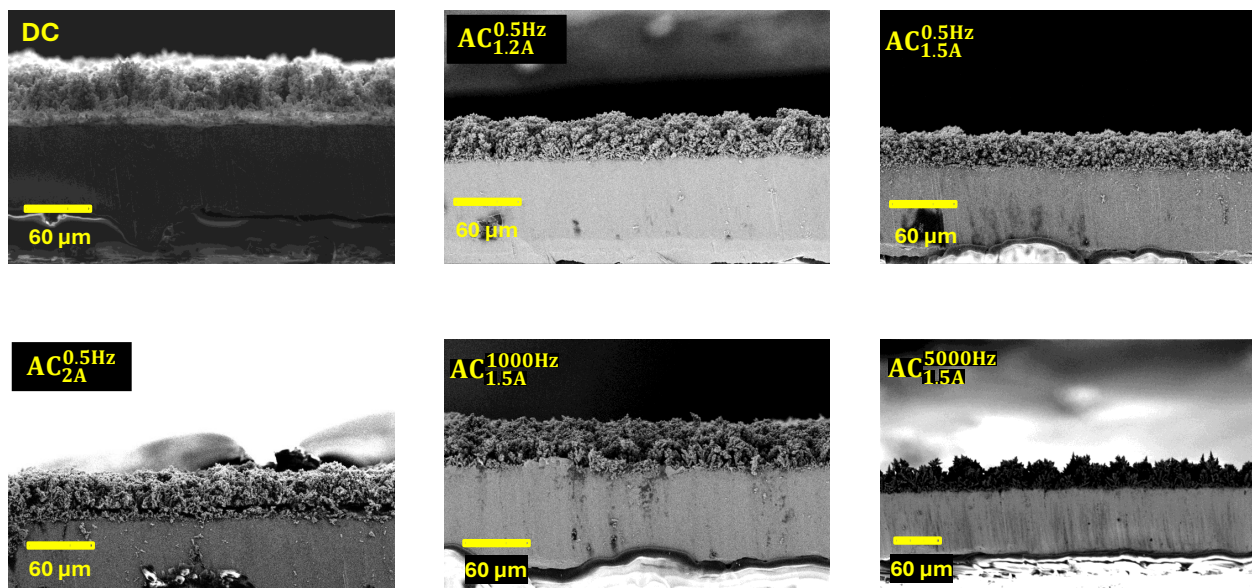


Figure 63: Examples of the cross-sectional SEM images of the AC samples, each collected at an appropriate magnification

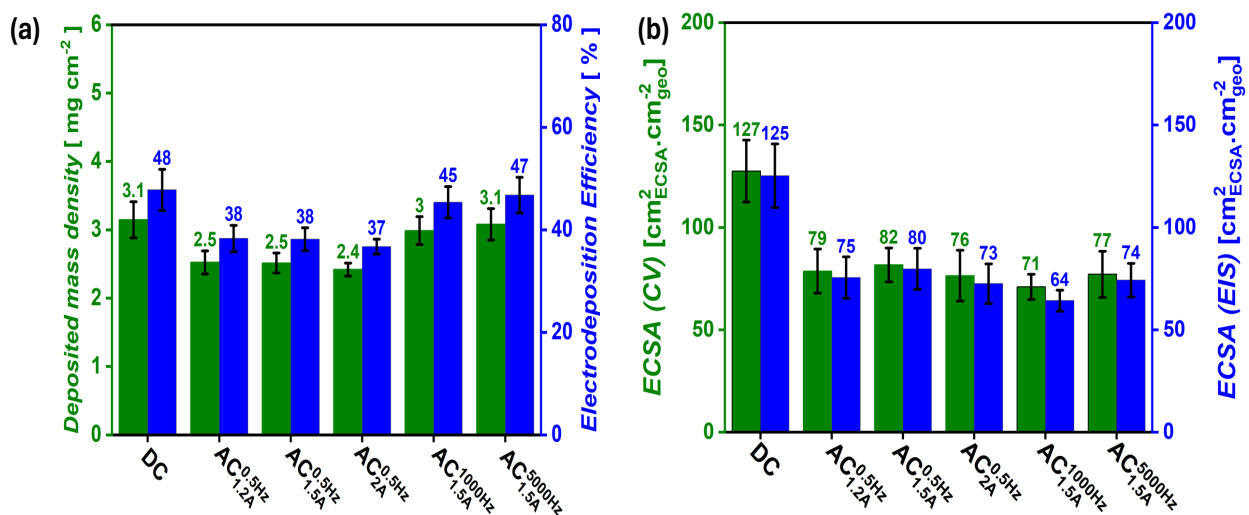


Figure 64: Gravimetric analysis (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis) of the alternating current series

CO_2RR FEs of the AC series are presented in Figure 65. The major products detected were formate, CO, ethylene, ethanol, 1-propanol, and parasitic H_2 . Methane was only observed at appreciable FEs at -1.05 V, with values of $\approx 4\text{-}9\%$. H_2 FEs for both the AC samples and DC reference increased steadily with increasing cathodic potential. For example, AC $_{1.5A}^{0.5\text{Hz}}$ showed a H_2 FE of $17 \pm 2\%$ at -0.6 V, rising to $74 \pm 0.1\%$ at -1.05 V. Conversely, CO and formate reached their highest FEs between -0.6 and -0.85 V and declined to negligible values between -0.95 and -1.05 V. For instance, AC $_{1.5A}^{0.5\text{Hz}}$ exhibited the highest CO FE in the AC series, $31 \pm 3\%$ at -0.6 V, which dropped to 0% at -1.05 V.

Similarly, $AC_{1.5A}^{1000Hz}$ showed a formate FE of $57 \pm 4\%$ at -0.6 V, which decreased to $4 \pm 1\%$ at -1.05 V. The largest C_{2+} product FEs were observed at -0.95 V. At less negative potentials, ethanol and 1-propanol reached FEs of up to $\approx 10\%$ for some samples, but their corresponding partial current densities were negligible, as will be discussed later. Therefore, comparisons between samples are more meaningful in the -0.95 to -1.05 V potential window, where C_{2+} partial current densities are maximal. At -0.95 V, the AC samples generally showed higher FEs for ethylene, ethanol, and 1-propanol than the DC reference. For example, $AC_{1.5A}^{0.5Hz}$ displayed FEs of $19 \pm 1\%$, $9 \pm 0\%$, and $7 \pm 0\%$ for ethylene, ethanol, and 1-propanol compared with $15 \pm 0\%$, $6 \pm 1\%$, and $5 \pm 1\%$ for the DC reference, respectively. Analogously, at -1.05 V, the AC samples outperformed the DC reference in C_{2+} selectivity. For example, the $AC_{1.5A}^{1000Hz}$ and the DC foams showed ethylene FEs of $13 \pm 2\%$ and $8 \pm 1\%$, respectively. Clearly, the AC mode improves C_{2+} product selectivity, but the improvement is modest compared with the PC and RC modes.

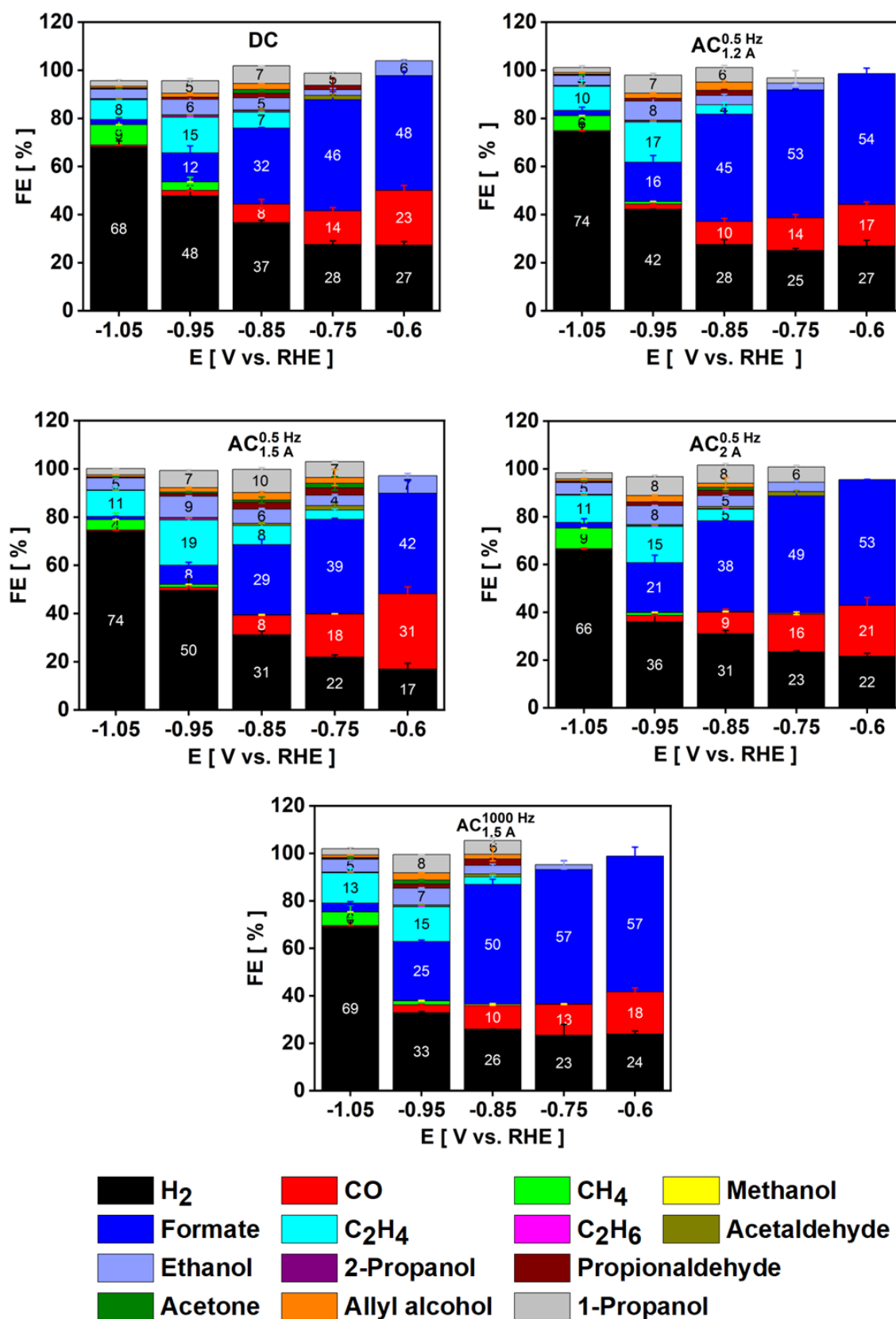


Figure 65: Faradaic efficiencies of CO₂RR products of the alternating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Figure 66 provides geometric-area-normalized partial current densities of C_1 products. Methanol showed negligible j_{geo} values across the applied potential range. CO also showed very low j_{geo} with maxima at -0.85 V of less than $1 \text{ mA cm}_{\text{geo}}^{-2}$. Methane displayed considerable j_{geo} only at -1.05 V, with maximum values observed from the DC ($6.0 \pm 2.2 \text{ mA cm}_{\text{geo}}^{-2}$) and $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$ ($5.0 \pm 1.8 \text{ mA cm}_{\text{geo}}^{-2}$). Formate was the most dominant C_1 product, with j_{geo} peaking either at -0.85 V for the $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$ sample or at -0.95 V for the other samples. The peak j_{geo} value for the AC samples and DC reference ranged between $2.6 \pm 0.0 \text{ mA cm}_{\text{geo}}^{-2}$ (obtained from $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$) and $3.8 \pm 0.2 \text{ mA cm}_{\text{geo}}^{-2}$ (obtained from $\text{AC}_{2\text{A}}^{0.5\text{Hz}}$).

Geometric-area-normalized partial current densities of C_{2+} products are provided in Figure 67. Ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol exhibited negligible j_{geo} across the applied potential range. Ethylene, ethanol, and 1-propanol showed considerable j_{geo} only in the potential window from -0.95 to -1.05 V. At -0.95 V, the DC, $\text{AC}_{1.2\text{A}}^{0.5\text{Hz}}$, and $\text{AC}_{1.5\text{A}}^{0.5\text{Hz}}$ samples exhibited the highest C_{2+} product j_{geo} values: 4.7 ± 1.5 , 3.2 ± 0.3 , and $4.9 \pm 0.7 \text{ mA cm}_{\text{geo}}^{-2}$ for ethylene; 2.0 ± 0.4 , 1.5 ± 0.0 , and $2.3 \pm 0.3 \text{ mA cm}_{\text{geo}}^{-2}$ for ethanol; and 1.6 ± 0.2 , 1.4 ± 0.0 , and $1.9 \pm 0.1 \text{ mA cm}_{\text{geo}}^{-2}$ for 1-propanol, respectively. At -1.05 V, no significant difference between the samples in C_{2+} j_{geo} was observed, with ethylene j_{geo} ranging between 5.1 and $6.5 \text{ mA cm}_{\text{geo}}^{-2}$, ethanol j_{geo} between 2.2 and $3.0 \text{ mA cm}_{\text{geo}}^{-2}$, and 1-propanol j_{geo} between 1.1 and $1.6 \text{ mA cm}_{\text{geo}}^{-2}$.

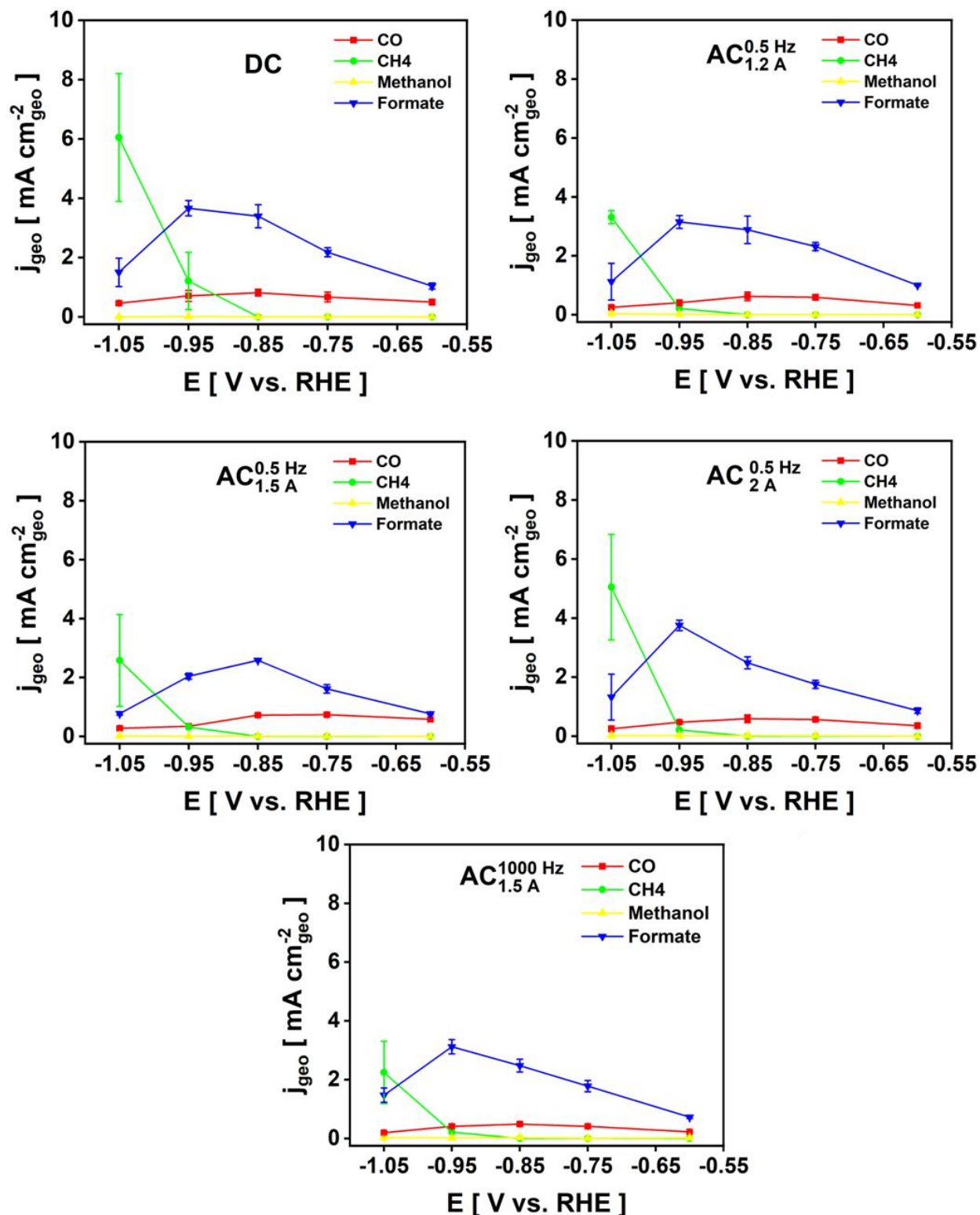


Figure 66: CO_2RR partial current densities of C_1 products of the alternating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

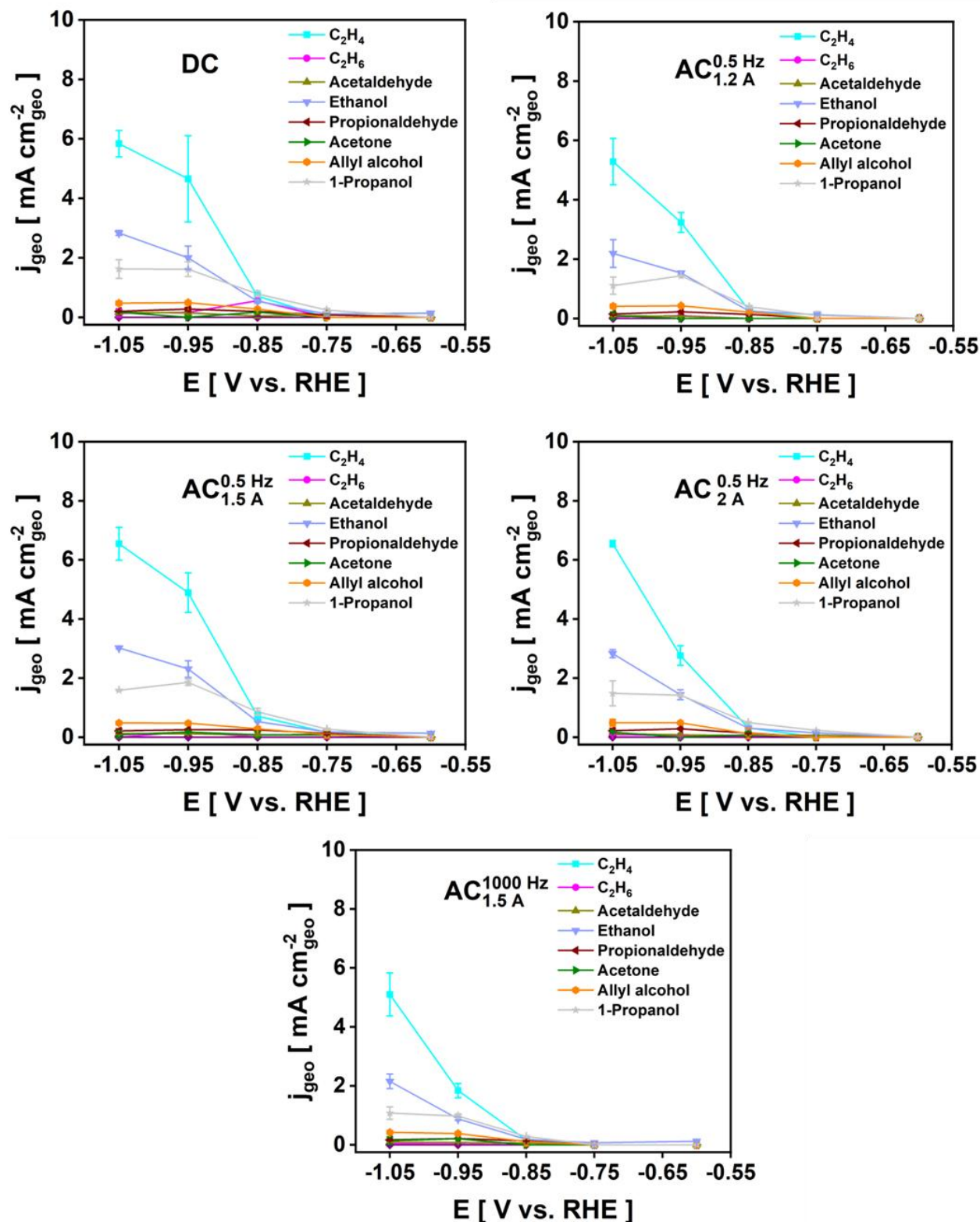


Figure 67: CO_2RR partial current densities of C_2^+ products of the alternating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

To exclude the influence of foam surface area on the measured partial current densities of CO₂RR products and to provide insights into the intrinsic activity of the AC Cu foams, partial current densities were normalized to the ECSA. ECSA-normalized partial current densities for C₁ products are presented in Figure 68. Similar to j_{geo} behavior, methane showed negligible j_{ECSA} values, while CO showed low j_{ECSA} values of less than $10 \mu\text{A cm}_{\text{ECSA}}^{-2}$. Methane also exhibited considerable j_{ECSA} only at -1.05 V, with values ranging between $31 \pm 19 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (observed from AC_{1.5A}^{0.5Hz}) and $59 \pm 21 \mu\text{A cm}_{\text{ECSA}}^{-2}$ (observed from AC_{2A}^{0.5Hz}). Again, formate j_{ECSA} followed a volcano-like trend, peaking in the potential range from -0.85 to -0.95 V. The AC foams and DC reference exhibited formate peak values in the range of approximately $30\text{-}45 \mu\text{A cm}_{\text{ECSA}}^{-2}$.

Figure 69 presents the ECSA-normalized partial current densities of C₂₊ products. Again, only at potentials more negative than -0.85 V, appreciable ethylene, ethanol, and 1-propanol j_{ECSA} values were obtained, while ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol showed negligible j_{ECSA} across the investigated potential window. At -0.95 V, the sample AC_{1.5A}^{0.5Hz} displayed the highest j_{ECSA} values for ethylene ($60 \pm 8 \mu\text{A cm}_{\text{ECSA}}^{-2}$), ethanol ($28 \pm 3 \mu\text{A cm}_{\text{ECSA}}^{-2}$), and 1-propanol ($23 \pm 1 \mu\text{A cm}_{\text{ECSA}}^{-2}$). In contrast to the j_{geo} values, which displayed only small differences at -1.05 V, the corresponding j_{ECSA} values indicate that all AC samples possessed higher intrinsic C₂₊ activity than the DC reference. For example, AC_{1.5A}^{0.5Hz} and AC_{2A}^{0.5Hz} exhibited ethylene j_{ECSA} of 80 ± 7 and $77 \pm 1 \mu\text{A cm}_{\text{ECSA}}^{-2}$, ethanol j_{ECSA} of 37 ± 0 and $33 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$, and 1-propanol j_{ECSA} of 19 ± 0 and $17 \pm 5 \mu\text{A cm}_{\text{ECSA}}^{-2}$, correspondingly. By comparison, the DC reference showed corresponding ethylene, ethanol, and 1-propanol j_{ECSA} of 46 ± 4 , 22 ± 1 , and $13 \pm 2 \mu\text{A cm}_{\text{ECSA}}^{-2}$.

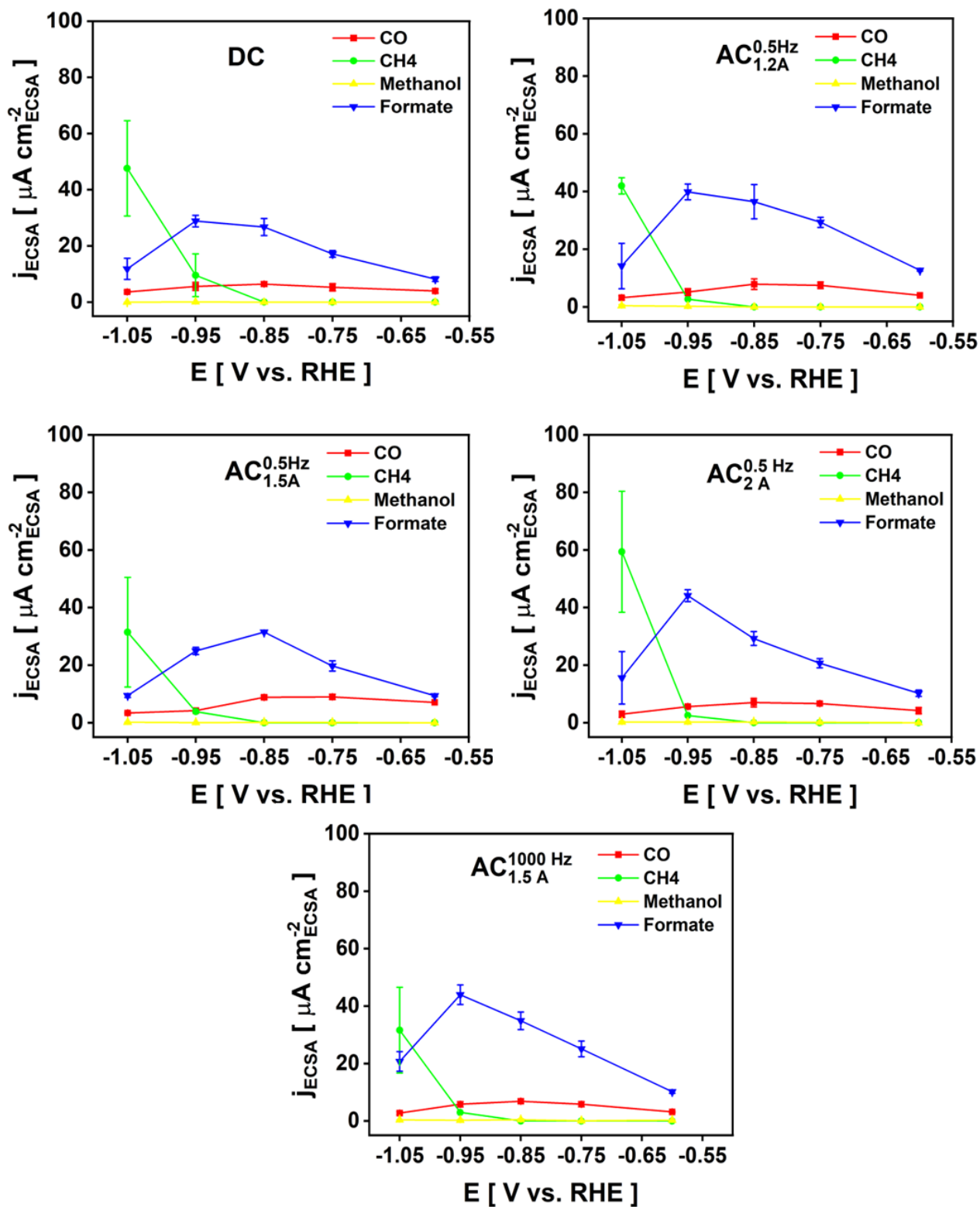


Figure 68: CO₂RR partial current densities of C_1 products of the alternating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

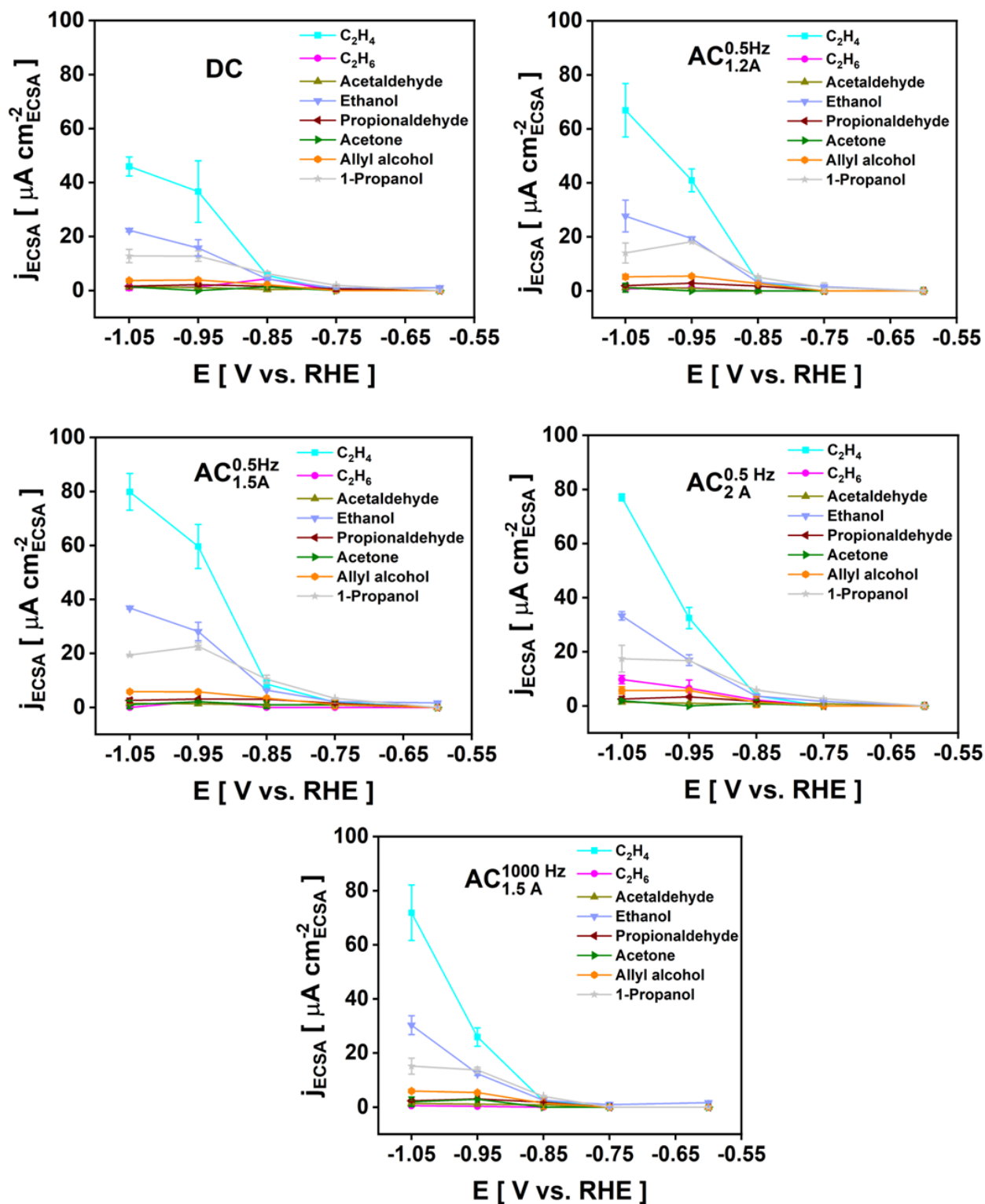


Figure 69: CO_2RR partial current densities of C_2^+ products of the alternating current series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

A comparison between the AC samples with respect to total C_{2+} product FEs and total C_{2+} product ECSA-normalized partial current densities is given in Figure 70. At potentials less negative than -0.95 V, differences between samples in $FE_{C_{2+}}$ can be observed, but the corresponding $j_{C_{2+}}$ values were all low, with very minor differences. At -0.95 V, all the AC samples showed higher $FE_{C_{2+}}$ values of up to $\approx 40\%$ compared to the DC counterpart ($\approx 30\%$). The corresponding $j_{C_{2+}}$ values at -0.95 V were higher for the AC samples produced at 0.5 Hz than for both the DC reference and $AC_{1.5A}^{1000Hz}$. The largest $j_{C_{2+}}$ at -0.95 V ($125 \pm 13 \mu A cm_{ECSA}^{-2}$) was obtained from the sample $AC_{1.5A}^{0.5Hz}$. At -1.05 V, both the AC samples and DC reference showed close total C_{2+} FEs of around 20%, while the corresponding $j_{C_{2+}}$ values for the AC samples were higher than those for the DC reference, with the highest values exhibited by the $AC_{1.5A}^{0.5Hz}$ and $AC_{2A}^{0.5Hz}$ ($\approx 150 \mu A cm_{ECSA}^{-2}$), whereas the DC samples exhibited $j_{C_{2+}}$ of $90 \pm 9 \mu A cm_{ECSA}^{-2}$.

The results of the AC series indicate that AC-DHBT enhances C_{2+} activity of the resulting Cu foams, as evidenced by higher FEs at -0.95 V and increased j_{ECSA} at -1.05 V. Nevertheless, PC- and RC-DHBT were demonstrated to be more effective at suppressing the parasitic H_2 evolution, promoting formate formation in the -0.6 to -0.85 V potential window, and substantially boosting C_{2+} activity at -1.05 V. The improved performance of the AC foams is consistent with the hypothesis that more compact Cu foams suffer less internal mass-transport limitation of CO_2 within the pore interiors, a point discussed in detail for the current-time, PC, and RC series. Compared with the DC reference, the AC foams generally exhibited smaller pore diameters, reduced thickness, and lower ECSA, which correlates with their superior CO_2RR selectivity relative to the DC sample.

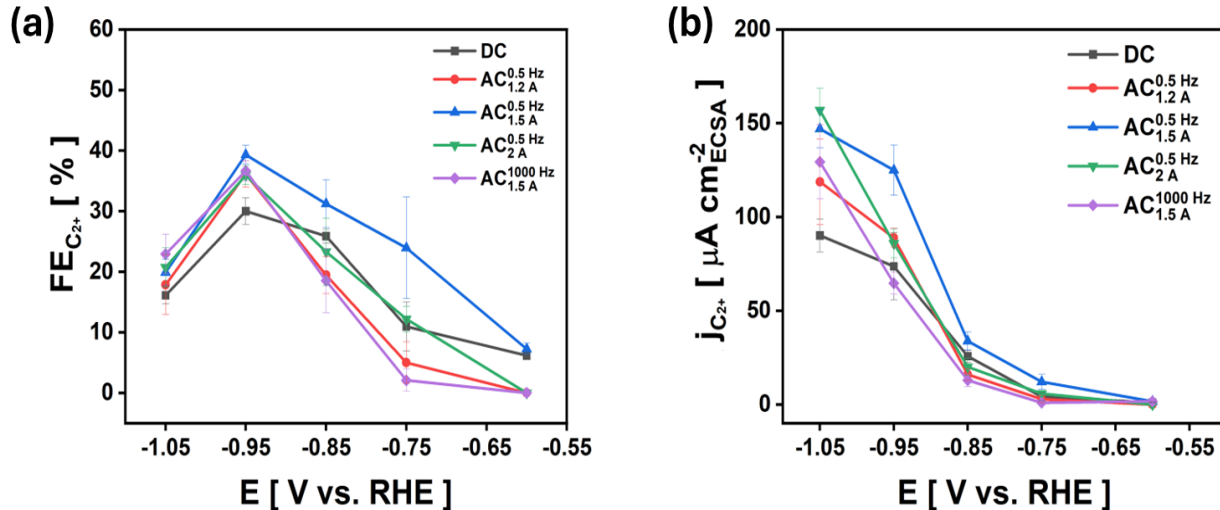


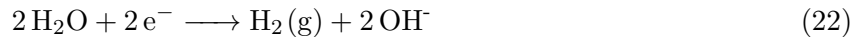
Figure 70: Comparison of the total Faradaic efficiencies (a) and total ECSA-normalized partial current densities (b) of C_{2+} products for the samples of the alternating current series

To summarize the findings of the current mode series, applying the PC mode, particularly at low pulse-to-pause ratios, provided an enhancement in CO_2RR activity toward formate in the potential range from -0.6 to -0.85 V and C_{2+} products at -1.05 V, compared to the DC reference. Under the same pulse separation, the RC mode exhibited superior C_{2+} activity at -1.05 V with respect to the PC reference while maintaining the same high formate activity at less negative potentials. The AC mode led to a modest increase in C_{2+} activity at -0.95 and -1.05 V with respect to the DC foam.

3.3 Chemical DHBT effect series

In this series, the influence of Cu^{2+} concentration, electrolyte pH, the addition of surfactants: sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), and the addition of Cu-complexing agents: 3,5-diamino-1,2,4-triazole (DAT) on DHBT-derived Cu foam morphology was examined. All deposits were produced under a continuous cathodic DC density of 1 A cm^{-2} for 20 s and were compared to a reference sample prepared under the same current and time conditions using the standard electrolyte described in Section 2.1.1.

SEM results (Figures 71 and 72) showed that lowering Cu^{2+} concentration from 0.2 M to 0.1 M or to 0.05 M produced non-uniform Cu agglomerates with reduced interconnectivity and finer nano-dendrites. Corresponding thicknesses declined from $50.6 \pm 5.3 \text{ }\mu\text{m}$ (0.2 M Cu^{2+}) to $30.3 \pm 2.0 \text{ }\mu\text{m}$ (0.1 M Cu^{2+}) and $22.9 \pm 10.2 \text{ }\mu\text{m}$ (0.05 M Cu^{2+}). The mean pore diameter at 0.1 M ($13.7 \pm 0.1 \text{ }\mu\text{m}$) was significantly smaller than that of the reference foam ($19.9 \pm 0.6 \text{ }\mu\text{m}$), while at 0.05 M, no foam structure was obtained; instead, agglomerates with predominant micro-to-nano porosity were formed. By contrast, raising the electrolyte pH from ≈ -0.5 (for reference) to ≈ 0.5 produced a thicker foam ($65.5 \pm 6.9 \text{ }\mu\text{m}$), a larger pore diameter ($28.4 \pm 2.4 \text{ }\mu\text{m}$), and increased nano-dendrite dimensions. Gravimetric measurements (Figure 74a) reveal that both the deposited Cu mass density and the electrodeposition FE decline as Cu^{2+} concentration decreases, with values of $3.1 \pm 0.3 \text{ mg cm}^{-2}$ and $48 \pm 4\%$ (0.2 M), $1.6 \pm 0.1 \text{ mg cm}^{-2}$ and $25 \pm 1\%$ (0.1 M), and $0.7 \pm 0.1 \text{ mg cm}^{-2}$ and $10 \pm 1\%$ (0.05 M). Increasing the pH to 0.5 raised the mass density and deposition FE to $3.8 \pm 0.2 \text{ mg cm}^{-2}$ and $58 \pm 4\%$. The enhanced H_2 evolution at low Cu^{2+} concentrations, as evidenced by reduced deposition FE, is consistent with the SEM results, where numerous very small H_2 bubbles were formed, providing limited local stirring and smaller nano-dendrites, and hindering the formation of an interconnected foam network. At pH 0.5, suppressed H_2 evolution, i.e., higher electrodeposition FE, leads to a smaller number of H_2 bubbles with a larger size, inducing stronger convective effects and promoting larger nano-dendrites. Notably, the honeycomb-like architecture appeared only at the highest Cu^{2+} concentration, supporting the hypothesis that forming interconnected foams via DHBT requires sufficiently high rates of both Cu electrodeposition and H_2 evolution, given the dependence of reaction rates on reactant concentration.^[89] Conversely, despite the tenfold decrease in H^+ concentration (from 3 M to 0.3 M) performed to raise the electrolyte pH from ≈ -0.5 to ≈ 0.5 , the foam morphology persisted. This observation supports the hypothesis that, during DHBT, HER can proceed via reduction of both H^+ ions and/or water molecules, as represented by Equations 22 and 23.^[89] Nevertheless, the observed rise in electrodeposition FE, pore diameter, and dendrite dimensions at pH 0.5 indicates that H_2 evolution remains partially hindered at lower proton concentrations. In this context, the pore diameter distribution of the (pH 0.5) foam may be interpreted as a bimodal distribution, with peaks around 20 μm and 40 μm . These two pore diameters may correspond to the sizes of H_2 bubbles produced by the reduction of H^+ and H_2O . In other words, the reference sample prepared at pH -0.5 exhibited a mean pore diameter of $\approx 20 \text{ }\mu\text{m}$. Increasing the pH to 0.5 produced a larger mean pore diameter of $\approx 30 \text{ }\mu\text{m}$ with a bimodal distribution with peaks at ≈ 20 and 40 μm . This observation might suggest that two distinct H_2 bubble sizes formed during the DHBT synthesis at pH 0.5: smaller bubbles originating from proton reduction and larger bubbles resulting from water reduction.



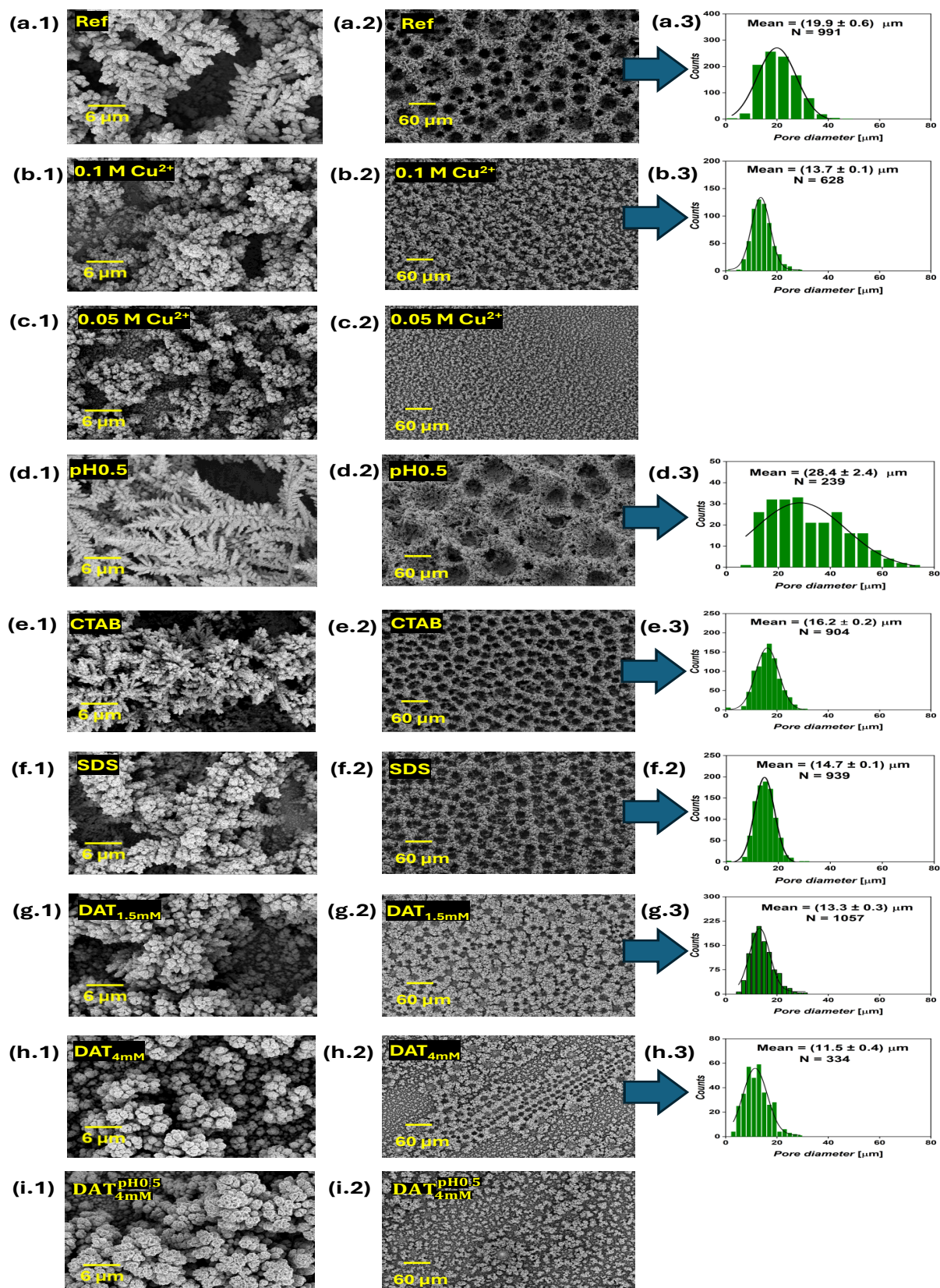


Figure 71: Top-view SEM images of Cu foam samples presenting the surface nano-structures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the reference sample (a), samples prepared at Cu²⁺ concentrations of 0.1 M (b) and 0.05 M (c), sample electrodeposited at pH 0.5 (d), samples synthesized in the presence of 0.25 mM of either CTAB (e) or SDS (f), samples synthesized in the presence of DAT at concentrations of 1.5 mM (g) and 4 mM (h), and sample prepared with 4 mM DAT at pH 0.5 (i), where N is the number of pores from which the pore diameter distribution was obtained. For the samples without a displayed pore diameter distribution, there were insufficient pore numbers to generate a reliable distribution

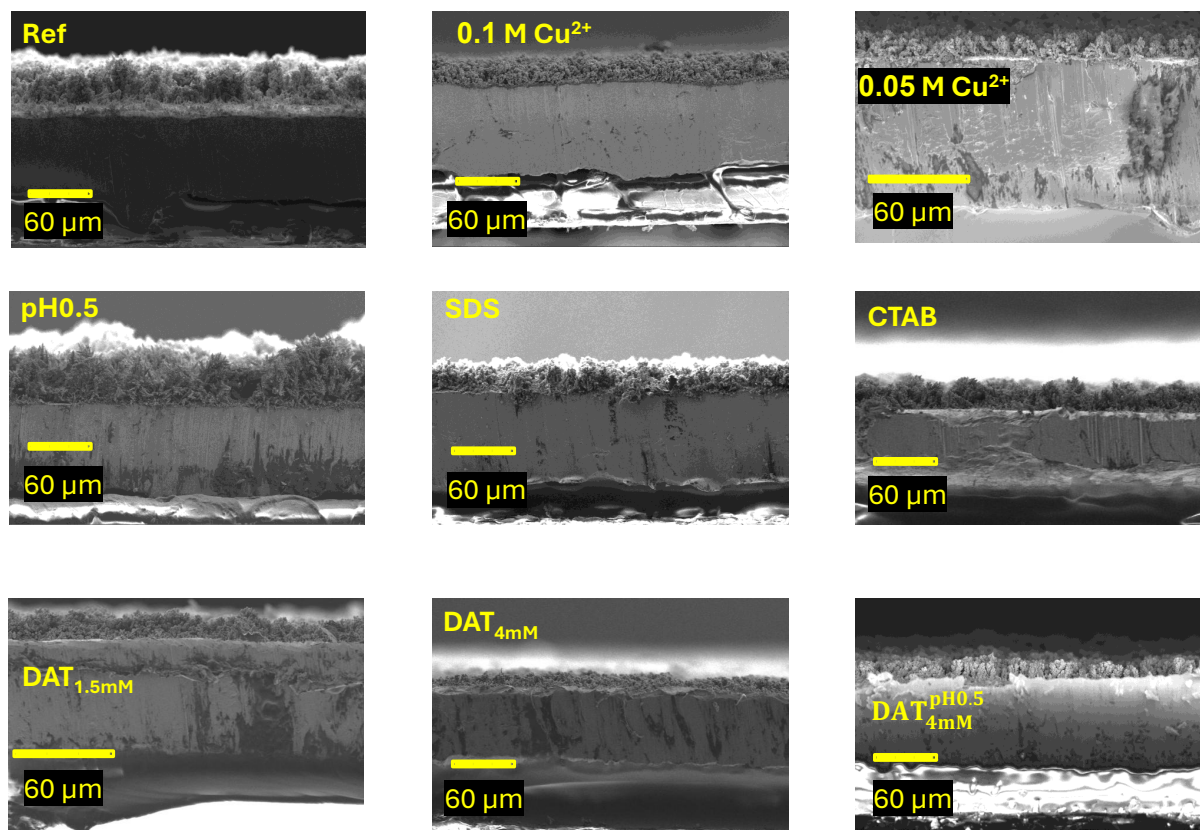


Figure 72: Examples of the cross-sectional SEM images of the chemical effect series, each collected at an appropriate magnification

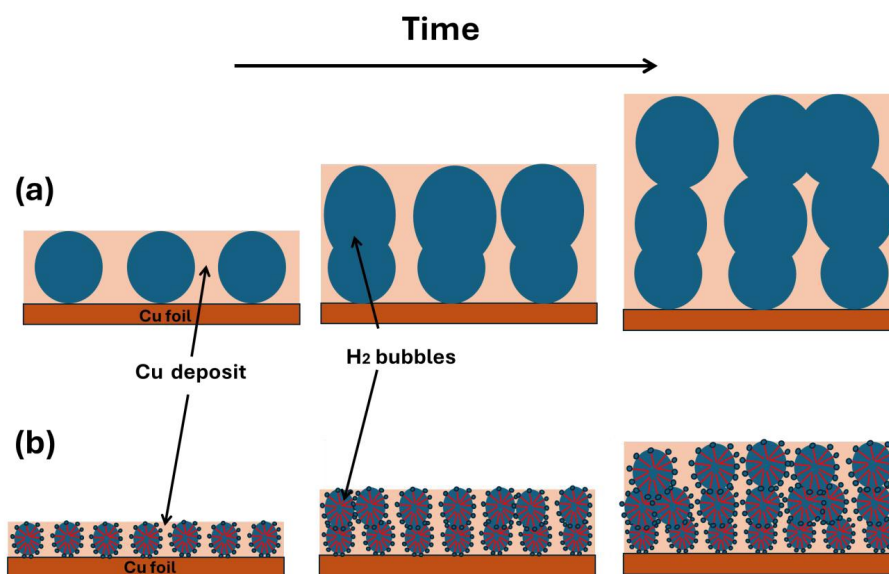


Figure 73: Schematic illustration of the DHBT process without (a) and with (b) surfactant addition to the DHBT electrolyte. The illustration highlights the presence of surfactant molecules on the bubble surface, affecting bubble size and the resulting Cu foam architecture

Introducing either SDS or CTAB at a 0.25 mM concentration into the DHBT electrolyte caused pronounced structural changes. Relative to the additive-free reference, surfactant-mediated samples exhibited smaller average pore diameters and reduced foam thicknesses, with respective values of $16.2 \pm 0.2 \mu\text{m}$ diameter and $30.5 \pm 1.6 \mu\text{m}$ thickness for CTAB, and $14.7 \pm 0.1 \mu\text{m}$ diameter and $33.3 \pm 2.6 \mu\text{m}$ thickness for SDS. Additionally, surfactants markedly increased pore densities to $1364 \text{ pore mm}^{-2}$ (CTAB) and $1063 \text{ pore mm}^{-2}$ (SDS), compared with 748 pore mm^{-2} for the reference. Deposited Cu mass densities and FEs decreased to $1.7 \pm 0.1 \text{ mg cm}^{-2}$ and $26 \pm 1\%$ for CTAB, and to $1.4 \pm 0.1 \text{ mg cm}^{-2}$ and $22 \pm 2\%$ for SDS. These trends are consistent with the well-known effect of surfactants in lowering electrolyte surface tension, which enhances HER, produces smaller H_2 bubbles, increases H_2 nucleation site density, and reduces the deposited mass density (see schematic representation in Figure 73).^[133] The compact foams with fine surface nano-dendrites formed in the presence of surfactants correspond to the elevated HER rates during DHBT, accompanied by smaller bubble templates and weaker local stirring. Although both SDS and CTAB reduced nano-dendrite size, their surface nano-structures differed. CTAB-mediated dendrites were highly branched and well-defined needles compared with the SDS-mediated counterparts. This suggests that SDS and CTAB affect Cu^{2+} diffusion dynamics differently, although both slow mass transport from the bulk electrolyte to the electrode relative to the additive-free reference foam.

Conversely, DAT had only a modest effect on the deposited Cu mass density and deposition FE, suggesting a limited influence on overall H_2 evolution but significant morphological changes. At 1.5 mM DAT (the sample denoted as $\text{DAT}_{1.5\text{mM}}$), the mean pore diameter and thickness decreased to $13.3 \pm 0.3 \mu\text{m}$ and $17.3 \pm 2.0 \mu\text{m}$, respectively, and cracks were observed within the foam walls. Increasing DAT concentration to 4 mM (the sample denoted as $\text{DAT}_{4\text{mM}}$) produced only isolated foam islands without uniform interconnectivity, with a mean pore diameter of $11.5 \pm 0.4 \mu\text{m}$ and a foam thickness of $16.6 \pm 4.1 \mu\text{m}$. When the electrolyte pH was raised to 0.5 at a 4 mM DAT concentration (the sample $\text{DAT}_{4\text{mM}}^{\text{pH}0.5}$), the foam morphology disappeared, and only Cu agglomerates were observed, consistent with prior studies reporting that the DAT chelating effect increases at higher pH values.^[107] At 1.5 mM DAT, the surface nano-dendrites were smaller than the reference sample, whereas the $\text{DAT}_{4\text{mM}}$ and $\text{DAT}_{4\text{mM}}^{\text{pH}0.5}$ samples developed cauliflower-like nano-structures. This may suggest that DAT hinders Cu electrodeposition in a manner analogous to the abrupt and periodic cathodic interruptions induced by the PC and RC DHBT regimes.

The ECSA results for the chemical effect series are shown in Figure 74b. The reference sample displayed an ECSA of $127 \pm 15 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$, which decreased upon the addition of any tested additives to $52 \pm 3 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (1.5 mM DAT), $44 \pm 5 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (4 mM DAT), $69 \pm 8 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (4 mM DAT and pH 0.5), $49 \pm 11 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (SDS), and $68 \pm 8 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (CTAB). Lowering Cu^{2+} concentration also reduced the ECSA to $51 \pm 6 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (0.1 M) and $31 \pm 3 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ (0.05 M). Increasing the electrolyte pH from -0.5 to 0.5 resulted in an ECSA of $125 \pm 5 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$, which is comparable to the reference sample.

The ability to tune foam dimensions and nano-morphology with additives such as DAT, SDS, and CTAB renders these materials attractive for electrocatalytic applications, including CO_2RR . Moreover, when foam architectures are undesirable and binder-free nano-particles are preferred, samples prepared with 4 mM DAT or 0.05 M Cu^{2+} provide suitable alternatives, as they do not form coherent structures.

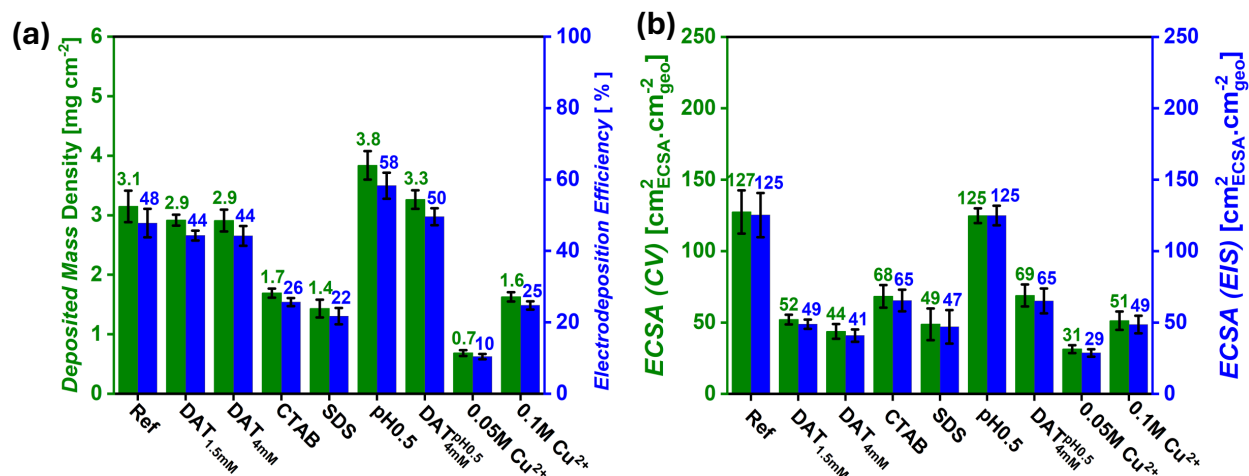


Figure 74: Gravimetric analysis (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis) of the chemical effect series

Figure 75 shows the CO₂RR FEs for the chemical effect series. The main products were formate, CO, ethylene, ethanol, 1-propanol, and the parasitic H₂. Methane exhibited appreciable FEs only at -1.05 V, with values between ≈ 7 and 11%, except for the DAT_{4mM}^{pH0.5} sample, which exhibited almost no activity for methane formation. Negligible FEs were obtained for allyl alcohol, acetone, propionaldehyde, acetaldehyde, ethane, and methanol. For both the reference and (pH 0.5) samples, the H₂ FE increased steadily as the applied potential became more negative. Specifically, the (pH 0.5) sample exhibited a H₂ FE of $35 \pm 4\%$ at -0.6 V, which rose to $68 \pm 5\%$ at -1.05 V. By contrast, the other samples in this series showed a V-shaped potential dependence of the H₂ FE, with a minimum at -0.75 or -0.85 V. For instance, the (0.05 M Cu²⁺) sample displayed a H₂ FE of $48 \pm 4\%$ at -0.6 V, which decreased to $18 \pm 1\%$ at -0.85 V, and then increased to $47 \pm 3\%$ at -1.05 V. Increasing the DHBT bath pH led to higher H₂ FEs, as seen by comparing DAT_{4mM}^{pH0.5} with DAT_{4mM}, and the reference sample with the (pH 0.5) sample. For example, at -1.05 V, DAT_{4mM}^{pH0.5} and DAT_{4mM} showed H₂ FEs of $82 \pm 1\%$ and $44 \pm 1\%$, respectively. Decreasing the Cu²⁺ concentration in the DHBT bath resulted in the reduction of H₂ FEs in the range from -0.85 to -1.05 V. At -1.05 V, H₂ FEs of $68 \pm 2\%$, $49 \pm 2\%$, and $47 \pm 3\%$ were obtained for samples electrodeposited at Cu²⁺ concentrations of 0.2, 0.1, and 0.05 M, respectively. Adding SDS or DAT (without raising the pH) to the DHBT bath decreased H₂ FEs between -0.85 and -1.05 V. For example, DAT_{1.5mM} and the reference sample displayed H₂ FEs of $39 \pm 4\%$ and $68 \pm 2\%$ at -1.05 V, respectively. Conversely, the CTAB sample favored higher H₂ FEs, exhibiting $56 \pm 1\%$ compared with $48 \pm 4\%$ for the reference sample at -0.95 V. CO and formate displayed their maximum FEs for each sample in the range from -0.6 to -0.85 V, decreasing at more negative potentials to much lower or negligible values. For example, the SDS sample showed a formate FE of $63 \pm 1\%$ at -0.85 V, which declined to $6 \pm 0\%$ at -1.05 V.

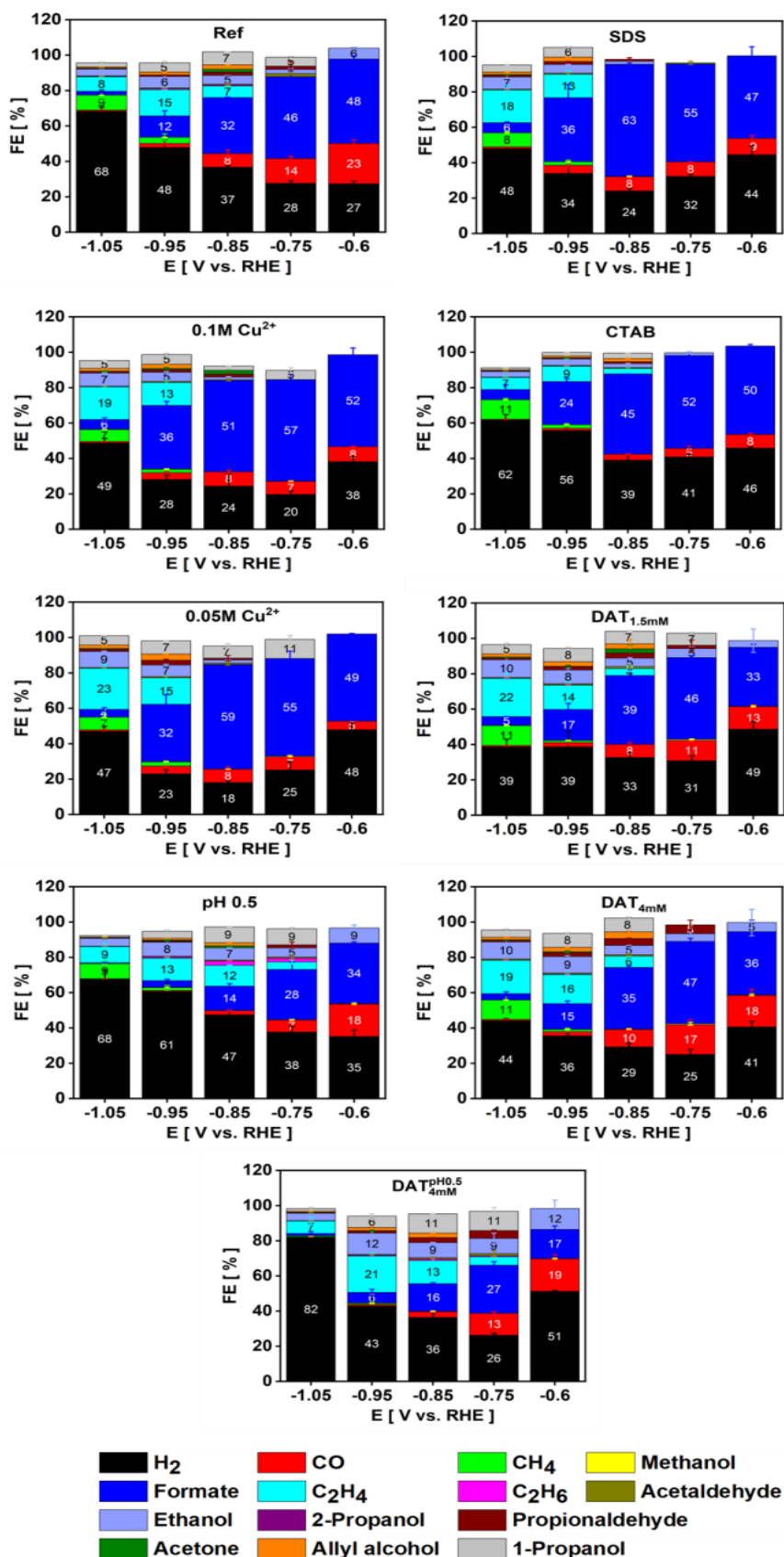


Figure 75: Faradaic efficiencies of CO₂RR products of the chemical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Generally, C_{2+} product FEs were remarkably higher in the potential range between -0.95 and -1.05 V, except for the (pH 0.5) foam, which showed a maximum total C_{2+} product FEs at -0.85 V. Although some samples exhibited considerable ethanol and 1-propanol FEs of up to $\approx 12\%$ in the potential range from -0.6 to -0.85 V, the corresponding partial current densities for these products in that range were negligible, as will be discussed later. Consequently, it is more meaningful to compare the C_{2+} product selectivity at more negative potentials, where significant partial current densities were measured. The addition of DAT (without increasing the pH), or SDS; or reducing Cu^{2+} concentration, did not result in a significant increase in the FEs of ethylene, ethanol, and 1-propanol at -0.95 V relative to the additive-free reference sample. However, at -1.05 V, a substantial increase in the C_{2+} product FEs was observed from the same samples. For example, the reference, (0.05 M Cu^{2+}), $DAT_{1.5mM}$, and SDS samples showed respective ethylene FEs of $8 \pm 1\%$, $23 \pm 2\%$, $22 \pm 3\%$, and $18 \pm 3\%$, ethanol FEs of $4 \pm 0\%$, $9 \pm 0\%$, $10 \pm 1\%$, and $7 \pm 1\%$, and 1-propanol FEs of $2 \pm 0\%$, $5 \pm 0\%$, $5 \pm 1\%$, and $4 \pm 0\%$ at -1.05 V. The $DAT_{4mM}^{pH0.5}$ sample showed higher C_{2+} FEs than the reference at -0.95 V, with an ethylene FE of $21 \pm 2\%$, ethanol FE of $12 \pm 1\%$, and 1-propanol FE of $6 \pm 1\%$, compared to respective FEs of $15 \pm 0.0\%$, $6 \pm 1\%$, and $5 \pm 1\%$ for the reference. The addition of CTAB significantly quenched C_{2+} product selectivity, with ethylene FEs of $9 \pm 0\%$ and $7 \pm 1\%$, ethanol FEs of $4 \pm 0\%$ and $3 \pm 0\%$, and 1-propanol FEs of $2 \pm 0\%$ and $1 \pm 0\%$ at -0.95 and -1.05 V, correspondingly. The sample (pH 0.5) exhibited its maximum C_{2+} FEs at -0.85 V; however, at this potential, very low C_{2+} product partial current densities of less than $1.5 \text{ mA cm}_{geo}^{-2}$ were obtained, as will be discussed later.

Figure 76 presents geometric-area-normalized partial current densities of C_1 products for the chemical effect series. CO and methanol exhibited negligible j_{geo} values for all samples across the investigated potential range. Methane showed considerable j_{geo} only at -1.05 V, with the highest values of 6.0 ± 2.2 , 4.9 ± 0.1 , 5.6 ± 1.7 , 5.3 ± 0.4 , and $7.9 \pm 0.2 \text{ mA cm}_{geo}^{-2}$ observed for the reference, $DAT_{1.5mM}$, DAT_{4mM} , (pH 0.5), and CTAB samples, respectively. Formate was the most dominant C_1 product, with j_{geo} following a volcano-like trend, peaking at either -0.95 V for the reference, (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), $DAT_{1.5mM}$, DAT_{4mM} , SDS, and CTAB samples, or at -0.85 V for the two samples produced at pH 0.5, namely $DAT_{4mM}^{pH0.5}$ and (pH 0.5). The highest formate j_{geo} values of 3.7 ± 0.3 , 5.9 ± 0.6 , 3.9 ± 0.5 , 4.9 ± 0.7 , and $7.7 \pm 0.1 \text{ mA cm}_{geo}^{-2}$ were observed for the reference, (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), SDS, and CTAB samples, respectively.

Figure 77 shows geometric-area-normalized partial current densities of C_{2+} products for the chemical effect series. Considerable C_{2+} product j_{geo} was obtained only between -0.95 and -1.05 V, while values at less negative potentials were negligible. At -0.95 V, the highest C_{2+} activity was exhibited by the reference, (pH 0.5), and $DAT_{4mM}^{pH0.5}$ samples, with corresponding j_{geo} values of 4.7 ± 1.5 , 4.0 ± 0.2 , and $4.2 \pm 0.4 \text{ mA cm}_{geo}^{-2}$ for ethylene; 2.0 ± 0.4 , 2.5 ± 0.2 , and $2.5 \pm 0.3 \text{ mA cm}_{geo}^{-2}$ for ethanol; and 1.6 ± 0.2 , 1.2 ± 0.1 , and $1.3 \pm 0.1 \text{ mA cm}_{geo}^{-2}$ for 1-propanol. At -1.05 V, the (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), $DAT_{1.5mM}$, DAT_{4mM} , and SDS samples showed superior C_{2+} activity. For instance, these five samples exhibited respective ethylene j_{geo} values of 8.5 ± 0.4 , 9.0 ± 0.4 , 9.3 ± 0.9 , 9.5 ± 0.6 , and $8.6 \pm 0.0 \text{ mA cm}_{geo}^{-2}$, while the reference sample exhibited ethylene j_{geo} of $5.8 \pm 0.4 \text{ mA cm}_{geo}^{-2}$. Elevating the DHBt bath pH (with or without DAT addition) and adding CTAB did not improve C_{2+} activity with respect to the reference sample. For example, at -1.05 V, the (pH 0.5) and $DAT_{4mM}^{pH0.5}$ samples exhibited ethylene j_{geo} values of 5.8 ± 0.3 and $3.5 \pm 0.2 \text{ mA cm}_{geo}^{-2}$, ethanol j_{geo} values of 2.8 ± 0.1 and $2.1 \pm 0.1 \text{ mA cm}_{geo}^{-2}$, and 1-propanol j_{geo} values of 0.6 ± 0.1 and $0.7 \pm 0.2 \text{ mA cm}_{geo}^{-2}$, respectively, which were comparable to or lower than the corresponding values for the reference sample.

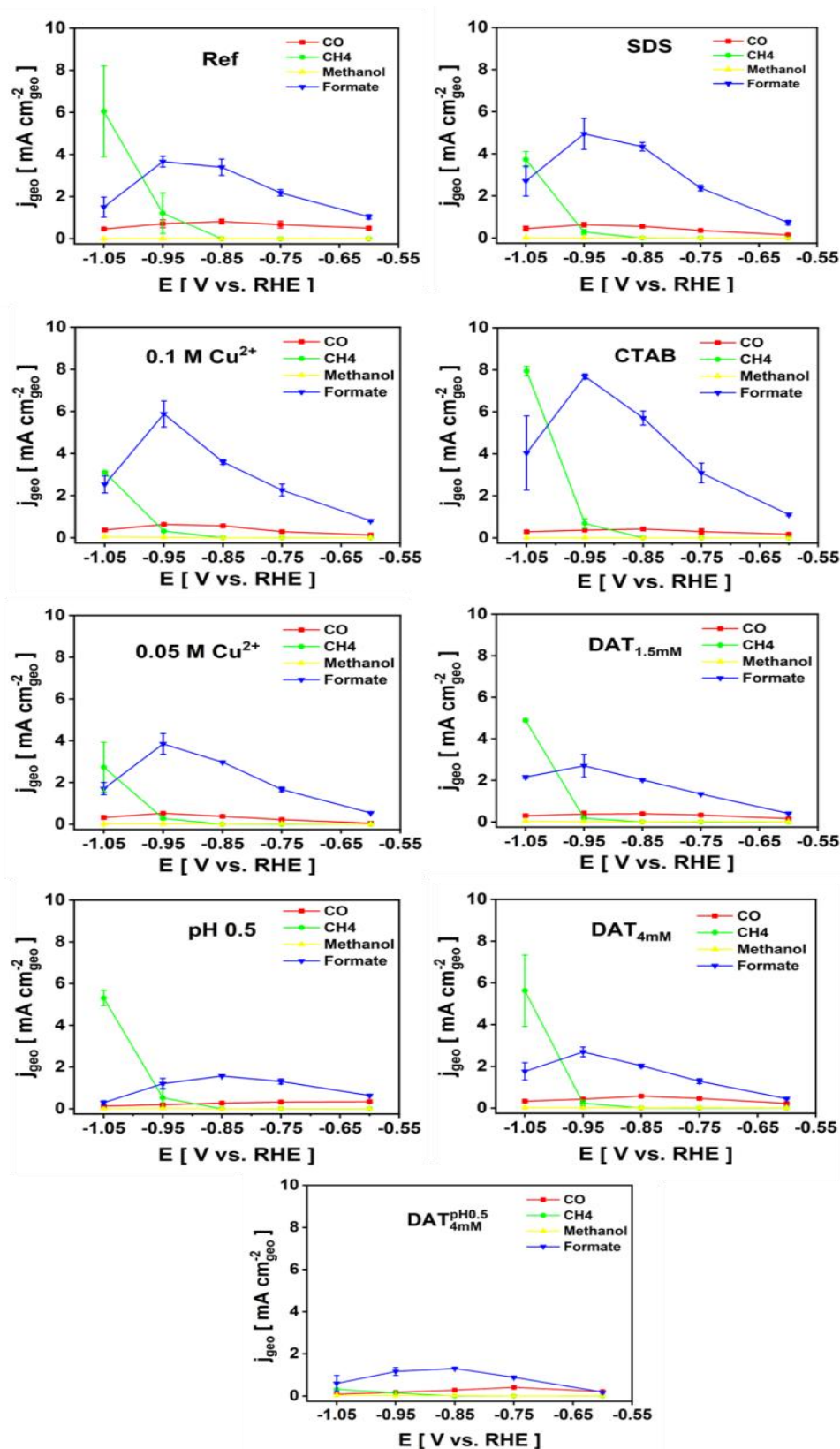


Figure 76: CO_2RR partial current densities of C_1 products of the chemical DHBt effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

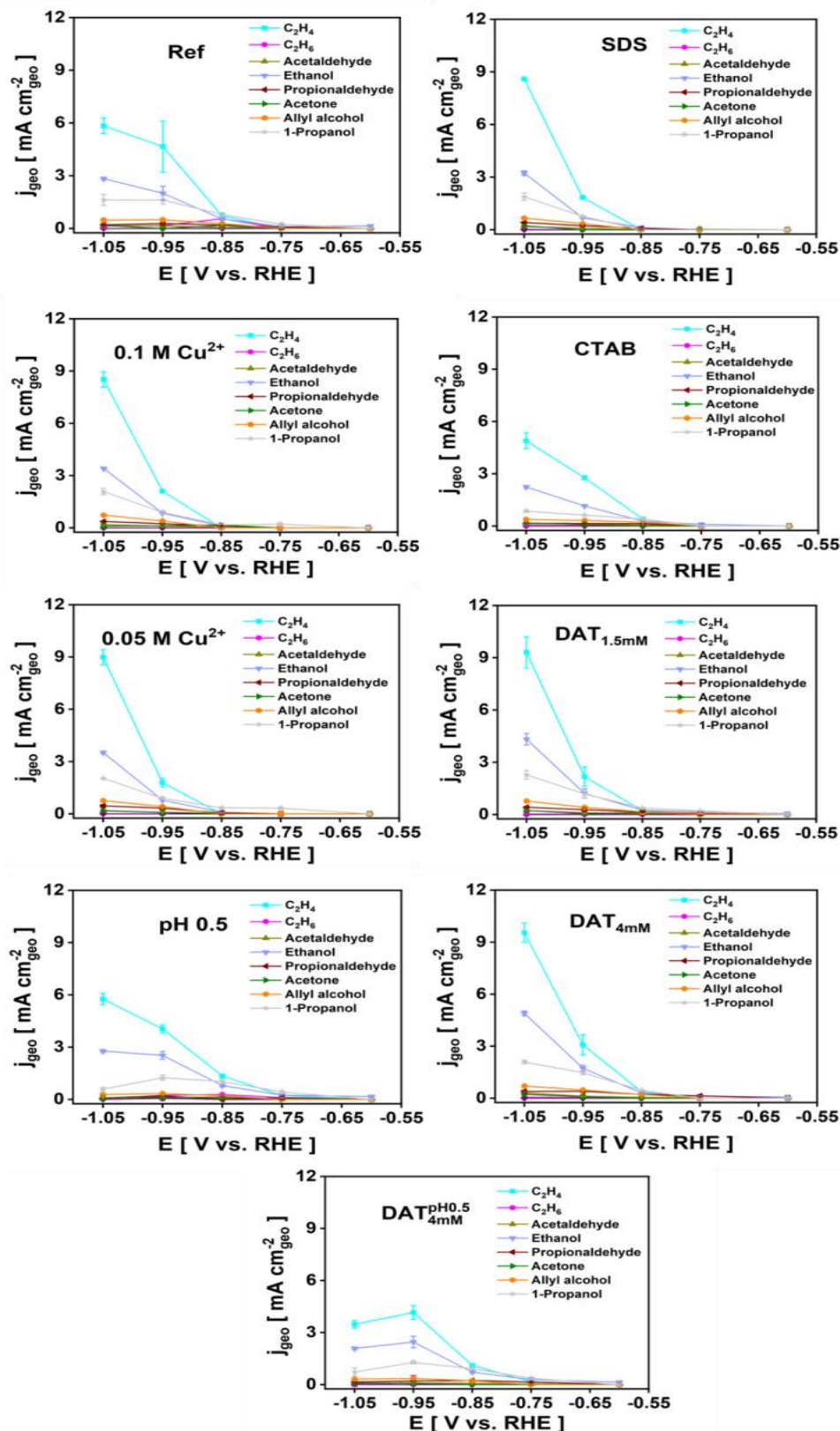


Figure 77: CO_2RR partial current densities of C_2^+ products of the chemical DHBt effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample geometric area**

Figure 78 presents the partial current densities of C_1 products of the chemical effect series normalized to ECSA. C_1 products j_{ECSA} followed similar trends as the corresponding j_{geo} . Specifically, CO and methanol exhibited negligible partial current densities; methane showed considerable current densities only at -1.05 V; and formate displayed a volcano-like partial current density, peaking at -0.85 V for the (pH 0.5) and $DAT_{4mM}^{pH0.5}$ samples, or at -0.95 V for the other samples. The (0.05 M Cu^{2+}), $DAT_{1.5mM}$, DAT_{4mM} , and CTAB samples exhibited the highest methane j_{ECSA} at -1.05 V with respective values of 88 ± 38 , 94 ± 1 , 128 ± 39 , and $117 \pm 3 \mu A cm_{ECSA}^{-2}$. The highest formate peak j_{ECSA} values of 115 ± 12 , 124 ± 16 , 101 ± 15 , and $113 \pm 2 \mu A cm_{ECSA}^{-2}$ were obtained from the (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), SDS, and CTAB foams.

ECSA-normalized partial current densities of C_{2+} products for the chemical effect series are presented in Figure 79. Across the entire applied potential range, ethane, acetaldehyde, propionaldehyde, acetone, and allyl alcohol exhibited negligible j_{ECSA} . At potentials less negative than -0.95 V, the C_{2+} products ethylene, ethanol, and 1-propanol showed negligible j_{ECSA} . Adding CTAB or elevating the DHBT bath pH, i.e., for both $DAT_{4mM}^{pH0.5}$ and the (pH 0.5) samples, did not significantly improve the intrinsic activity of the resulting Cu foams toward C_{2+} products in the potential range between -0.95 and -1.05 V. Conversely, the (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), $DAT_{1.5mM}$, DAT_{4mM} , and SDS samples showed a remarkable enhancement in C_{2+} product j_{ECSA} at -1.05 V. For instance, ethylene j_{ECSA} values were 167 ± 9 , 290 ± 14 , 179 ± 17 , 217 ± 13 , and $175 \pm 1 \mu A cm_{ECSA}^{-2}$ at -1.05 V for the (0.1 M Cu^{2+}), (0.05 M Cu^{2+}), $DAT_{1.5mM}$, DAT_{4mM} , and SDS samples, respectively. By comparison, the reference sample exhibited ethylene j_{ECSA} of $46 \pm 4 \mu A cm_{ECSA}^{-2}$ at -1.05 V.

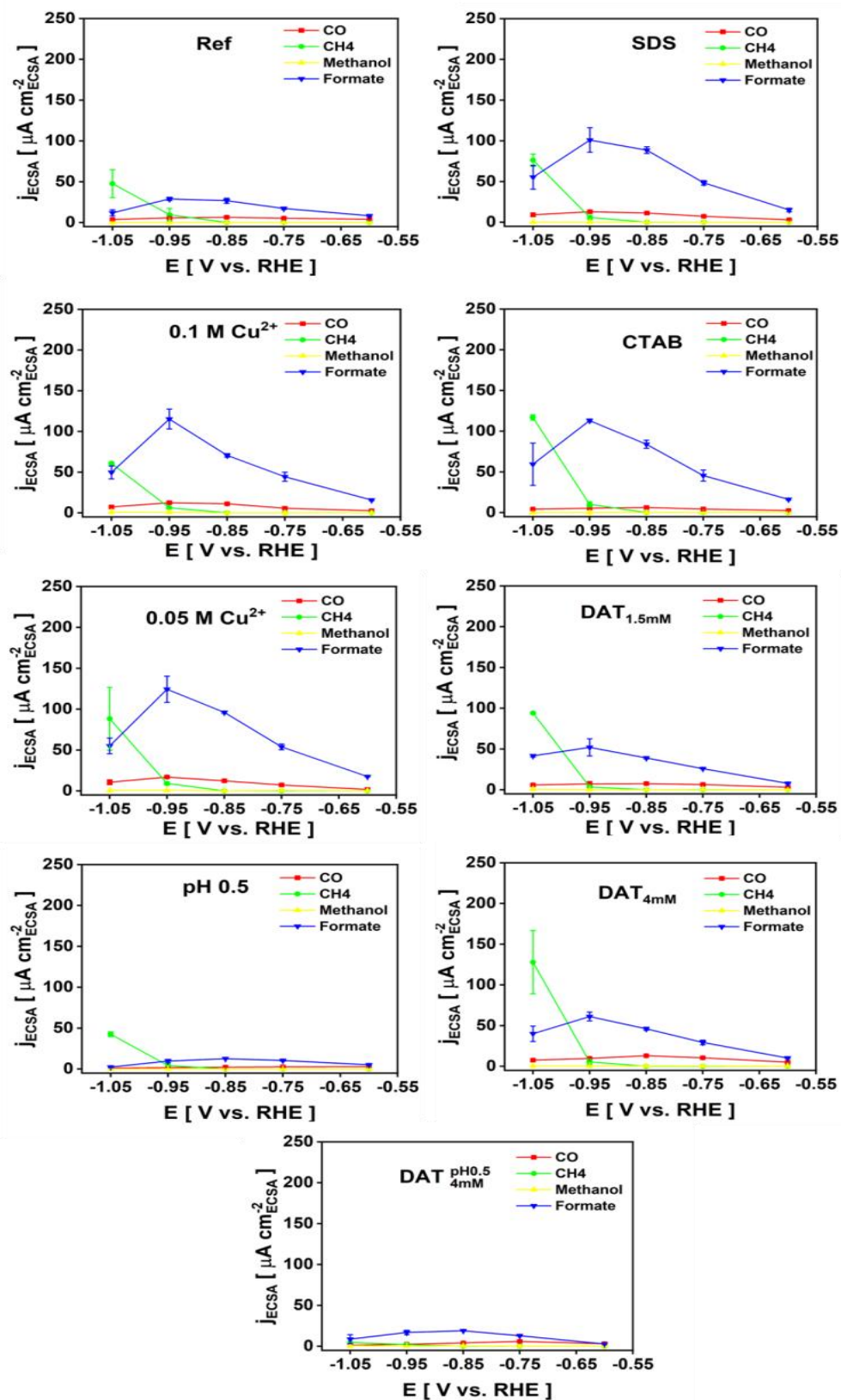


Figure 78: CO₂RR partial current densities of C₁ products of the chemical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

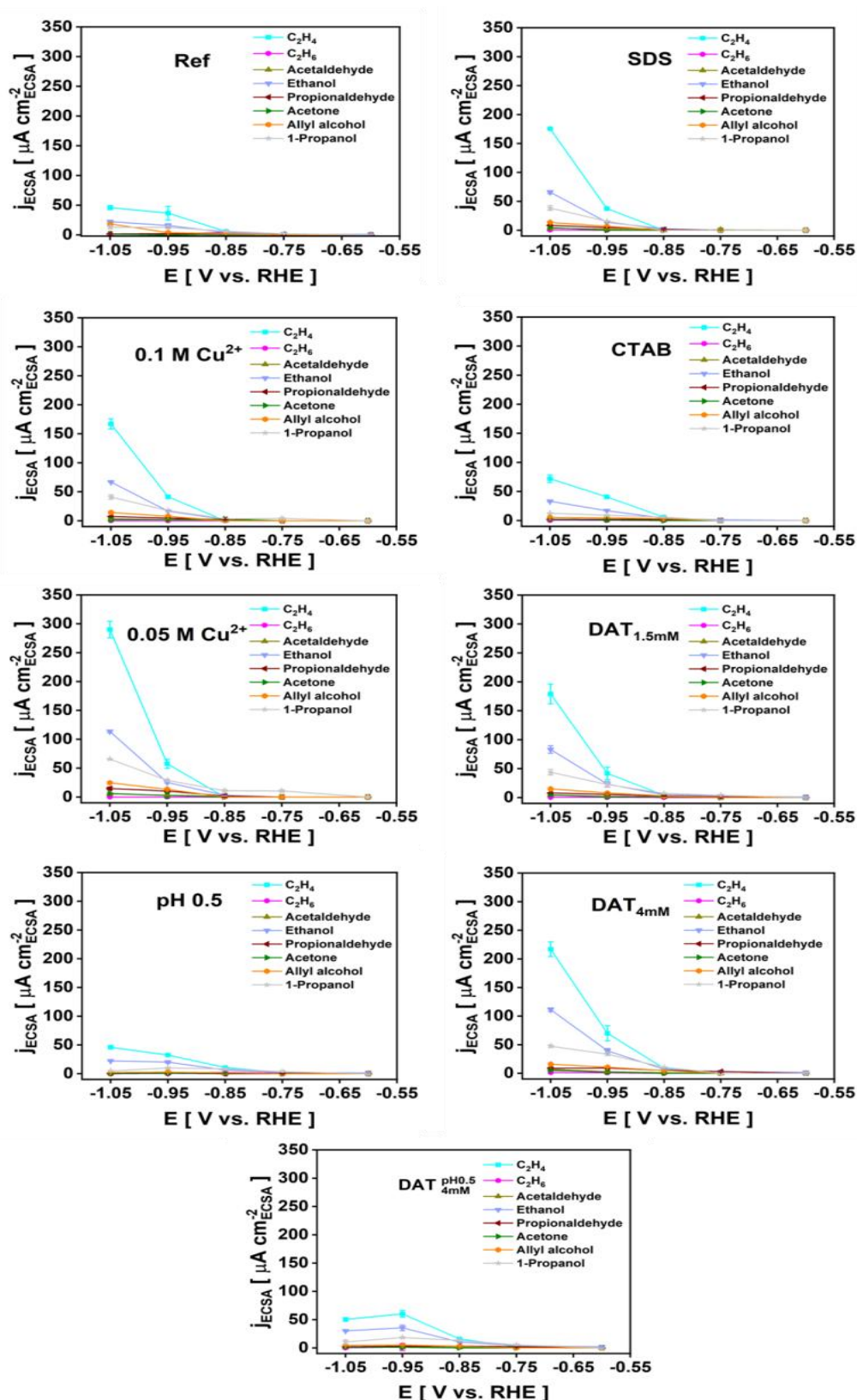


Figure 79: CO₂RR partial current densities of C₂⁺ products of the chemical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, **normalized to the sample electrochemically active surface area**

Figure 80 provides a comparison between the samples of the chemical effect series in terms of total C_{2+} product FEs and total C_{2+} product ECSA-normalized partial current densities. In the potential range between -0.6 and -0.85 V, the samples showed different $FE_{C_{2+}}$ values; however, the corresponding $j_{C_{2+}}$ values were negligible. At -0.95 V, all samples exhibited overlapping $FE_{C_{2+}}$ of about 30-45%, except for the CTAB sample, which showed a reduced $FE_{C_{2+}}$ of $\approx 16\%$. At -0.95 V, the $j_{C_{2+}}$ values overlapped between 70 and 170 $\mu A cm_{ECSA}^{-2}$, approximately. At -1.05 V, the samples diverged markedly in C_{2+} product activity. Lowering the Cu^{2+} concentration from 0.2 M to 0.1 M or 0.05 M promoted C_{2+} formation, with $FE_{C_{2+}}$ of $16 \pm 1\%$, $33 \pm 1\%$, and $42 \pm 3\%$ and $j_{C_{2+}}$ of 90 ± 9 , 302 ± 17 , and $520 \pm 20 \mu A cm_{ECSA}^{-2}$ for the three concentrations at -1.05 V, correspondingly. Conversely, increasing the DHBt bath pH disfavored C_{2+} formation, where the (pH 0.5) and $DAT_{4mM}^{pH0.5}$ samples showed $FE_{C_{2+}}$ values of $16 \pm 3\%$ and $14 \pm 4\%$ and $j_{C_{2+}}$ values of 77 ± 6 and $100 \pm 13 \mu A cm_{ECSA}^{-2}$ at -1.05 V, respectively. Adding surfactants resulted in different outcomes. SDS promoted C_{2+} activity, providing a total C_{2+} FEs of $33 \pm 4\%$, corresponding to $j_{C_{2+}}$ of $310 \pm 10 \mu A cm_{ECSA}^{-2}$ at -1.05 V. In contrast, the addition of CTAB was not beneficial for C_{2+} performance, with $FE_{C_{2+}}$ of $12 \pm 1\%$ and $j_{C_{2+}}$ of $130 \pm 10 \mu A cm_{ECSA}^{-2}$ obtained at -1.05 V. Remarkably, the (0.05 M Cu^{2+}) sample exhibited the highest C_{2+} activity among the chemical effect samples in terms of both FEs and ECSA-normalized partial current densities.

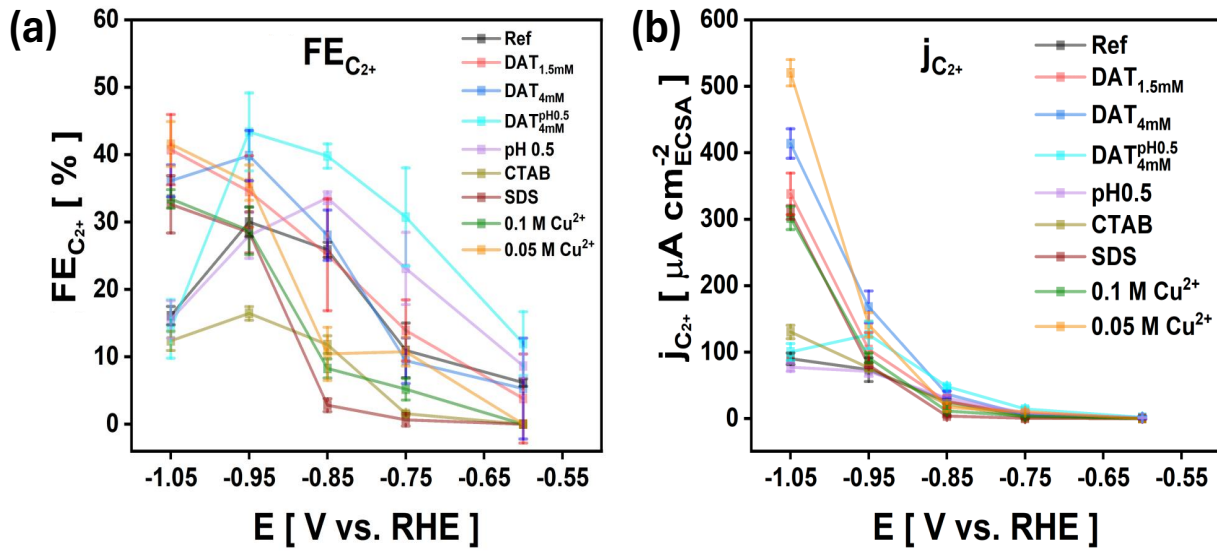


Figure 80: Comparison of the total Faradaic efficiencies (a) and total ECSA-normalized partial current densities (b) of C_{2+} products for the samples of the chemical effect series

Operando SERS measurements were conducted by Prof. Holger Dau's group at Freie Universität Berlin. These measurements were enabled by the surface nano-structures of the Cu foam samples and provided molecular-level monitoring of adsorbates and surface species during CO_2RR . In addition to identifying surface intermediates, operando SERS can also probe local alkalization by tracking the relative intensities of HCO_3^- and CO_3^{2-} species, as detailed in Section 2.5.2. Operando SERS was conducted at various potentials, starting at the OCP and stepping from 0 to -0.9 V. At OCP, the DAT_{4mM} foam exhibited additional peaks in the wavenumber range $1000-1600 cm^{-1}$, which were not observed in the reference sample and were attributed to incorporated surface DAT species (Figure 81). Additionally, these peaks were observed for the DAT_{4mM} sample in a N_2 -saturated electrolyte,

which rules out their association with CO_2RR intermediates.

As presented in Figure 82, When the applied potential was sequentially stepped from 0 V to more negative potentials, the Cu_xOH_y peaks at $\approx 500\text{ cm}^{-1}$ disappeared within a few seconds at 0 to -0.1 V for both the $\text{DAT}_{4\text{mM}}$ and reference samples, indicating a rapid reduction of the surface oxides at low negative potentials, in agreement with previous works.^[99] At more negative potentials, several additional bands evolved. The intensities of the DAT peaks increased markedly when small negative potentials were applied, potentially due to Cu surface reduction. Specifically, metallic Cu nanoparticles typically produce stronger SERS enhancement than Cu oxide counterparts because metallic Cu supports localized surface plasmons more effectively, which can account for the enhancement in DAT signal intensities when the Cu foam surface was reduced.^[134] The peak at $\approx 1070\text{ cm}^{-1}$ corresponds to CO_3^{2-} formed by the deprotonation of HCO_3^- . The peak at $\approx 2055\text{ cm}^{-1}$ is attributed to the adsorbed $\ast\text{CO}$ intermediate. Notably, the $\ast\text{CO}$ peak appears at more negative potentials for the reference sample than for the $\text{DAT}_{4\text{mM}}$ sample, as quantified by the integrated areas of this peak, as depicted in Figure 83. The $\text{DAT}_{4\text{mM}}$ sample showed a steady increase in the $\ast\text{CO}$ peak area as the potential was shifted from 0 to more negative values, reaching a steady state at -0.3 V with a peak area of around 35 a.u., which remained approximately constant until -0.8 V; beyond which the peak area decreased to ≈ 30 a.u. at -0.9 V. Conversely, the reference sample exhibited a negligible $\ast\text{CO}$ peak area from 0 to -0.4 V, followed by a sudden increase to a maximum of about 45 a.u. at -0.7 V, and then a rapid decrease to 30 a.u. at -0.9 V. These findings clearly indicate that $\text{DAT}_{4\text{mM}}$ displayed a lower overpotential for $\ast\text{CO}$ formation. The C-H peak at $\approx 2800\text{ cm}^{-1}$ started to evolve at low negative potentials for both the reference and $\text{DAT}_{4\text{mM}}$ samples in the range from 0 to -0.1 V, which agrees with chromatographic results showing a significant formation of formate at potentials less negative than -0.95 V, and then the formation of hydrocarbons in the range from -0.95 to -1.05 V.

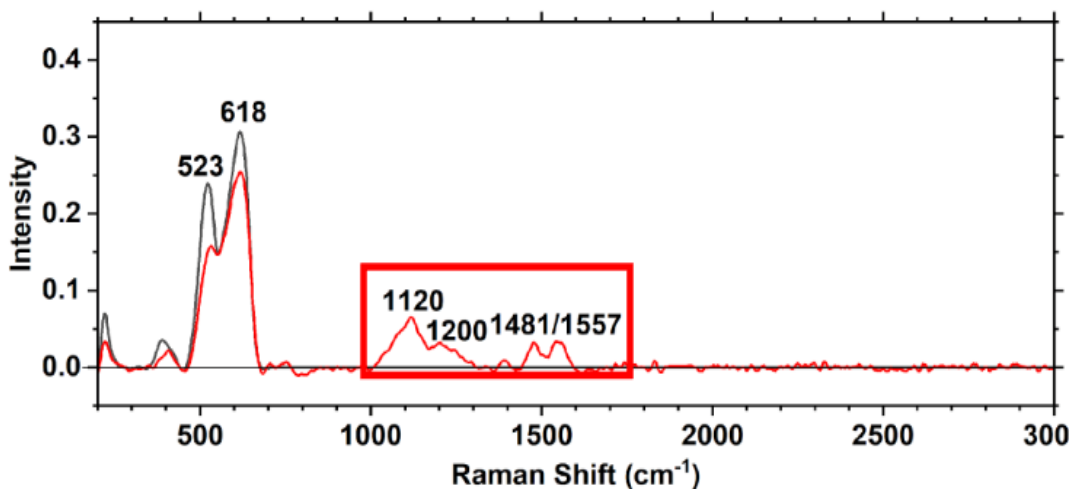


Figure 81: Surface-enhanced Raman spectra collected at the open circuit potential for the reference (black) and $\text{DAT}_{4\text{mM}}$ (red) samples

For monitoring local alkalization of the reference and $\text{DAT}_{4\text{mM}}$ foams, operando SERS pH measurements were performed based on tracking the intensities of HCO_3^- and CO_3^{2-} peaks, as detailed in Section 2.5.2. The Raman laser was focused at two locations to probe spatial differences in alkalization: the Cu foam surface and bottom. During one hour of electrolysis at -5 mA cm^{-2} , the

DAT_{4mM} sample exhibited a higher local pH both at the foam surface and bottom (≈ 9.4 - 9.8) than the reference sample (≈ 9.2 - 9.6), consistent with the increased activity and more suppressed parasitic H₂ evolution on the DAT_{4mM} foam relative to the reference counterpart.

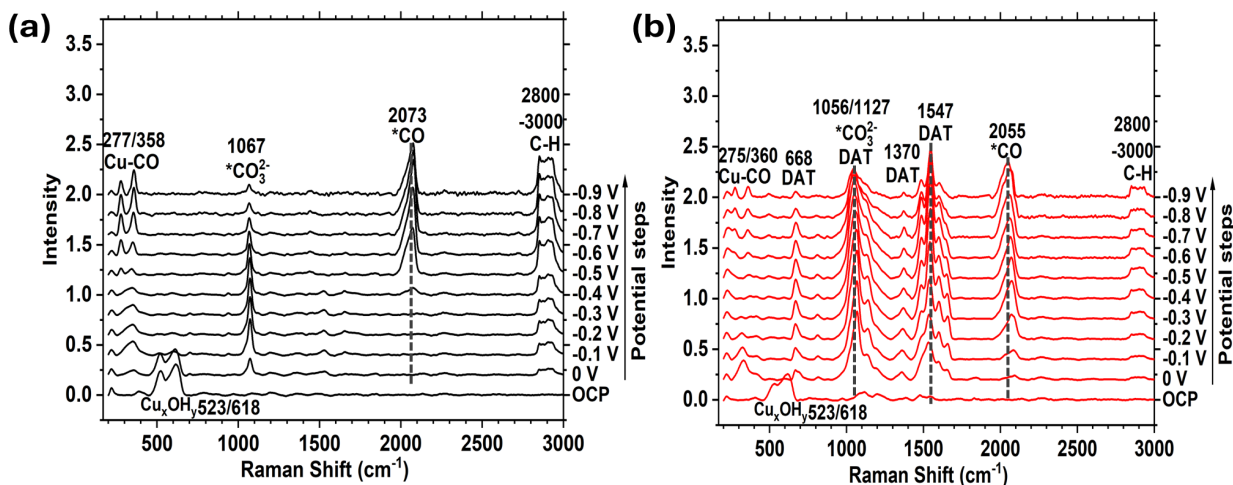


Figure 82: Potential-dependent surface-enhanced Raman spectra of the reference (a) and DAT_{4mM} samples (b) collected at the open circuit potential and in the potential range from 0 V to -0.9 V

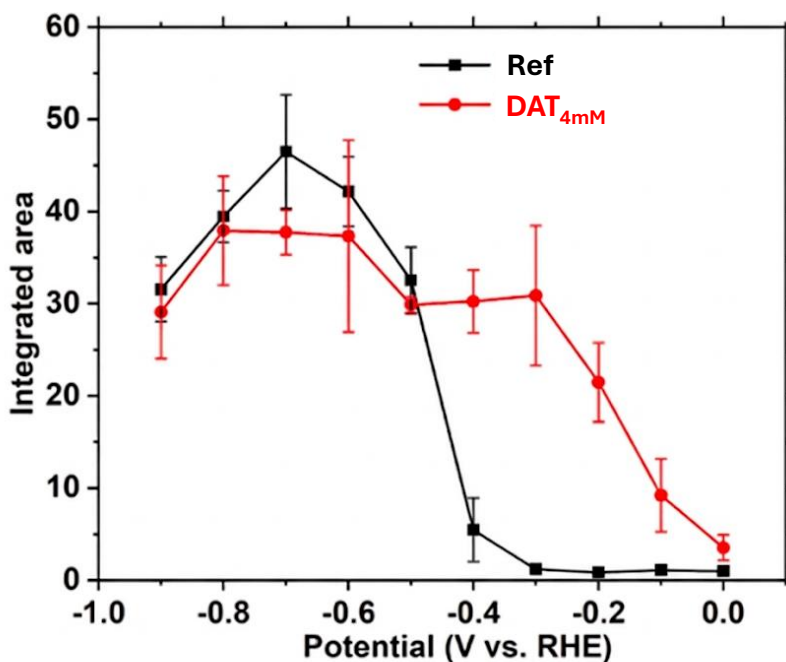


Figure 83: The integrated area for the *CO adsorption band in the range 1950-2150 cm⁻¹ for the reference (black) and DAT_{4mM} (red) samples

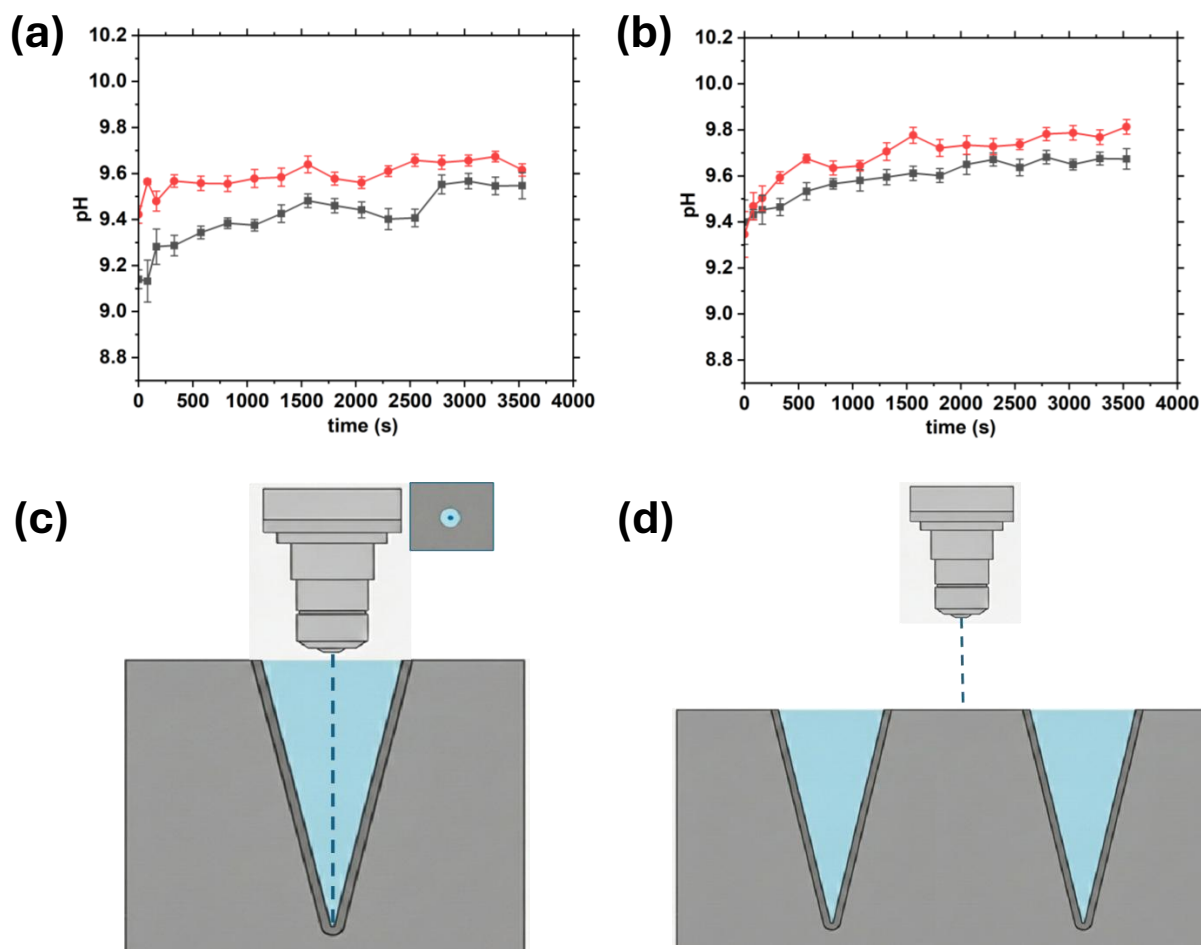


Figure 84: pH change during CO₂RR at an applied current density of -5 mA cm^{-2} for the reference (a) and DAT_{4mM} (b) samples measured at the foam bottom (red) and surface (black), as well as schematic representation of the sample positions probed by surface-enhanced Raman spectroscopy: the Cu sample bottom (c) and surface (d)

Based on the chromatographic and operando SERS results obtained for the DAT-mediated and reference foams, a schematic comparison between both foams is presented in Figure 85. Incorporation of DAT into Cu active sites increases the adsorption affinity and residence time of $\ast\text{CO}$ intermediates on the catalyst surface, leading to a higher $\ast\text{CO}$ surface coverage, as evidenced by enhanced SERS band intensity at low negative overpotentials between 0 and -0.5 V . This accumulation of $\ast\text{CO}$ promotes C-C coupling by increasing the probability of adjacent $\ast\text{CO}$ species encountering one another and by stabilizing key dimerization transition states, which in turn raises the selectivity and activity toward C_{2+} products, such as ethylene.

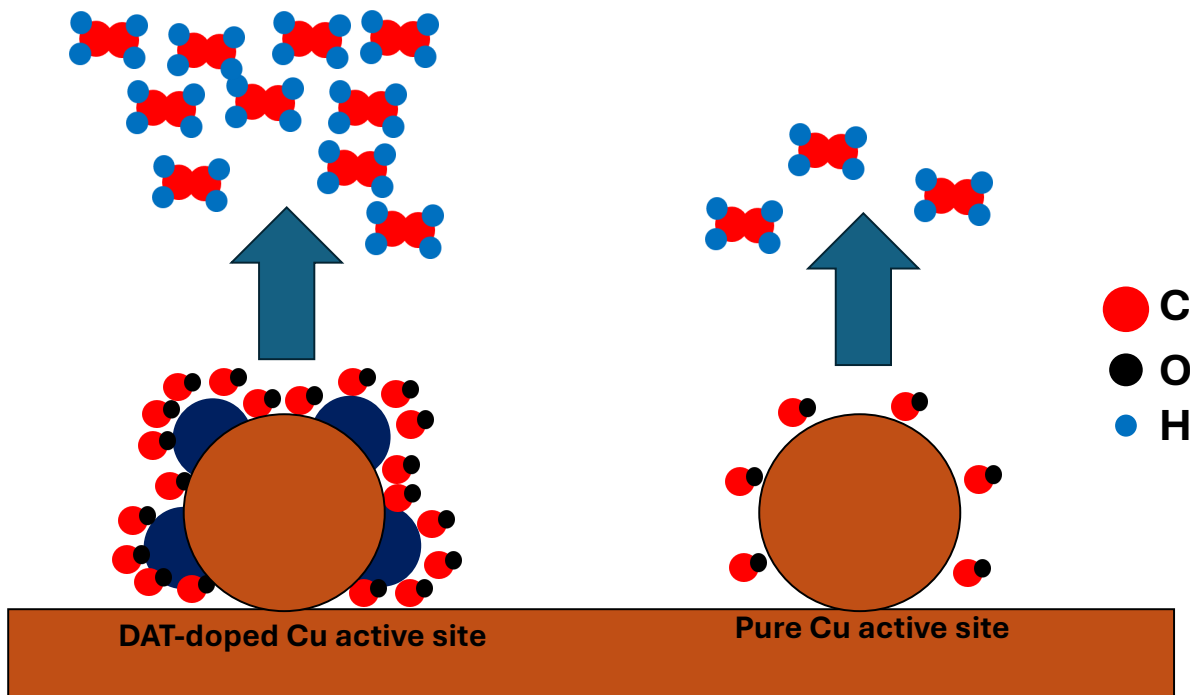


Figure 85: Schematic illustration of the DAT-modified and DAT-free Cu active sites, showing the extent of accumulation and stabilization of $^*\text{CO}$ intermediates on each, and the subsequent formation and release of C_{2+} products, represented by ethylene

To summarize the important findings of the chemical effect series and the conclusions obtained:

1. The dramatically enhanced activity of the (0.05 M Cu^{2+}) sample, which lacked the foam interconnected skeleton, demonstrates again that honeycomb-like foams exhibit CO_2 concentration polarization between the pore surface and bottom, which is more pronounced with larger pore diameters and increased thicknesses.^[125] The (0.05 M Cu^{2+}) sample consisted mainly of micro-to-nano-structured Cu agglomerates with very low thickness and ECSA; consequently, it suffered from the least CO_2 depletion at the active sites. This highlights that the surface nano-structures of the Cu foams provide the crucial active sites for CO_2RR , while the foam skeleton serves primarily as a binder-free support for the nano-structures. These nano-particle substrates need to be engineered carefully to enable efficient supply of CO_2 to the catalyst active sites and promote CO_2RR performance.
2. The addition of DAT to the DHBT bath (without elevating pH) was beneficial for C_{2+} product activity. In addition to the fact that the DAT-mediated samples are markedly less open than the reference sample, ex-situ XPS (as discussed in Section 3.5) and operando SERS demonstrated that DAT was incorporated into the Cu foam structure. The incorporated DAT species were found to lower the overpotential of $^*\text{CO}$ formation, stabilize the $^*\text{CO}$ intermediates, and facilitate C-C coupling. Additionally, the incorporated DAT was demonstrated to lower the local pH at the electrode surface, thereby quenching the parasitic H_2 FE and promoting CO_2RR . Specifically, surface amino groups can form hydrogen bonds or coordinate weakly to adsorbed $^*\text{CO}$ intermediates, thereby lowering their desorption rate and increasing their residence time on the catalyst surface. The resulting higher surface $^*\text{CO}$ coverage induced by the surface DAT species increases the probability of C-C coupling, and consequently, the formation of C_{2+} products. Moreover, the protonation of the surface amino species can

effectively lower the local pH and suppress the evolution of parasitic H_2 during CO_2RR . The findings of DAT-mediated foams (without elevating pH) agree with previous works reporting that surface amino-based species are beneficial for C_{2+} products selectivity.^[106,107]

3. At an elevated pH of 0.5, the obtained samples were not remarkably more active towards C_{2+} product formation. This can be attributed to their reduced mechanical stability. At pH 0.5, both the (pH 0.5) and $DAT_{4mM}^{pH0.5}$ samples showed Cu precipitates during DHBT (see Figure 86), which may cause a rapid decline in their performance during operation.

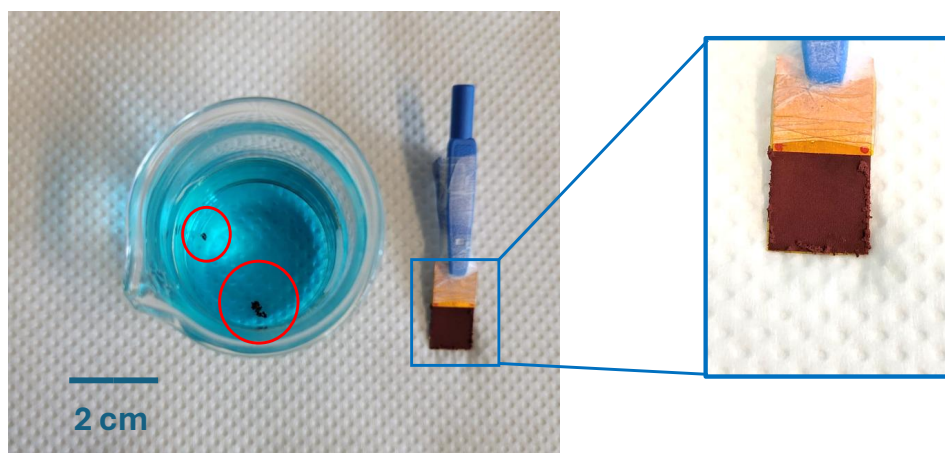


Figure 86: Digital photos of a Cu foam sample synthesized at pH 0.5, showing detached Cu particles in the DHBT electrolyte (red circles) and on the sample edges

4. Surfactants led to more compact structures with respect to the additive-free reference sample; however, only the SDS-mediated foam exhibited the expected enhancement of C_{2+} product activity, while CTAB addition was detrimental to C_{2+} product formation. Ex-situ XPS on the as-prepared SDS- and CTAB-mediated foams did not provide evidence for incorporation of both species into the Cu foam structure or for residual surfactants on the Cu foam surface, as detailed later in Section 3.5. The reduced C_{2+} activity of the CTAB sample can be attributed to alterations of the active-site structure in the presence of CTAB. Specifically, CTAB is a cationic surfactant composed of a cetyltrimethylammonium (CTA^+) headgroup and a bromide (Br^-) counter-ion. Halide ions have been reported to modify the surface morphology during Cu electrodeposition by reducing the density of step edges and grain boundaries, producing smoother, defect-poor surfaces and thereby lowering the Cu foam's C_{2+} activity.^[135]

3.4 Physical DHBT effect series

Various physical parameters were varied systematically to determine their effect on the morphology of the Cu foams produced by DHBT. To investigate the influence of the Cu^{2+} diffusion layer thickness on surface nano-dendrite formation, an effect previously identified in the previous DHBT series, electrodeposition was performed under vigorous electrolyte stirring at ≈ 1350 rpm using a magnetic stirrer to enhance the mass transport of Cu^{2+} from the bulk electrolyte to the electrode interface. To assess the role of electrode orientation, a custom DHBT cell was designed to enable the horizontal alignment of the WE and CE with a collateral electrical connection (Figure 18). Since elevating the DHBT bath temperature above room temperature was shown to promote H_2 bubble coalescence and thereby enlarge foam dimensions^[136], the effect of electrolyte temperature was more thoroughly investigated here by performing DHBT at two controlled temperatures: 5 °C (using an ice bath) and 60 °C (using a heated water bath). Since annealing promotes the oxidation of the Cu foam surface and can modify CO_2RR performance^[99], the impact of post-deposition annealing was examined using two annealing protocols: 300 °C for 15 minutes and 150 °C for 30 minutes. These annealed samples were denoted $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ and $\text{An}_{30\text{min}}^{150^\circ\text{C}}$, respectively. All samples in this series were electrodeposited under a continuous cathodic DC density of 1 A cm^{-2} for 20 s and were compared to a reference foam prepared under identical current and time conditions but at room temperature in a quiescent solution with vertical electrode alignment and without post-deposition annealing.

Top-view SEM images at low and high magnification for the physical effect series are presented in Figure 87, and the corresponding cross-sectional SEM images are shown in Figure 88. Gravimetric analysis for this series appears in Figure 89a. Introducing mechanical stirring to the DHBT bath produced only minor changes to the Cu foam skeleton relative to the reference sample, where mean pore diameters of 19.9 ± 0.6 μm and 20.4 ± 0.4 μm , foam thicknesses of 50.6 ± 5.3 μm and 49.4 ± 5.3 μm , deposited Cu masses of 3.1 ± 0.3 and 3.3 ± 0.3 mg cm^{-2} , and deposition FEs of $48 \pm 4\%$ and $50 \pm 4\%$ were observed for the reference and stirred foams, respectively. In contrast to the modest changes in the foam architecture, stirring markedly increased the size of the surface nano-dendrites. This supports the interpretation that enhanced mass transport of Cu^{2+} to the electrode, i.e., a lower diffusion layer thickness, raises the limiting current density, reduces the electrodeposition overpotential, and favors the rapid growth of larger nano-dendritic features. In the quiescent DHBT electrolyte, convective effects arise merely from the natural dynamics of H_2 bubble formation and detachment, as noted in the earlier DHBT series.

Horizontal electrode alignment produced larger pores and thicker foams, with a mean pore diameter 22.4 ± 1.1 μm , thickness 64.1 ± 8.1 μm , deposited Cu mass density 4.4 ± 0.7 mg cm^{-2} , and deposition FE $66 \pm 11\%$, compared to the vertical reference. These effects can be attributed to gravity opposing the buoyant rise of H_2 bubbles, which forces bubbles to grow and coalesce into larger sizes before detachment. Again, larger bubble templates in the horizontal orientation enhance local convection and increase Cu^{2+} transport from the bulk to the electrode, promoting the growth of larger nano-dendrites. These results are consistent with previous studies in which the horizontal orientation of the WE during HER, which was a parasitic reaction during the electrochemical reduction of $\text{K}_3\text{Fe}(\text{CN})_6$, resulted in enhanced mass transport of $\text{K}_3\text{Fe}(\text{CN})_6$ to the electrode surface.^[137] Moreover, a simulation study of H_2 bubble evolution on vertical and horizontal micro-electrodes, which took into account different forces: contact pressure, surface tension, buoyancy, thermal Marangoni forces, hydrostatic pressure, and shear lift, found that detachment in the horizontal configuration requires a substantially larger bubble diameter than in the vertical case, consistent with our experimental DHBT results.^[138]

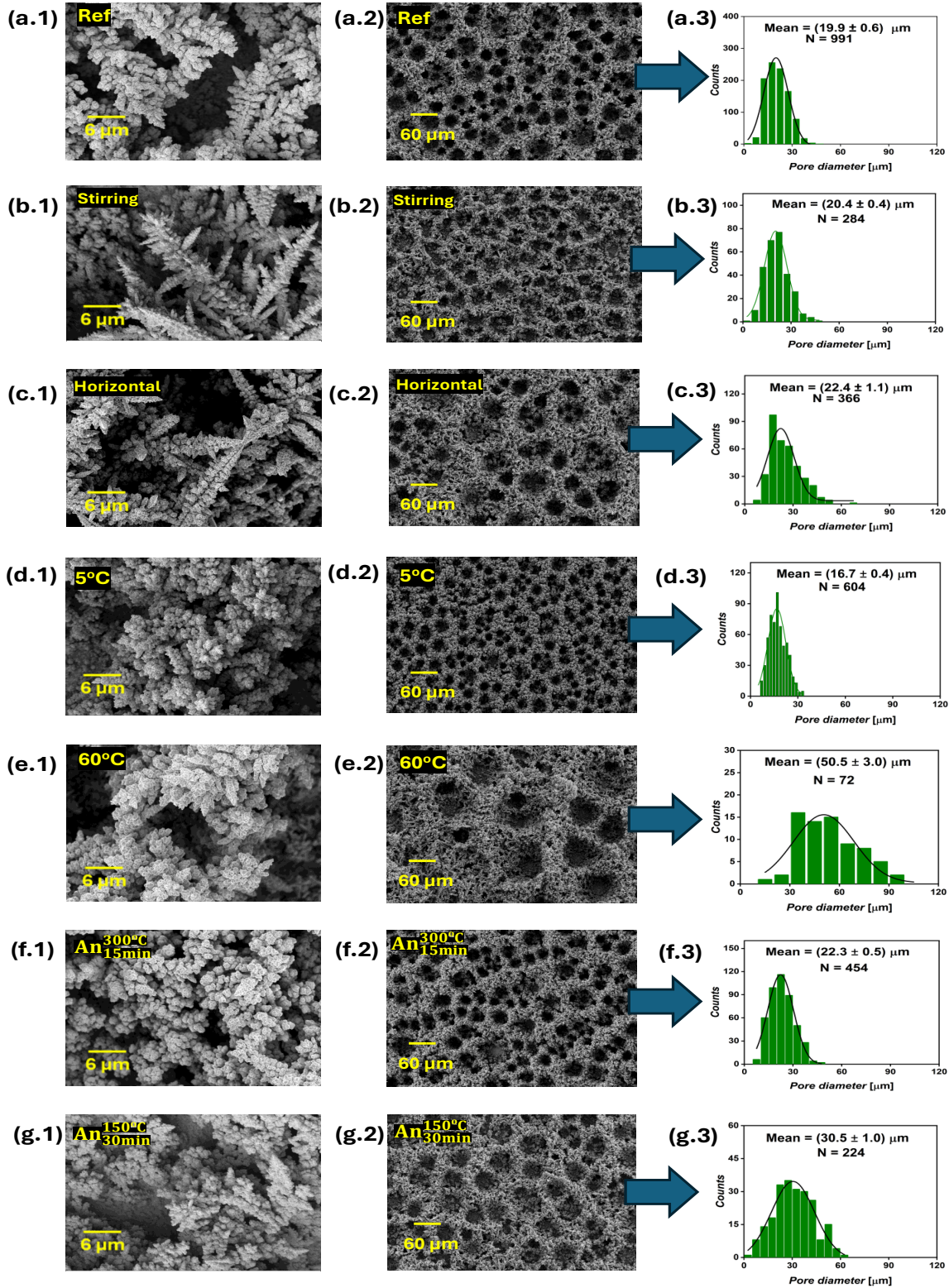


Figure 87: Top-view SEM images of Cu foam samples presenting the surface nano-structures at a magnification of 3000x (first column), foam structure at a magnification of 200x (second column), and pore diameter distribution obtained from the 200x images (third column) of the reference sample (a), stirred sample (b), horizontally-aligned sample (c), sample produced at 5 °C (d), sample produced at 60 °C (e), sample annealed at 300 °C for 15 minutes (f), and sample annealed at 150 °C for 30 minutes (g), where N is the number of pores from which the pore diameter distribution was obtained

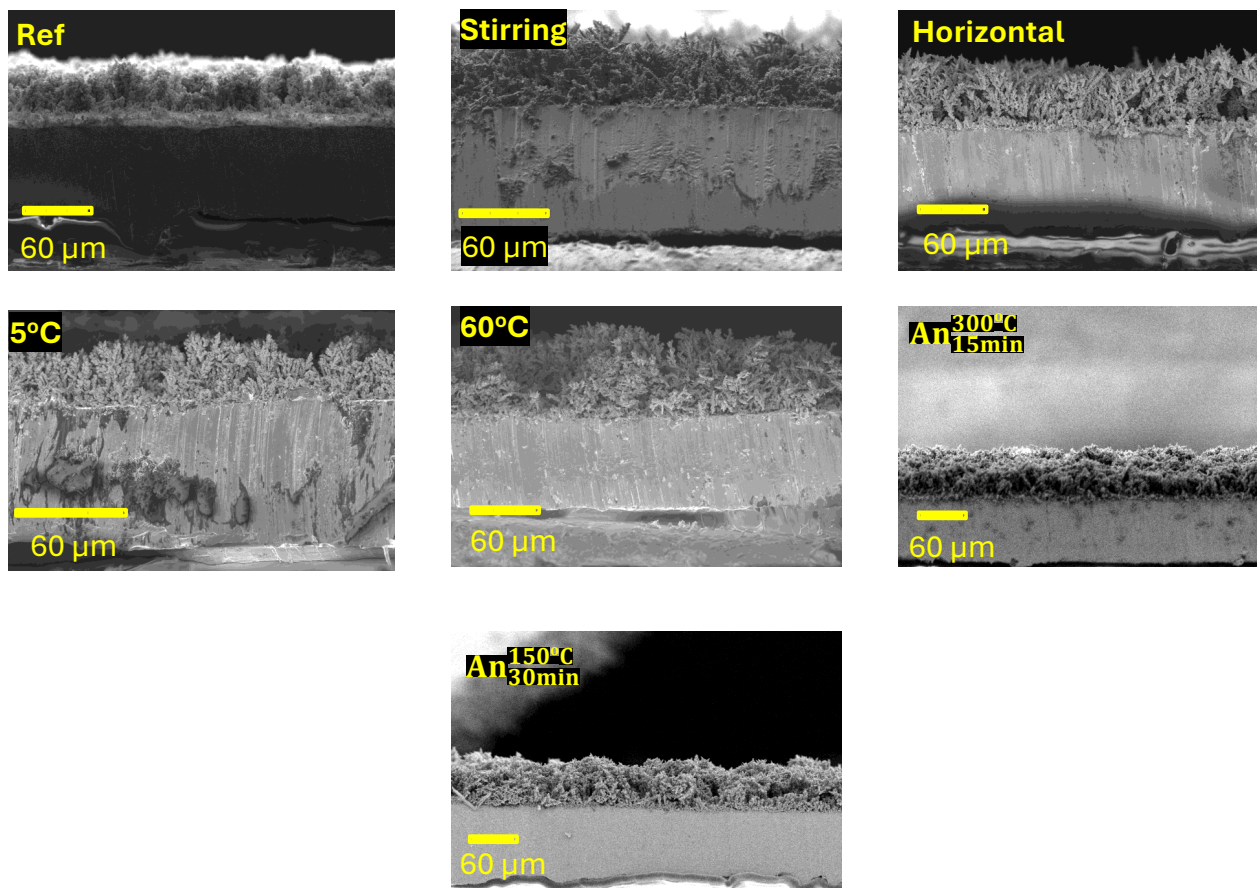


Figure 88: Examples of the cross-sectional SEM images of the physical effect series, each collected at an appropriate magnification

Raising the DHBT bath temperature produced a progressive increase in all morphological descriptors. For the three foams deposited at 5 °C, room temperature, and 60 °C, the mean pore diameters were 16.7 ± 0.4 , 19.9 ± 0.6 , and 50.5 ± 3.0 μm ; foam thicknesses were 38.2 ± 4.1 , 50.6 ± 5.3 , and 69.6 ± 7.8 μm ; and deposited Cu mass densities were 2.6 ± 0.1 , 3.1 ± 0.3 , and 4.0 ± 0.3 mg cm^{-2} , with corresponding FEs of $39 \pm 2\%$, $48 \pm 4\%$, and $61 \pm 4\%$, respectively. These trends indicate that higher bath temperatures favor larger H_2 bubble templates, consistent with earlier work that provided similar findings, which attributed this behavior to enhanced HER rates at elevated temperatures.^[136] However, in our experiments, the increase in electrodeposition FE with temperature suggests a relative reduction in concurrent HER activity. Therefore, the larger H_2 bubbles at 60 °C are more likely to be caused by temperature-dependent factors, such as reduced electrolyte viscosity, which promotes bubble coalescence.

Nano-dendrite size also increased with temperature, an effect attributable to a reduction in Cu electrodeposition overpotential due to both the enhanced convective transport and higher temperature. Notably, the rise in nano-dendrite size at 60 °C occurred mainly by increasing the size of the dendrite needles. By contrast, stirring and horizontal electrode orientation led to an increase in the nano-dendrites along the dendrite branch axis. This indicates that different physical parameters modify hydrodynamic conditions and Cu^{2+} mass transport in distinct ways.

The two samples to be annealed exhibited mass densities nearly identical to the reference counterpart ($\approx 3.2 \text{ mg cm}^{-2}$) before annealing, which is expected due to identical DHBT conditions. After annealing, both samples showed a modest increase in mass density of ($\approx 0.2 \text{ mg cm}^{-2}$), reflecting surface oxidation during heat treatment in air. Annealing also produced a clear expansion of the foam architecture, where mean pore diameters increased to $22.3 \pm 0.5 \text{ }\mu\text{m}$ and $30.5 \pm 1.0 \text{ }\mu\text{m}$, while foam thicknesses reached $71.7 \pm 4.8 \text{ }\mu\text{m}$ and $68.5 \pm 3.7 \text{ }\mu\text{m}$ for $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ and $\text{An}_{30\text{min}}^{150^\circ\text{C}}$, respectively. In contrast to the enlarged foam skeleton, the surface nano-dendrites were substantially reduced in size, consistent with annealing-induced recrystallization processes.^[139] The broad pore diameter distribution of the $\text{An}_{30\text{min}}^{150^\circ\text{C}}$ foam indicates a reduced pore diameter uniformity for this sample. The influence of annealing on the oxidation state of both the foam bulk (based on XRD results) and the foam surface (based on XPS results) was studied. The $\text{Cu}_2\text{O}(111)/\text{Cu}(111)$ intensity ratios were 0.076, 0.045, and 0.264, while the micro-strain values were 1.7, 0.3, and 1.0 for the reference, $\text{An}_{30\text{min}}^{150^\circ\text{C}}$, and $\text{An}_{15\text{min}}^{300^\circ\text{C}}$, respectively. In addition, XPS showed that only $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ exhibited a surface CuO layer, whereas the reference and $\text{An}_{30\text{min}}^{150^\circ\text{C}}$ foams displayed surface Cu_2O . These observations indicate that annealing at 300°C for 15 minutes effectively oxidizes both the Cu foam surface and bulk, while producing a relatively smaller expansion of the foam dimensions. In contrast, annealing at 150°C for 30 minutes leads to greater dimensional expansion and a larger release of micro-strain but does not significantly change the bulk or surface oxidation state compared with the reference sample. These results are detailed in Section 3.5.

The ECSA results for the physical DHBT effect series are shown in Figure 89b. Horizontal substrate alignment during DHBT increased the ECSA to $134 \pm 2 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ with respect to the reference sample, which exhibited an ECSA of $127 \pm 15 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$. The ECSA rose gradually with increasing DHBT bath temperature, with values of 68 ± 7 , 127 ± 15 , and $155 \pm 6 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ for foams formed at 5°C , room temperature, and 60°C , correspondingly, while mechanical stirring resulted in an ECSA of $114 \pm 15 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$. Annealing had two different effects on ECSA, where the $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ sample displayed an increased ECSA of $167 \pm 8 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$, whereas the $\text{An}_{30\text{min}}^{150^\circ\text{C}}$ foam showed a reduced ECSA of $81 \pm 15 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$. These differences reflect the dominant micro-structural transformations at each temperature. Partial surface recrystallization at 150°C can smoothen the surface and lower the active-site density, while the more effective re-crystallization and surface reconstruction at 300°C can increase defect density, active sites, and overall surface area.^[140]

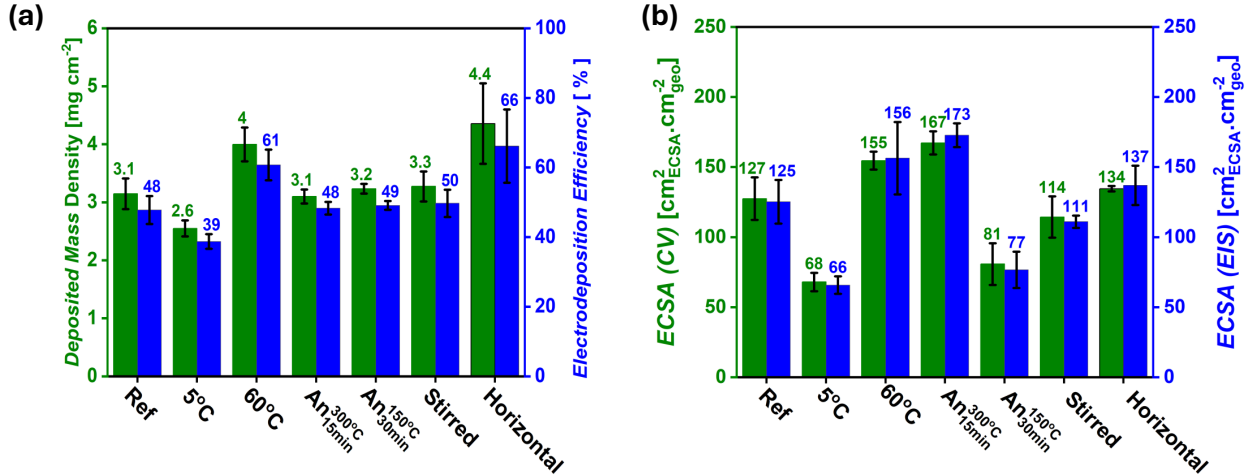


Figure 89: Gravimetric analysis (a), showing electrodeposited mass densities (green axis), with corresponding electrodeposition Faradaic efficiencies (blue axis), and the electrochemically active surface areas (b) determined by cyclic voltammetry (green axis) and electrochemical impedance spectroscopy (blue axis) of the physical effect series

CO₂RR FEs of the physical effect series are shown in Figure 90. As in the other series, the major products were formate, CO, ethylene, ethanol, 1-propanol, and parasitic H₂. Significant methane FEs were observed only at -1.05 V for the 5 °C, horizontally aligned, and reference samples, with respective values of $11 \pm 1\%$, $8 \pm 0\%$, and $9 \pm 3\%$. Allyl alcohol, acetone, propionaldehyde, acetaldehyde, ethane, and methanol showed negligible FEs across the applied potential range. For all samples in this series, H₂ FEs were lower between -0.6 and -0.85 V and rose sharply at more negative potentials between -0.95 and -1.05 V. For example, the An_{15min}^{300 °C} sample exhibited a H₂ FE of $24 \pm 1\%$ at -0.6 V, which increased steadily with more negative potentials to reach $91 \pm 0\%$ at -1.05 V. Among the physical DHBT effect samples, the stirred, 60 °C, An_{15min}^{300 °C}, and An_{30min}^{150 °C} samples showed the highest H₂ FEs in the -0.95 to -1.05 V potential window, dramatically quenching CO₂RR activity in this potential range. Specifically, H₂ FEs of $91 \pm 2\%$, $84 \pm 1\%$, $91 \pm 0\%$, and $92 \pm 3\%$ were measured at -1.05 V for these four samples, respectively. Conversely, formate and CO exhibited high FEs between -0.6 and -0.85 V that decreased markedly in the potential range from -0.95 to -1.05 V. The largest formate FE in this series was observed for the 60 °C sample at -0.75 V ($56 \pm 4\%$), which dropped to a negligible value at -1.05 V ($\approx 1\%$). Similarly, the highest CO FE was obtained for An_{15min}^{300 °C} at -0.6 V ($24 \pm 3\%$) and decreased to a negligible value at -1.05 V (0%). For all samples except An_{15min}^{300 °C}, the maximum ethylene and ethanol FEs were obtained at -0.95 V, with the largest ethylene FEs of 15 ± 0 , 15 ± 0 , and $12 \pm 1\%$, and ethanol FEs of 6 ± 1 , 10 ± 1 , and $7 \pm 0\%$ for the reference, 5 °C, and 60 °C samples, respectively. Some samples displayed appreciable 1-propanol and ethanol FEs between -0.6 and -0.85 V, reaching values of up to 11%; however, the corresponding partial current densities at these potentials were negligible, as discussed later. At -0.95 V, the highest 1-propanol FE ($9 \pm 1\%$) was obtained for the 5 °C foam, with high corresponding partial current densities. Clearly, the best C₂₊ product performance in this series was exhibited by the 5 °C sample at -0.95 V. The An_{15min}^{300 °C} foam exhibited its maximum ethylene, ethanol, and 1-propanol FEs between -0.6 and -0.85 V, with FE values of $9 \pm 0\%$ for ethylene at -0.85 V, $8 \pm 1\%$ for ethanol at -0.6 V, and $8 \pm 0\%$ for 1-propanol at -0.75 V. Nevertheless, these values also correspond to very low partial current densities, as discussed later.

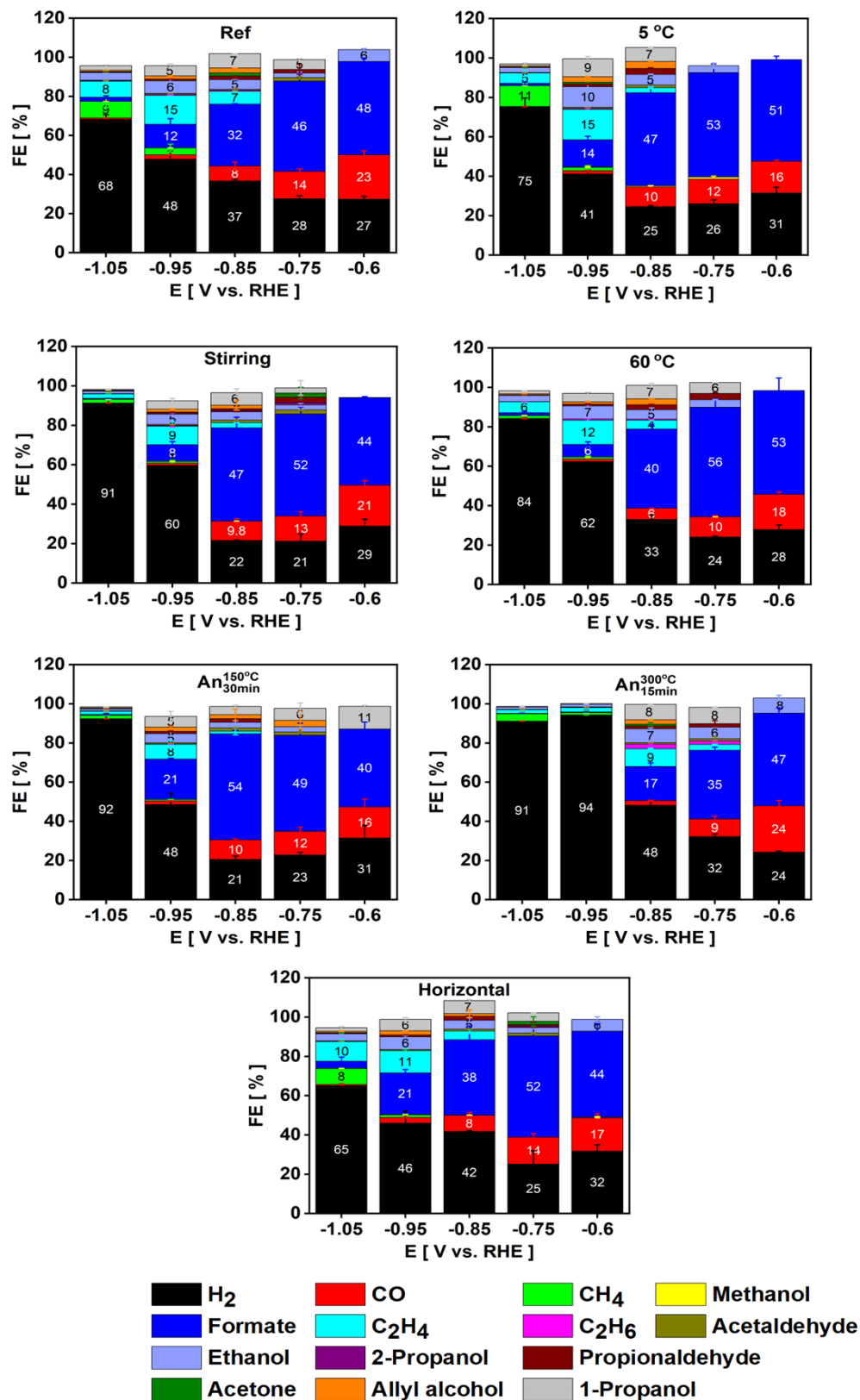


Figure 90: Faradaic efficiencies of CO₂RR products of the physical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V

Figure 91 shows the geometric-area-normalized partial current densities of C_1 products for the physical effect series. All samples exhibited negligible j_{geo} for CO and methanol. Methane produced appreciable j_{geo} only at -1.05 V, with the largest values observed for the reference, horizontally aligned, and 5 °C samples: 6.0 ± 2.2 , 4.5 ± 0.9 , and 5.4 ± 0.1 mA cm $_{\text{geo}}^{-2}$, respectively. Formate j_{geo} followed a volcano-like trend, peaking at -0.95 V for the reference and horizontal foams, or at -0.85 V for the other samples, where peak values ranged from 2 to 3.5 mA cm $_{\text{geo}}^{-2}$, approximately.

C_{2+} product geometric-area-normalized partial current densities are presented in Figure 92. C_{2+} product j_{geo} values were negligible at potentials less negative than -0.95 V. At -0.95 V, the reference, 5 °C, and 60 °C foams showed the highest partial current densities: ethylene j_{geo} of 4.7 ± 1.5 , 2.9 ± 0.1 , and 3.5 ± 0.2 mA cm $_{\text{geo}}^{-2}$; ethanol j_{geo} of 2.0 ± 0.4 , 2.0 ± 0.4 , and 1.9 ± 0.1 mA cm $_{\text{geo}}^{-2}$; and 1-propanol j_{geo} of 1.6 ± 0.2 , 1.7 ± 0.3 , and 1.2 ± 0.1 mA cm $_{\text{geo}}^{-2}$, respectively. At -1.05 V, the largest j_{geo} values were measured for the reference, horizontally aligned, and 60 °C samples: ethylene j_{geo} of 5.8 ± 0.4 , 5.7 ± 1.8 , and 3.7 ± 0.3 mA cm $_{\text{geo}}^{-2}$; ethanol j_{geo} of 2.8 ± 0.1 , 2.0 ± 0.2 , and 2.1 ± 0.2 mA cm $_{\text{geo}}^{-2}$; and 1-propanol j_{geo} of 1.6 ± 0.3 , 0.9 ± 0.2 , and 1.0 ± 0.1 mA cm $_{\text{geo}}^{-2}$, correspondingly. Annealed samples showed quenched C_{2+} j_{geo} values, indicating that annealing does not favor C_{2+} selectivity.

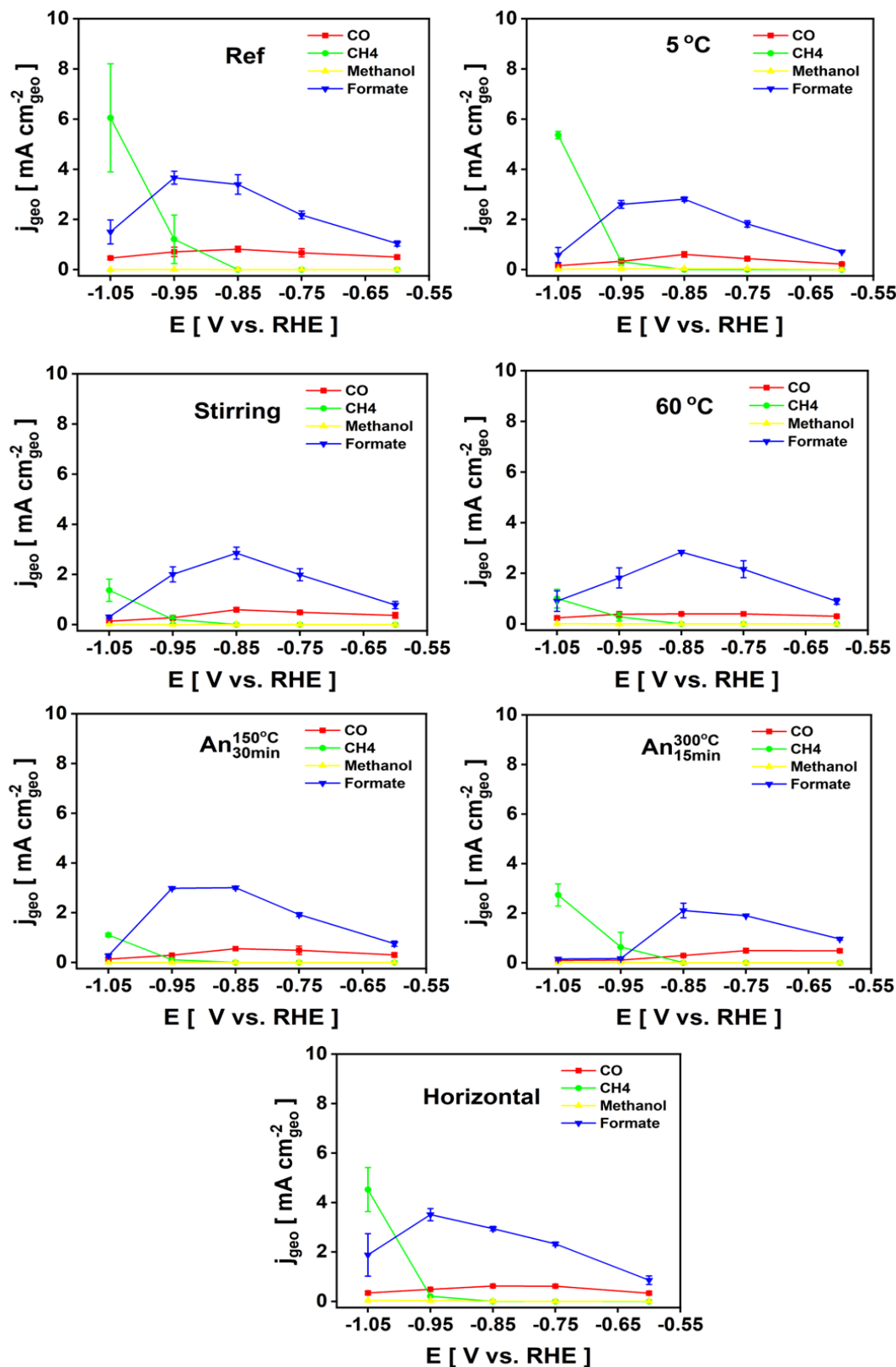


Figure 91: CO_2RR partial current densities of C_1 products of the physical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, normalized to the sample geometric area

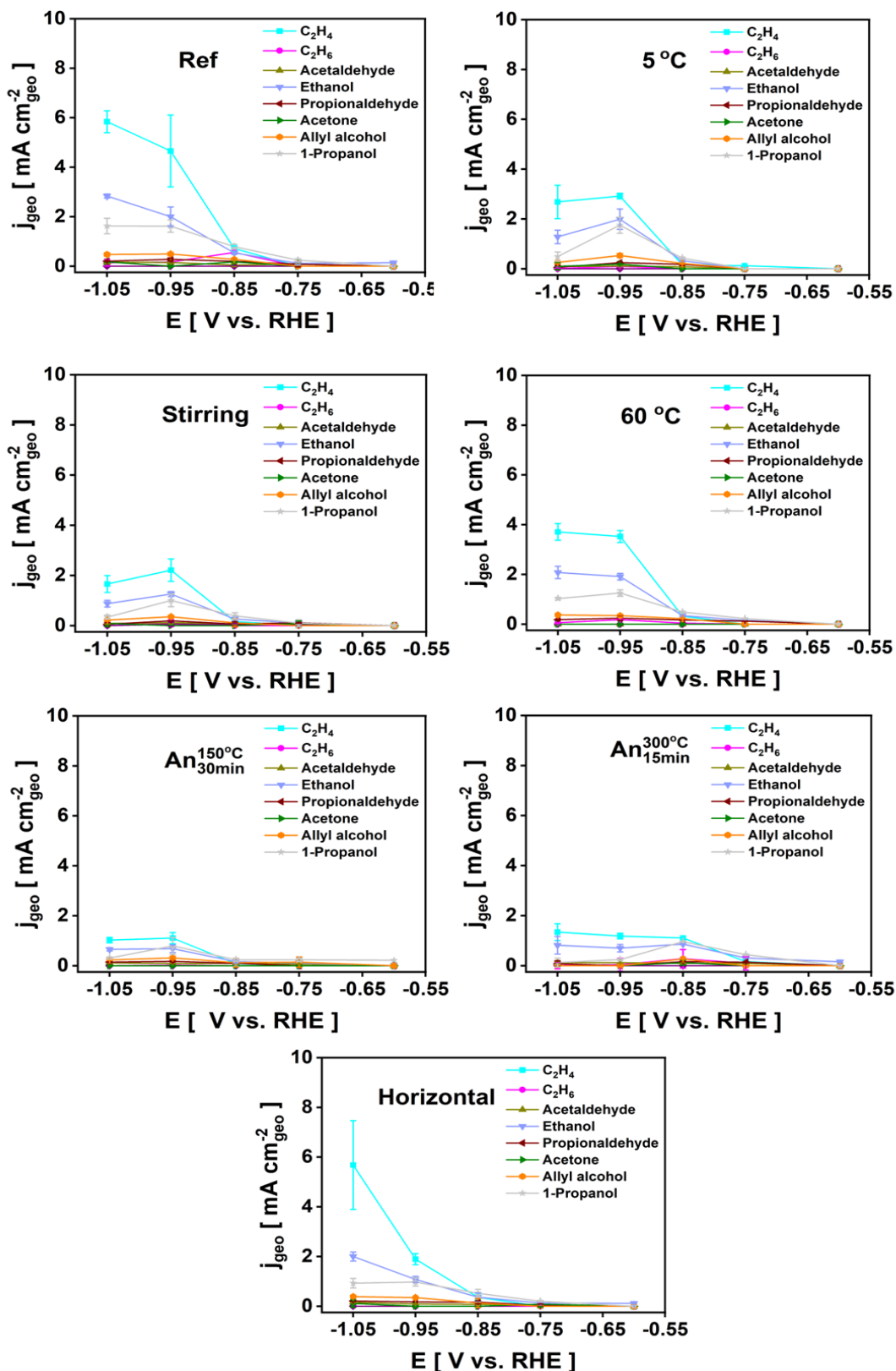


Figure 92: CO_2RR partial current densities of C_2^+ products of the physical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, normalized to the sample geometric area

To assess the intrinsic activity of this series, partial current densities were normalized to the ECSA, as shown in Figure 93 (C_1 products) and Figure 94 (C_{2+} products). The behavior of C_1 product j_{ECSA} was similar to that of j_{geo} , with CO and methanol exhibiting negligible j_{ECSA} . Also, CH_4 displayed appreciable j_{ECSA} only at -1.05 with the maximum values exhibited by the reference ($48 \pm 17 \mu A cm_{ECSA}^{-2}$), 5 °C ($79 \pm 2 \mu A cm_{ECSA}^{-2}$), and horizontally aligned ($34 \pm 7 \mu A cm_{ECSA}^{-2}$) foams. The largest formate peak j_{ECSA} values were observed for the 5 °C foam ($41 \pm 1 \mu A cm_{ECSA}^{-2}$) and $An_{30min}^{150^\circ C}$ ($37 \pm 1 \mu A cm_{ECSA}^{-2}$).

C_{2+} j_{ECSA} values were very low for the annealed samples across the applied potential range. At -0.95 V, the reference and 5 °C samples exhibited the highest C_{2+} j_{ECSA} : ethylene j_{ECSA} of 37 ± 11 and $43 \pm 2 \mu A cm_{ECSA}^{-2}$, ethanol j_{ECSA} of 16 ± 3 and $29 \pm 6 \mu A cm_{ECSA}^{-2}$, and 1-propanol j_{ECSA} of 13 ± 2 and $26 \pm 5 \mu A cm_{ECSA}^{-2}$. At -1.05 V, the best intrinsic C_{2+} activities were shown by the reference, 5 °C, and horizontal foams: ethylene j_{ECSA} of 46 ± 4 , 39 ± 10 , and $42 \pm 13 \mu A cm_{ECSA}^{-2}$; ethanol j_{ECSA} of 22 ± 1 , 19 ± 4 , and $15 \pm 1 \mu A cm_{ECSA}^{-2}$; and 1-propanol j_{ECSA} of 13 ± 2 , 7 ± 3 , and $7 \pm 1 \mu A cm_{ECSA}^{-2}$. Stirring and increasing the DHBT bath temperature produced intermediate C_{2+} j_{ECSA} values between those of the reference/horizontal/5 °C samples and the annealed counterparts.

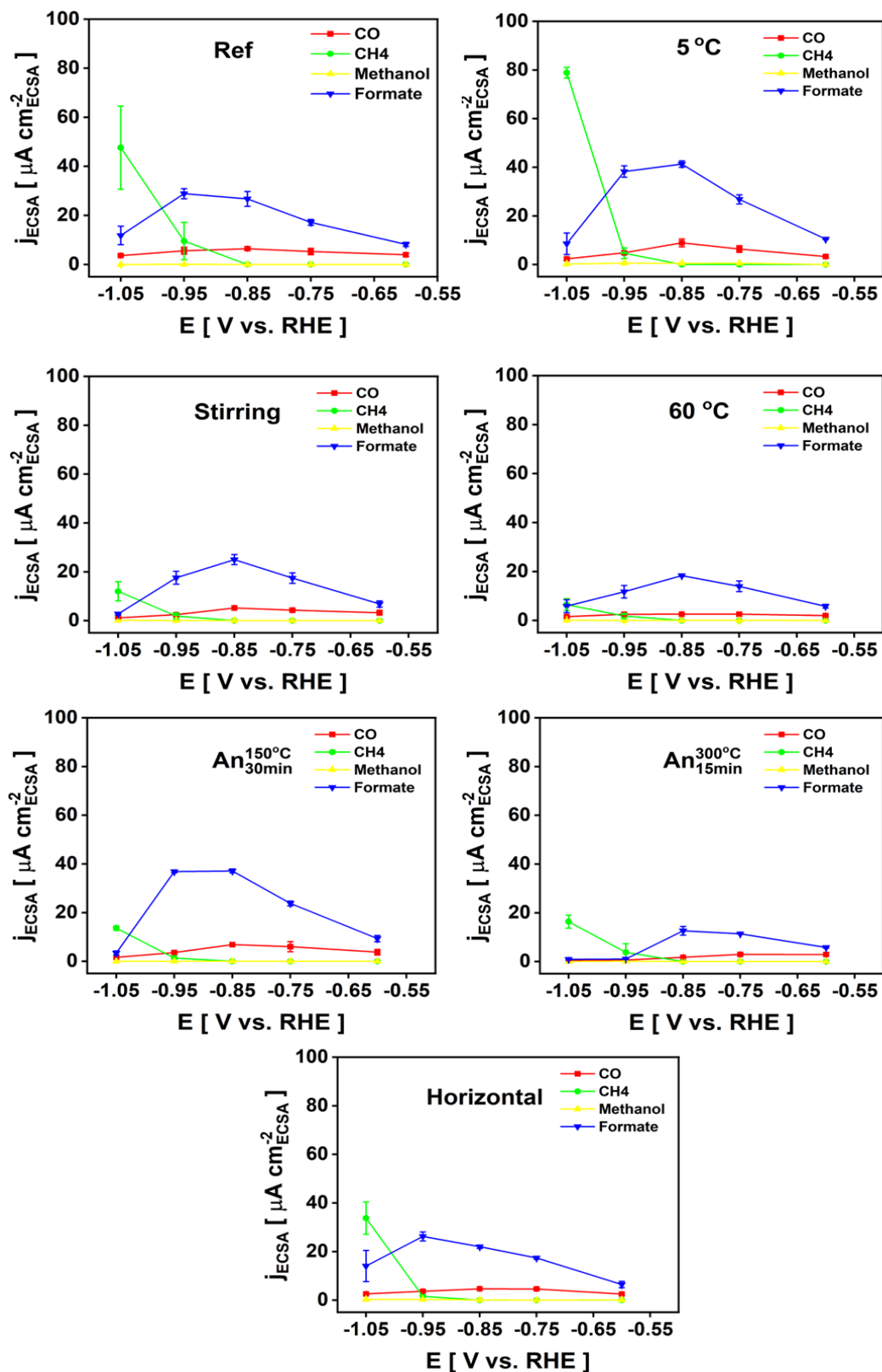


Figure 93: CO₂RR partial current densities of C_1 products of the physical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, normalized to the sample electrochemically active surface area

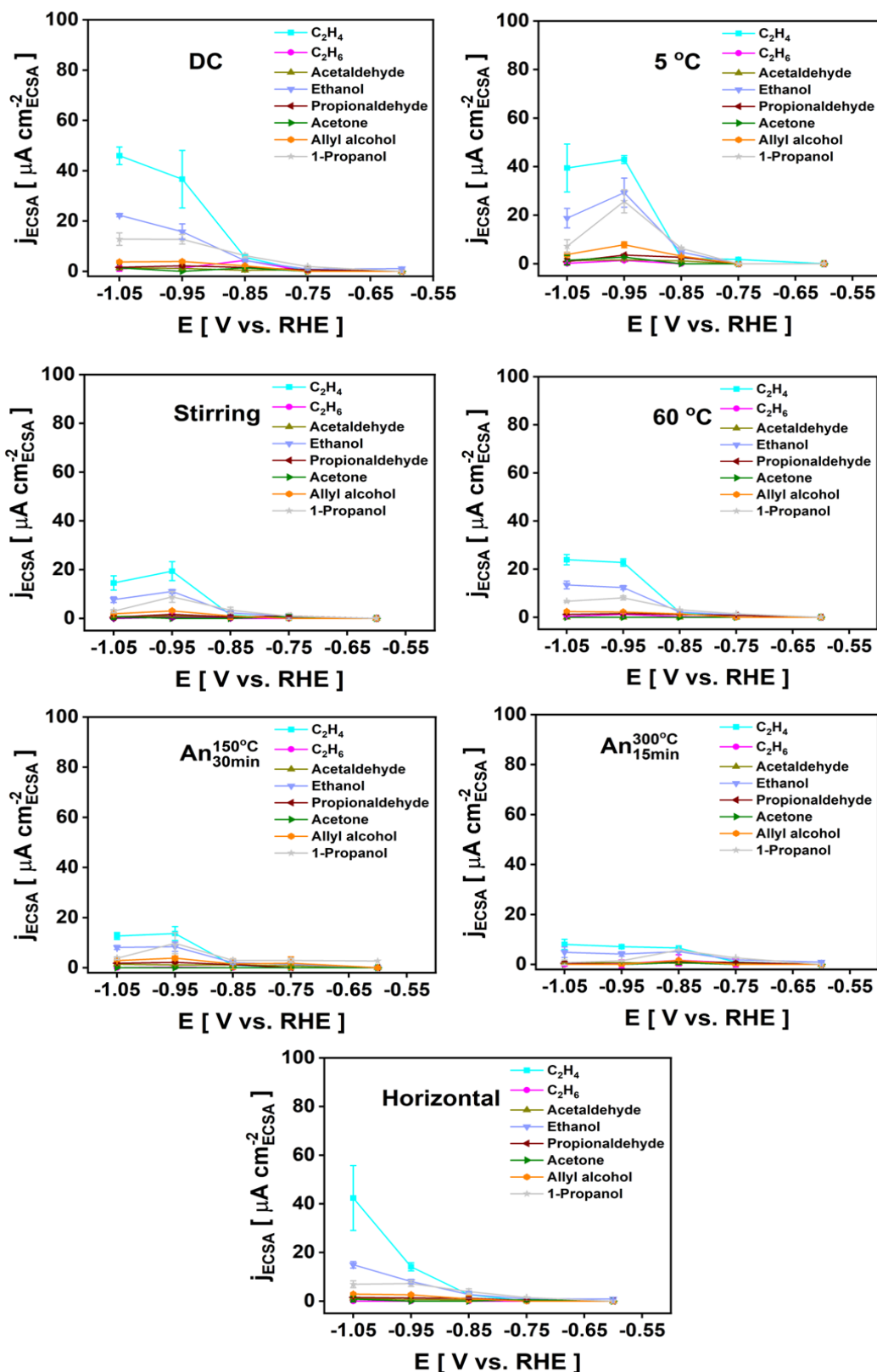


Figure 94: CO_2RR partial current densities of C_2^+ products of the physical effect series, measured in an H-cell setup in the potential range from -0.6 to -1.05 V, normalized to the sample electrochemically active surface area

Figure 95 compares the total C_{2+} product FEs and total C_{2+} product ECSA-normalized partial current densities of the samples of the physical effect series. Except for $An_{15min}^{300^{\circ}C}$, all samples showed a gradual increase in $FE_{C_{2+}}$ with more negative potentials, reaching maxima at -0.95 V and then dropping again at -1.05 V. The $An_{15min}^{300^{\circ}C}$ foam exhibited the highest $FE_{C_{2+}}$ at -0.85 V ($32 \pm 2\%$) compared to the other samples, but the corresponding $j_{C_{2+}}$ was very low ($23 \pm 3 \text{ cm}_{ECSA}^{-2}$), reflecting no actual enhancement in C_{2+} activity. At -0.95 V, the highest $FE_{C_{2+}}$ was observed for the $5^{\circ}C$ sample ($41 \pm 4\%$), corresponding to a superior $j_{C_{2+}}$ ($115 \pm 15 \text{ } \mu\text{A cm}_{ECSA}^{-2}$). The $An_{15min}^{300^{\circ}C}$ samples exhibited the lowest $FE_{C_{2+}}$ and $j_{C_{2+}}$ at -0.95 V with values of $4 \pm 1\%$ and $14 \pm 3 \text{ } \mu\text{A cm}_{ECSA}^{-2}$. The other samples in this series exhibited moderate activity at -0.95 V, with $FE_{C_{2+}}$ between 22 and 30% and $j_{C_{2+}}$ in the range of 34-49 $\mu\text{A cm}_{ECSA}^{-2}$.

In summary, among the physical parameters tested, decreasing the DHBT bath temperature was the most effective strategy to improve C_{2+} product selectivity and intrinsic activity. This supports the hypothesis that more compact foams are more active for CO_2RR because they minimize CO_2 concentration polarization between the foam surface and pore bottom, considering that the $5^{\circ}C$ sample was the most compact foam in this series. The series also highlights the influence of surface nano-features on activity. **Specifically, the reference and stirred samples possessed comparable foam skeletons in terms of pore diameter, foam thickness, and ECSA, as detailed earlier, but they exhibited different dendrite sizes. The reference sample, with smaller dendrites, was more active toward C_{2+} products than the stirred sample with larger dendrites,** which agrees with previous works focusing on the influence of Cu nano-particle size on C_{2+} activity.^[52] At -0.95 V, the $FE_{C_{2+}}$ and $j_{C_{2+}}$ were $22 \pm 5\%$ and $46 \pm 9 \text{ } \mu\text{A cm}_{ECSA}^{-2}$ for the stirred sample, and $30 \pm 2\%$ and $74 \pm 18 \text{ } \mu\text{A cm}_{ECSA}^{-2}$ for the reference sample. This reflects that the surface nano-dendrite size plays a significant role in determining C_{2+} product activity in addition to the foam's overall skeleton. Clearly, the pre-electrolysis Cu oxide species, as will be detailed later in Section 3.5, do not lead to an enhancement in C_{2+} selectivity.

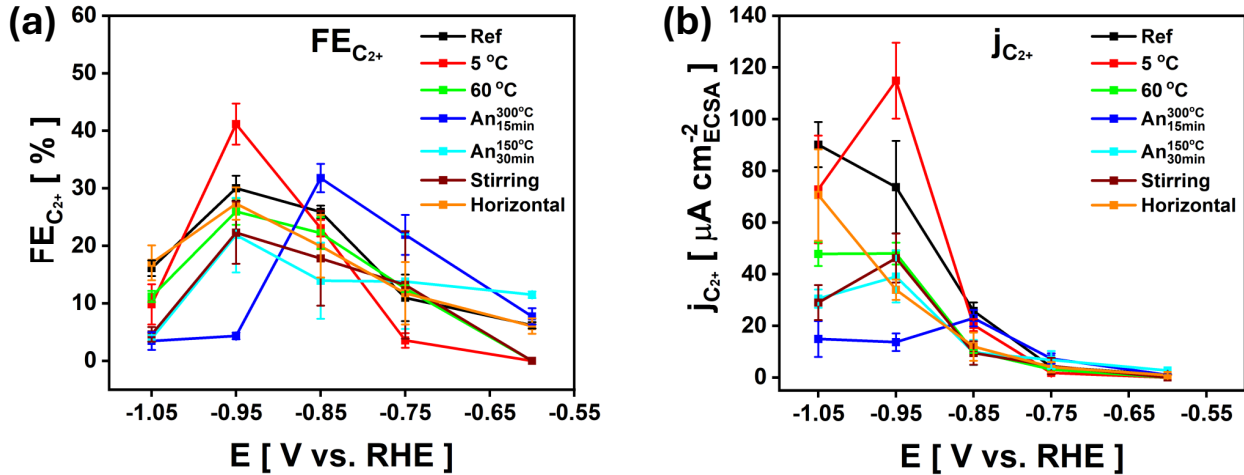


Figure 95: Comparison of the total Faradaic efficiencies (a) and total ECSA-normalized partial current densities (b) of C_{2+} products for the samples of the physical effect series

3.5 X-ray Analysis of Model Cu Foams

XRD was employed to probe the crystal structure of the electrodeposited Cu foams. XRD results of Cu samples were previously correlated to their CO₂RR performance. For instance, smaller crystallite sizes, indicated by broader XRD peaks, were found to enhance C₂₊ selectivity by increasing the density of active sites and promoting *CO adsorption and subsequent dimerization.^[141] Similarly, elevated micro-strain values were reported to facilitate *CO hydrogenation and C-C coupling while inhibiting the H₂ evolution, as demonstrated by operando XRD studies on Cu-based catalysts.^[141] Furthermore, higher intensities of the pre-electrolysis Cu₂O(111) XRD reflection were correlated with improved C₂₊ activity. Analogously, more pronounced Cu(100) reflections were associated with enhanced C-C coupling and increased selectivity toward C₂₊ products.^[141]

In this work, the Cu foams exhibited thicknesses of up to ≈ 70 μm and were electrodeposited on 100 μm Cu foils. Consequently, a contribution from the substrate to the XRD results cannot be fully excluded, considering that XRD is a bulk technique. Although the Cu foil substrate displayed a markedly different XRD pattern from the Cu foam samples, as shown in Figure 96, the XRD results should be interpreted with caution.

All samples were dominated by the metallic face-centered cubic (fcc) Cu, with a minor but distinct simple-cubic Cu₂O phase, likely formed by oxidation due to exposure to air after synthesis.^[96,99] No clear evidence for the CuO phase existence was observed under the applied conditions. The Williamson-Hall method was applied to estimate crystallite size and micro-strain, as detailed in Section 2.3.2. XRD-derived crystallite sizes and micro-strain values, as well as XRD peak intensities normalized to the Cu(111) peak intensity, are listed in Table 4.

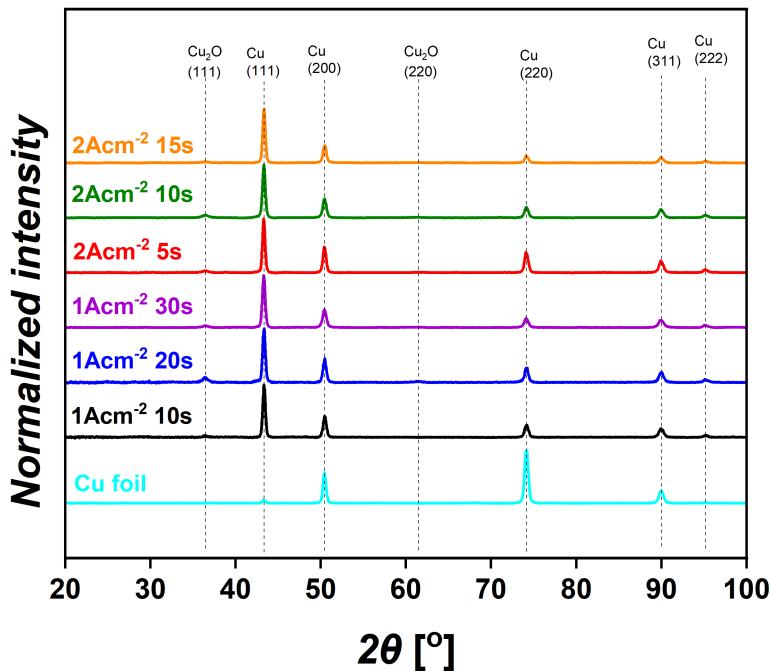


Figure 96: XRD patterns of the DHBT current-time series and Cu foil substrate

Figure 96 shows the XRD patterns of the current-time series. In this series, crystallite sizes ranged

from 41 nm, obtained from the (1Acm^{-2} 30 s) sample, to 139 nm, observed from the (2Acm^{-2} 5 s) counterpart, while micro-strain values ranged from 0.7×10^{-3} , for the (2Acm^{-2} 15s) foam, up to 1.7×10^{-3} , for both the (1A cm^{-2} 20s) and (2Acm^{-2} 5s) samples. The dominant phase in this series was fcc Cu.

X-ray diffractograms of the current-mode series are presented in Figure 97. In this series, the smallest crystallite size, 29 nm, was obtained from the $\text{RC}_{1\text{mC}}$ foam, while the other RC samples exhibited crystallite sizes of 37 nm ($\text{RC}_{3\text{mC}}$) and 60 nm ($\text{RC}_{6\text{mC}}$). The largest crystallite size in this series was 116 nm, obtained from the $\text{PC}_{20:200}$ sample. Micro-strain values in this series varied from 0.5×10^{-3} ($\text{RC}_{1\text{mC}}$) to 1.8×10^{-3} ($\text{AC}_{1.5\text{A}}^{1000\text{Hz}}$). The PC samples deposited with small pulse-to-pause ratios showed relatively larger crystallites. AC samples generally displayed stronger Cu_2O reflections while retaining fcc Cu as the principal phase. This can be attributed to partial surface oxidation during the anodic half-cycles. The dominant phase in this series was fcc Cu.

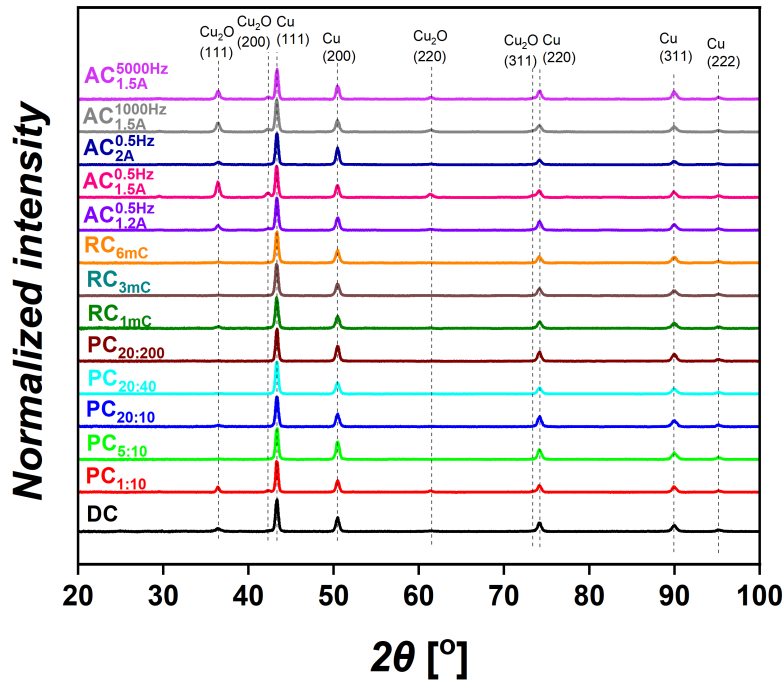


Figure 97: XRD patterns of the DHBT current mode series

Figure 98 represents the XRD results of the physical effect series. For this series, crystallite sizes ranged from 36 nm ($\text{An}_{30\text{min}}^{150^\circ\text{C}}$) to 99 nm (60°C), and micro-strain ranged from 0.3×10^{-3} ($\text{An}_{30\text{min}}^{150^\circ\text{C}}$) to 1.3×10^{-3} (stirred sample). Metallic Cu was the dominant Cu phase in this series, with the (60°C) and $\text{An}_{30\text{min}}^{150^\circ\text{C}}$ foams exhibiting the strongest Cu_2O (111) reflections, most likely due to atmospheric oxidation. [95,96,99]

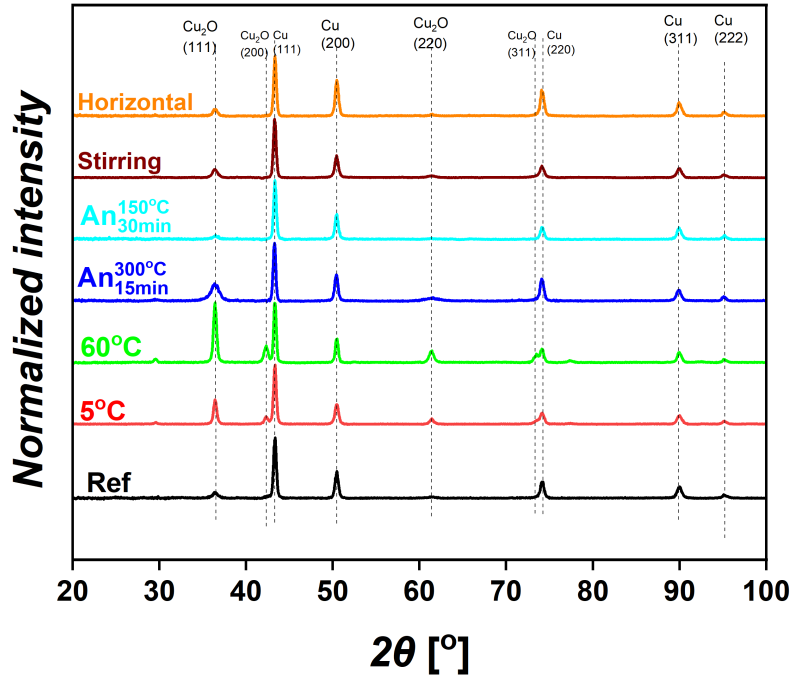


Figure 98: XRD patterns of the DHBT physical effect series

Figure 99 depicts the X-ray diffractograms of the chemical effect series. In this series, DAT-mediated samples exhibited notably smaller crystallite sizes (from 7 to 20 nm) and reduced micro-strain values (from 0 to -1.5×10^{-3}) relative to other samples in this series. The negative micro-strain values observed in the DAT samples were previously reported for Al-Zn-0.4%Cu alloys and were attributed to compressive strain effects,^[142] while other studies interpreted negative micro-strain as an indication of negligible micro-strain contribution to peak broadening.^[143] The largest micro-strain value (1.2×10^{-3}) was exhibited by the SDS and (0.05 M Cu^{2+}) samples, and the highest crystallite size (66 nm) was obtained from the SDS sample. The dominant Cu phase in this series was metallic Cu.

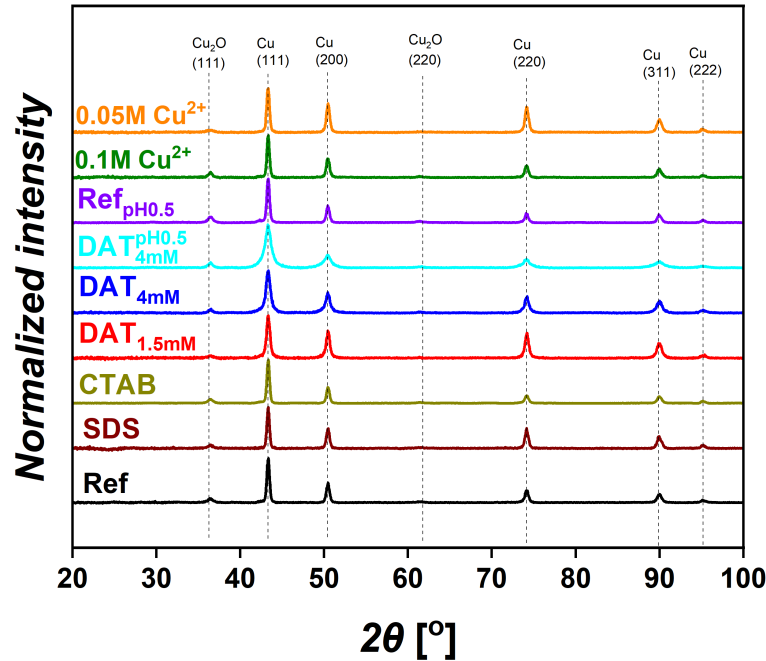


Figure 99: XRD patterns of the DHBT chemical effect series

In summary, the XRD patterns of the produced samples are broadly similar, and the dominant phase is metallic Cu. The largest relative contributions from the Cu₂O phase were observed for AC_{1.5A}^{1000Hz}, AC_{1.5A}^{5000Hz}, 5 °C, 60 °C, stirred, and An_{15min}^{300°C}, with respective Cu₂O(111)/Cu(111) ratios of 0.265, 0.238, 0.372, 0.918, 0.198, and 0.264. There is no clear correlation between the pre-electrolysis bulk Cu₂O content and the C₂₊ product activity. For example, both the 5 °C and 60 °C samples showed strong Cu₂O peaks, but the 5 °C sample exhibits substantially higher C₂₊ activity than the 60 °C sample. The (0.05 M Cu²⁺) sample has very low bulk Cu₂O content (Cu₂O(111)/Cu(111) = 0.027) but was the most active sample in this study. No general correlation is apparent between the intensities of the Cu(200) and Cu(220) peaks and C₂₊ activity; nevertheless, it is worth noticing that the (0.05 M Cu²⁺) foam exhibited the highest Cu(200)/Cu(111) and Cu(220)/Cu(111) ratios (0.606 and 0.519) and was the most active sample toward C₂₊ formation.

Crystallite sizes ranged between 7 and 154 nm, with no evident general correlation to the DHBT condition or to C₂₊ activity. The DAT-mediated samples, which showed remarkable C₂₊ activity, exhibited the smallest crystallite sizes (7-11 nm), whereas the (0.05 M Cu²⁺) sample displayed a larger crystallite size (48 nm) but showed higher activity than the DAT-mediated samples.

Similarly, micro-strain values ranged from -1.5×10^{-3} to 2.1×10^{-3} , and no general correlation between micro-strain, DHBT parameters, and C₂₊ performance was evident. For instance, it is notable that the DAT-mediated samples showed negative micro-strain values (between 0 and -1.5×10^{-3}), which might indicate the presence of compressive strain and might correlate to their good C₂₊ activity.^[142,144] Nevertheless, the (0.05 M Cu²⁺) sample exhibited a higher micro-strain (1.2×10^{-3}) despite its superior C₂₊ activity.

Table 4: Summarized XRD results of the Cu foam samples synthesized in this study: crystallite size, micro-strain, and XRD peak intensities of Cu₂O(111), Cu(200), Cu(220), and Cu(311) reflections each normalized to the Cu(111) peak intensity

Sample	Crystallite size [nm]	Micro-strain [x 10 ⁻³]	Cu ₂ O(111)*	Cu(200)*	Cu(220)*	Cu(311)*
1Acm ⁻² 10s	82	1.4	0.025	0.364	0.210	0.142
1Acm ⁻² 20s, DC, Ref	92	1.7	0.076	0.403	0.245	0.166
1Acm ⁻² 30s	41	1.1	0.028	0.307	0.155	0.128
2Acm ⁻² 5s	139	1.7	0.028	0.449	0.356	0.196
2Acm ⁻² 10s	50	1.2	0.041	0.329	0.184	0.143
2Acm ⁻² 15s	46	0.7	0.016	0.305	0.123	0.088
PC _{1:10}	107	1.4	0.153	0.340	0.180	0.152
PC _{5:10}	63	1.4	0.011	0.519	0.287	0.182
PC _{20:10}	36	0.6	0.037	0.364	0.284	0.177
PC _{20:40}	50	1.4	0.013	0.334	0.179	0.143
PC _{20:200}	116	1.6	0.000	0.442	0.258	0.195
RC _{1mc}	29	0.5	0.048	0.344	0.184	0.138
RC _{3mc}	37	1.0	0.013	0.341	0.203	0.143
RC _{6mc}	60	1.7	0.021	0.359	0.181	0.166
AC _{1.2A} ^{0.5Hz}	58	1.4	0.135	0.370	0.249	0.160
AC _{1.5A} ^{0.5Hz}	69	1.2	0.441	0.363	0.195	0.157
AC _{2A} ^{0.5Hz}	87	1.6	0.074	0.489	0.130	0.095
AC _{1.5A} ^{1000Hz}	58	1.8	0.265	0.333	0.172	0.143
AC _{1.5A} ^{5000Hz}	50	0.6	0.238	0.401	0.254	0.236
5°C	41	0.9	0.372	0.313	0.164	0.129
60°C	99	1.1	0.918	0.377	0.198	0.156
Stirring	50	1.3	0.198	0.327	0.190	0.140
Horizontal	53	0.9	0.098	0.560	0.394	0.195
An _{30min} ^{150°C}	36	0.3	0.045	0.380	0.179	0.166
An _{15min} ^{300°C}	66	1.0	0.264	0.411	0.341	0.154
SDS	66	1.2	0.063	0.417	0.386	0.233
CTAB	46	0.7	0.079	0.341	0.159	0.139
DAT _{1.5mM}	20	0	0.042	0.550	0.501	0.296
DAT _{4mM}	11	-1.5	0.167	0.373	0.316	0.223
DAT _{4mM} ^{pH0.5}	7	-1.2	0.095	0.230	0.150	0.108
0.1 M Cu ²⁺	50	1.0	0.098	0.405	0.238	0.158
0.05 M Cu ²⁺	48	1.2	0.027	0.606	0.519	0.265
pH 0.5	53	0.9	0.117	0.343	0.178	0.135

XPS measurements were performed on the as-deposited Cu foams to identify surface species and oxidation states. The O 1s spectra (Figure 100) exhibited pronounced oxide-related features with binding-energy maxima in the range 529.5–531.2 eV, attributed to overlapping contributions from lattice and defect oxygen in Cu_2O and CuO surface species.^[145–148] Notably, the DAT- and CTAB-modified foams, as well as the $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ and $\text{PC}_{20:200}$ samples, showed enhanced overall oxide peak intensities relative to the other samples.

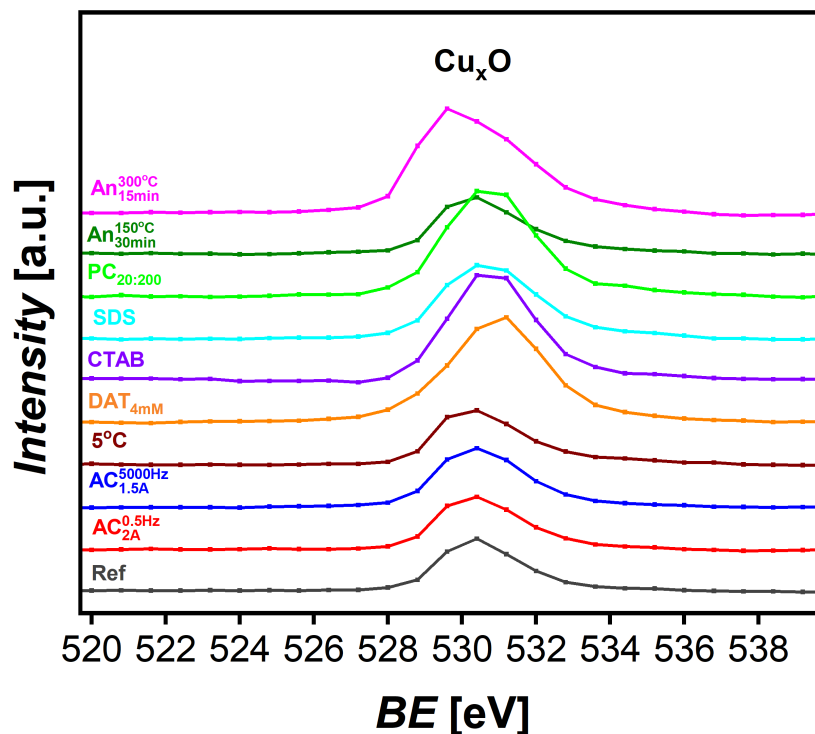


Figure 100: XPS spectra for O 1s region of selected Cu foam samples

The Cu 2p spectra (Figure 101) displayed main peaks at 932.2 eV ($2p_{3/2}$) and 952.0 eV ($2p_{1/2}$) for most samples, consistent with overlapping signals from metallic Cu and Cu_2O , indicating that the surface is dominated by metallic Cu and/or cuprous oxide.^[145–148] DAT- and CTAB-mediated samples displayed additional, weaker shoulders at 934.4 eV and 954.0 eV, assignable to CuO, and consistent with their stronger O 1s oxide intensities. These two samples also exhibited pronounced shake-up satellite features in the $\approx 938\text{--}945$ eV and $\approx 959\text{--}966$ eV ranges, diagnostic of surface CuO.^[145–148] In contrast, the $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ foam showed dominant peaks at 933.7 eV and 954.0 eV (from CuO), with weaker shoulders at 932.2 eV and 952.0 eV (from metallic Cu/ Cu_2O), and very intense shake-up satellites, indicating that annealing at 300 °C promotes substantial surface oxidation to CuO.^[145–148]

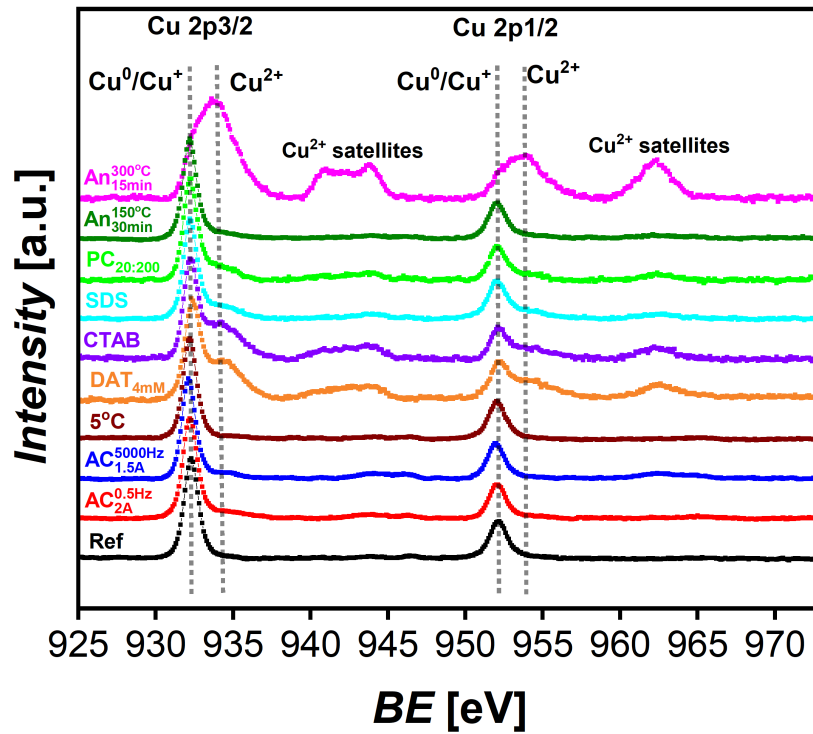


Figure 101: XPS spectra for Cu 2p region of selected Cu foam samples

Cu LMM Auger spectra (Figure 102) exhibited a kinetic-energy maximum at 917.0 eV for most samples, reflecting a surface dominated by Cu_2O , while the $\text{An}_{15\text{min}}^{300^\circ\text{C}}$ sample showed a shifted maximum at 917.7 eV, confirming that the surface is dominated by CuO .

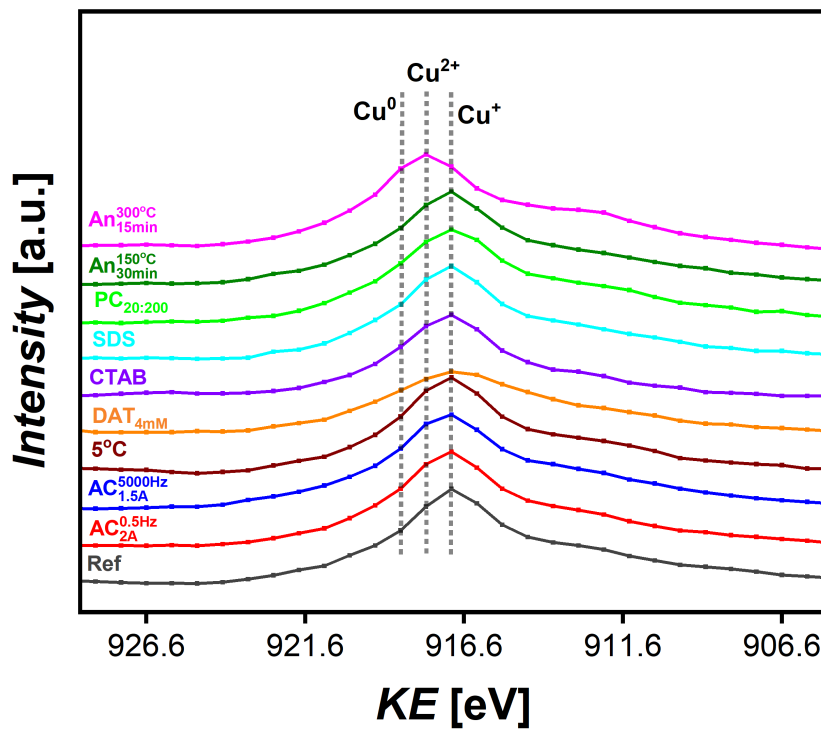


Figure 102: XPS spectra for Cu LMM Auger region of selected Cu foam samples

The N 1s spectrum of the DAT-mediated sample (see Figure 103) showed a peak at 399.7 eV that was absent in the additive-free reference. This peak is attributed to contributions from amino and/or triazole nitrogen atoms of surface-bound DAT.^[149] No bromine, sulfur, nitrogen, or sodium signals were detected for the CTAB- and SDS-mediated samples. Accordingly, only DAT species appear to be incorporated into the structure of the Cu foams, while there is no evidence of incorporation of CTAB or SDS. Therefore, the enhanced C_{2+} activity of the DAT-mediated foams can be attributed to surface DAT-species, as detailed earlier and confirmed by operando SERS measurements. Moreover, there is no indication that surface CTAB species block the catalyst active sites.

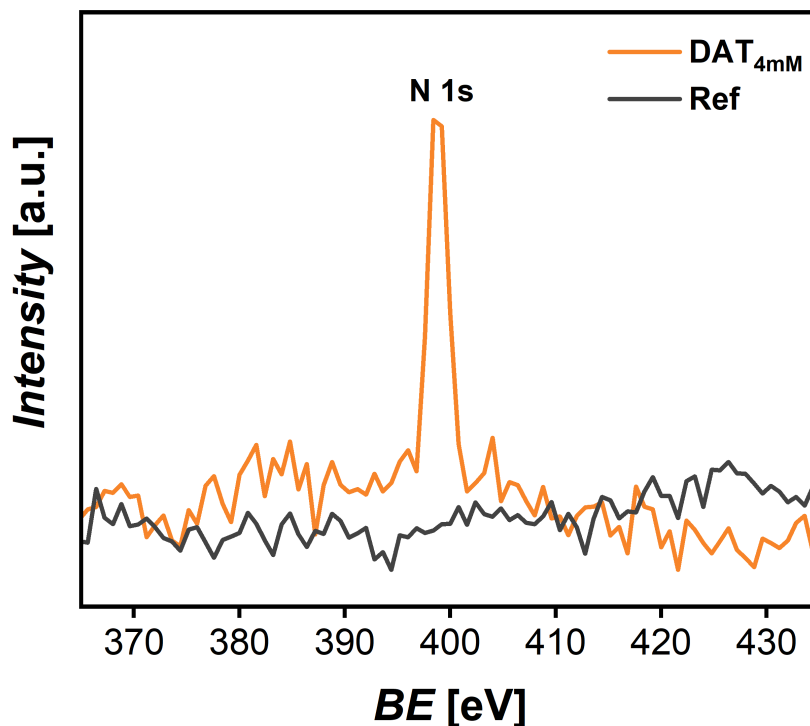


Figure 103: XPS spectra for N 1s region of DAT_{4mM} and Ref samples

Except for the N 1s XPS results of the DAT-mediated samples, pre-electrolysis XPS results do not correlate with CO₂RR performance. The pre-electrolysis surface CuO observed for An_{15min}^{300°C} did not provide an enhancement in C_{2+} activity. Therefore, quasi in-situ XPS analysis is recommended in future work to monitor surface changes of annealed Cu foams during CO₂RR and to provide a direct, more meaningful understanding of their influence on CO₂RR performance.^[150] Additionally, collecting XPS spectra with smaller step sizes and measuring reference substances for the CuO, Cu₂O, and DAT species should be considered in future work.

3.6 Synthesis, Morphology, and Activity Relationships

After a comprehensive study of the influence of various DHBT parameters on Cu foam morphology, synthesis-morphology relationships were established. These relationships enable the targeted synthesis of Cu foam structures for CO₂RR or other applications. Overall, conditions that enhanced H₂ evolution during DHBT, as shown by the decrease in electrodeposition FE, increased the number of H₂ nucleation sites and produced many smaller bubble templates. This led to compact Cu foam structures with smaller pore diameters, or to only micro-to-nano agglomerates without an interconnected foam structure, reduced foam thickness, lower ECSA, decreased mass density, and finer surface nano-dendrites. In contrast, conditions that suppressed HER during DHBT yielded a lower number of larger H₂ bubbles, resulting in more open foam architectures and larger surface nano-dendrites, as represented schematically in Figure 104. A notable exception is the PC mode, where repeated interruptions of the cathodic signal strongly suppressed HER and produced mass-dense foams composed of dominant micro-to-nano agglomerates with limited interconnectivity. Another exception concerns surface nano-particle morphology: the PC and RC samples, as well as foams prepared in the presence of DAT, developed surface nano-cauliflowers instead of nano-dendrites, indicating altered local hydrodynamic conditions under these DHBT settings. Finally, stirring the DHBT bath has only a minor effect on the foam skeleton but causes a pronounced increase in surface nano-dendrite size, supporting the role of hydrodynamic conditions in shaping and sizing surface nano-structures.

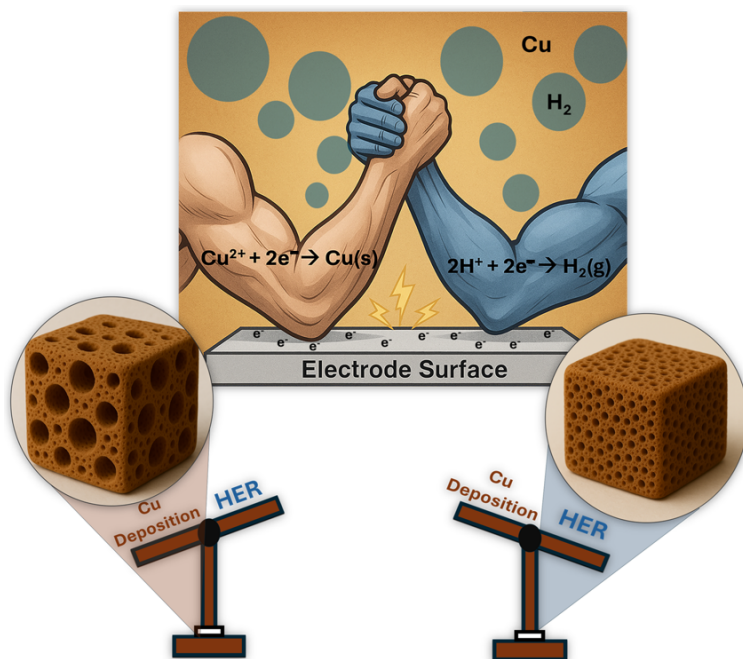


Figure 104: General illustration of the competition between H₂ evolution and Cu electrodeposition during DHBT and its influence on the synthesized foam morphology

It is widely accepted that nano-particle morphology and size critically influence electrocatalysis. Different nano-particles expose distinct crystal facets, edges, and corners, each characterized by unique arrangements of under-coordinated atoms. These atomic variations modify reactant adsorption and intermediate stabilization, generate diverse active sites, and thus substantially affect electrocatalytic performance.^[131] On this basis, the two distinct nano-structures observed in this work, nano-

cauliflowers and nano-dendrites, were further examined at higher magnification ($10,000\times$), as presented in Figure 105. The SEM images show that both nano-structures comprise particles, kinks, and edges ranging from a few microns to sub-microns, which enclose pores and cavities at the nano-scale. Accordingly, samples whose surfaces were dominated mainly by these features were described in this work as exhibiting dominant micro-to-nano porosity.

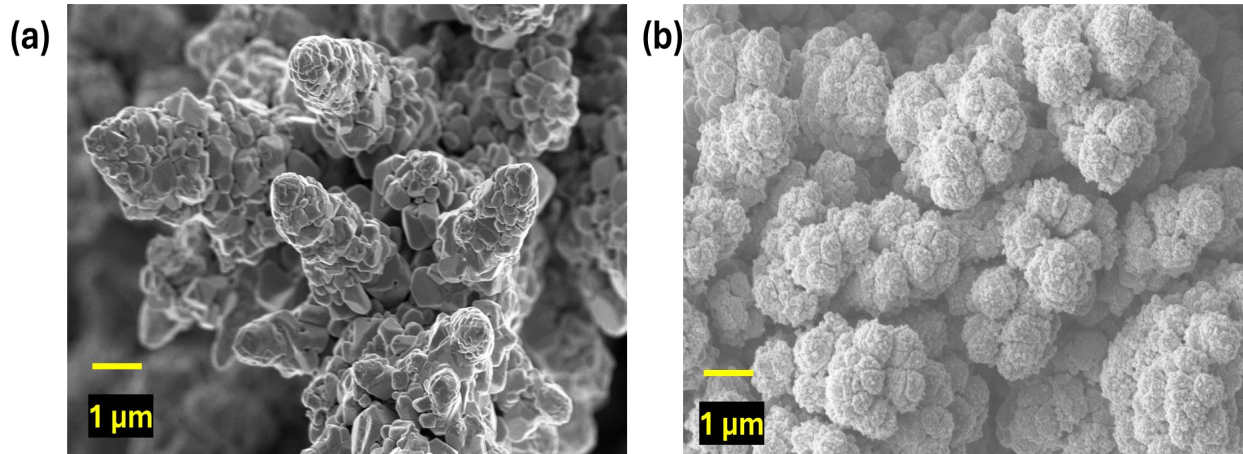


Figure 105: $10,000\times$ magnification SEM images of the two different nano-structures observed in this study: nano-dendrites (a) and nano-cauliflowers (b)

Figure 106 presents a decision flow chart to guide the synthesis of Cu foam samples with desired structural features. The chart first separates two primary targeted morphologies: honeycomb-like structures and only micro-to-nano porous deposits. For honeycomb-like architectures, the next branch addresses the desired surface nano-structures: nano-dendrites or nano-cauliflowers. Both the RC and PC modes can produce cauliflower morphologies. To obtain honeycomb-like morphologies, higher pulse-to-pause ratios (in the PC mode) or cathodic-to-anodic pulse ratios (in the RC mode) are required. Moreover, the foam architecture can be tuned gradually by adjusting the ΔC parameter in the RC regime. For nano-dendrite surfaces, the flow chart asks whether an open or compact foam is desired. For open structures, DC-DHBT combined with long deposition times, low current densities, elevated temperatures, mechanical stirring (to promote dendrite growth when large dendrites are targeted), and/or higher pH can be applied. The pH range studied here was from -0.5 to 0.5. If open foams with small nano-dendrites are required, post-synthesis annealing can be applied.

Compact metallic foams are obtained using the DC mode with low temperature, high current densities, short deposition times, and/or additives such as DAT (at low concentrations), SDS, or CTAB. In this study, one concentration of 0.25 mM for both SDS and CTAB, and two DAT concentrations of 1.5 and 4 mM were tested. Additionally, low- and moderate-frequency AC-DHBT (0.5 - 1000 Hz) can produce compact structures. If only micro-to-nano-porosity is required, the chart asks whether uniformity is important. When uniformity is not critical, and only the application of nano-structures is required, high DAT concentrations (with or without elevated pH) can be used; whereas when uniformity is essential, PC mode with low pulse-to-pause ratios or DC mode at low Cu^{2+} concentrations can be employed.

These recommendations are intended as guidelines rather than restrictive protocols. Differences between laboratories were observed in the structure of the obtained Cu foams, which may arise from

distinctions in potentiostat models, Cu foil preparation, etching procedures, and Cu foil suppliers. Therefore, the flow chart should be used as a directional framework, followed by systematic optimization under the specific onsite experimental conditions. Additionally, it is recommended to visit the previous Results & Discussion subsections and the Experimental part before applying the flow chart. Suppose the targeted architecture is an open, honeycomb-like Cu foam with large nano-dendrites, large pores, and substantial thickness for use as a current collector in a battery. The flow chart gives the following recommendations: honeycomb-like? $\rightarrow$ yes, surface nano-dendrites? $\rightarrow$ yes, open structure? $\rightarrow$ yes, large dendrites? $\rightarrow$ yes, the chart recommendations include using the DC mode at low current densities, with the possibility to control the foam thickness and pore diameter simply via electrodeposition times.

For CO₂RR particularly, Table 5 offers a parameter-focused overview, illustrating how each parameter influences the electrodeposited Cu mass density, electrodeposition FE, pore diameter, foam thickness, and the shape and size of surface nano-structures. Importantly, it provides the impact of each DHBT parameter on CO₂RR activity toward C₂₊ products, reported as the increase or decrease in the highest total C₂₊ ECSA-normalized partial current densities ($j_{C_{2+}}^{\text{Max}}$) exhibited by the resulting Cu foams. Strategies that improve C₂₊ activity include applying the DC mode at high current densities for short times, using the PC mode at low pulse-to-pause ratios, employing the RC mode with large ΔC values, using the AC mode at low frequencies, and adding SDS or DAT to the DHBT bath. Clearly, all parameters that suppress Cu foam openness increase C₂₊ products activity. To present the synthesis, morphology, and activity numerically, a summary of the pore diameter, foam thickness, pore density, ECSA, mass density, and $j_{C_{2+}}^{\text{Max}}$ values is given in Table 6. The values from Table 6 were used to establish useful correlations.

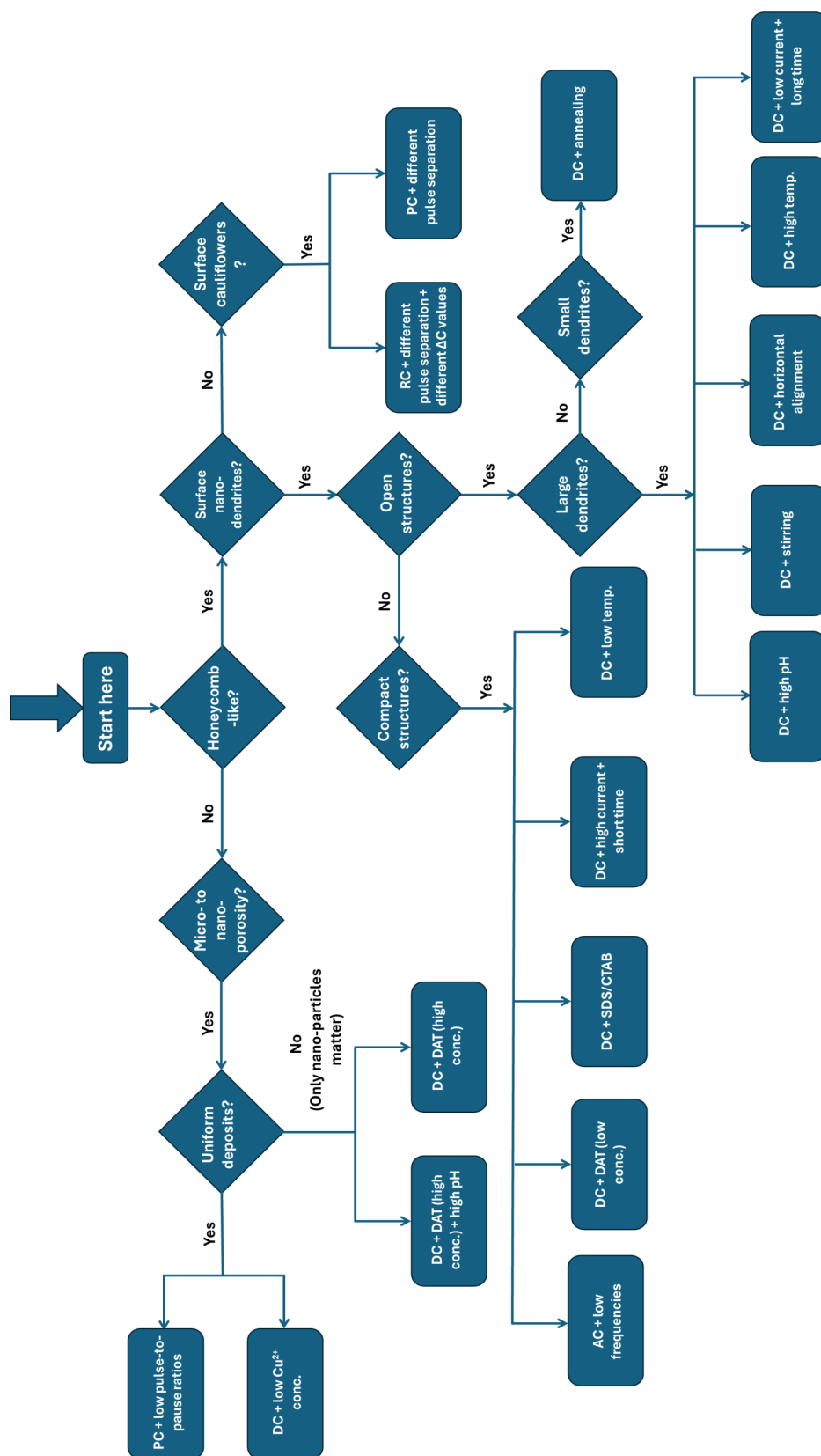


Figure 106: Flow chart for guiding the synthesis of Cu foam samples with tailored properties, based on the results obtained in this work

Table 5: Detailed correlation of the DHBT conditions and various properties of the electrodeposited Cu foams: deposited Cu mass, electrodeposition Faradaic efficiency (deposition FE), pore diameter, foam thickness, the shape and size of surface nano-dendrites, and highest total C_{2+} jECSA values ($j_{C_{2+}}^{Max}$). An upward arrow ($\uparrow$) signifies an increase, a downward arrow ($\downarrow$) indicates a decrease, and a dash (-) represents no clear correlation between the property and the applied DHBT condition

DHBT parameter	Mass density	Deposition FE	Pore diameter	Thickness	nano-dendrite shape	nano-dendrite size	$j_{C_{2+}}^{Max}$
DC + time $\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	dendrites	$\uparrow$	$\rightarrow$
DC + current density $\uparrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	dendrites	$\downarrow$	$\uparrow$
PC + pulse-to-pause ratio $\downarrow$	$\uparrow$	$\uparrow$	$\downarrow^a$	$\downarrow$	cauliflower	-	$\uparrow$
RC + $\Delta C \uparrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	cauliflower	-	$\uparrow$
AC + frequency $\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	-	dendrites	$\uparrow$	$\downarrow$
AC + amplitude $\uparrow$	-	-	$\uparrow$	-	dendrites	-	$\uparrow$
Mechanical stirring	-	-	-	-	dendrites	$\uparrow$	$\rightarrow$
Horizontal alignment	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	dendrites	$\uparrow$	$\rightarrow$
Temperature $\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	dendrites	$\downarrow$	$\rightarrow$
Annealing	-	-	$\uparrow$	$\uparrow$	dendrites	$\downarrow$	$\rightarrow$
SDS	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	dendrites	$\downarrow$	$\uparrow$
CTAB	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	dendrites	$\downarrow$	$\rightarrow$
DAT	-	-	$\downarrow^b$	$\downarrow$	dendrites	$\downarrow$	$\rightarrow$
Cu ²⁺ concentration $\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	dendrites or cauliflower ^b	-	$\uparrow$
pH $\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	dendrites	$\uparrow$	$\rightarrow$
					dendrites	$\uparrow$	$\rightarrow$

^{a)} Depends on the pulse-to-pause ratio. At very low pulse-to-pause ratios, no honeycomb-like structures were obtained (refer to Section 3.2.1 for more information).

^{b)} Depends on DAT concentration and pH (refer to Section 3.3 for more information).

Table 6: Summarized results of the model Cu foam samples investigated in this study: pore diameter, foam thickness, pore density, mass density, ECSA (measured via CV), and highest total C₂₊ product ECSA-normalized partial current densities

Sample	Diameter [μm]	Thickness [μm]	Pore density [pore mm^{-2}]	Mass density [mg cm^{-2}]	ECSA [$\text{cm}^2_{\text{ECSA}} \cdot \text{cm}^{-2}_{\text{geo}}$]	$j_{\text{C}_{2+}}^{\text{Max}}$ [$\mu\text{A cm}^{-2}_{\text{ECSA}}$]
1Acm ⁻² 10s	11.5 $\pm$ 0.3	24.8 $\pm$ 1.7	1824	1.5 $\pm$ 0.1	41 $\pm$ 1	118 $\pm$ 44
1Acm ⁻² 20s, DC, Ref	19.9 $\pm$ 0.6	50.6 $\pm$ 5.3	748	3.1 $\pm$ 0.3	127 $\pm$ 15	90 $\pm$ 9
1Acm ⁻² 30s	36.7 $\pm$ 0.5	62.0 $\pm$ 4.7	346	4.8 $\pm$ 0.2	179 $\pm$ 12	27 $\pm$ 6
2Acm ⁻² 5s	9.4 $\pm$ 0.1	23.0 $\pm$ 1.5	3541	1.2 $\pm$ 0.1	41 $\pm$ 7	347 $\pm$ 54
2Acm ⁻² 10s	15.5 $\pm$ 0.1	26.2 $\pm$ 2.4	1360	2.4 $\pm$ 0.2	85 $\pm$ 13	88 $\pm$ 32
2Acm ⁻² 15s	20.1 $\pm$ 0.2	55.6 $\pm$ 4.6	806	3.8 $\pm$ 0.2	132 $\pm$ 12	62 $\pm$ 9
PC _{1:10}	-	19.7 $\pm$ 3.7	-	4.7 $\pm$ 0.1	39 $\pm$ 2	199 $\pm$ 32
PC _{5:10}	-	23.8 $\pm$ 5.3	-	3.8 $\pm$ 0.2	45 $\pm$ 2	195 $\pm$ 7
PC _{20:10}	17.4 $\pm$ 0.4	46.2 $\pm$ 5.2	631	3.4 $\pm$ 0.1	56 $\pm$ 6	100 $\pm$ 26
PC _{20:40}	-	25.7 $\pm$ 3.5	-	3.6 $\pm$ 0.1	37 $\pm$ 4	391 $\pm$ 87
PC _{20:200}	-	19.0 $\pm$ 1.6	-	4.4 $\pm$ 0.1	28 $\pm$ 3	364 $\pm$ 35
RC _{1mC}	15.7 $\pm$ 0.2	39.1 $\pm$ 2.1	733	3.4 $\pm$ 0.1	53 $\pm$ 5	307 $\pm$ 20
RC _{3mC}	15.0 $\pm$ 0.1	29.4 $\pm$ 9.1	588	3.3 $\pm$ 0.1	43 $\pm$ 2	281 $\pm$ 25
RC _{6mC}	13.1 $\pm$ 0.1	24.8 $\pm$ 5.3	936	3.1 $\pm$ 0.1	37 $\pm$ 1	372 $\pm$ 27
AC _{0.5Hz} 1.2A	11.3 $\pm$ 0.3	47.3 $\pm$ 3.8	1379	2.5 $\pm$ 0.2	79 $\pm$ 11	119 $\pm$ 23
AC _{0.5Hz} 1.5A	12.1 $\pm$ 0.3	37.4 $\pm$ 2.0	1215	2.5 $\pm$ 0.1	82 $\pm$ 8	147 $\pm$ 10
AC _{0.5Hz} 2A	14.5 $\pm$ 0.4	43.0 $\pm$ 3.1	913	2.4 $\pm$ 0.1	76 $\pm$ 12	157 $\pm$ 12
AC _{1000Hz} 1.5A	13.5 $\pm$ 0.2	40.7 $\pm$ 5.5	1013	3.0 $\pm$ 0.2	71 $\pm$ 6	129 $\pm$ 20
AC _{5000Hz} 1.5A	20.4 $\pm$ 0.5	44.0 $\pm$ 4.1	613	3.1 $\pm$ 0.2	77 $\pm$ 11	-
5 °C	16.7 $\pm$ 0.4	38.2 $\pm$ 4.1	911	2.6 $\pm$ 0.1	68 $\pm$ 7	115 $\pm$ 15
60 °C	50.5 $\pm$ 3.0	69.6 $\pm$ 7.8	54	4.0 $\pm$ 0.3	155 $\pm$ 6	48 $\pm$ 4
Stirred	20.4 $\pm$ 0.4	49.4 $\pm$ 5.3	430	3.3 $\pm$ 0.3	114 $\pm$ 15	46 $\pm$ 9
Horizontal	22.4 $\pm$ 1.1	64.1 $\pm$ 8.1	276	4.4 $\pm$ 0.7	134 $\pm$ 2	71 $\pm$ 18
An _{15min} ^{300°C}	22.3 $\pm$ 0.5	71.7 $\pm$ 4.8	514	3.1 $\pm$ 0.1	167 $\pm$ 8	23 $\pm$ 3
An _{30min} ^{150°C}	30.5 $\pm$ 1.0	68.5 $\pm$ 3.7	253	3.2 $\pm$ 0.1	81 $\pm$ 15	39 $\pm$ 10
SDS	14.7 $\pm$ 0.1	33.3 $\pm$ 2.6	1063	1.4 $\pm$ 0.1	49 $\pm$ 11	310 $\pm$ 10
CTAB	16.2 $\pm$ 0.2	30.5 $\pm$ 1.6	1364	1.7 $\pm$ 0.1	68 $\pm$ 8	130 $\pm$ 10
0.1 M Cu ²⁺	13.7 $\pm$ 0.1	30.3 $\pm$ 2.0	948	1.6 $\pm$ 0.1	51 $\pm$ 6	302 $\pm$ 17
0.05 M Cu ²⁺	-	22.9 $\pm$ 10.2	-	0.7 $\pm$ 0.1	31 $\pm$ 3	520 $\pm$ 20
DAT _{1.5mM}	13.3 $\pm$ 0.3	17.3 $\pm$ 2.0	797	2.9 $\pm$ 0.1	52 $\pm$ 3	338 $\pm$ 31
DAT _{4mM}	11.5 $\pm$ 0.4	16.6 $\pm$ 4.1	302	2.9 $\pm$ 0.2	44 $\pm$ 5	414 $\pm$ 22
DAT _{4mM} ^{pH0.5}	-	26.4 $\pm$ 5.2	-	3.3 $\pm$ 0.2	69 $\pm$ 8	126 $\pm$ 21
pH 0.5	28.4 $\pm$ 2.4	65.5 $\pm$ 6.9	216	3.8 $\pm$ 0.2	125 $\pm$ 5	77 $\pm$ 6

Figure 107 shows the relationship between foam thickness and pore diameter, excluding the values of annealed samples because their dimensions reflect post-deposition thermal effects rather than pure DHBT conditions. A clear linear relationship across the pore range $\approx 10\text{--}30\text{ }\mu\text{m}$ was observed. This linear trend may indicate that, within the specified range, the DHBT mechanism remains essentially unchanged and that the applied DHBT parameters primarily scale the extent of the process rather than altering its fundamental character. For pore diameters above $30\text{ }\mu\text{m}$, the $(1\text{Acm}^{-2}\text{ }30\text{s})$ and $60\text{ }^\circ\text{C}$ samples deviate from the linear trend. This may arise from experimental error; therefore, these points might be treated as outliers. Alternatively, the dependence can be described by an exponential relation with two distinct DHBT regimes separated by an inflection point at a $\approx 60\text{ }\mu\text{m}$ thickness and a $\approx 30\text{ }\mu\text{m}$ diameter, suggesting a change in the dominant growth mechanism before and after this thickness.

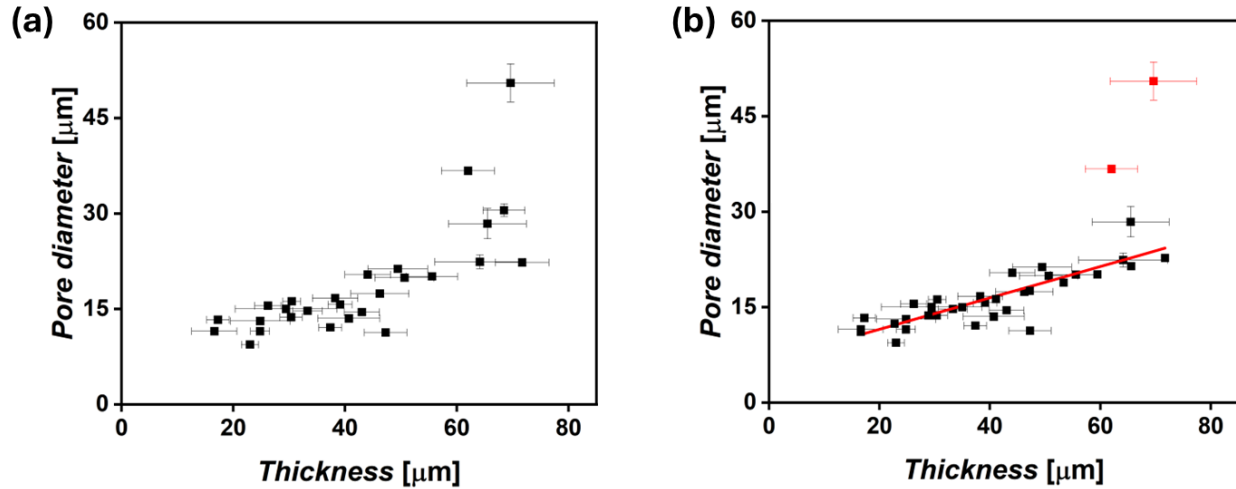


Figure 107: Relationship between foam thickness and pore diameter for the Cu foam samples investigated in this study (a), and the corresponding linear fit (b), with the outliers shown in red

The relationships between three morphology descriptors, namely ECSA, pore diameter, and foam thickness, each treated individually as the independent variable, and the C_{2+} activity, expressed as $j_{\text{C}_{2+}}^{\text{Max}}$, as the dependent variable, are presented in Figure 108. For the three descriptors, the data are best described by an exponential trend, with larger values of the independent variable corresponding to low $j_{\text{C}_{2+}}^{\text{Max}}$, and below a characteristic inflection point, $j_{\text{C}_{2+}}^{\text{Max}}$ increased sharply.

Specifically, for ECSA values above $\approx 45\text{ }\mu\text{m}^2$, the C_{2+} activity was very low (below $150\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$). The decrease in ECSA below $\approx 45\text{ }\mu\text{m}^2$ resulted in a sudden increase in $j_{\text{C}_{2+}}^{\text{Max}}$, reaching more than $500\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$. Similarly, pore diameters above $\approx 17.5\text{ }\mu\text{m}$ corresponded to low $j_{\text{C}_{2+}}^{\text{Max}}$ ($\approx 50\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$), which rose dramatically as pore diameters decreased below $17.5\text{ }\mu\text{m}$ to values above $400\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$. Thickness values above $\approx 25\text{ }\mu\text{m}$ corresponded to low $j_{\text{C}_{2+}}^{\text{Max}}$ (below $100\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$), whereas the decrease in thickness values below $35\text{ }\mu\text{m}$ was associated with a steep increase in activity to more than $500\text{ }\mu\text{A cm}^{-2}_{\text{ECSA}}$.

These important findings confirm the hypothesis proposed throughout this work that more open Cu foams, characterized by a larger pore diameter, greater thickness, and higher ECSA, are less active than more compact foams with smaller values for these three parameters. This behavior suggests that, in addition to the expected CO_2 mass-transport limitation between the bulk electrolyte and the electrode surface, an additional mass-transport limitation of CO_2 exists for the Cu foam samples

between the foam surface and pore interior. This results in CO_2 concentration polarization along the pore axis, which is more pronounced for very open foams. Once each morphology descriptor drops below its respective inflection point, the CO_2 concentration polarization across the pore becomes less significant, and CO_2RR performance improves remarkably.^[125]

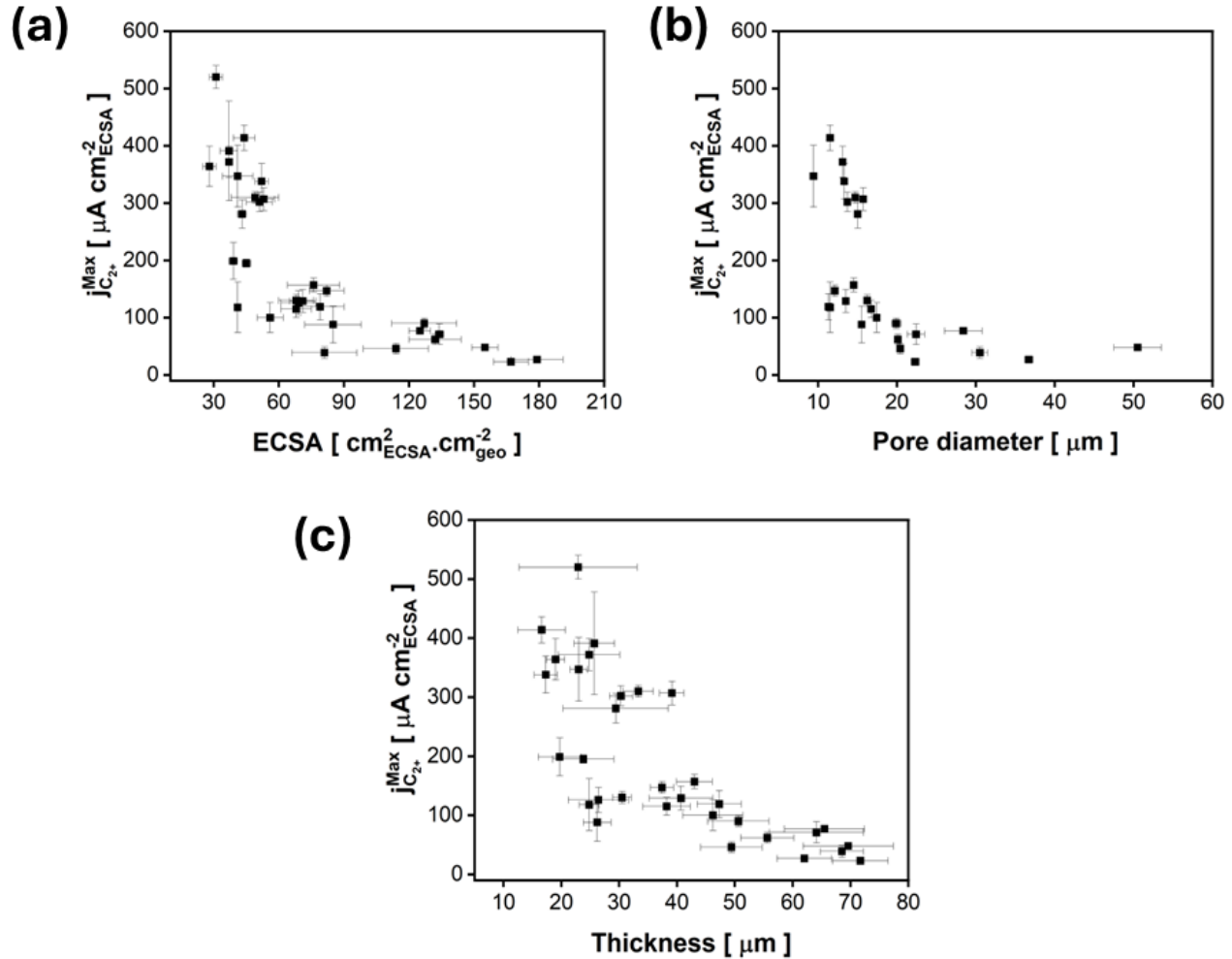


Figure 108: Relationships between ECSA (a), pore diameter (b), and thickness (c), each as the independent variable, and C_{2+} activity expressed as the highest total C_{2+} product ECSA-normalized partial current densities, as the dependent variable

The mass-transport limitations of CO_2 between the bulk electrolyte and the Cu foam surface, together with the internal diffusion constraints within the pore, are represented in Figure 109. The schematic depicts how concentration gradients develop from the bulk electrolyte toward the pore bottom, producing regions inside the pores that become depleted of CO_2 , where HER consequently dominates the local electrochemistry. As a result, foams with more open, widely spaced pore structures are more susceptible to pronounced internal mass-transport limitations and larger extents of CO_2 depletion relative to more compact foams, which is a difference that can significantly affect selectivity and overall catalytic performance.

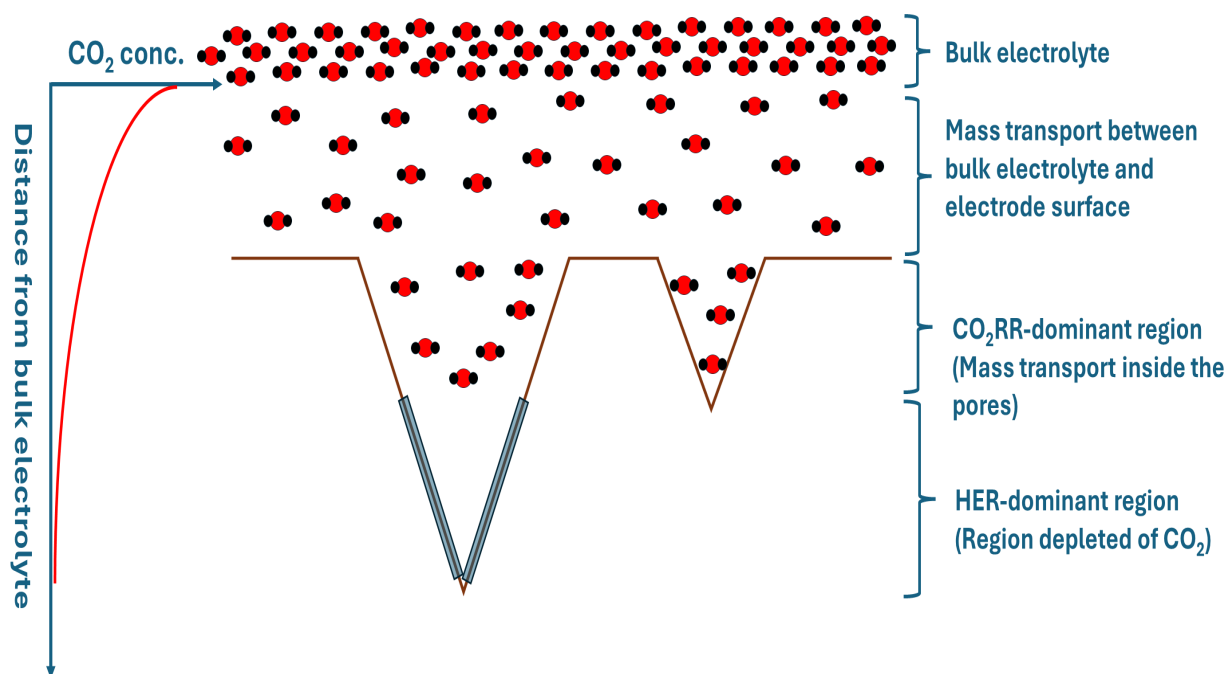


Figure 109: Schematic representation of CO_2 diffusion from the bulk electrolyte to the Cu foam surface and through the pore, highlighting pore regions depleted of CO_2 where HER predominates, with a comparison between open and compact foams, and the pore geometry represented as a V-shaped morphology

Attempts to make morphology-activity correlations between C_{2+} activity and other morphology descriptors, namely mass density, micro-strain, crystallite size, and $\text{Cu}_2\text{O}(111)/\text{Cu}(111)$, $\text{Cu}(200)/\text{Cu}(111)$, $\text{Cu}(220)/\text{Cu}(111)$, and $\text{Cu}(311)/\text{Cu}(111)$ XRD peak intensity ratios are provided in Figure 110. In contrast to the parameters presented in Figure 108, the specified parameters in this Figure 110 do not show a significant correlation to C_{2+} activity. The absence of correlation between C_{2+} activity and mass density was expected, as mass dense samples such as $\text{PC}_{20:40}$ ($j_{\text{C}_{2+}}^{\text{Max}} = 391 \pm 87 \mu\text{A cm}_{\text{ECSA}}^{-2}$) showed comparable activity to that of less dense samples, e.g., $\text{DAT}_{4\text{mM}}$ ($j_{\text{C}_{2+}}^{\text{Max}} = 414 \pm 22 \mu\text{A cm}_{\text{ECSA}}^{-2}$).

XRD results of Cu samples were correlated in previous studies to CO_2RR performance. For example, smaller crystallites (inferred from broader XRD peaks) were reported to enhance C_{2+} selectivity by increasing active-site density and favoring *CO adsorption and dimerization.^[141] Analogously, a high micro-strain was shown to promote *CO hydrogenation and C-C coupling while suppressing HER, as observed by operando XRD on Cu-based catalysts.^[141] Also, higher pre-electrolysis $\text{Cu}_2\text{O}(111)$ XRD reflection intensities were associated with enhanced C_{2+} activity. Similarly, stronger $\text{Cu}(100)$ reflections were linked to improved C-C coupling and higher activity toward C_{2+} products.^[141] The lack of a general correlation between C_{2+} activity and XRD-derived descriptors in this work may indicate the following: (1) bulk XRD metrics are less relevant for CO_2RR performance of Cu foam samples, (2) ex-situ XRD observations obtained here do not reflect the operando catalyst crystal structure, (3) XRD measurement parameters were not optimized enough to equally exclude the effect of substrate contribution to XRD response for each sample, and/or (4) the Cu foam skeleton (and its associated mass-transport limitations) is the dominant factor determining CO_2RR performance and C_{2+} activity in our samples.

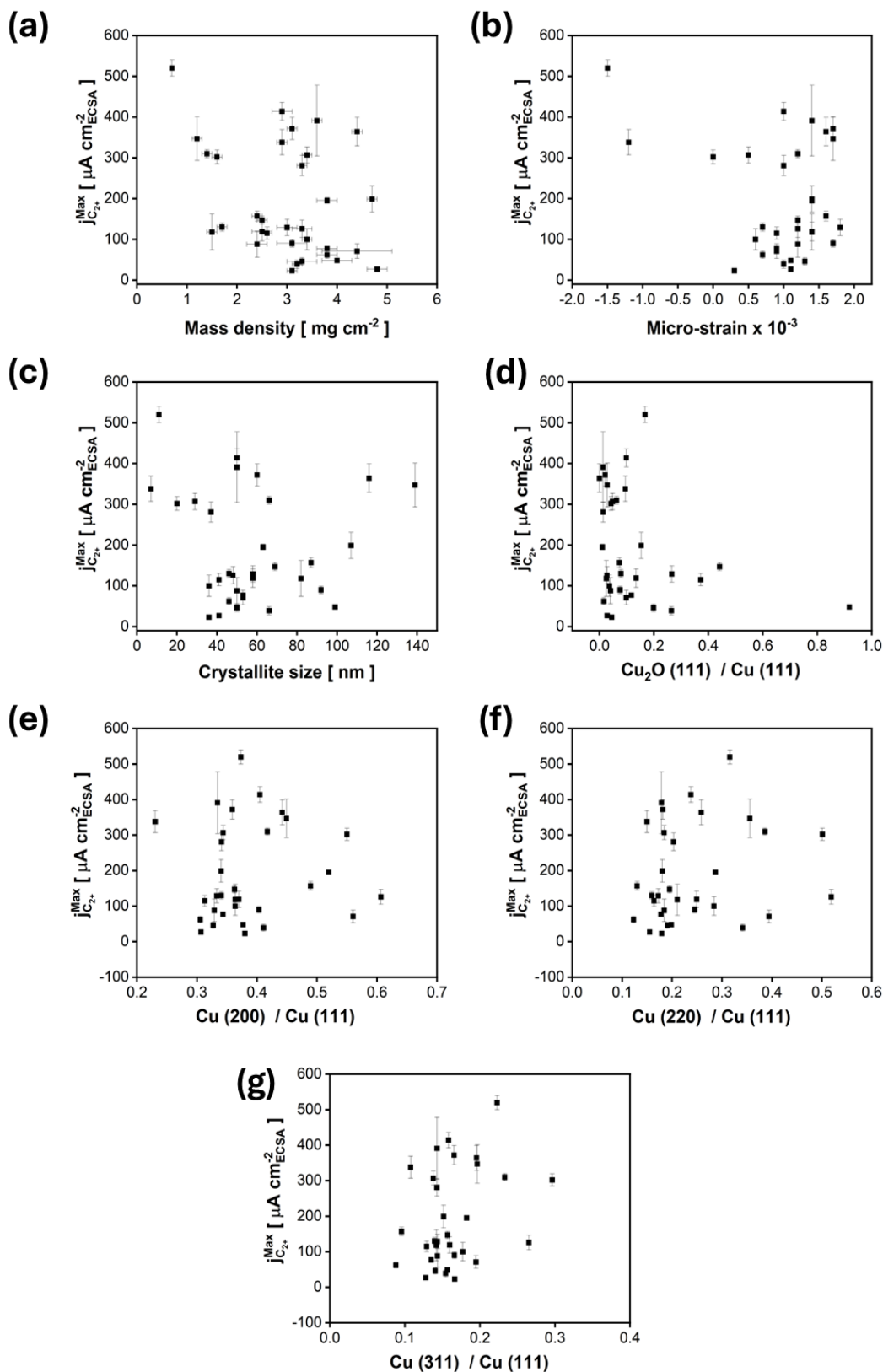


Figure 110: Relationships between mass density (a), micro-strain (b), crystallite size (c), XRD reflection ratios of Cu₂O(111)/Cu(111) (d), Cu(200)/Cu(111) (e), Cu(220)/Cu (111), and Cu(311)/Cu(111), each as the independent variable, and C₂₊ activity expressed as the highest total C₂₊ product ECSA-normalized partial current densities, as the dependent variable

3.7 DHBT-Derived Cu Foam Gas Diffusion Electrodes for CO₂ Reduction

To demonstrate the practicality and simplicity of the DHBT method for producing electrodes compatible with industrially relevant setups, a concise three-step protocol was developed to prepare Cu foam GDEs for CO₂RR (Figure 19). This protocol was inspired by a previously reported procedure for the fabrication of Ag foam GDEs.^[82] Initially, 3 × 4 cm PTFE/PP bilayer fabric substrates were sputter-coated on the PTFE side with a 480 nm Ag layer. The DHBT synthesis was then applied to grow porous Cu foam structures directly onto the Ag-coated substrates. Finally, ionomer infiltration was carried out to render the Cu foam GDEs hydrophobic, as detailed in Section 2.2.

Nine Cu foam GDEs were prepared to systematically probe the influence of electrodeposition parameters on the morphology and CO₂RR performance of the Cu foams at the GDE level. First, to compare the DC and PC DHBT modes, two electrodes were deposited at a cathodic charge density of 30 C cm⁻², one using the DC mode and the other using the PC counterpart. These two samples were denoted as DC_{30 C cm⁻²} and PC_{30 C cm⁻²}. Second, to evaluate the influence of charge density, two more PC samples were produced at charge densities of 60 C cm⁻² and 90 C cm⁻², labeled as PC_{60 C cm⁻²} and PC_{90 C cm⁻²}. Third, the effect of additives was examined by adding either 4 mM DAT or Ag₂SO₄ at concentrations of 1, 2, and 4 mM (equivalent to Ag⁺ concentrations of 2, 4, and 8 mM). These additive-modified GDEs were referred to as PC_{30 C cm⁻²}^{DAT}, PC_{30 C cm⁻²}^{2 mM Ag⁺}, PC_{30 C cm⁻²}^{4 mM Ag⁺}, and PC_{30 C cm⁻²}^{8 mM Ag⁺}. Lastly, to assess the effect of lowering the DHBT bath temperature, a GDE was synthesized under the PC mode at a cathodic charge density of 30 C cm⁻² using an ice bath adjusted to 4 °C. This sample was abbreviated as PC_{30 C cm⁻²}^{4 °C}. The synthesis of bimetallic Ag-Cu foam GDEs was inspired by previous studies showing that trace concentrations of Ag⁺ (≈4 mM) produced a marked enhancement of C₂₊ activity.^[109] Conversely, higher Ag⁺ concentrations (≈10-50 mM) favored CO production and rendered Ag-Cu foams more cost-effective than pure Ag foams while maintaining high CO activity.^[95] Because the primary aim of this work is to improve C₂₊ activity, we investigated trace Ag⁺ concentrations between 2 and 8 mM.

Figure 111 shows the EDX cross-sectional mapping of a Cu foam GDE produced by the protocol developed in this work before ionomer infiltration. The map reveals a layered structure composed of the Cu foam layer (top), sputtered Ag inter-layer (middle), and PTFE substrate (bottom), with PTFE identified by the fluorine signal. The successful conversion of DHBT-derived Cu foams into GDEs, together with the reproducible formation of Cu foams on Ag-sputtered PTFE, reflects the versatility and scalability of DHBT. Importantly, the DHBT approach is effective on both planar and porous supports, which is advantageous for energy storage and conversion devices. In the obtained GDE architecture, the Cu foam served as the CL, while the PTFE and PP fabric layers acted as the micro- and macro-porous diffusion layers, respectively.

The hydrophobicity of the Cu foam GDEs after ionomer infiltration was evaluated by contact angle measurements. Figure 112 provides representative contact angle images of the DC_{30 C cm⁻²} sample before and after ionomer treatment. Prior to infiltration, the sample exhibited complete wettability, with water droplets being absorbed immediately by the Cu foam. After ionomer application and complete dryness, the sample showed a distinctly stable hydrophobic response, with a contact angle of approximately 120°, confirming the GDE suitability for operation in a CO₂RR flow-cell configuration.

Figure 113 presents top-view SEM images of the samples DC_{30 C cm⁻²}, PC_{30 C cm⁻²}, PC_{30 C cm⁻²}^{DAT}, PC_{30 C cm⁻²}^{4 °C}, and PC_{30 C cm⁻²}^{2 mM Ag⁺}. Among them, only the DC_{30 C cm⁻²} GDE exhibited a continuous, interconnected foam network. By contrast, the PC_{30 C cm⁻²} and PC_{30 C cm⁻²}^{DAT} samples consisted of

isolated foam islands. Adding DAT to the DHBT bath led to noticeably smaller pores within these foam islands. Lowering the DHBT bath temperature to 4 °C inhibited foam formation, producing Cu agglomerates with dominant micro-to-nano porosity instead for the sample $PC_{30}^{4\text{ }^{\circ}\text{C}}_{\text{cm}^{-2}}$. Introducing 2 mM Ag^+ resulted in a less uniform foam skeleton with enhanced macro-porosity for the sample $PC_{30}^{2\text{ mM Ag}^+}_{\text{cm}^{-2}}$.

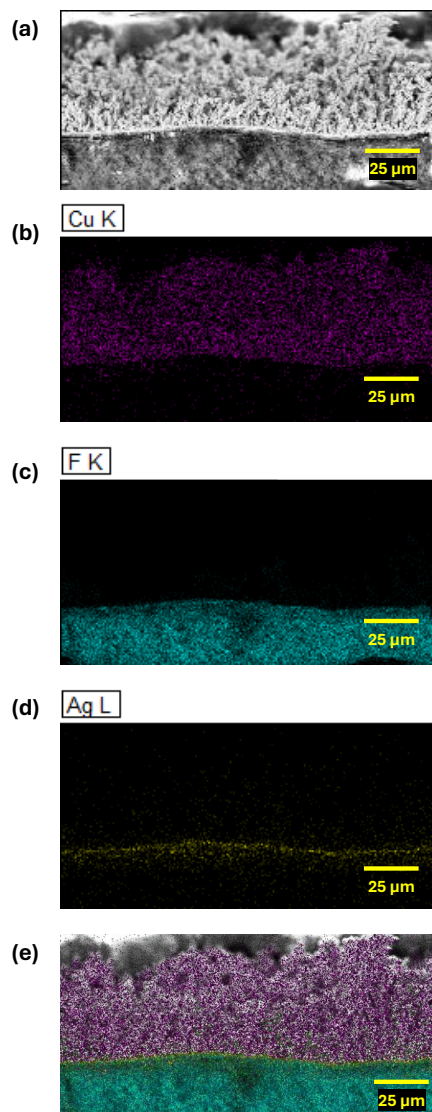


Figure 111: Cross-sectional EDX elemental mapping of a Cu foam GDE, showing the distribution of Cu (catalytic layer), Ag (sputtered conductive inter-layer), and F from the PTFE fabric substrate

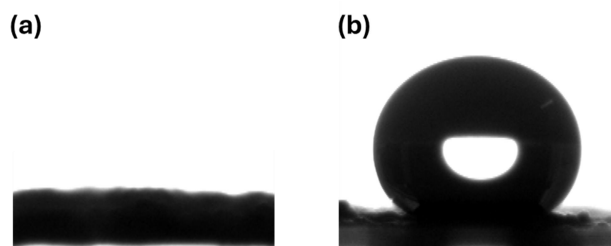


Figure 112: Contact angle images of the $\text{DC}_{30}\text{C}_{\text{cm}-2}$ sample before (a) and after (b) ionomer infiltration

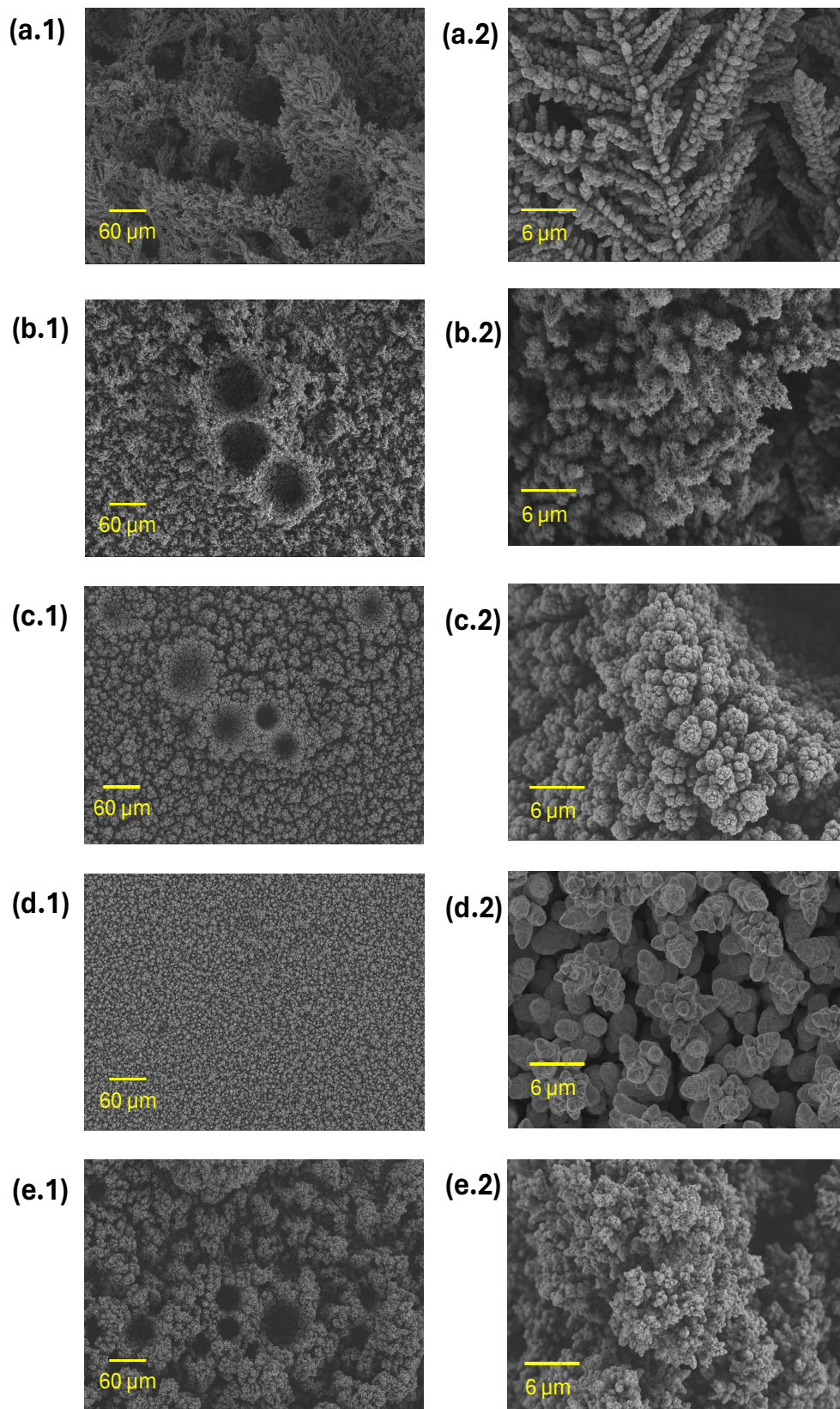


Figure 113: Top-view SEM images of Cu foam GDEs, showing the foam structure at 200x magnification (first column) and surface nano-structures at 3000x magnification (second column) for the samples: DC_{30C cm⁻²} (a), PC_{30C cm⁻²} (b), PC_{30C DAT cm⁻²} (c), PC_{30C 4°C cm⁻²} (d), and PC_{30C 2mM Ag⁺ cm⁻²} (e)

At higher magnification, the $\text{DC}_{30\text{C cm}^{-2}}$ sample showed surface nano-dendrites, consistent with the model DC Cu foams. The $\text{PC}_{30\text{C cm}^{-2}}$ GDE displayed cactus-like nano-structures, which differ from the nano-cauliflower morphology observed for the model PC electrodes. This difference is likely due to the change of the DHBT substrate from a planar Cu foil to a porous Ag-sputtered PTFE fabric. The $\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$ sample exhibited surface nano-cauliflowers similar to those observed from the model DAT-mediated Cu foam ($\text{DAT}_{4\text{mM}}$). Surface nano-features for $\text{PC}_{30\text{C cm}^{-2}}^{4^\circ\text{C}}$ and $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$ can be described as fine conical nano-structures and extremely small nano-dendrites, correspondingly.

Top-view EDX elemental maps for the Ag-Cu GDEs (after ionomer infiltration) are shown in Figure 114, with the respective quantitative compositions in Table 7-9. EDX maps reveal that Ag was uniformly distributed across all the Ag-Cu GDE surfaces, with the darker regions in the Ag maps indicating recessed porous regions, as can be seen by the comparison of the Ag maps with the corresponding SEM images. Low oxygen content was detected and attributed to the atmospheric oxidation of Cu. Additionally, very weak F and C signals were also observed and attributed to the PFSA ionomer used for the hydrophobic treatment of the GDEs.

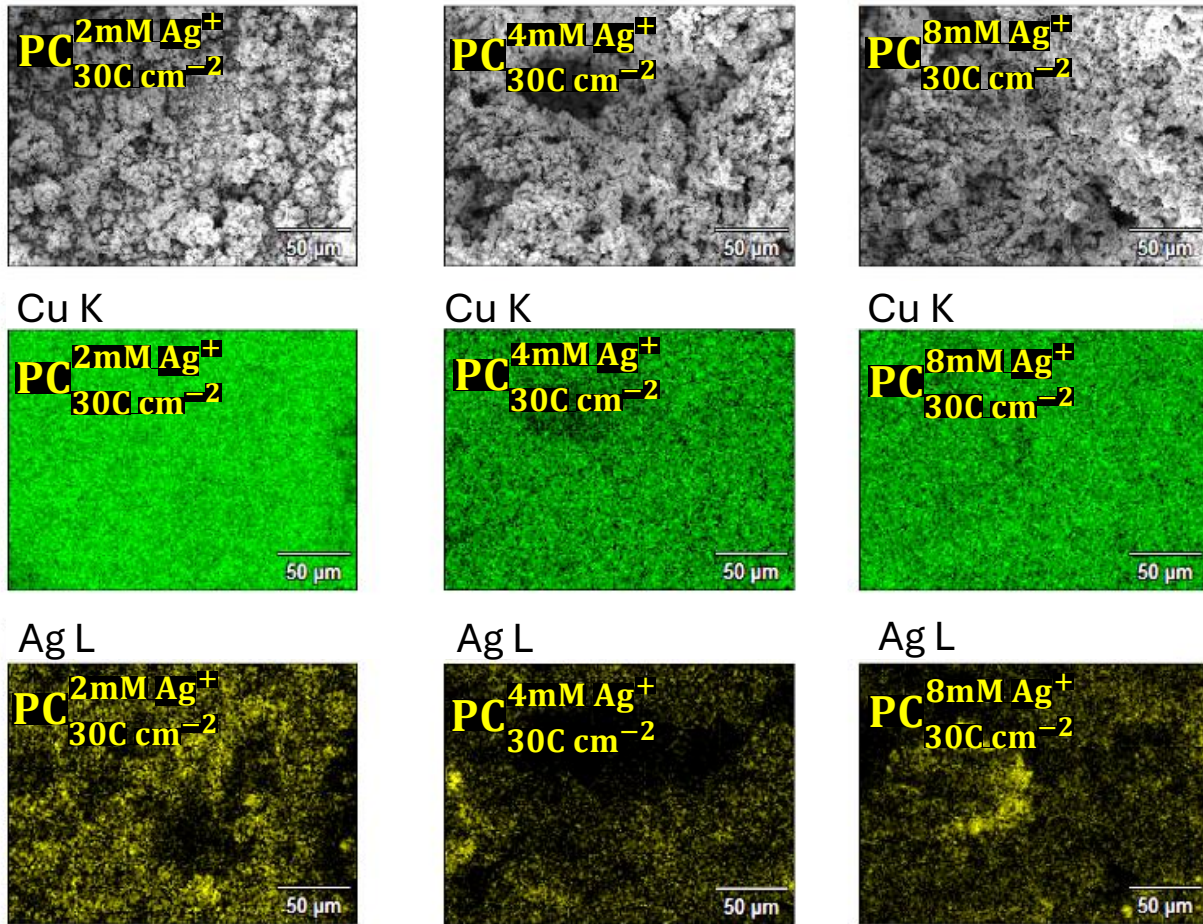


Figure 114: EDX elemental mapping of the samples: $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$ (first column), $\text{PC}_{30\text{C cm}^{-2}}^{4\text{mM Ag}^+}$ (second column), and $\text{PC}_{30\text{C cm}^{-2}}^{8\text{mM Ag}^+}$ (third column)

Quantitative EDX analysis provides atomic Cu/Ag ratios of 65.6, 37.9, and 18.3 for $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$,

$\text{PC}_{30\text{C cm}^{-2}}^{4\text{mM Ag}^+}$, and $\text{PC}_{30\text{C cm}^{-2}}^{8\text{mM Ag}^+}$, respectively. These measured values contrast with the theoretical Cu/Ag ratios of 100, 50, and 25 calculated from the respective DHBT bath composition for each sample (refer to Section 2.2). Such deviations are commonly observed in Ag-Cu co-electrodeposition and are attributed to the more favorable electrochemical reduction of Ag^+ compared with Cu^{2+} , where Ag has a more positive standard reduction potential and typically electrodeposits at lower overpotentials than Cu, promoting preferential Ag incorporation under identical deposition conditions.^[151,152] Importantly, the successful fabrication of Cu-Ag foam GDEs via DHBT confirms that the DHBT approach can be extended to multi-metallic foam synthesis on gas diffusion porous substrates, not only on planar model electrodes^[95], which is important for more industrially relevant applications.^[82]

Table 7: Weight and atomic percent extracted from the EDX spectrum of the Cu foam GDE electrodeposited in the presence of 2 mM Ag^+

Element	Net Counts	Weight %	Atom %
C K	9471	0.5	2.6
O K	21032	0.8	2.9
F K	13943	0.3	1.1
Cu K	762385	95.8	91.9
Ag L	84352	2.5	1.4

Table 8: Weight and atomic percent extracted from the EDX spectrum of the Cu foam GDE electrodeposited in the presence of 4 mM Ag^+

Element	Net Counts	Weight %	Atom %
O K	165395	6.2	20.9
F K	18488	0.5	1.5
Cu K	685561	89.4	75.7
Ag L	127021	3.9	2.0

Table 9: Weight and atomic percent extracted from the EDX spectrum of the Cu foam GDE electrodeposited in the presence of 8 mM Ag^+

Element	Net Counts	Weight %	Atom %
O K	113634	9.7	30.0
F K	14283	1.0	2.7
Cu K	291478	81.8	63.9
Ag L	114747	7.5	3.5

ECSA results of the Cu foam GDEs are presented in Figure 115. It is important to report that the GDE results represent the initial successful conversion and measurement of the model Cu foams into GDEs after a long series of optimization steps. Consequently, some of the ECSA results were not repeated sufficiently for robust statistics, as mentioned in Section 2.6. As expected, increasing the DHBT charge density increased the ECSA, with values of 91, 196, and 318 $\text{cm}_{\text{ECSA}}^2 \text{cm}_{\text{geo}}^{-2}$ for DHBT charge densities of 30, 60, and 90 C cm^{-2} , respectively. Consistent with the model electrode results, the DC-DHBT produced larger ECSA values than the PC-DHBT. Specifically, the $\text{DC}_{30\text{C cm}^{-2}}$

sample showed an ECSA of $147 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ compared with $91 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$ for the $\text{PC}_{30} \text{ C cm}^{-2}$ counterpart. The DAT-modified GDE exhibited a markedly lower ECSA ($57 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$) than the other GDEs. Despite the dominant micro-to-nano porosity of the $\text{PC}_{30}^{\text{4}^\circ\text{C}} \text{ cm}^{-2}$ sample, it showed an ECSA of $89 \text{ cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$, which is comparable to that of the reference $\text{PC}_{30} \text{ C cm}^{-2}$ sample. This unexpected similarity may reflect inaccuracies in the obtained ECSA for $\text{PC}_{30}^{\text{4}^\circ\text{C}} \text{ cm}^{-2}$ GDE due to insufficient statistical repetition. The Ag-Cu GDEs displayed higher ECSA values (120-189 $\text{cm}_{\text{ECSA}}^2 \text{ cm}_{\text{geo}}^{-2}$) than the reference GDE, consistent with the increased total metal concentration in the DHBT baths of the Ag-Cu samples.

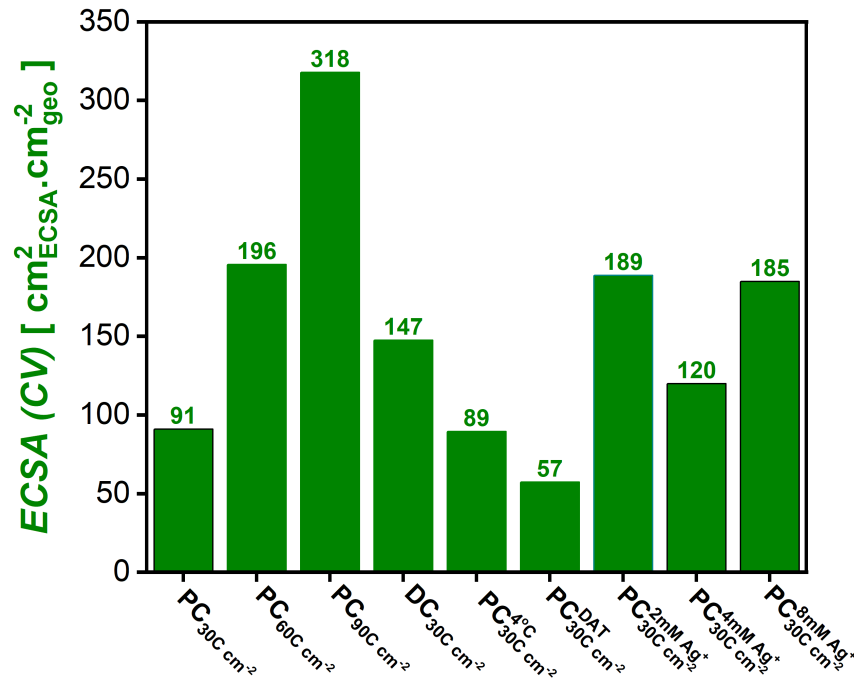


Figure 115: CV-based electrochemically active surface area values of the Cu foam GDE samples

CO_2RR activity of the Cu foam GDEs was tested in a flow cell setup, comprising cathode and anode compartments separated by a Selemion AEM. The cathode compartment consisted of separate electrolyte and gas chambers, between which the GDE was sandwiched, with the CL facing the electrolyte and the macro-porous PP layer facing the CO_2 -purged gas chamber. The outlet gas stream was switched via a three-port valve to an online GC (every 15 minutes) or a bubble flow meter to monitor the actual flow rate between injections, which was found to be crucial for the accurate estimation of CO_2RR FEs. Chronopotentiometric CO_2RR experiments were performed at current densities of 50, 100, 150, and 200 mA cm^{-2} for 1.5 hours each. Flow cell design, chromatographic analysis, and CO_2RR calculations are described in Section 2.4.2. Representative FE results of the gas products detected over the 1.5-hour interval of the chronopotentiometric run are displayed in Figure 116, where FEs rose progressively and approached a quasi steady-state after about 1.25 hours for most electrodes.

Figure 117 shows the FEs of CO_2RR products at 1.5 hours of electrolysis, at the specified applied current densities, together with the mean potential recorded during each chronopotentiometric run. The major CO_2RR products detected were CO, formate, ethylene, ethanol, propionaldehyde, 1-propanol, and the parasitic H_2 . The comparison between the GDEs prepared at different DHBT charges ($\text{PC}_{30} \text{ cm}^{-2}$, $\text{PC}_{60} \text{ cm}^{-2}$, $\text{PC}_{90} \text{ cm}^{-2}$) reveals that lower DHBT charges are more beneficial

for CO₂RR performance. The performance of the PC_{60C cm⁻²} and PC_{90C cm⁻²} samples was largely dominated by H₂ evolution (H₂ FEs: 73-90%), while the PC_{30C cm⁻²} sample exhibited better CO₂RR activity, with H₂ FEs not exceeding 62%. The DC-derived GDE displayed poorer CO₂RR activity than the PC_{30C cm⁻²} counterpart, with maximum H₂ FEs of 70% and 62% at 100 mA cm⁻² for both samples, respectively. For the PC_{30C cm⁻²} GDE, CO and formate FEs declined correspondingly from 11% and 24% at 50 mA cm⁻² to 5% and 5% at 200 mA cm⁻². The DC_{30C cm⁻²} sample showed a comparable trend (CO: 11% → 5%; formate: 25% → 4%) over the same current range. By contrast, ethylene and ethanol FEs were negligible at 50 mA cm⁻² and increased gradually with the elevation of the applied current density, reaching corresponding maxima of 21% and 11% for PC_{30C cm⁻²} and 14% and 6% for the DC counterpart at 200 mA cm⁻².

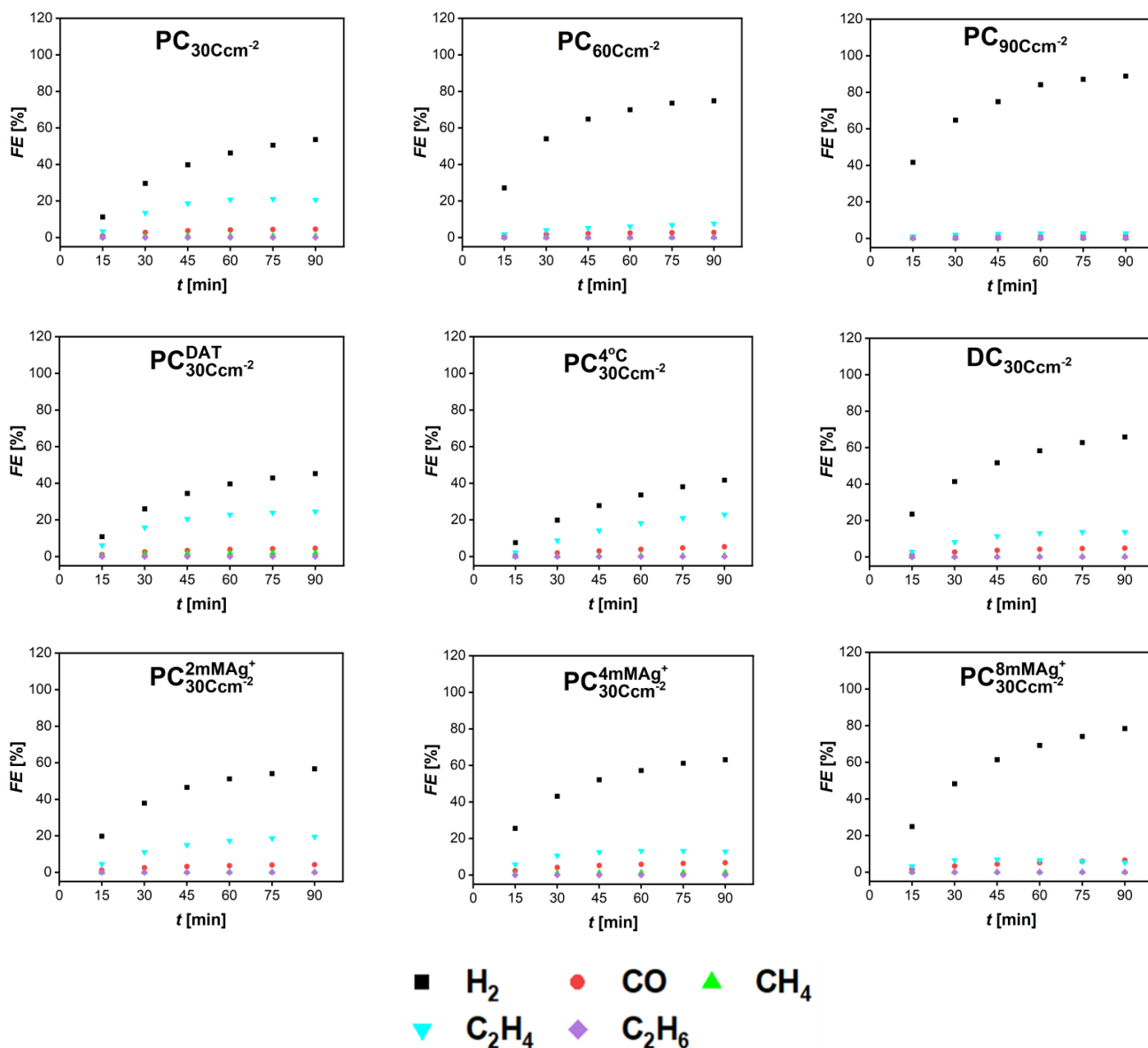


Figure 116: Faradaic efficiencies of CO₂RR gaseous products obtained from the Cu foam GDEs, measured every 15 minutes during chronopotentiometric runs at 200 mA cm⁻² for 1.5 hours

The addition of 2 mM Ag^+ to the DHBT bath enhanced the CO_2RR activity of the resulting GDEs, whereas higher Ag^+ levels (4 and 8 mM) reduced activity. At 100 mA cm^{-2} , H_2 FEs were 62%, 56%, 60%, and 77% for Ag^+ concentrations of 0, 2, 4, and 8 mM, respectively. At 150 mA cm^{-2} , ethylene FEs were 16%, 21%, 12%, and 4%; ethanol FEs were 4%, 10%, 6%, and 1% for the same four Ag^+ concentrations, correspondingly. C_1 products detected from the Ag-modified GDEs followed the Ag-free reference ($\text{PC}_{30\text{C cm}^{-2}}$) pattern, exhibiting maximum FEs at 50 mA cm^{-2} and becoming negligible at 200 mA cm^{-2} . For instance, CO and formate FEs for the $\text{PC}_{30\text{C cm}^{-2}}^{4\text{mM Ag}^+}$ GDE were 26% and 21% at 50 mA cm^{-2} , dropping to corresponding values of 7% and 2% at 200 mA cm^{-2} . Among Ag-modified samples, the $\text{PC}_{30\text{C cm}^{-2}}^{8\text{mM Ag}^+}$ GDE exhibited the largest CO FE (34% at 50 mA cm^{-2}), while $\text{PC}_{30\text{C cm}^{-2}}^{4\text{mM Ag}^+}$ showed the highest formate FE (21% at 50 mA cm^{-2}).

The $\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$ and $\text{PC}_{30\text{C cm}^{-2}}^{4^\circ\text{C}}$ samples showed the best overall CO_2RR performance, with reduced parasitic H_2 FEs of 37% and 41% at 100 mA cm^{-2} , and improved C_{2+} activity. The two samples ($\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$ and $\text{PC}_{30\text{C cm}^{-2}}^{4^\circ\text{C}}$) exhibited respective ethylene FEs of 31% and 26%, at 150 mA cm^{-2} , and ethanol FEs of 17% and 14%, at 200 mA cm^{-2} . Moreover, propionaldehyde FEs of 22% (at 50 mA cm^{-2}) for $\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$ and 9% (at 200 mA cm^{-2}) for $\text{PC}_{30\text{C cm}^{-2}}^{4^\circ\text{C}}$ were observed.

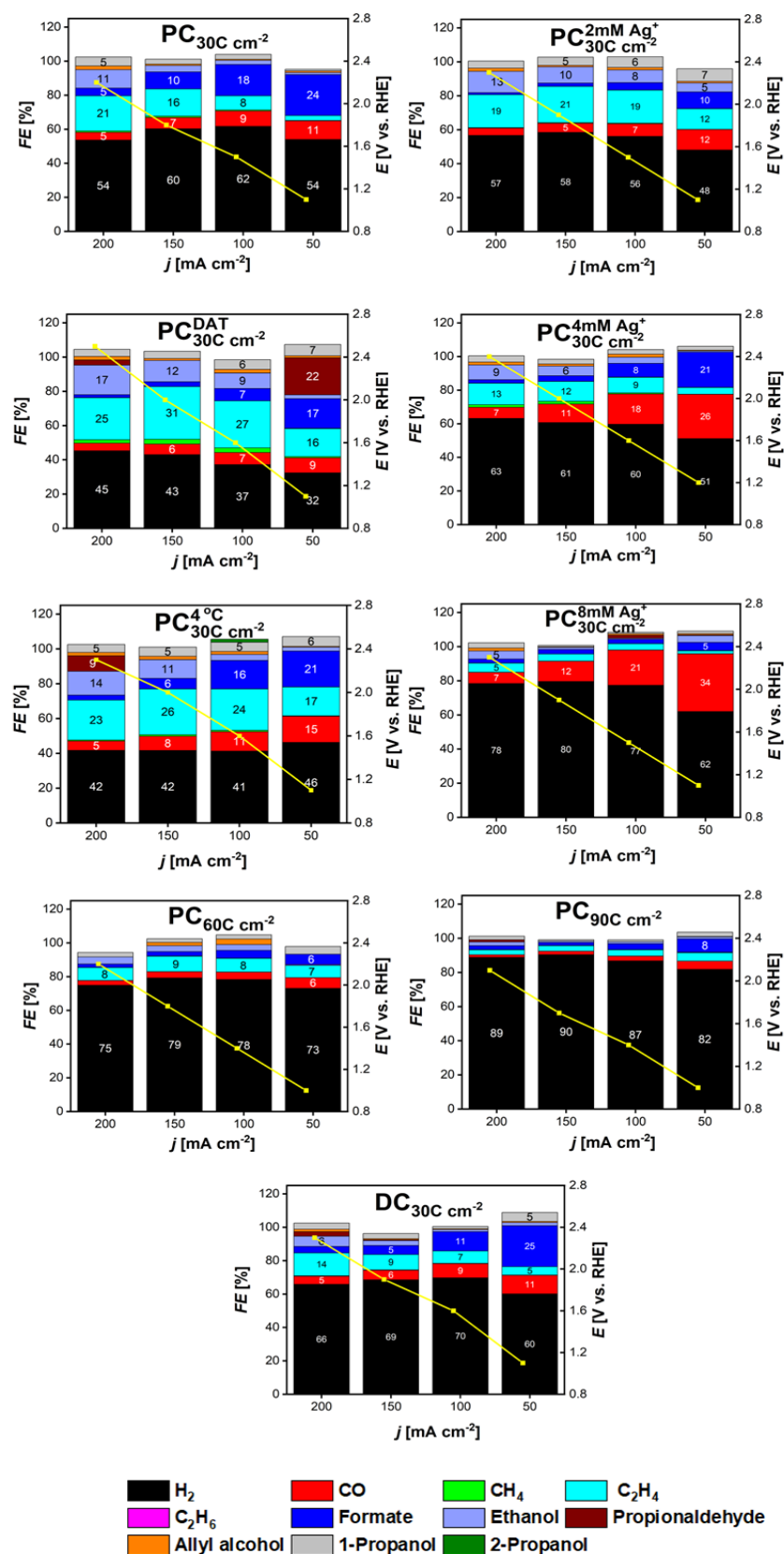


Figure 117: Faradaic efficiencies of CO₂RR products at 1.5 hours of electrolysis for the Cu foam GDEs investigated in this work, showing the average potential recorded at each applied current density

Figure 118 compares the total C_{2+} products and ethylene activity for the nine GDEs. The $PC_{30C\text{cm}^{-2}}^{2mM\text{Ag}^+}$, $PC_{30C\text{cm}^{-2}}^{\text{DAT}}$, and $PC_{30C\text{cm}^{-2}}^{4^\circ\text{C}}$ electrodes achieved the highest C_{2+} activity, with respective total FEs of 38%, 51%, and 52% at 200 mA cm^{-2} ($\approx 2.4\text{ V}$), corresponding to C_{2+} product j_{geo} of 76, 102, and 104 mA cm^{-2} . These three samples also delivered superior ethylene production at 150 mA cm^{-2} ($\approx 2.0\text{ V}$) with FEs of 21%, 31%, and 26% and partial current densities of 32, 47, and 39 mA cm^{-2} , respectively.

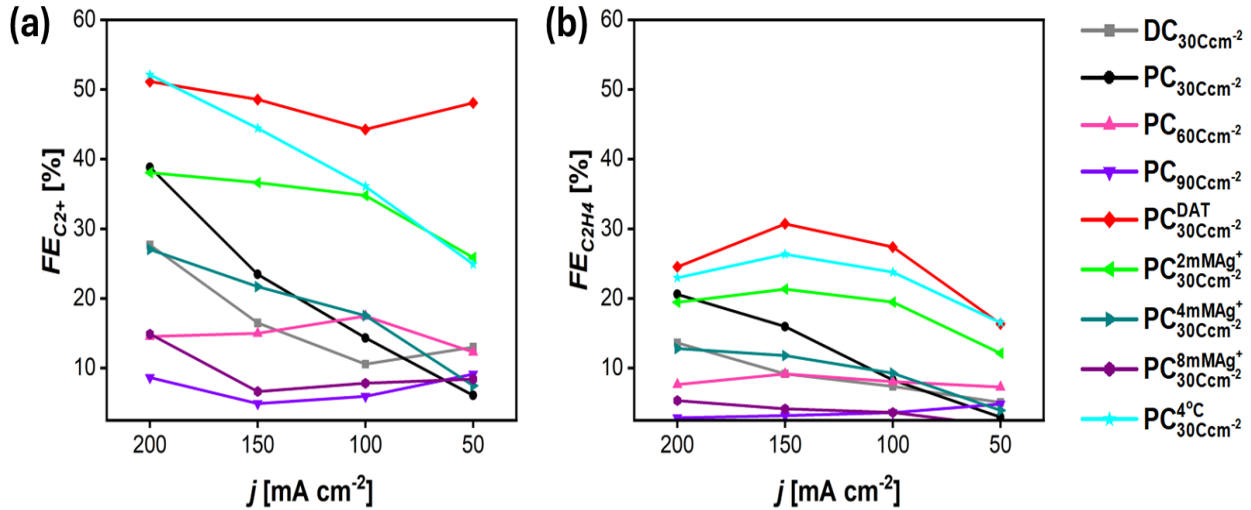


Figure 118: Total C_{2+} products (a) and ethylene (b) Faradaic efficiencies measured at 1.5 hours of electrolysis for the Cu foam GDEs

The Cu foam GDE findings indicate again that the micro-to-nano porosity, which dominates the PC samples, offers better C_{2+} product selectivity than macro-porosity, which dominates the DC samples. Earlier studies showed that PC-derived Ag foams were more active for CO_2 electrochemical reduction into CO than DC-derived counterparts deposited at the same charge densities.^[82] Thus, it is repeatedly and consistently plausible that highly macro-porous and thicker foam structures (e.g., DC, $PC_{60C\text{cm}^{-2}}$, and $PC_{90C\text{cm}^{-2}}$) suffer strong internal mass-transport limitations. At high current densities, the effective CO_2 concentration inside deep or tortuous pores drops, shifting the reaction toward the readily available water reduction in the CO_2 -depleted regions.^[125] This hypothesis not only explains the excellent performance of the PC GDE synthesized at 4°C , but also supports the argument that CO_2RR at GDEs can proceed via a two-phase boundary between the electrolyte (where CO_2 is dissolved) and the CL, rather than a pure three-phase boundary involving gaseous CO_2 , liquid electrolyte, and the catalyst layer, in particular for the flow-by electrolysis mode applied here.^[153]

The diffusion limitations of CO_2 associated with Cu foam GDEs are schematically represented in Figure 119. CO_2 molecules travel through the GDE micro-porous layer to the pore surface; here, it is the pore throat in contact with the micro-porous layer, and then they diffuse inside the pore, creating a concentration gradient along the pore axis. These effects produce internal regions that become progressively depleted of CO_2 , altering the local reaction environment and favoring HER that is more readily available. The extent of depletion and the severity of mass-transport limitations depend strongly on the Cu foam GDE architecture. More open foam GDEs, with larger, more widely spaced pores and greater exposed surface areas, tend to exhibit larger depletion zones because mass transport into deep pore regions is limited, and diffusive replenishment is relatively slow. By

contrast, more compact Cu foam GDE structures provide shorter effective diffusion paths and a more confined pore structure, which can mitigate local CO_2 depletion and help maintain higher reactant availability at active sites.

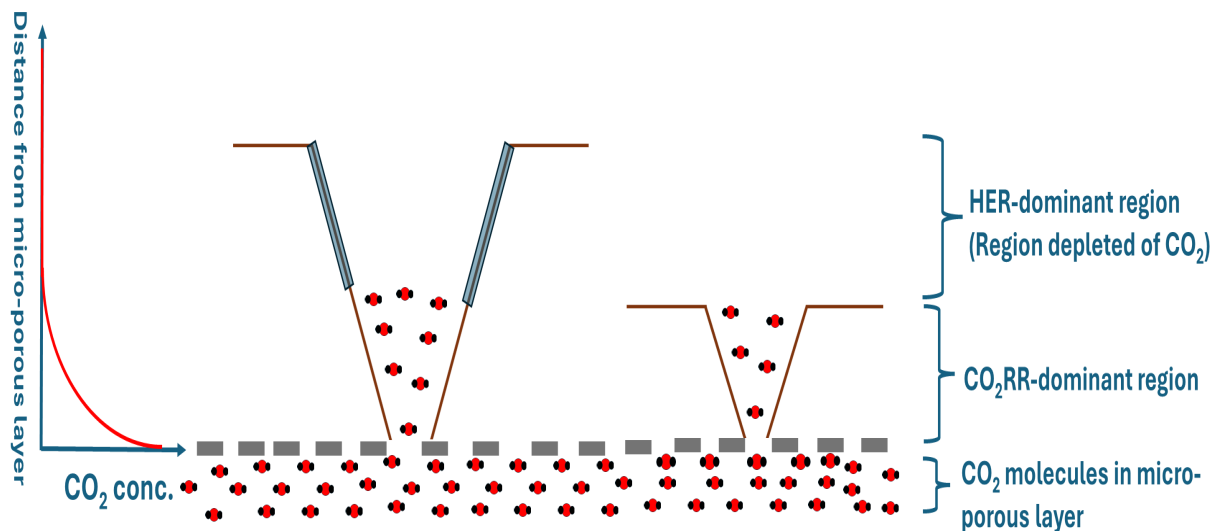


Figure 119: Schematic representation of CO_2 diffusion processes associated with Cu foam GDEs through the GDE micro-porous layer into the pore throat, and then along the pore axis, with the pore geometry represented as a V-shaped morphology

The enhanced C_{2+} performance of the $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$ and $\text{PC}_{30\text{C cm}^{-2}}^{\text{DAT}}$ samples can be attributed to chemical contributions. On the one hand, amino-based surface species, as indicated by XPS and operando SERS results of the DAT-modified model samples, were found to stabilize the $^*\text{CO}$ intermediate on the electrode surface, increase local alkalization, and facilitate the C-C coupling, as detailed earlier. On the other hand, Ag has a high selectivity for reducing CO_2 to CO because it binds CO weakly, favoring CO desorption over further reduction. This creates a high local concentration of $^*\text{CO}$ intermediates at the catalyst surface, which spill over to adjacent Cu sites, where Cu moderates $^*\text{CO}$ binding strength, enabling $^*\text{CO}$ dimerization, which is typically the rate-determining step for C_{2+} product pathways. At optimal Cu/Ag ratios, bimetallic interfacial sites are abundant, enabling effective Cu-Ag synergistic performance. Increasing the Ag content above the optimal ratio dilutes Cu active sites, reduces the number of effective Cu-Ag interfaces, and weakens $^*\text{CO}$ binding on the Cu surface through ligand effects, thereby making C-C dimerization less favorable.^[154] Accordingly, among the Cu/Ag ratios studied here, the ratio of 65.6 observed for the $\text{PC}_{30\text{C cm}^{-2}}^{2\text{mM Ag}^+}$ sample is suggested to be the most favorable for the synergistic interaction between Cu and Ag active sites, and deviations above this ratio lead to reduced C_{2+} activity.

The role of Ag at optimal Cu:Ag ratios in enhancing the C_{2+} activity of Cu foams is schematically illustrated in Figure 120. The diagram shows the sequence of elementary processes that produce the observed promotion in C_{2+} product formation: (1) diffusion of CO_2 to the catalyst surface, (2) efficient formation and release of $^*\text{CO}$ at Ag active sites, (3) spillover of $^*\text{CO}$ from Ag onto adjacent Cu active sites, (4) efficient C-C coupling on Cu, and (5) desorption of C_{2+} products, represented here by ethylene. Clearly, the effectiveness of this synergistic pathway between Ag and Cu depends critically on the spatial separation and relative abundance of their sites. At optimal Cu:Ag ratios, Ag provides a high local flux of $^*\text{CO}$ that can readily migrate to neighboring Cu sites, thereby increasing the probability of $^*\text{CO}$ - $^*\text{CO}$ dimerization and stabilizing transition states for C_{2+} product

formation. Conversely, when the Ag content becomes excessive, the cooperative mechanism breaks down, as $^*\text{CO}$ can be formed and released independently at Ag-rich regions, reducing the fraction of $^*\text{CO}$ that spills over to Cu and diminishing the population of adjacent Cu active sites required for effective dimerization. This results in a decline in C_{2+} activity, consistent with the reduced C_{2+} performance observed experimentally at elevated Ag^+ concentrations of 4 and 8 mM.

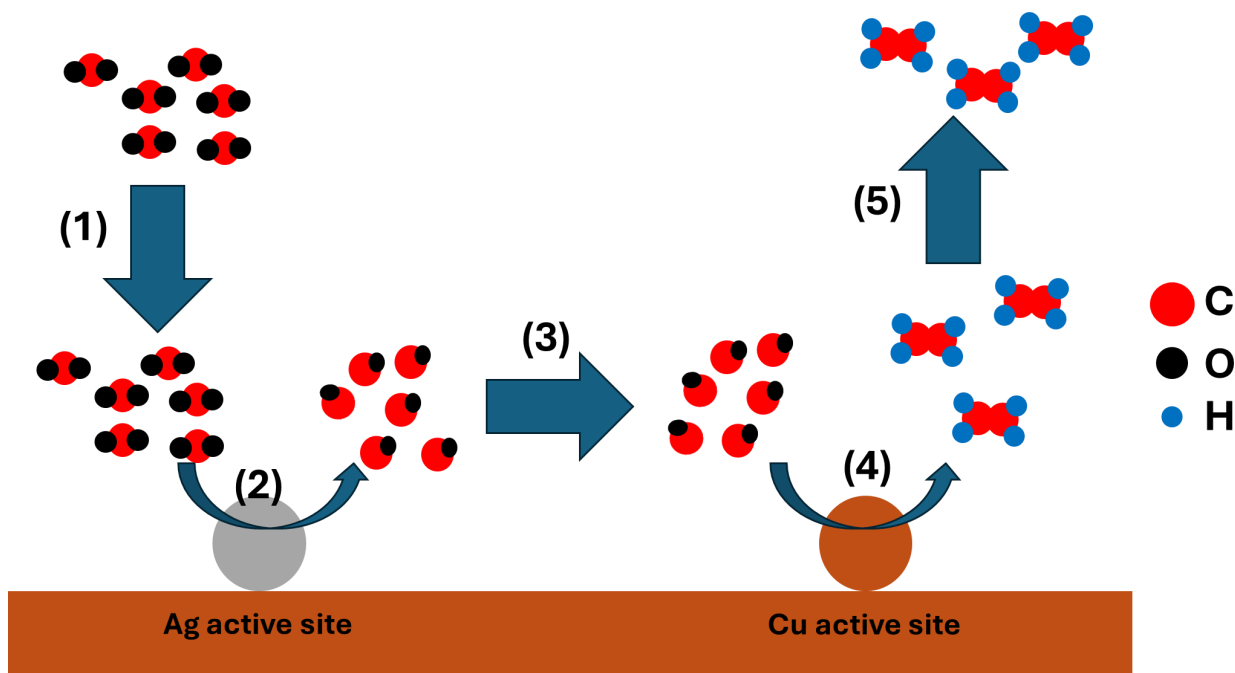


Figure 120: Schematic illustration of the synergistic effect between adjacent Ag-Cu active sites that enhances C_{2+} formation: (1) CO_2 adsorption; (2) CO_2 conversion to $^*\text{CO}$ on Ag; (3) $^*\text{CO}$ spillover to Cu; (4) C-C coupling on Cu; and (5) desorption of C_{2+} products (represented by ethylene)

To assess the operational stability of the GDEs produced by the described protocol, a DAT-modified GDE was prepared and treated with 15 μL of ionomer solution for each geometric 1 cm^2 of the GDE surface. The performance of this GDE was monitored during a 12-hour chronopotentiometric experiment at 150 mA cm^{-2} , with the gaseous CO_2RR products analyzed every 15 minutes by the online GC, as shown in Figure 121. Evidently, the recorded potential remained nearly constant at approximately -1.5 V for the 12-hour duration. Ethylene FE increased gradually to reach a plateau at about 39% after 2.5 hours and remained almost stable, decreasing only to 37% after 12 hours. CO FE reached a plateau near 9% after 1.25 hours and remained constant thereafter. Methane showed a maximum FE of 8.5% at 1.25 hours, which declined gradually to approximately 4% after 12 hours.

Superior C_{2+} product performance for Cu-based GDEs was reported in the literature compared with the GDE results obtained in this study. For example, an ethylene FE of 87% was reported at -0.47 V for Cu GDEs doped with poly-N-(6-aminohexyl)acrylamide; however, the ethylene activity decreased rapidly after three hours of operation.^[106] Additionally, bimetallic Cu-Al GDEs identified by machine learning achieved an ethylene FE of 75% at an applied current density of 600 mA cm^{-2} with stable performance tested for 50 h.^[78] These electrodes, however, were tested in very concentrated electrolytes (e.g., 10 M KOH) and represent optimized end points after series of multiple development steps. By contrast, the Cu foam GDEs reported here represent an initial, successful conversion

of model Cu foams into GDEs and already exhibited promising activity. Several parameters that were not optimized within the time frame of this work, such as the ionomer type and loading, pore dimensions of the bilayer substrate, sputtered metal type and thickness, CO₂RR electrolyte, and the cell design, are expected to substantially enhance the performance of the Cu foam GDEs upon systematic optimization.

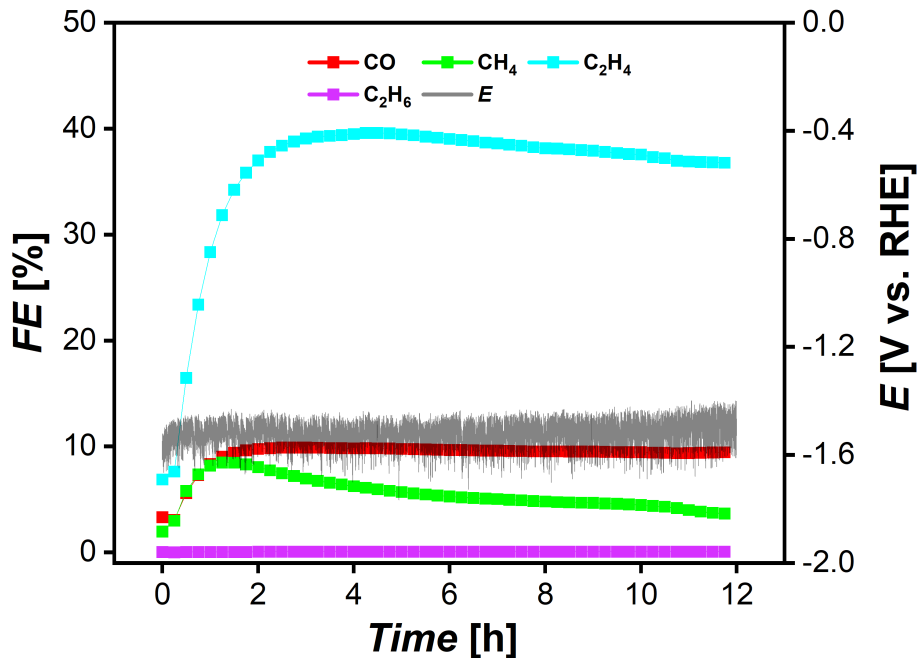


Figure 121: Faradaic efficiencies of CO₂RR gaseous products of the DAT-modified GDE, and the measured potential, recorded for 12 hours at an applied current density of 200 mA cm⁻²

In summary, a three-step protocol for the DHBT synthesis of pure Cu and bimetallic Ag-Cu foam GDEs was developed. The resulting GDEs exhibited high hydrophobicity after ionic infiltration and stable CO₂RR performance tested for 12 hours. Consistent with the model Cu foam results, increasing the DHBT charge resulted in poor CO₂RR performance, and the DC-derived foams were less active toward C₂₊ products than the PC counterparts synthesized at the same charge densities. Adding Ag⁺ at a trace concentration of 2 mM, applying DAT, and lowering the DHBT bath temperature were found to be effective strategies for enhancing C₂₊ activity, yielding FE_{C₂₊} of up to $\approx 50\%$ at -1.1 V and j_{C₂₊} of up to ≈ 100 mA cm⁻² at -2.5 V.

4 Conclusions & Outlook

The aim of this study was to explore the optimum Cu foam structures for enhanced C_{2+} activity. Accordingly, the study was planned to provide a fundamental and comprehensive understanding of how tailored DHBT conditions influence the morphology and CO_2RR performance of model Cu foams, revealing practical synthesis-morphology and morphology-activity relationships. To translate these insights toward industrially relevant devices, a simple three-step protocol was developed to upscale the most promising Cu foam architectures into Cu foam GDEs.

4.1 Synthesis-Morphology Relationship

First, the influence of the most elementary DHBT parameters, current density and deposition time, was examined in a current-time series. Compact foams were obtained at higher current densities combined with shorter deposition times. These compact structures were characterized by small pore diameters, reduced foam thicknesses, high pore densities, low ECSAs, and small surface nano-dendrites. By contrast, lower DHBT current densities combined with longer deposition durations produced open foams with large pore diameters, high foam thicknesses, high ECSAs, lower pore densities, and large surface nano-dendrites. For example, the ($1Acm^{-2}$ 30s) sample exhibited a pore diameter of $36.7 \pm 0.5 \mu m$, a foam thickness of $62.0 \pm 4.7 \mu m$, a pore density of 346 pore mm^{-2} , a mass density of $4.8 \pm 0.2 \text{ mg cm}^{-2}$, and an ECSA of $179 \pm 12 \text{ cm}_{ECSA}^2 \text{ cm}_{geo}^{-2}$, whereas the ($2Acm^{-2}$ 5s) foam showed corresponding values of $9.4 \pm 0.1 \mu m$, $23.0 \pm 1.5 \mu m$, $3541 \text{ pore mm}^{-2}$, $1.2 \pm 0.1 \text{ mg cm}^{-2}$, and $41 \pm 7 \text{ cm}_{ECSA}^2 \text{ cm}_{geo}^{-2}$. These results indicate that higher current densities with shorter deposition times favor HER during DHBT in the form of numerous H_2 nucleation sites with small H_2 bubble sizes, and vice versa. This trend was confirmed by the electrodeposition FE, where the ($2Acm^{-2}$ 5s) and ($1Acm^{-2}$ 30s) samples exhibited deposition FEs of $36 \pm 4\%$ and $49 \pm 2\%$, respectively, indicating a higher HER FE for the former sample compared with the latter. Additionally, the local hydrodynamic conditions during DHBT were found to be crucial for determining the size and shape of surface nano-features. Larger H_2 bubble templates led to an intensified stirring effect, which reduced the diffusion-layer thickness and thus lowered the overpotential of Cu electrodeposition. The reduced overpotential for Cu electrodeposition resulted in larger surface nano-dendrites, whereas smaller bubble templates produced the opposite effect.

Second, since different current modes were reported in the literature for Cu electrodeposition, their effects on the DHBT synthesis of Cu foams were investigated in a current mode series. The PC mode suppressed H_2 templates evolution, yielding mass-dense Cu foams dominated by micro-to-nano porosity and reduced macro-porosity. The surface nano-features produced under the PC mode were nano-cauliflowers, in contrast to the nano-dendrites formed under the DC mode. This difference was attributed to modified diffusion layer hydrodynamics caused by the periodic interruption of the cathodic signal in the PC-DHBT. The quenching of H_2 templates by the PC mode was more remarkably pronounced at lower pulse-to-pause ratios. For example, at the same total electrodeposition charge density, the PC sample fabricated with a 1 ms pulse and a 10 ms pause ($PC_{1:10}$) showed no interconnected honeycomb-like skeleton but only micro-to-nano Cu agglomerates, a reduced thickness of $19.7 \pm 3.7 \mu m$, a higher mass density of $4.7 \pm 0.1 \text{ mg cm}^{-2}$, and a reduced ECSA of $39 \pm 2 \text{ cm}_{ECSA}^2 \text{ cm}_{geo}^{-2}$, compared with the DC reference, which exhibited an evident interconnected honeycomb-like skeleton with a pore diameter of $19.9 \pm 0.6 \mu m$, greater foam thickness of $50.6 \pm 5.3 \mu m$, lower mass density of $3.1 \pm 0.3 \text{ mg cm}^{-2}$, and larger ECSA of $127 \pm 15 \text{ cm}_{ECSA}^2 \text{ cm}_{geo}^{-2}$. Remarkably, the $PC_{1:10}$ sample displayed a higher electrodeposition FE ($72 \pm 2\%$) than the DC counterpart ($48 \pm 4\%$), demonstrating a substantially lower HER contribution during the synthesis

of the PC_{1:10} sample.

The RC-DHBT mode enabled gradual control of the Cu foam morphologies by tuning the anodic charge density per single anodic pulse (ΔC). Higher ΔC values appear to further suppress HER compared with the PC mode by interrupting the cathodic signal with short anodic pulses. At the same total electrodeposition charge density and pulse separation, the RC mode produced more compact structures than the PC mode. For example, the RC_{6mC} sample exhibited a pore diameter of $13.1 \pm 0.1 \mu\text{m}$, foam thickness of $24.8 \pm 5.3 \mu\text{m}$, pore density of 936 pore mm^{-2} , and an ECSA of $37 \pm 1 \text{ cm}^2_{\text{ECSA}} \text{ cm}_{\text{geo}}^{-2}$, whereas the PC_{20:10} reference that shared the same pulse separation showed corresponding values of $17.4 \pm 0.4 \mu\text{m}$, $46.2 \pm 5.2 \mu\text{m}$, 631 pore mm^{-2} , and $56 \pm 6 \text{ cm}^2_{\text{ECSA}} \text{ cm}_{\text{geo}}^{-2}$. The RC samples retained the nano-cauliflower surface morphology observed in the PC samples.

In the AC-DHBT, Cu foam structures were strongly affected by the portion of the applied charge consumed by capacitive processes. A higher capacitive contribution, at larger AC amplitudes or frequencies, produced more open structures, whereas a lower capacitive contribution yielded more compact morphologies. This behavior suggests that capacitive processes attenuate the applied cathodic signal, mimicking the effect of applying low current densities in DC-DHBT. For example, at the same applied frequency (0.5 Hz), the two samples produced at amplitudes of 1.2 and 2 A cm⁻², namely AC_{1.2A}^{0.5Hz} and AC_{2A}^{0.5Hz}, exhibited pore diameters of 11.3 ± 0.3 and $14.5 \pm 0.4 \mu\text{m}$ and pore densities of about 1379 and 913 pore mm⁻², respectively. The two AC samples deposited at the same amplitude (1.5 A cm⁻²) but at different frequencies (0.5 and 5000 Hz), namely AC_{1.5A}^{0.5Hz} and AC_{1.5A}^{5000Hz}, showed corresponding pore diameters of 12.1 ± 0.3 and $20.4 \pm 0.5 \mu\text{m}$ and pore densities of 1215 and 613 pore mm⁻². The AC samples displayed surface nano-dendrites, indicating that the nano-cauliflowers observed in the PC and RC modes require an abrupt interruption of the cathodic signal to form. By contrast, the smooth transition between cathodic and anodic phases in the AC mode reproduces the local hydrodynamic conditions of the DC mode and favors nano-dendrite formation.

Third, the influence of the DHBT bath composition was examined in a chemical effect series, focusing on Cu²⁺ concentration, pH, additives that affect HER (e.g., surfactants), and additives that modify Cu electrodeposition behavior (e.g., complexing agents). It was demonstrated that a relatively high Cu²⁺ concentration (0.2 M) is required to drive HER and Cu electrodeposition at comparable rates, and thereby obtain the honeycomb-like interconnected foam structures when desired. Lower Cu²⁺ concentrations reduced foam interconnectivity and overall openness. For example, the (0.05 M Cu²⁺) sample showed no interconnected network but only Cu agglomerates with dominant micro-to-nano porosity, a reduced thickness of $22.9 \pm 10.2 \mu\text{m}$, low mass density of $0.7 \pm 0.1 \text{ mg cm}^{-2}$, and ECSA of $31 \pm 3 \text{ cm}^2_{\text{ECSA}} \text{ cm}_{\text{geo}}^{-2}$, along with very small surface nano-dendrites. In comparison, the reference sample (prepared at 0.2 M Cu²⁺) exhibited an interconnected honeycomb-like structure (pore diameter = $19.9 \pm 0.6 \mu\text{m}$), a larger thickness ($50.6 \pm 5.3 \mu\text{m}$), larger mass density ($3.1 \pm 0.3 \text{ mg cm}^{-2}$), higher ECSA ($127 \pm 15 \text{ cm}^2_{\text{ECSA}} \text{ cm}_{\text{geo}}^{-2}$), and larger surface nano-dendrites. In contrast to the effect of Cu²⁺ concentration, reducing the H⁺ concentration by a factor of ten (increasing the pH from -0.5 to 0.5) preserved the honeycomb-like morphology, indicating that H₂ bubbles during DHBT can originate from both water and proton reduction. Surfactants (SDS and CTAB) increased the number of H₂ nucleation sites, and raised the FE of H₂ evolution. This effect was attributed to the reduced surface tension at the bubble/liquid interface in the presence of surfactants and was reflected in the low electrodeposition FEs obtained for SDS ($22 \pm 2\%$) and CTAB ($26 \pm 1\%$) foams, corresponding to an HER FE of roughly 75%. Consequently, surfactant-mediated samples were very compact. For instance, the SDS sample exhibited a pore diameter of $14.7 \pm 0.1 \mu\text{m}$, foam thickness of $33.3 \pm 2.6 \mu\text{m}$, pore density of $1063 \text{ pore mm}^{-2}$, ECSA of $49 \pm 11 \text{ cm}^2_{\text{ECSA}} \text{ cm}_{\text{geo}}^{-2}$, and very small surface nano-dendrites. DAT hindered Cu electrodeposition, producing compact morphologies, with

pore diameters of 13.3 ± 0.3 and 11.5 ± 0.4 μm , foam thicknesses of 17.3 ± 2.0 and 16.6 ± 4.1 μm , and reduced ECSA values of 52 ± 3 and 44 ± 5 $\text{cm}_{\text{ECSA}}^2 \text{cm}_{\text{geo}}^{-2}$ for DAT concentrations of 1.5 and 4 mM, respectively. The DAT samples exhibited cauliflower-like surface nano-structures, suggesting that DAT acts similarly to the periodic interruption of the cathodic signal (as in PC and RC modes) in modifying local deposition dynamics.

Fourth, the effect of different physical parameters was examined in a physical effect series. Stirring the DHBT bath had a modest effect on the foam skeleton but markedly increased the nano-dendrite size. This observation highlights the importance of local hydrodynamic conditions and diffusion layer thickness in determining the shape and size of surface nano-features. Specifically, stirring enhances the transport of Cu^{2+} from the bulk electrolyte to the electrode surface, reduces the diffusion layer thickness, lowers the overpotential for Cu electrodeposition, and accelerates Cu electrodeposition, resulting in large nano-dendrites. For the stirred sample, Cu^{2+} mass transport is enhanced by both the applied forced convection and generated H_2 bubbles, while for other samples, local hydrodynamics are driven only by H_2 bubble templates. Across all the Cu foam samples synthesized in this study (except for annealed samples that underwent post-synthesis morphological changes during heat treatment), pore diameter correlated with nano-dendrite size, confirming the role of local stirring in shaping the surface nano-structures. Inhibiting Cu electrodeposition either by adding DAT, or by applying either the PC or RC modes, led to distinct nano-features (nano-cauliflowers). Lowering the DHBT bath temperature increased foam compactness. For example, foams prepared at 5 °C and 60 °C exhibited pore diameters of 16.7 ± 0.4 and 50.5 ± 3.0 μm , foam thicknesses of 38.2 ± 4.1 and 69.9 ± 7.8 μm , pore densities of ≈ 911 and 54 pore mm^{-2} , mass densities of 2.6 ± 0.1 and 4.0 ± 0.3 mg cm^{-2} , and ECSA values of 68 ± 7 and 155 ± 6 $\text{cm}_{\text{ECSA}}^2 \text{cm}_{\text{geo}}^{-2}$, correspondingly. Additionally, the 5 °C sample showed very small nano-dendrites, whereas the 60 °C counterpart exhibited very large dendrites. These findings indicate that lower temperatures favor HER during DHBT in the form of numerous small H_2 nucleation sites with mild local stirring, while higher temperatures favor fewer, larger bubbles and stronger local stirring. This agrees with electrodeposition FE values which were $39 \pm 2\%$ at 5 °C and $61 \pm 4\%$ at 60 °C, indicating higher HER FEs during DHBT at lowered temperatures. Horizontal alignment of the DHBT substrate produced large H_2 bubble templates, resulting in large surface nano-dendrites and more open samples. Specifically, the horizontal sample showed a larger pore diameter of 22.4 ± 1.1 μm , higher foam thickness of 64.1 ± 8.1 μm , elevated mass density of 4.4 ± 0.7 mg cm^{-2} , and greater ECSA of 134 ± 2 $\text{cm}_{\text{ECSA}}^2 \text{cm}_{\text{geo}}^{-2}$, with respect to the reference sample. Post-DHBT annealing increased overall foam dimensions relative to the non-annealed reference, but reduced nano-dendrite size due to recrystallization. For example, $\text{An}_{30\text{min}}^{150^\circ\text{C}}$ exhibited a high pore diameter of 30.5 ± 1.0 μm , large foam thickness of 68.5 ± 3.7 μm , and reduced pore density of 253 pore mm^{-2} , compared with reference sample values of 19.9 ± 0.6 μm , 50.6 ± 5.3 μm , and 748 pore mm^{-2} .

The thorough investigation of Cu foam morphologies in this work enabled the establishment of synthesis-morphology correlations, which were translated into a practical flow chart to guide the synthesis of targeted Cu foams with specific structural descriptors (Figure 106).

4.2 Morphology-Activity Relationship

CO_2RR performance of the model Cu foam samples was determined by three main factors:

1. **Overall Cu foam skeleton:** Cu foam dimensions were a primary determinant of CO_2RR performance and C_2^+ product activity. Across the synthesized samples, more open foam structures (larger pore diameter, greater thickness, and higher ECSA) generally exhibited

poorer CO₂RR selectivity for C₂₊ products, whereas more compact samples with smaller values of these morphological descriptors showed substantially improved performance, as presented graphically in Figure 108. This trend was attributed to an additional CO₂ mass-transport limitation along the pore axis, in addition to the conventional mass-transport limitation between the bulk electrolyte and the electrode surface. In very thick and highly porous foams, CO₂ is largely depleted in the pore interior, favoring the readily available HER in the CO₂-depleted regions and reduces C₂₊ production.^[125] This hypothesis accounts for most of the observed sample-to-sample variation in CO₂RR performance:

- (a) In the current-time series, more open foams deposited at lower current densities for longer times showed lower C₂₊ activity than the more compact counterparts prepared at higher current densities for shorter times.
- (b) In the PC series, dense Cu foams obtained at low pulse-to-pause ratios (0.5 or 0.1), characterized by very small thickness and negligible macro-porosity, exhibited suppressed H₂ FEs during CO₂RR and enhanced C₂₊ selectivity. The RC samples, which were more compact than the PC reference prepared at the same pulse separation and total charge density, exhibited relatively superior C₂₊ performance. Similarly, the AC samples generally exhibited smaller foam dimensions than the DC counterpart, and thus, displayed improved C₂₊ performance.
- (c) In the chemical effect series, the addition of SDS or DAT, and lowering the Cu²⁺ concentration, reduced the produced samples openness, and enhanced their C₂₊ activity.
- (d) In the physical effect series, the sample deposited at 5 °C was the most compact and showed the best CO₂RR performance.

It is important to point out that the negative correlation between foam dimensions and CO₂RR activity is probably specific to gas-phase reactants and therefore may not extend to reactions without gaseous precursors (for example, OER and HER). Additionally, in PEM CO₂RR configurations, where diffusion limitations are relatively irrelevant, Cu foam GDEs could exhibit different activity trends, and the larger surface area might be beneficial.

2. **Surface nano-features (shape and size):** There was a negative correlation between surface nano-dendrites size and C₂₊ performance, agreeing with the literature.^[52] Although this effect is partially coupled to the effect of foam dimensions discussed above, the lower C₂₊ activity of the stirred sample, which displayed larger surface nano-dendrites but almost similar foam skeleton dimensions with respect to the reference sample, indicates that an influence of the surface nano-features on the CO₂RR activity significantly exists. In this study all samples with smaller nano-dendrites exhibited better C₂₊ performance, with the CTAB sample as the sole outlier. Additionally, samples displaying nano-cauliflower morphologies (PC, RC, and DAT-mediated samples) tended to show superior C₂₊ activity. When the nano-cauliflower morphology coincided with a high mass density, as in PC samples, an outstanding activity toward formate was observed in the potential range between -0.6 and -0.85 V. Given that the less open foams are the more active, the foam skeleton can be regarded primarily as a binder-free support for the nano-particles, and thus, careful engineering of the skeleton is required to avoid internal mass-transport limitations, allowing the genuine surface nano-particle active sites to perform its catalytic function.
3. **Chemical effects:** Ex-situ XPS and operando SERS confirmed the incorporation of DAT into the surface of the DAT-modified foams. Surface-integrated DAT species promoted the formation and stabilization of *CO intermediates, enhanced C-C coupling, and increased the

local alkalization. This led to lowering the parasitic HER FEs and improving C_{2+} products activity. DAT samples also exhibited the lowest micro-strain values (0 to -1.5×10^{-3}), reflecting compressive strain, and the smallest crystallite sizes (7-20 nm) among the studied samples, which might be correlated to their superior C_{2+} performance.

Other morphology descriptors, such as surface oxides (detected by ex-situ XPS), both Cu and Cu_2O XRD peak intensities, and mass densities did not show clear correlations with CO_2RR activity across the studied samples. The lack of correlation between C_{2+} activity and both ex-situ XPS and XRD results likely reflects catalyst reconstruction under CO_2RR conditions, which produces different Cu and Cu_xO phases that are not captured by ex-situ measurements.

4.3 Transforming Model Cu Foams into Cu Foam Gas Diffusion Electrodes

Cu foam GDEs preserved the activity trends observed for the model foams. The open DC-derived GDEs were less active than the more compact PC-derived counterparts prepared at the same electrodeposition charge density. Thicker PC GDEs obtained at high DHBT charge densities (60 and 90 C cm^{-2}) were less active than the PC GDE obtained at 30 C cm^{-2} . The $PC_{30 \text{ C cm}^{-2}}^{DAT}$ and $PC_{30 \text{ C cm}^{-2}}^{4^\circ C}$ GDEs showed the best C_{2+} activity among all tested GDEs, with total C_{2+} FEs of 51% and 52% at an applied current density of 200 mA cm^{-2} ($\approx -2.5 \text{ V}$), corresponding to total C_{2+} partial current densities of 102 and 104 mA cm^{-2} . Moreover, the DAT-modified GDE exhibited excellent operational stability tested for 12 h.

4.4 Outlook

This study identifies several promising directions for future research to advance the rational design of nano-structured Cu foams for CO_2RR . First, integrating machine learning to quantify and predict synthesis-morphology-activity relationships could provide deeper insights and accelerate the optimization of Cu foam electrodes for CO_2RR . Second, a systematic exploration of other triazole-based additives, including 3-amino-1,2,4-triazole, 5-amino-1,2,4-triazole, 1,2,4-triazole, 1,2,3-triazole, 3-amino-1,2,3-triazole, 5-amino-1,2,3-triazole, and 3,5-diamino-1,2,3-triazole, can elucidate the specific role of triazoles in enhancing C_{2+} activity and potentially further improve the C_{2+} performance. Third, the application of AC mode at frequencies exceeding 5000 Hz and the RC mode at ΔC values larger than 6 mC cm^{-2} might result in the synthesis of Cu foams with controlled Cu_xO content. Fourth, to address mass-transport limitations, numerical simulations of internal CO_2 transport along the pore axis, utilizing Fick's law and reaction kinetics within a macroscopic porous-electrode model, can confirm the experimental observations obtained in this work. Finally, further optimization of the Cu foam GDE synthesis protocol, in terms of the bilayer substrate dimensions, type and thickness of the sputtered metal, type and loading of the infiltrated ionomer, selection of model Cu foam architectures for upscaling, and exploration of multi-metallic foams, is expected to remarkably enhance the C_{2+} activity of the Cu foam GDEs.

Ultimately, this study demonstrated that the DHBT approach is a time-efficient, straightforward, and reproducible route to produce binder-free nano-structured self-supporting Cu foams with a highly controllable morphology and CO_2RR activity. These foams can be directly transformed into GDEs and readily scaled to sizes relevant for industrial applications while retaining the structural and electrochemical properties required for efficient CO_2RR performance.

5 References

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6 List of Publications

6.1 Papers

M. Attia, C. Zhao, M. Lindner, P. Hawe, and C. Roth, Engineering Hierarchically Nano-Structured Cu Foams: Dynamic Hydrogen Bubble Templated Binder-Free Freestanding Electrodes for Energy Applications. *Small*, 22, e09389; (2026).

M. Attia, Z. Zhu, H. Dau and C. Roth, Effect of 3,5-Diamino-1,2,4-triazole on the Morphology and C_{2+} Product Activity of Cu Foams Synthesized by the Dynamic Hydrogen Bubble Templating Method, in preparation (2026).

M. Attia, Z. Zhu, H. Dau and C. Roth, Effect of the Pulsating Current Mode on the Morphology and CO_2 Reduction Performance of Cu Foams Synthesized by the Dynamic Hydrogen Bubble Templating Method, in preparation (2026).

J. Zander, M. F. Fink, **M. Attia**, C. Roth, and R. Marschall, Selective optimization of catalytic activity by tuning the structural composition in nanoparticulate $CuFe_2O_4$. *Sustain. Energy Fuels*, 8, 4848–4863, (2024).

6.2 Conference contributions

M. Attia, Z. Zhu, H. Dau and C. Roth, Surfactant-Based Tailoring of Cu Foam Electrodes Performance Towards CO_2 Reduction. GDCh Electrochemistry Conference, Braunschweig, Germany, 2024, Poster.

M. Attia, Z. Zhu, H. Dau and C. Roth, Effect of Different Current Modes in Dynamic Hydrogen Bubble Templating on Cu Foams Morphology and CO_2 Reduction Activity. ISE Conference, Mainz, Germany, 2025, Poster.

C. Roth, **M. Attia**, M. Lindner, S. Lechner and H. Hoffmann, Transferring Insights Obtained on 2D Metal Foams Synthesized by Dynamic Hydrogen Bubble Templating to 3D Gas Diffusion Electrodes. GDE Conference, Berlin, Germany, 2025, Presentation.

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