



Improving critical current density and cycling stability of NaSICON solid electrolytes by powder aerosol deposited CuO interlayers

Mutlucan Sozak^{a,e,*}, Kim Bennet Wiedemann^{a,e}, Ganga Sasikumar^{d,e}, Fariza Kalyk^c, Nella M. Vargas-Barbosa^{b,e}, Matteo Bianchini^{d,e}, Ralf Moos^{a,e}

^a Department of Functional Materials, Universität Bayreuth, Universitätsstraße 30, Bayreuth, 95447, Germany

^b Department of Electrochemistry, Universität Bayreuth, Universitätsstraße 30, Bayreuth, 95447, Germany

^c Institute of Energy Materials and Devices (IMD), IMD-4: Helmholtz-Institute Münster, Forschungszentrum Jülich, Münster, 48149, Germany

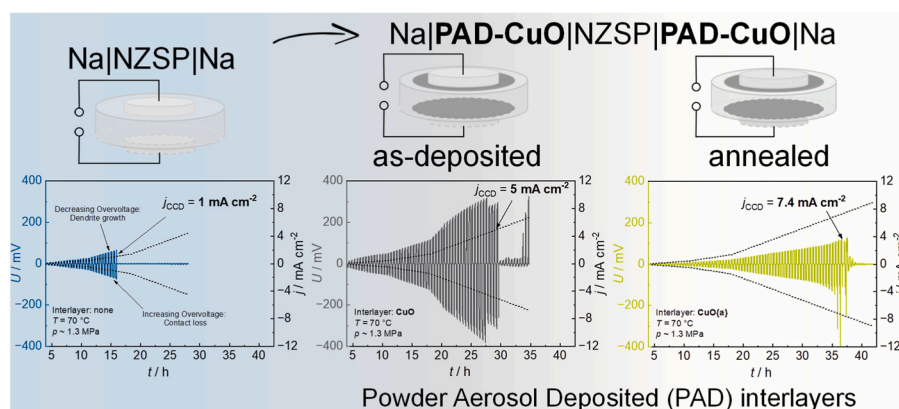
^d Department of Biology, Chemistry and Earth Sciences, Universität Bayreuth, Universitätsstraße 30, Bayreuth, 95447, Germany

^e Bavarian Center for Battery Technology (BayBatt), Universität Bayreuth, Weiherstraße 26, Bayreuth, 95448, Germany

HIGHLIGHTS

- Dense NZSP solid electrolytes ($\sim 500 \mu\text{m}$ thick) fabricated.
- Powder Aerosol Deposition (PAD) was employed to fabricate interlayers.
- Conversion-type CuO interlayers ($\sim 650 \text{ nm}$) reduced interfacial resistances.
- High critical current density up to 7.4 mA cm^{-2} has been achieved.
- PAD-CuO interlayers provided cycling stability over ten days at 30°C .

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Critical current density
NaSICON solid electrolyte
Interlayer engineering
Powder aerosol deposition (PAD)

ABSTRACT

Solid-solid interfacial instabilities remain major obstacles for the industrialization of cost-effective, high energy density solid-state sodium batteries (SSSB). In this work, a conversion-type CuO interlayer was successfully deposited onto both sides of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) solid electrolyte (SE) discs by powder aerosol deposition (PAD) to enhance the interfacial compatibility between sodium metal and SE. While unmodified symmetric cells suffer from progressive interfacial degradation, and limited critical current density, incorporating PAD-CuO interlayers on NZSP SE discs significantly reduces interfacial resistance and increases the critical current density up to 5.0 mA cm^{-2} . This value is further increased to 7.4 mA cm^{-2} by thermal post-treatment. Long-term galvanostatic cycling demonstrates stabilized overvoltages during plating/stripping experiments, indicating progressive interphase activation and improved Na^+ transport. Overall, these results demonstrate that PAD

* Corresponding author. Department of Functional Materials, Universität Bayreuth, Universitätsstraße 30, Bayreuth, 95447, Germany.

E-mail address: functional.materials@uni-bayreuth.de (M. Sozak).

<https://doi.org/10.1016/j.jpowsour.2026.240631>

Received 27 February 2026; Received in revised form 23 May 2026; Accepted 4 June 2026

Available online 12 June 2026

0378-7753/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

enables the fabrication of functional interlayers for stabilizing the Na|NZSP interface and may provide a foundation for fully PAD-processed scalable architectures in next-generation SSSBs.

1. Introduction

Solid-state sodium batteries (SSSBs) hold great potential as a cost-effective and safe storage solution for future electromobility and stationary energy storage applications [1]. NaSICON (Sodium Super Ionic Conductor) solid electrolytes (SE) are a promising class of materials to realize SSSBs due to their high sodium ion conductivity and good thermal stability [2]. Amongst them, the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (NZSP) system [3] is extensively studied because it enables fast Na^+ -ion transport at room temperature and exhibits good chemical and ambient air stability. When using NaSICON-based SEs, sodium metal can be incorporated into the SSSB architecture as the negative electrode, providing a high theoretical capacity of 1165 mAh g^{-1} while offering a wide electrochemical stability window [4]. As a result, pairing sodium metal with NaSICON may lead to high volumetric energy density cells, especially when thin NaSICON separators are used in Na|NaSICON|Cathode cells.

Such SSSB configurations, however, face significant challenges at the Na|NaSICON interface, namely, high interfacial resistances due to insufficient contact at the interface caused by poor wettability of sodium metal on the SE surface, and the dendrite formation/penetration through the SE, owing to inhomogeneous ion transport across the interface which leads to short circuits [5,6]. Moreover, when NZSP is brought into contact with sodium metal, chemical instabilities at the interface arise and they may form undesired interphases. Such reactions produce by-products that increase interfacial resistances and give rise to non-uniform plating/stripping of sodium metal. This leads to a degraded performance and reduced lifetime of SSSB [7,8].

Wenzel et al. [9] described three possible interphases that can occur between electrolyte and electrode materials: (1) a “stable interface” refers to a thermodynamically stable SE and interface without unwanted parasitic side reactions or interphases, therefore, the resistance does not increase over time; (2) a “mixed-conducting interphase” relates to solid electrolyte reduction where both ions and electrons are mobile at the interface, and (3) a “solid-electrolyte interphase (SEI)” indicates passivating decomposition products that are ionically conductive but electronically insulating. Moreover, the authors reported that Na_3PS_4 SE reacts with sodium to form resistive decomposition interphases that grow over time. Therefore, it was concluded that a protective interlayer strategy is required.

Interface modifications via “interlayers” play a crucial role to overcome the above-mentioned interfacial issues and to enhance the cycling stability. An interlayer is a deliberately introduced thin film coating between an alkali metal anode and the SE that aims to improve the wettability of sodium at the interface for a better contact. It reduces the interfacial resistance, stabilizes and/or prevents parasitic interfacial reactions, and suppresses the dendrite formation at the interfaces of Na|SE [10–12].

In general, interlayer materials can be classified into three main categories. Conversion-type interlayers are based on reactive precursors such as CuO [7] and SnO_2 [13,14], which react with alkali metal to form ionically and electronically conductive interlayers to stabilize sodium plating/stripping. This process follows the general reaction: $\text{MO} + 2\text{Na} \rightarrow \text{Na}_2\text{O} + \text{M}$ (M: Post-/transition metal). Secondly, an alloying-type interlayer can react with the alkali-metal anode (or the plated metal) to form a metal alloy (or intermetallic compounds) that remains in intimate contact with the solid electrolyte, enabling uniform metal plating/stripping. For example, a metallic interlayer on the electrolyte surface can form a sodium-tin (Na-Sn) alloy during cycling, which mitigates dendrite penetration and stabilizes the interface [15,16], or a sodium-gallium (Na-Ga) alloy can be generated by rolling the metal Ga on Na to improve sodiophilicity [17]. Lastly, a protective-type interlayer

acts primarily as a passive barrier or buffer layer: it remains chemically and mechanically stable at the interface, suppresses undesired side reactions, limits the growth of voids or dendrites at the interface and maintains good physical contact between alkali metal and solid electrolyte [18,19].

Duchène et al. [20] reviewed borohydride materials as an underexplored class of SEs, and reported their remarkable cycling stability. Borohydrides exhibit a unique mechanical deformability that allows them to wet the sodium metal anode more effectively than rigid ceramic oxide. Since they provide high stability and ionic conductivity, they can also serve as an interlayer. When utilized as an interlayer, they can bridge the gap between a NaSICON electrolyte and the Na metal to ensure a uniform sodium ion flux with one major drawback: their high production costs compared with traditional ceramics.

Interlayers can be formed in situ, as demonstrated by Li et al. [21] where Na-K alloy was formed at the Na|NZSP interface through the electrochemical migration and reduction of K^+ from a K-doped $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ electrolyte. Ex situ formation of protective layers on the surface of the solid electrolyte are also possible via various methods, such as atomic layer deposition (ALD) [22,23], physical vapor deposition (PVD) [24], chemical vapor deposition (CVD) [5], pulsed laser deposition (PLD) [25], or ultrasound solid welding [26,27].

The powder aerosol deposition method (abbrev. PAD or ADM) is a ceramic powder spraying technique that enables the fabrication of dense ceramic thin or thick layers at room temperature in short processing times, without the use of binders, solvents, or post-sintering steps [28, 29]. Its low cost, low-temperature operation, and simple equipment setup offers major advantages over methods such as ALD and PVD. The fundamentals of the PAD process have been described elsewhere, e.g., in Refs. [30,31].

Nazareus et al. [32] demonstrated that introducing a manually applied graphite interlayer (with a graphite rod) between PAD fabricated $\text{Al}_{0.2}\text{Li}_{6.025}\text{La}_3\text{Zr}_{1.625}\text{Ta}_{0.375}\text{O}_{12}$ (ALLZTO) and lithium metal substantially improves the electrochemical properties. While the polished as-deposited film showed a critical current density of $670 \mu\text{A cm}^{-2}$ at 70°C , applying a graphite interlayer enabled cycling up to $1000 \mu\text{A cm}^{-2}$ under identical conditions, with noticeably stable voltage behavior and reduced voltage peaks.

In this work, we demonstrate for the first time the utilization of Powder Aerosol Deposition (PAD) method to fabricate CuO conversion-type interlayers on Na-based ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ or NZSP) solid electrolytes. This approach is designed to stabilize plating/stripping behavior at the Na|SE interface. To evaluate the impact of these PAD interlayers, we use Electrochemical Impedance Spectroscopy (EIS) to investigate interfacial resistances within symmetric cell configurations of Na|PAD-CuO|NZSP|PAD-CuO|Na. Finally, we assess how the PAD-CuO interlayers enhance the critical current density and long-term cycling stability of NZSP compared to pristine Na|NZSP|Na cells.

2. Experiment & methods

2.1. Preparation of sintered NZSP solid electrolyte discs

The solid-state synthesis route to obtain $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ powders was carried out according to our previous work [33]. The obtained powder with the desired NZSP phase was then compacted into cylindrical green pellets ($\varnothing 13 \text{ mm}$, $\sim 3 \text{ g}$ each) using a uniaxial hand press (Werkstattspresse WPS 10C, Raptor Maschinen, Germany). Each pellet was held under pressure for 5 min at a pressure of $\sim 220 \text{ MPa}$. Sintering was carried out in alumina crucibles covered with Pt-foil and an alumina-lid on top. The temperature profile during sintering was set to 2 K min^{-1} up

to 1215 °C with a dwell time of 10 h at the target temperature, and subsequent cooling with 1.8 K min⁻¹ down to 150 °C. The temperature was held constant at 150 °C until the removal of the sintered NZSP pellets from the furnace (LHT08/16, Nabertherm GmbH, Germany).

The obtained sintered NZSP pellets (9.3 ± 0.13 mm in height, Ø11.2 mm) were then mounted in a circular saw machine (Accutom-50, Struers GmbH, Germany) to slice ~500 µm thick NZSP solid electrolyte discs using a metal-bonded diamond blade (DiaCut005, Cloeren Technology GmbH, Germany). Demineralized water containing four percent cooling lubricant additive (Cooli Additive, Struers GmbH, Germany) was circulated to cool down the blade during the cutting process. The cut NZSP discs were then collected from the saw machine and immersed in isopropanol to prevent any progressive reaction between water and NZSP [34,35]. Prior to polishing, the notch on the NZSP discs from the cutting process was ground by SiC abrasive paper (FEPA P#1200, Struers GmbH, Germany) at 50 rpm with demineralized water as medium using a grinding/polishing machine (TegraPol-11, Struers GmbH, Germany). The NZSP discs were subsequently polished to reduce the surface roughness on both sides with FEPA P#2000. After the surface-finish processes, the NZSP discs were again immersed in isopropanol and cleaned in an ultrasonic bath (Ultrasonic Cleaner USC-TH, VWR International GmbH, Germany) to remove residual surface contaminants. They were then dried at 80 °C for 10 min, measured five times per disc with a digital caliper to assess the average thickness, and stored in an argon-filled glovebox until further processing. The final NZSP discs resulted in a mean thickness of 484.9 ± 11.8 µm.

2.2. Powder aerosol deposition of interlayers

A custom-made PAD apparatus [31] was used to fabricate thin film interlayers. For that, copper (II) oxide (CuO, ≥94%, technical, VWR International S.A.S) was chosen to be deposited on NZSP SE discs via the powder aerosol deposition method. The powders were sieved through a 90 µm mesh size and then stored in a drying oven at 200 °C for at least three days prior to deposition. For each run, the aerosol flask was filled with 7 g of powder. The powder in the aerosol flask was mixed with oxygen to create a free-flowing aerosol while shaking the aerosol flask with the vibration table. The particles inside the aerosol were then transferred into the deposition chamber, through a converging nozzle (10 × 0.5 mm²) at high velocities of up to 500 m s⁻¹ [31]. The NZSP SE discs were briefly dry polished using SiC sand paper (FEPA P#2000) to reveal a fresh surface and further attached to the substrate holder. The particles hit the NZSP substrates, which moved in the x-y direction at a constant scan speed, forming thin interlayer coatings layer by layer. The parameter set to deposit CuO material on NZSP samples is shown in Table 1.

First, CuO powder was sprayed onto one side of the NZSP disc, and the same procedure was then applied to the other side. Some of the NZSP discs coated with CuO interlayers on both sides were subjected to thermal post-treatment. The annealing temperature (T_{ann}) was calculated using the empirical equation (1) derived by Exner et al. [36], which indicates that T_{ann} depends on the melting point (T_{mp}) of the powder aerosol deposited material. Considering the T_{mp} of CuO (1326 °C), T_{ann} was calculated to be 723 °C, therefore, annealing was carried out at 720 °C in a muffle furnace with a heating/cooling rate of 5 K min⁻¹ and a dwell time of 20 min at the target temperature.

Table 1
Powder aerosol deposition parameters for CuO deposition on NZSP discs.

Parameter	Value
Distance (nozzle to substrate)	2 mm
Carrier gas	O ₂
Gas flow	8 l min ⁻¹
Scan speed	5 mm s ⁻¹

$$T_{ann} = \frac{1}{6}T_{mp} + 730 \text{ K} \quad \text{Eq. 1}$$

2.3. Analysis methods

The Archimedes' principle was employed to determine the density of sintered NZSP pellets by measuring the mass of the sample in air and in water at room temperature, using a balance (Sartorius LA 120 S, Kit YDK01, Sartorius AG, Germany) equipped with a density determination kit. The density was calculated based on the buoyant force, which is proportional to the mass of the water displaced by the sample. The particle size of the CuO powder was measured by laser scattering (Mastersizer 2000, Malvern Instruments Ltd., UK) prior to the deposition process. Crystal structure analysis was conducted by X-Ray diffraction (XRD) to assess whether water-exposed NZSP underwent structural changes. Diffraction analyses were carried out using Bragg-Brentano configuration (Bruker D8 Discovery A25, Bruker AXS GmbH, Germany) in 2θ range of 10 – 120°, exposure time of 5 s with 0.01° step size for the synthesized NZSP powder. For the sintered NZSP pellets, the parameter set was 10 – 55°, 0.75 s with 0.02°, respectively. For the CuO phase analysis, XRD measurements of both the initial CuO powder and CuO films deposited on Si wafers (911 orientation) were conducted in the 2θ range of 30 – 70° using an exposure time of 1.5 s and a step size of 0.01°. The cross-section of the powder aerosol deposited CuO interlayers (PAD-CuO|NZSP) was examined by scanning electron microscopy (SEM, FEI Quanta FEG 250, ThermoFisher Sci., USA). The PAD-CuO|NZSP discs were manually broken in half and analyzed in SEM from the emerged cross-sections. Surface roughness of NZSP discs with and without interlayers was determined by stylus profilometry (Waveline W20, Jenoptik, Germany) according to DIN EN ISO 4287:1998 standard to determine the average roughness R_a and the average maximum height of the profile R_z .

X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded using a Versa Probe III XPS Microprobe (Physical Electronics PHI, Japan) equipped with a monochromatic Al Kα X-ray source (1486.6 eV) and operated with the SmartSoft-VP software. XPS survey scans and core-level spectra were obtained with constant pass energies of 280 eV and 26 eV, respectively. The XPS data were processed using CasaXPS, while the binding energies of all core-level spectra were calibrated using the C 1s peak at 284.8 eV as a reference.

The ionic conductivity of pristine NZSP discs (~500 µm) was measured by electrochemical impedance spectroscopy (EIS, Alpha-A, Novocontrol Tech. GmbH & Co. KG, Germany) applying gold ion-blocking electrodes (~200 nm thickness, ~Ø9 mm) sputtered on both sides of the NZSP discs. The sputtered NZSP discs were then packed into pouch cells in a glovebox with an Al contact placed on top of the gold layers as explained in Ref. [37]. A clamp was attached to the pouch cells to provide a better contact between electrode and the current collectors. EIS was conducted in a frequency range from 1 MHz to 1 Hz at various temperatures (−10, 0, 10, 20, and 70 °C) applying a voltage amplitude of 50 mV with 10 steps per decade.

Time-resolved impedance spectroscopy (TR-EIS) was performed at room temperature for Na|NZSP|Na and Na|PAD-CuO|NZSP|PAD-CuO|Na configurations in electrochemical test cells (PAT-Cell, EL-Cell GmbH, Germany) inserted in a docking station (PAT-Stand-1, EL-Cell, Germany) using a Novocontrol impedance analyzer. TR-EIS measurement parameters were 1 MHz to 0.1 Hz and 50 mV for the frequency range and the voltage amplitude, respectively.

Configuration-wise, two types of symmetric cells were assembled for galvanostatic cycling: without an interlayer (Na|NZSP|Na), and with powder aerosol deposited interlayers (Na|PAD-CuO|NZSP|PAD-CuO|Na). The cells of NZSP discs with annealed CuO interlayers are designated with {a} (Na|PAD-CuO{a}|NZSP|PAD-CuO{a}|Na). For the sake of clarity, all abbreviations are listed below in Table 2.

Sodium metal (99.9%, Sigma Aldrich) was prepared from sodium

Table 2

Symmetric cell configurations in this study. {a} denotes an NZSP disc with powder aerosol deposited CuO interlayers on both sides that were additionally annealed.

Symmetric cell configuration	Abbreviation
Na NZSP Na	Na@NZSP
Na PAD-CuO NZSP PAD-CuO Na	CuO@NZSP
Na PAD-CuO{a} NZSP PAD-CuO{a} Na	CuO{a}@NZSP

cubes by removing the oxide layer on the surfaces using a scalpel, and then rolled in between low-density polyethylene (LDPE) foils to a thickness of ~ 0.5 mm. The circular electrodes ($\varnothing 4$ mm) were punched from the sodium metal foil and attached to both sides of NZSP discs to fabricate the above-mentioned symmetric cell configurations. The Na electrode diameter was enlarged because of pressure inside the PAT cell and heat in the climate chamber and determined to be ~ 6.5 mm in post-mortem analysis upon cell disassembly (which corresponds to an area of ~ 0.33 cm²). Based on the thickness of cell stack (~ 0.6 mm – Na|NZSP|Na), a stack pressure of 1.34 MPa in the PAT-Cell setup was calculated using the equation provided by the manufacturer [38].

All the electrochemical test cells were cycled in PAT-Cells in a climate chamber operated at 30 °C or 70 °C, inserted in the docking station (PAT-Stand-4) and connected to PAT-Channel-1 (galvanostat/potentiostat/EIS analyzer) controlled by PAT-Controller-8 unit. The schemes of the galvanostatic cycling protocols are shown in Figure S-1 in the Supporting Information. The protocols started after the initial 4 h waiting time in the climate chamber to achieve a steady state. Potentiostatic electrochemical impedance spectroscopy (PEIS) was performed at the end of the initial waiting time.

The critical current densities (j_{CCD}) of symmetric cell configurations were determined by staircase galvanostatic plating/stripping protocols (Figure S-1a). The cells were cycled in a current range from 20 μ A to 2960 μ A with gradually increasing current density (Table 3). A constant current was applied in both directions for 10 min with a relaxation period of 2 min after each constant current step, following a PEIS step at the end of each full cycle.

Galvanostatic long-term cycling stability tests (Figure S-1b) were performed by applying 20 min of constant current (CC) in each direction for plating/stripping with 5 min relaxation after each CC step, followed by a PEIS step at the end of each full cycle. The protocol includes 135 full cycles, which corresponds to ~ 5.25 days of cycling duration. The same protocol was applied for approx. 10 days to test the cycling stability of the annealed PAD-CuO interlayer (CuO{a}@NZSP) under practical operating conditions (30 °C) in the extended long-term cycling experiment.

3. Results & discussion

3.1. Characterization of NZSP solid electrolyte

Crystal structures of sintered NZSP SE discs before and after the cutting process with water, as well as the powder utilized to produce NZSP discs were investigated by X-ray diffraction analysis as shown in Figure S-2 in the Supporting Information. The desired phases were confirmed in the synthesized powders based on the position of the

Table 3

Staircase galvanostatic cycling protocol to determine the critical current density (j_{CCD}).

Current range/ μ A	Step Size/ μ A	Corresponding current density ^a /mA cm ⁻²
20 to 160	10	0.06 to 0.48
180 to 460	20	0.54 to 1.38
510 to 2960	50	1.54 to 8.92

^a Calculated based on a corresponding sodium metal electrode area ($\sim \varnothing 6.5$ mm, ~ 0.33 cm²).

reflections and the relative intensities. Minor reflections corresponding to ZrO₂ were detected, indicating the secondary phase. The secondary phase is attributed to residual, unreacted ZrO₂, as a result of decomposition/volatilization of Na and P containing species, which lead to ZrO₂ segregation at the grain boundaries during sintering [39,40]. The crystal structure was preserved after sintering of NZSP pellets. Moreover, the water-cut NZSP discs did not show additional reflections, meaning that no significant reaction occurs in NZSP when it is briefly exposed to water [35,41].

The NZSP SE powders prior to the sintering process exhibit a bimodal particle size distribution, with a small fraction of particles larger than 10 μ m. Milling the NZSP SE powder for 8 h resulted in a D_{50} value of ~ 1.7 μ m. The particle size distribution of CuO powder is also bimodal with a significant fraction of larger particles with a D_{50} value of ~ 11.5 μ m (see Supporting Information, Figure S-3).

The relative density of sintered NZSP pellets is 98% measured by the Archimedes method using water as the liquid medium. The theoretical density value of 3.27 g cm⁻³ [42] was taken for Na₃Zr₂Si₂PO₁₂ to calculate the relative density.

Surface roughness values of sintered NZSP pellets and after each process step (cutting, grinding, and polishing) were measured using a stylus profilometer. After polishing the NZSP discs with 10 μ m SiC sandpaper, the surface roughness decreased to $R_a \approx 0.12 \pm 0.02$ μ m and $R_z \approx 1.36 \pm 0.32$ μ m, compared to $R_a \approx 0.64 \pm 0.13$ μ m and $R_z \approx 5.08 \pm 0.86$ μ m for the as-fired NZSP pellets (see Supporting Information, Figure S-4).

Total resistance (R_{total}) values of the NZSP discs were investigated using impedance spectroscopy at -10 , 0 , 10 , 20 , and 70 °C. The impedance spectra were evaluated using different equivalent circuits depending on the distinguishable processes at different temperatures (Supporting Information, Figure S-5 and Table S-1). At low temperatures (-10 to 20 °C), the spectra exhibit separable bulk and grain-boundary contributions. The data were accordingly fitted using an equivalent circuit consisting of R_{bulk} , R_{gb} || CPE_{gb} , and a low-frequency polarization related constant phase element (CPE_{pol}). An inductive element (L1) was included when necessary to elucidate instrumental or wiring-related inductive contributions. At 70 °C, the characteristic frequencies shift to higher values and the bulk and grain-boundary responses overlap within the measured frequency range, therefore a reliable separation of the two individual processes is no longer possible. For this reason, a simplified model containing R_{total} and CPE_{pol} was used. The use of constant phase elements instead of ideal capacitors accounts for the non-ideal response, which may be caused by inhomogeneity and porosity in solid electrolyte and non-uniform interfacial contact at the interfaces [43].

The ionic conductivities of NZSP discs were calculated in an Au|NZSP|Au setup according to equation (2) using the thickness of the NZSP disc (d_{disc}), the area of the gold electrode (A_{Au}), and the total resistance (R_{total}) which is the sum of bulk resistances (R_{bulk}) and grain-boundary resistances (R_{gb}).

$$\sigma_{ion} = \frac{d_{disc}}{R_{total} \cdot A_{Au}} \quad \text{Eq. 2}$$

The calculated ionic conductivity of NZSP SE discs depending on the measurement temperature are shown in the Supporting Information, Figure S-6a. An ionic conductivity of $9.5 \cdot 10^{-4}$ S cm⁻¹ at ambient temperature and $5.5 \cdot 10^{-3}$ S cm⁻¹ at 70 °C were achieved for NZSP SE discs. An activation energy of $\sim 0.3 \pm 0.03$ eV for NZSP SE discs was calculated from the Arrhenius plot (Figure S-6b).

3.2. Critical current density of Na@NZSP symmetric cells

The critical current densities (j_{CCD}) of symmetrical cells without interlayers (Na@NZSP) were evaluated using a staircase galvanostatic cycling protocol at 70 °C with an internal stack pressure of ~ 1.34 MPa. In total, six cells were assembled in symmetric cell configuration

without interlayer. They were designated as Na@NZSP-C1 to C6. Fig. 1a shows the cycling of Na@NZSP-C1. During the plating/stripping half-cycles in both directions, up to current densities of 0.54 mA cm^{-2} , slight drops were observed in the overvoltage. In the positive overvoltage half-cycle, these drops indicate the onset of dendrite formation, while in the negative overvoltage half-cycle, the drops suggest a contact loss at the Na|NZSP interface [7]. With the increasing current density, decrease in the overvoltage drops in each positive (upper) half-cycle gets more pronounced, showing the insufficient creepage and diffusion of sodium metal to refill the voids formed at the interface due to poor wettability of the NZSP SE [5,6]. This is a major issue that limits the performance of solid-state batteries with metal electrodes [10,44]. Temperature and stack pressure applied to the cells play an important role in this problem and influence the contact at the interface of metal electrode and solid electrolyte [44,45]. Dendrite-induced voltage drops are noticeable after 11.2 h of cycling in Fig. 1b. The overvoltage decreases from 27.4 to 26.7 mV after 5 min of plating/stripping in one direction, followed by a slight increase to 27.5 mV until the end of constant current step. Formation of sodium metal dendrites can be related to those overvoltage drops, which reduced the internal cell resistance by partly shorting the cell [46,47]. A sudden drop from 64.7 to 0.8 mV at the current density of 1.08 mA cm^{-2} indicates a short circuit due to sodium metal dendrites connecting metal electrodes all along the NZSP SE [47].

The remaining cells (Na@NZSP-C2 to C5) were examined using the same cycling procedure and they all exhibited different critical current densities of (C2) 2.74 mA cm^{-2} , (C3) did not short-circuit up to 4.4 mA cm^{-2} , (C4) 1.38 mA cm^{-2} , and (C5) 3.94 mA cm^{-2} , respectively. The critical current density plot of the cells C2 to C5 can be seen in the Supporting Information, Figure S-7. EIS data collected from the cycling procedure were examined to elucidate the difference in critical current densities of these cells. Nyquist plots of the cells Na@NZSP-C1 to C3 are shown in the Supporting Information, Figure S-8, each derived after applying specific current densities. The high-frequency intercept of the spectra is attributed to the total resistance of NZSP SE ($R_{\text{bulk}} + g_{\text{b}}$). The interfacial resistance ($2R_{\text{int}}$) is modelled in parallel with a constant phase element (CPE_{int}) to describe the non-ideal capacitive behavior at the Na|NZSP SE interface. Therefore, the depressed semicircles observed at 0.1 MHz to $\sim 793 \text{ Hz}$ are attributed to an interfacial resistance ($2R_{\text{int}} || \text{CPE}_{\text{int}}$) [48]. In symmetric cell configuration, the interfacial resistance is represented as $2R_{\text{int}}$ since metal electrodes are placed on both sides of the solid electrolyte and their contribution to the interfacial resistance can be considered as equal [5,14]. In Figure S-8a, the total resistance ($R_{\text{bulk}} + g_{\text{b}} + 2R_{\text{int}}$) of the cell Na@NZSP-C1 is measured to be 164.3Ω at 0.06 mA cm^{-2} . The total resistance continuously decreases at each subsequent cycle until the cell is shorted at a j_{CCD} of 1.08 mA cm^{-2} . The cell Na@NZSP-C2 in Figure S-8b exhibits a slight increase in total

resistance at the j_{CCD} of 0.18 mA cm^{-2} , and then the resistance decreases similar to the cell C1. In contrast to cells C1 and C2, the cell Na@NZSP-C3 Figure S-8c shows a slight decrease in total resistance at the j_{CCD} of 0.18 mA cm^{-2} , following a continuous increase in resistance at each subsequent current density step without a short at the end of the j_{CCD} of 4.4 mA cm^{-2} . Therefore, a significant discrepancy was observed in total resistance and critical current density values between the three cells.

In Fig. 2, the calculated resistance values from the impedance measurements above are plotted as a function of the applied current density after the first and every fifth applied current density step, including the resistance value at the critical current density step just before the short. Fig. 2a shows the sum of bulk and grain boundary resistances of the cells Na@NZSP-C1 to C5. It can be seen that the $R_{\text{bulk}} + g_{\text{b}}$ resistances remain constant through the course of cycling for all the cells except cell C2, which exhibits a slightly decreasing $R_{\text{bulk}} + g_{\text{b}}$, which can be attributed to excessive dendrite growth and break-up. For the cells C2 to C5, the $R_{\text{bulk}} + g_{\text{b}}$ value is between 34Ω and 40Ω at the beginning. Contrary to cells C2 to C5, cell C1 shows a higher initial $R_{\text{bulk}} + g_{\text{b}}$ value of 55.2Ω , which is stable until the cell is shorted. The slightly higher $R_{\text{bulk}} + g_{\text{b}}$ resistance of cell C1 compared to cells C2 to C5 can be explained by the microstructural aspects such as the distributions of inhomogeneity (impurities, closed porosity) of the sintered NZSP SE discs [49].

The interfacial resistances ($2R_{\text{int}}$) extracted from fitted EIS data of the cells Na@NZSP-C1 to C5 are shown in Fig. 2b as a function of the applied current density (j). As can be seen, the higher the interfacial resistance, the lower the critical current density of the NZSP SE discs. Cells C1 and C4 exhibit high interfacial resistances of $\sim 100 \Omega$ and $\sim 150 \Omega$, respectively. Consequently, cell failure occurs when low currents are applied. Cells C3 and C5 with lower interfacial resistances between $\sim 25 \Omega$ and $\sim 75 \Omega$ can withstand higher applied current densities. Cell C3 with the lowest initial interfacial resistance of $\sim 25 \Omega$ survived until the end of the galvanostatic staircase plating/stripping procedure up to 4.5 mA cm^{-2} . Cell C2 exhibits a j_{CCD} of $\sim 2.74 \text{ mA cm}^{-2}$, however $2R_{\text{int}}$ of C2 is not stable due to severe dendrite formation.

To explain why the interfacial resistances vary significantly, one needs to consider the time elapsed between cell assembly and the start of cycling. While some cells were cycled right after the assembly in PAT-Cells, the others were left at open-circuit conditions after the assembly up to four days due to the unavailability of the cell cyclers. The open-circuit conditions may have caused degradation of the NZSP SE interfaces when brought in contact with sodium metal electrodes, as for instance reported in Ref. [50]. Zhang et al. [4] reported that at open-circuit conditions for symmetric cells (0 V vs. Na^+/Na), $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ undergoes an irreversible reduction in the presence of sodium. Therefore, decomposition products that exhibit a lower ionic conductivity compared to NZSP formed at the Na|NZSP SE interface.

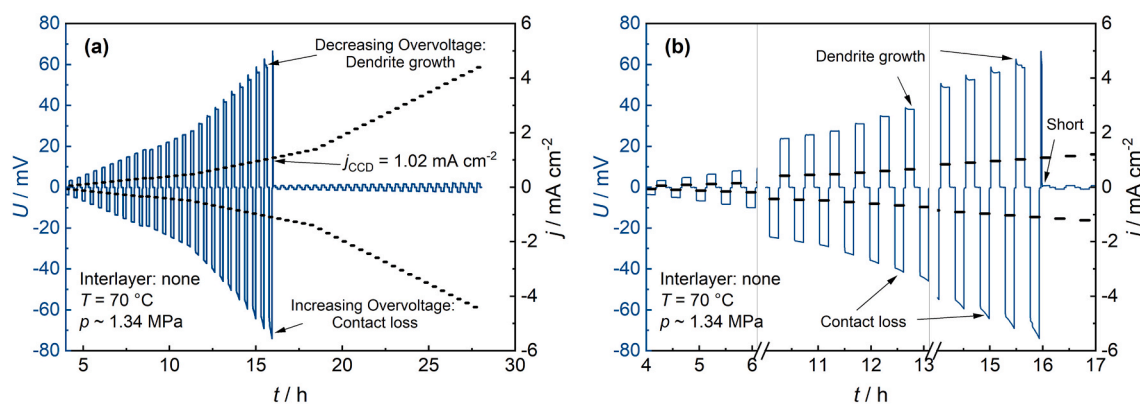


Fig. 1. Staircase galvanostatic cycling of Na@NZSP-C1; a) total cycling profile, b) zoomed in timeslots to display overvoltage responses. The black lines show the plating/stripping current density (j) plateaus and the blue curve is the measured voltage (U) response. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

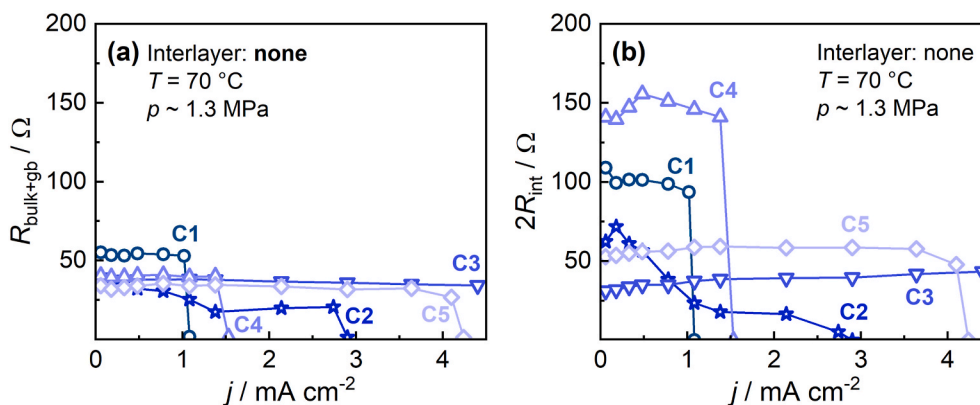


Fig. 2. Resistance values from fitted data as a function of applied current density in symmetric cells Na@NZSP-C1 to C5, a) Bulk + grain boundary resistances, b) Interface resistances. The straight lines between the data points are for the eye guidance.

Sodium-ion transport across the interface would then be impeded [10].

Furthermore, time resolved impedance spectroscopy (TR-EIS) was used to validate the interfacial degradation of Na@NZSP symmetric cells over time. Fig. 3a shows the evolution of the impedance spectra of the cell Na@NZSP-C6 over 19 days at room temperature. The impedance spectra were analyzed using the equivalent circuit shown in Fig. 3a. The high-frequency intercept on the real axis was assigned to the bulk resistance of the NZSP pellet (R_{bulk}). The depressed semicircle in the high-frequency region was attributed to the grain boundary contribution and modelled by R_{gb} in parallel with a constant phase element (CPE_{gb}) [48]. The larger depressed semicircle at intermediate frequencies was assigned to the total interfacial resistance of the two Na|NZSP interfaces ($2R_{\text{int}}$) and fitted using $R_{\text{int}}||\text{CPE}_{\text{int}}$. Constant phase elements were used instead of ideal capacitors to account for the non-ideal response of the system, which arises from surface heterogeneity and non-uniform interfacial contact. This equivalent circuit provided the most physically meaningful description in the measured frequency range. The fitting results show that the bulk and grain-boundary resistance remain nearly unchanged during open-circuit conditions, whereas the interfacial contribution increases over time. Specifically, the total interfacial resistance increased from 2480 Ω for the freshly assembled cell to 8126.5 Ω after 19 days at open-circuit conditions. This is an indication of the formation of poorly conductive interphases at the interface of Na|NZSP SE and the assignment of the individual processes was based on their characteristic frequency ranges, consistent with previous reports [4,10].

The discrepancy in the varying critical current densities of the different cells can be understood based on the TR-EIS experiment, as it was revealed that interfacial resistance increases over time. With regard

to the time elapsed after cell assembly at open-circuit conditions, cells may exhibit different interfacial resistances (Fig. 3b) due to the different degrees of degradation at the Na|NZSP interface [8,9]. As prolonged resting was found to lead to progressive interfacial degradation, affecting the measured critical current density, all forthcoming CuO@NZSP and CuO@{a}@NZSP symmetric cell measurements were performed immediately after assembly to ensure reproducibility and a fair comparison between different cell configurations.

3.3. Critical current density of CuO@NZSP symmetric cells

Interlayers of CuO on both sides of NZSP SE discs were fabricated by powder aerosol deposition. The cross-sectional and the top-view SEM images of the CuO interlayer are shown in Fig. 4. The interlayers appear to be dense and well adhered to the NZSP SE with a thickness of approx. 650 nm. The uniform, but crater-like [51] surface morphology, as it is typical for aerosol deposition, can be observed from the top-view SEM images. The surface roughness of the CuO interlayers increased from $R_a \approx 0.1 \pm 0.03 \mu\text{m}$ and $R_z \approx 0.66 \pm 0.3 \mu\text{m}$ to $R_a \approx 0.17 \pm 0.02 \mu\text{m}$ and $R_z \approx 1.65 \pm 0.29 \mu\text{m}$ after tempering the PAD-CuO layers. The interlayer thickness remained unchanged, indicating that roughening is primarily due to the grain growth during annealing [36] (see Supporting Information, Figure S-9).

CuO serves as a conversion-type interlayer material according to the following reaction [7]:



The same galvanostatic staircase cycling procedure was applied to the symmetric cells with as-deposited and annealed CuO interlayers. The

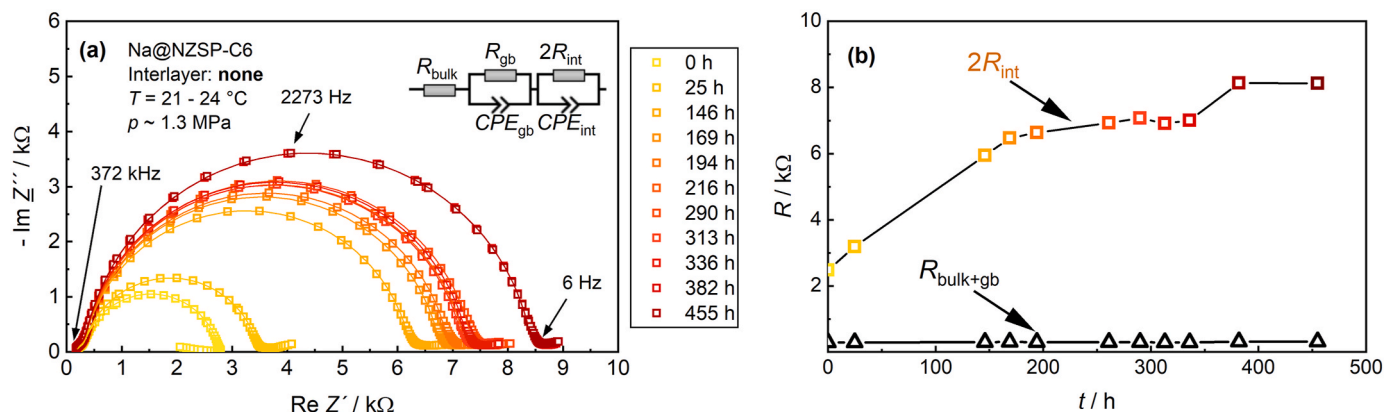


Fig. 3. a) TR-EIS of the cell Na@NZSP-C6. The impedance spectra were recorded under open-circuit conditions at RT (the straight lines represent the fit to the data), b) separated resistance values ($2R_{\text{int}}$ and $R_{\text{bulk}} + R_{\text{gb}}$) from fitted data, where the black line is for the eye guidance.

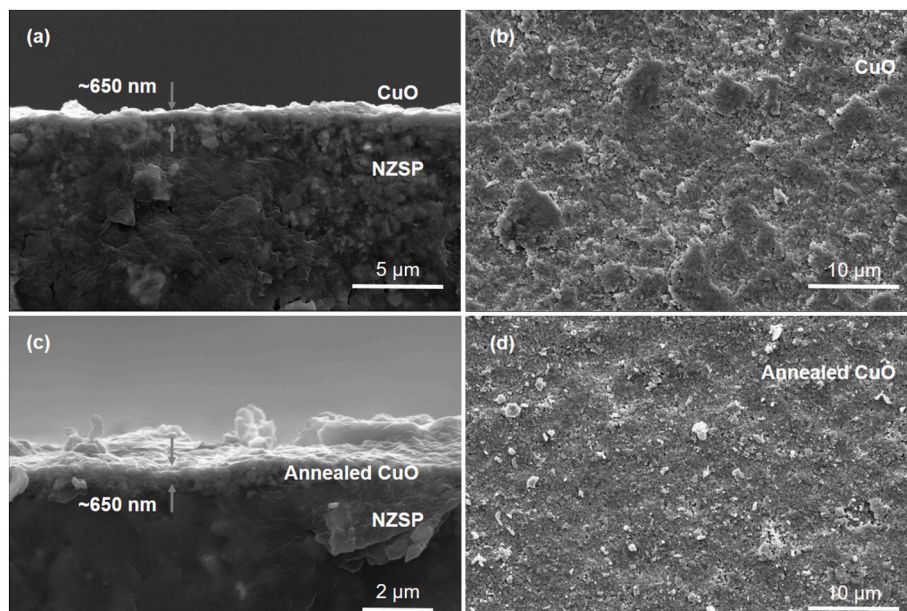


Fig. 4. SEM images of powder aerosol deposited CuO interlayers on NZSP SE in the as-deposited and annealed states, where (a, c) cross-section and (b, d) top-view.

galvanostatic cycling results of as-deposited CuO@NZSP-C1 are shown in Fig. 5a. A critical current density of 5.0 mA cm^{-2} was achieved with an as-deposited CuO interlayer without any indication of severe contact loss in the overvoltage-time plot. Overvoltage slightly increases within each half cycle during both plating and stripping, indicating that the

contact loss occurs more slowly compared to NZSP without interlayer (Fig. 1a). A sudden overvoltage drop was observed at 27.7 h of plating/stripping. It can be attributed to sodium dendrite formation and growth [47]. On the other hand, gradually increasing overvoltages during constant current steps for both half cycles refer to progressive contact

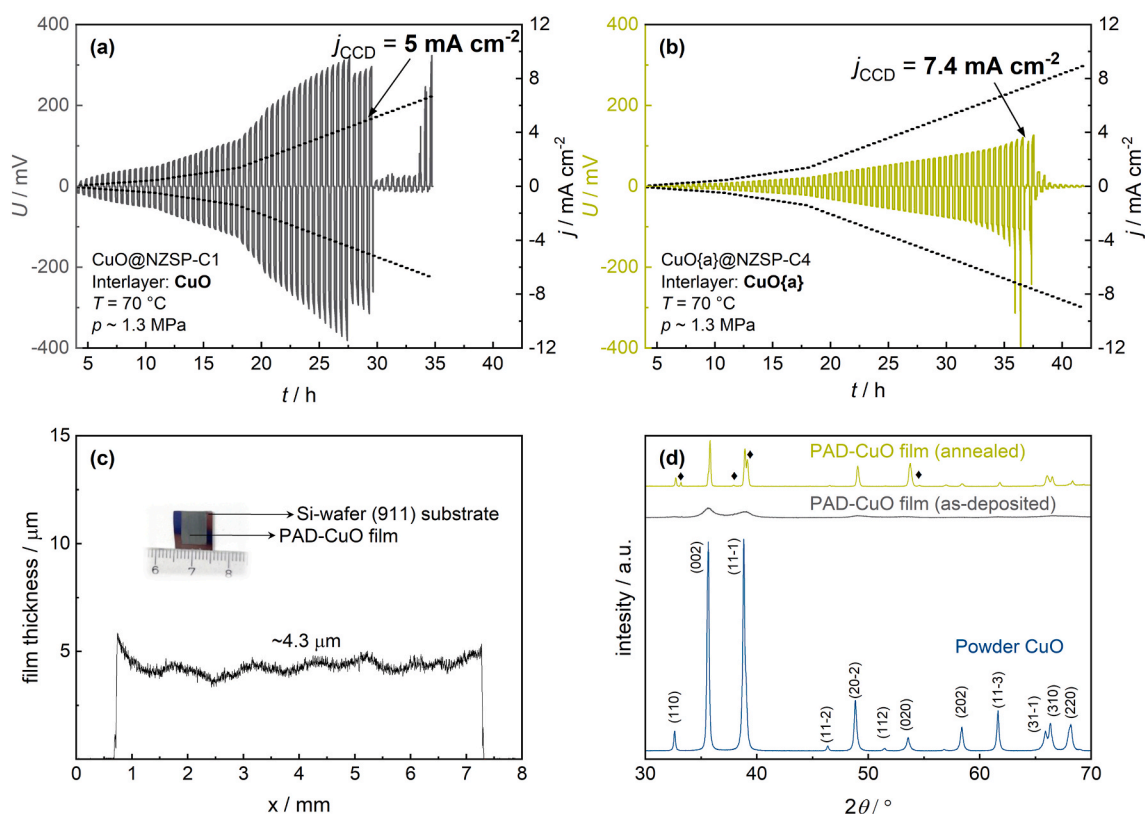


Fig. 5. Galvanostatic cycling of a) CuO@NZSP-C1 (as-deposited PAD interlayer), and b) CuO(a)@NZSP-C4 (annealed PAD interlayer) at gradually increasing current densities. Scaling was kept constant for comparability. c) Stylus-profilometer profile of the PAD-CuO film on a silicon (Si) wafer. The inset image shows the PAD-deposited CuO on a Si-wafer (911 orientation), d) X-ray diffraction analysis of the initial powder, the PAD-CuO film in its as-deposited state, and the PAD-CuO film after annealing. The reflections marked with “♦” belong to the impurity byproducts. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

loss [46,47]. The other two symmetric cells with as-deposited CuO interlayers (CuO@NZSP-C2 and C3) exhibited critical current densities of 5.75 mA cm^{-2} , and 5.3 mA cm^{-2} , respectively, showing the reproducibility of results obtained from powder aerosol deposited CuO interlayers on NZSP SE (Supporting Information, Figure S-10).

Fig. 5b shows data of the galvanostatic staircase cycling of CuO{a}@NZSP-C4 SE with annealed CuO interlayers. A critical current density of 7.4 mA cm^{-2} was reached with thermally post-treated CuO interlayers on NZSP SE. In addition, it is observed that this configuration exhibits a lower overvoltage at each half-cycle in comparison to the as-deposited CuO interlayers in Fig. 5a. Therefore, the critical current density of NZSP SE can be further improved by a thermal post-treatment of PAD-CuO interlayers. Exner et al. [36,52] reported that functional properties (e.g. ionic and electronic conductivity) of powder aerosol deposited ceramic layers can be improved by releasing the microstrain in PAD layers (induced from the deposition process) by thermal post-treatment. The further increase in j_{CCD} of NZSP SE with annealed CuO interlayers can therefore be explained by the release of microstrain in the PAD-CuO interlayers. An additional cell with the same configuration (CuO{a}@NZSP-C5) showed a j_{CCD} of 7.1 mA cm^{-2} demonstrating the reproducibility of the annealing process (Supporting Information, Figure S-11).

To further elucidate the effect of annealing on the PAD-deposited CuO interlayer, additional structural characterization was performed using X-ray diffraction. Since the CuO layer deposited on NZSP is relatively thin ($\sim 650 \text{ nm}$), its reflections are dominated by the underlying bulk-NZSP substrate and cannot be clearly distinguished. Therefore, CuO films were deposited on Si wafers (911 orientation) to enable reliable structural analysis (Fig. 5c). The as-deposited CuO film exhibits very broad diffraction peaks (Fig. 5d), indicating a highly

nanocrystalline structure with increased microstrain. This observation is consistent with the characteristic mechanism of powder aerosol deposition, where particles impact the substrate at high velocity and undergo fragmentation, resulting in dense films composed of nanocrystallites. Rietveld refinement (Supporting Information, Figure S-12 & Table S-2 to S-5) reveals that the initial CuO powder possesses a crystallite size of approx. 88 nm with negligible microstrain (0.13%), whereas the as-deposited film shows a significantly reduced crystallite size of $\sim 8 \text{ nm}$ and increased microstrain ($\sim 1\%$). Upon annealing in ambient air at 720°C (with a heating/cooling rate of 5 K min^{-1} , dwell time of 20 min), the reflections became significantly sharper, indicating crystallite growth and the relaxation of internal strain. Additional reflections were observed in the annealed PAD-CuO at 2θ positions of 33.2° , 37.9° , 39.1° and 54.6° , which may possibly belong to byproducts that emerged as a result of copper diffusion onto the silicon wafer according to Cu-O-Si system [53], which we could not fully resolve these reflections. Rietveld analysis confirms an increase in crystallite size to $\sim 450 \text{ nm}$ accompanied by a substantial reduction in microstrain. This microstructural evolution is expected to improve the structural integrity and interfacial contact of the CuO interlayer, which is consistent with the enhanced electrochemical performance and stable interfacial behavior observed for the annealed CuO{a}@NZSP samples.

The EIS data collected during the galvanostatic cycling of CuO@NZSP-C1 (Fig. 5a) were analyzed to separate the interfacial contribution from the bulk and grain boundary resistance of the cell. The same equivalent circuit as shown in Fig. 3a was used for fitting, and the corresponding impedance spectra are provided in the Supporting Information (Figure S-13). In this equivalent circuit, the high-frequency real-axis intercept together with the first depressed semicircle was assigned to the combined bulk and grain boundary resistance ($R_{\text{bulk}} +$

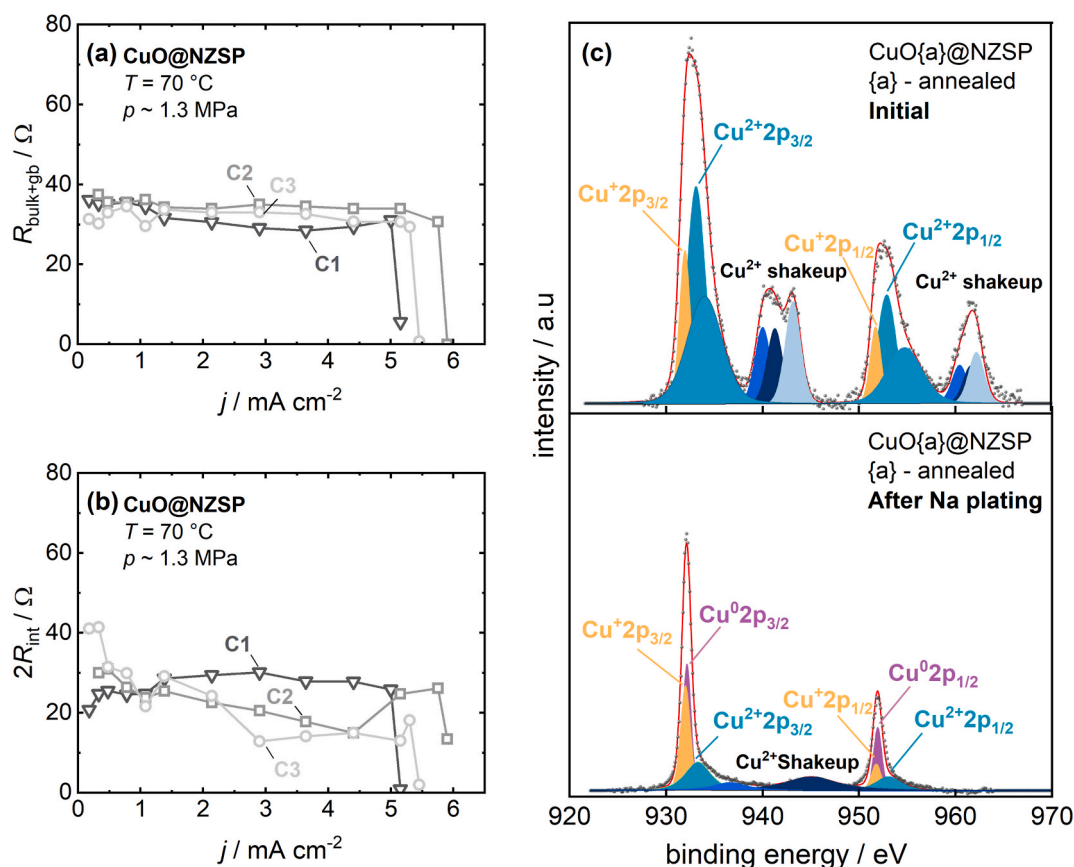


Fig. 6. Resistance values from fitted data as a function of applied current density in symmetric cells CuO@NZSP-C1 to C3, a) bulk + grain boundary resistances, b) interface resistances. c) Comparison of Cu 2p photoemission spectra of CuO{a}@NZSP before and after Na plating/stripping. All spectra were calibrated according to C 1s spectra of carbon (Binding energy = 284.8 eV).

R_{gb}), whereas the second semicircle at lower frequencies, modelled by $R_{int}|CPE$, was attributed to the total interfacial resistance contribution ($2R_{int}$). The assignment of the low-frequency semicircle to the interfacial process is also consistent with previous literature [7]. The resistance contributions, as extracted from fitted EIS data, are shown in Fig. 6. The $R_{bulk} + R_{gb}$ resistances for all three cycled cells are in good agreement with each other and also with those of the cells without interlayer (Fig. 2a), remaining almost constant throughout the experiment in the range of approx. 30–40 Ω as shown in Fig. 6a. In contrast, the interfacial resistances ($2R_{int}$, Fig. 6b) vary in the range of 20–30 Ω , presumably due to ongoing interfacial reactions during the EIS measurements, but remain lower than in the corresponding symmetric cells without interlayer (Na@NZSP-C1 to C3). Furthermore, unlike the pristine Na@NZSP cells, in which the second semicircle continuously increases over time, the semicircle at the low frequencies attributed to the total interfacial resistance ($2R_{int}$) in CuO@NZSP cells remains comparatively stable even with increasing applied current density. This indicates that the PAD-CuO interlayer primarily reduces and stabilizes the Na|NZSP interfacial resistance, while the bulk and grain boundary transport in the NZSP electrolyte remain constant. Consequently, the reduced interfacial resistances in symmetric cells containing PAD-CuO interlayer lead to higher critical current densities for NZSP. Moreover, the in situ conversion of CuO into Cu and Na₂O is proposed to form a porous, mixed electronic/ionic conductive interphase at the Na|NZSP SE interface during cycling, which improves sodium metal stripping and plating as, e. g., explained by Miao et al. [7]. Post-mortem analyses of the cycled CuO@NZSP symmetric cells showed that CuO-PAD interlayers exhibit a porous morphology, and that the products (Cu + Na₂O) resulted from the conversion of CuO at the interface can easily be wiped off from the NZSP SE surface (see Supporting Information, Figure S-14).

To reveal the conversion-reaction mechanism occurring at the PAD-CuO interface, X-ray photoelectron spectroscopy (XPS) was used to analyze CuO{a}@NZSP samples before and after sodium plating. Fig. 6c shows the high-resolution XPS spectrum (see Supporting Information, Table S-6 & S-7 for fitting results). The high-resolution Cu 2p spectrum exhibits Cu 2p_{3/2} and Cu 2p_{1/2} peaks at 933.58 eV and 953.33 eV, respectively, consistent with Cu²⁺ and thus with PAD-CuO interlayer. An impurity phase of Cu₂O was also observed at around 932.19 eV and 951.94 eV [54], indicating that the oxide layer contains copper in a mixed valence state. Two sets of shake-up satellites were also observed at 934.00 eV (S1), 940.01 eV (S2), 941.27 eV (S3), 943.15 eV (S4) and 954.15 eV (S5), 960.41 eV (S6), 961.41 eV (S7), and 962.15 eV (S8) and they were fitted as reported by Torres-Ochao et al. [54]. After sodium plating/stripping, all Cu peaks decreased in intensity, and new Cu species emerged at lower binding energy with a narrower full width at half maximum (FWHM). This suggests the formation of metallic copper. Therefore, this result can be interpreted as evidence of a conversion-reaction mechanism for the PAD-CuO interlayer when it is in contact with Na metal at the Na|NZSP interface. However, because the binding energies of Cu⁺ and Cu⁰ are very similar (932.02 eV and 932.18 eV, respectively), it is difficult to distinguish between residual Cu₂O and metallic copper in the spectrum [7].

The time-resolved impedance spectra were collected for the CuO@NZSP and CuO{a}@NZSP symmetric cells up to 455 h and 305 h, respectively. The TR-EIS spectra of the NZSP symmetric cell with as-deposited PAD-CuO interlayers (CuO@NZSP) are shown in the Supporting Information, Figure S-15a. The impedance response of freshly assembled cell shows a loop that turns inward instead of the usual semicircle or arcs. This kind of behavior may indicate that the system is not at steady state. Diffusion processes may be responsible for the inward curl at the low frequencies during interfacial changes while sodium reacts in presence of a conversion type interlayer. This phenomenon often happens when the electrochemical reactions are coupled by the formation of intermediate species absorbed on the electrode surface [55]. Post-mortem analyses of PAD-CuO interlayers with porous morphology after cycling support this hypothesis. In the

following hours of TR-EIS analysis, the impedance response shows reduced resistances from corresponding mid-frequency semicircle attributed to the interfacial resistance ($2R_{int}$) and over the time, the interfacial resistance exhibits stable behavior. Especially, in comparison to the TR-EIS of bare NZSP symmetric cell (Na@NZSP-C6 in Fig. 3a), semicircles attributed to the interfacial resistance do not expand over time, which would indicate increasing resistances, but in contrast, the interfacial resistances slightly decrease over time (Figure S-15b) to resistance values of less than 1 k Ω . Therefore, this result shows that powder aerosol deposited CuO interlayers reduce the interfacial resistance and prevent further degradation between sodium and NZSP SE.

The TR-EIS results of annealed PAD-CuO interlayers (CuO{a}@NZSP) show a similar trend, with only one semicircle followed by diffusion-limited behavior at low frequencies (see Supporting Information, Figure S-16).

Electrochemical impedance spectroscopy (EIS) is widely used to assess interfacial resistance in symmetric solid-state cells, as it isolates the behavior of a single electrolyte/metal interface without contributions from a dissimilar counter electrode [45,56]. While Zhang et al. [48] define the interfacial resistance (R_{int}) as the transport resistance across the electrode interface, distinct from the charge-transfer resistance (R_{ct}), other studies interpret R_{int} more broadly. Kasemchainan et al. [57] and Yang et al. [6] describe it as the combined impedance of the solid-electrolyte interphase (R_{SEI}), which includes degradation products and intermediate phases [58], together with R_{ct} . Under this framework, the R_{int} defined by Zhang et al. [48] corresponds to the R_{SEI} component described above. Krauskopf et al. [59] further emphasized that interfacial resistance should encompass all impedance contributions arising from the interfacial region. In NZSP interlayer studies, this value is often reported as the total R_{int} of the symmetric cell without dividing by two [6,7,60], underscoring its use as an umbrella term. We used the term “interfacial resistance” to express the resistance contributions from both interfaces ($2R_{int}$) in the symmetric cell configurations tested in this study. The variability in definitions across the literature highlights the need to explicitly state the chosen interpretation and modelling approach when evaluating interfacial resistance in solid-state systems.

In Fig. 7, the interfacial resistance contributions obtained from the

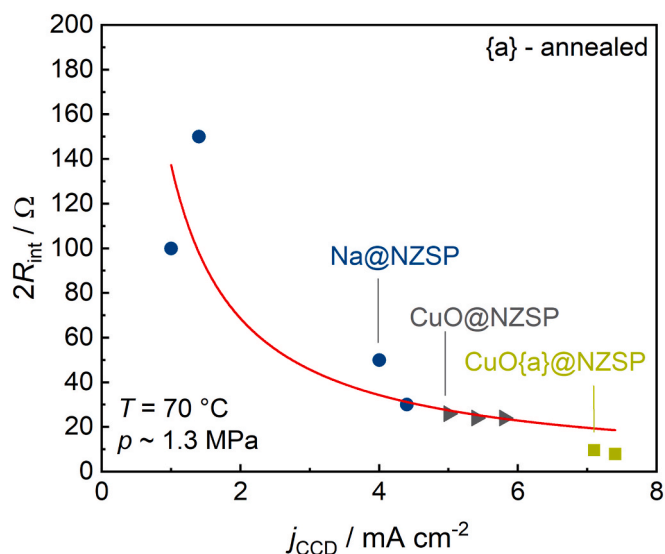


Fig. 7. Interfacial resistances of Na@NZSP, CuO@NZSP, and CuO{a}@NZSP as a function of critical current density (j_{CCD}). The data follow an inverse relation described by $R = a/j$ as dashed red-curve, consistent with relationship $R = (1/j)$ (U/A) with A being the electrode area, a voltage (U). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

impedance spectra collected at the current density immediately before the onset of overvoltage collapse (which corresponds to the critical current density) are plotted as a function of the critical current density (j_{CCD}). The experimental data points follow an inverse dependence that is well described by the fitted model $R \propto j^{-1}$ (red-line in Fig. 7) according to equation (4) below (see the Supporting Information for the derivation of the equation), where U is the voltage, A is the area, j is the current density, and R is the resistance:

$$R = \frac{1}{j} \frac{U}{A} \quad \text{Eq. 4}$$

The alignment of the interfacial resistance data with the nonlinear expression $R = a/j$ in Fig. 7 suggests enhanced Na wetting and uniform plating/stripping, leading to reduced overvoltages across a wide range of current densities. The best-fit parameter calculated to be $a = 137.8 \Omega \text{ mA cm}^{-2}$, indicating that polarization resistance scales inversely with current density and is regulated by the area-normalized voltage drop (U/A). An interfacial resistance barrier can be calculated back from the parameter a , using the area A of 0.33 cm^2 , which yields $\sim 45 \Omega$, which can be attributed to an interfacial resistance barrier to sustain relatively smooth Na plating/stripping process.

3.4. Galvanostatic long-term cycling of the symmetric cells with and without interlayers

The plating/stripping stability of NZSP SE discs was tested with the long-term cycling procedure at current densities of 0.1 mA cm^{-2} and 0.3 mA cm^{-2} . Fig. 8a–c shows long-term plating/stripping data obtained at 0.1 mA cm^{-2} of the symmetric cells Na@NZSP, CuO@NZSP, and CuO{a}@NZSP, respectively. The overvoltage gradually increases from 3.2 mV to 5.1 mV in the Na@NZSP cell without the interlayer (Fig. 8a), indicating interfacial degradation throughout the cycling [61]. In contrast, the cell CuO@NZSP exhibits initially a higher overvoltage, which decreases progressively from 62 mV to 6.5 mV. This high voltage at the initial cycles can be attributed to the conversion reaction (equation (3)) [7], that forms a mixed electron/ion conduction interphase that improves sodium ion transport across the Na|NZSP interface. Therefore, this process can be regarded as an interfacial activation [6] of the Na|PAD-CuO|NZSP interface. Plating/stripping is highly stable in the annealed symmetric cell of CuO{a}@NZSP, exhibiting a low overvoltage of $\sim 2 \text{ mV}$ at a current density of 0.1 mA cm^{-2} (Fig. 8c). Remarkably, this annealed cell shows the lowest overvoltage of $\sim 2 \text{ mV}$ and this value

remains constant from the beginning to the end of the experiment after 130 h. Fig. 8d displays all three symmetric cell configurations that cycled at 0.1 mA cm^{-2} in a zoomed-in range (110 to 120 h of cycling) to better illustrate the overvoltage responses in half cycles in both current directions. At a higher current density of 0.3 mA cm^{-2} (Fig. 8e–g), the effect of the PAD-CuO interlayer on the reduction of the interfacial resistance becomes even more pronounced. While the overvoltage during the cycling of Na@NZSP without interlayer increases from 15.1 mV to 25.4 mV (Fig. 8e), the CuO@NZSP cell exhibits an overvoltage of 10.2 mV at the end of the cycling procedure (Fig. 8f). Moreover, annealed PAD interlayers (CuO{a}@NZSP, Fig. 8g) yield highly stable plating/stripping leading to only $\sim 5.7 \text{ mV}$ overvoltage in the course of plating/stripping at the current density of 0.3 mA cm^{-2} . This value is roughly three times higher than the $\sim 2 \text{ mV}$ overpotential observed at 0.1 mA cm^{-2} .

To assess the functionality of the PAD-CuO interlayer at practical operating conditions, an additional long-term plating/stripping experiment was conducted using the annealed PAD-CuO sample (CuO{a}@NZSP) at 30°C and a current density of 0.3 mA cm^{-2} for over ten days. Fig. 8h shows a direct comparison of CuO{a}@NZSP samples cycled at 30°C and 70°C . The light green data points represent the sample cycled at 70°C , while the dark cyan long-term cycling data represents the sample cycled at 30°C . Even at 30°C , the cell still exhibited highly stable plating/stripping behavior over 10 days of cycling. Initial overvoltage response was approx. 18 mV and remained almost constant at 17.5 mV throughout the cycling procedure. The zoomed-in overvoltage response for these samples is shown in the Supporting Information (Figure S-17). This result indicates the beneficial effect of the annealed PAD-CuO interlayers under practical operating conditions.

4. Conclusions

This work demonstrates that powder aerosol deposition enables the fabrication of dense ceramic interlayers directly onto $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ solid electrolyte surfaces at room temperature without the need for solvents, binders, or high-temperature processing. We provide a promising PAD route towards scalable interphase engineering for SSSBs.

Symmetric Na@NZSP (Na|NZSP|Na) cells without an interlayer exhibited progressive interfacial degradation, revealed by TR-EIS measurements, which showed a continuous increase in interfacial resistance over time under open-circuit conditions. Therefore, the instability of the Na|NZSP interface contact was confirmed along with declining critical

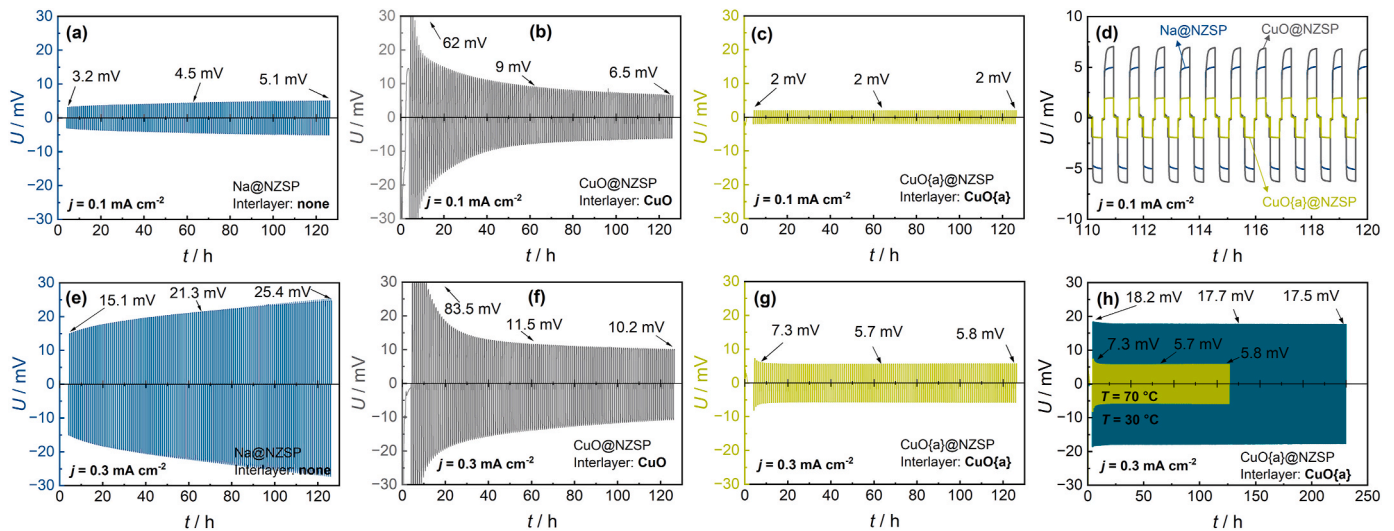


Fig. 8. Galvanostatic long-term Na plating/stripping of symmetric cells at constant current density. a) Na@NZSP, b) CuO@NZSP, and c) CuO{a}@NZSP cycled at 0.1 mA cm^{-2} . d) Enlarged timeslot from 110 to 120 h to compare the overvoltage responses of the three cell configurations shown. e) Na@NZSP, f) CuO@NZSP, and g) CuO{a}@NZSP cycled at 0.3 mA cm^{-2} . h) Comparison of CuO{a}@NZSP cycled at 70°C (for ~ 5 days) and 30°C (for ~ 10 days) at 0.3 mA cm^{-2} .

current densities during galvanostatic cycling. The CuO interlayers with a thickness of approximately 650 nm were successfully deposited by PAD on both sides of NZSP SE. Highly effective interfaces were obtained by the conversion of CuO into a mixed electronic/ionic conducting Cu + Na₂O interphase, confirmed by XPS analysis, enabling significantly reduced interfacial resistances and enhanced critical current densities up to 7.4 mA cm⁻² when thermally post-treated. The interfacial resistance values were found to follow an inverse relationship with the critical current density of NZSP SE, $R_{int} \propto 1/j_{CCD}$. Galvanostatic long-term cycling showed further stabilization with the PAD-CuO-derived interphase, supporting its beneficial role in maintaining intimate contact between sodium metal and solid electrolyte, suppressing dendrite formation, and providing uniform plating/stripping across the surface. The annealed CuO interlayer also enabled stable Na plating/stripping at 30 °C over 10 days, with relatively low overvoltages of ~18 mV remaining almost unchanged at a current density of 0.3 mA cm⁻². These results indicate that the interfacial stabilization is maintained under conditions closer to those of practical operation.

These findings show CuO as a highly promising PAD-processable interlayer for enabling stable Na-metal cycling with NZSP solid electrolytes. Owing to its low-cost, low-temperature operation, and simple equipment requirements (advantages over vapor-phase methods such as ALD and PVD), PAD also offers a practical route for scalable fabrication of such interlayers. Future studies should focus on optimizing the thermal post-treatment conditions of PAD-fabricated interlayers, particularly finding the optimal temperature where no further improvements in the critical current density or the long-term cycling stability can be observed. Further validation under longer-term, higher current density and lower-temperature cycling conditions is still needed. PAD-fabricated NZSP solid electrolytes, combined with PAD-derived interlayers and cathode composites, may represent a viable pathway towards next-generation Na solid-state batteries.

Ethical approval

Not applicable.

CRediT authorship contribution statement

Mutlucan Sozak: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. **Kim Bennet Wiedemann:** Formal analysis, Investigation, Writing – review & editing. **Ganga Sasikumar:** Formal analysis, Investigation, Writing – review & editing. **Fariza Kalyk:** Formal analysis, Validation, Writing – review & editing. **Nella M. Vargas-Barbosa:** Validation, Writing – review & editing. **Matteo Bianchini:** Validation, Writing – review & editing. **Ralf Moos:** Conceptualization, Funding acquisition, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

5. Acknowledgements

The project is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 508497297. Support by the BayBatt Cell Technology Center is gratefully acknowledged, funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – INST 91/452-1 LAGG.

The authors are grateful to the KeyLab Electron and Optical Microscopy of the Bavarian Polymer Institute (BPI) for the SEM images, and for the access to the XPS/UPS facility (PHI 5000 VersaProbe III system) at the Device Engineering KeyLab (we thank W. Reichstein for the help

with XPS analysis), to G. Jena of the Chair of Applied Mechanics and Fluid Mechanics (J. Sesterhenn) for the particle size distribution measurements, to the Chair of Metals and Alloys (U. Glatzel) for enabling the XRD measurements, to Dr. Martin Hämmerle for proofreading and valuable remarks, to Lukas Hennerici M.Sc., Daniel Paulus M.Sc., Nils Donker M.Sc., Jürgen Schneider M.Sc., Dr.-Ing. Daniela Schönauer-Kamin, Dr.-Ing. Jaroslaw Kita for insightful discussions and their help with analytical instruments, to Monika Daubinger for the instructions on sample preparation devices (cutting, polishing).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2026.240631>.

Data availability

Data will be made available on request.

References

- [1] B.L. Ellis, L.F. Nazar, Sodium and sodium-ion energy storage batteries, *Curr. Opin. Solid State Mater. Sci.* 16 (2012) 168–177, <https://doi.org/10.1016/j.cossms.2012.04.002>.
- [2] M. Guin, F. Tietz, Survey of the transport properties of sodium superionic conductor materials for use in sodium batteries, *J. Power Sources* 273 (2015) 1056–1064, <https://doi.org/10.1016/j.jpowsour.2014.09.137>.
- [3] H.-P. Hong, Crystal structures and crystal chemistry in the system Na_{1+x}Zr₂Si_xP_{3-x}O₁₂, *Mater. Res. Bull.* 11 (1976) 173–182, [https://doi.org/10.1016/0025-5408\(76\)90073-8](https://doi.org/10.1016/0025-5408(76)90073-8).
- [4] Z. Zhang, S. Wenzel, Y. Zhu, J. Sann, L. Shen, J. Yang, X. Yao, Y.-S. Hu, C. Wolverton, H. Li, et al., Na₃Zr₂Si₂PO₁₂: a stable Na⁺-ion solid electrolyte for solid-state batteries, *ACS Appl. Energy Mater.* 3 (2020) 7427–7437, <https://doi.org/10.1021/acsaelm.0c00820>.
- [5] E. Matios, H. Wang, C. Wang, X. Hu, X. Lu, J. Luo, W. Li, Graphene regulated ceramic electrolyte for solid-state sodium metal battery with superior electrochemical stability, *ACS Appl. Mater. Interfaces* 11 (2019) 5064–5072, <https://doi.org/10.1021/acsami.8b19519>.
- [6] J. Yang, Z. Gao, T. Ferber, H. Zhang, C. Guhl, L. Yang, Y. Li, Z. Deng, P. Liu, C. Cheng, et al., Guided-formation of a favorable interface for stabilizing Na metal solid-state batteries, *J. Mater. Chem. A* 8 (2020) 7828–7835, <https://doi.org/10.1039/D0TA01498B>.
- [7] R. Miao, C. Wang, D. Li, C. Sun, J. Li, H. Jin, Uniform Na metal plating/stripping design for highly reversible solid-state Na metal batteries at room temperature, *Small* 18 (2022) e2204487, <https://doi.org/10.1002/sml.202204487>.
- [8] D. Li, X. Wang, Q. Guo, X. Yu, S. Cen, H. Ma, J. Chen, D. Wang, Z. Mao, C. Dong, Atomically bonding Na anodes with metallized ceramic electrolytes by ultrasound welding for high-energy/power solid-state sodium metal batteries, *Carbon Energy* 5 (2023) e299, <https://doi.org/10.1002/cey2.299>.
- [9] S. Wenzel, T. Leichtweiss, D.A. Weber, J. Sann, W.G. Zeier, J. Janek, Interfacial reactivity benchmarking of the sodium ion conductors Na₃PS₄ and sodium β-Alumina for protected sodium metal anodes and sodium all-solid-state batteries, *ACS Appl. Mater. Interfaces* 8 (2016) 28216–28224, <https://doi.org/10.1021/acsami.6b10119>.
- [10] Le Xiang, X. Li, J. Xiao, L. Zhu, X. Zhan, Interface issues and challenges for NASICON-based solid-state sodium-metal batteries, *Adv. Powder Mater.* (2024) 100181, <https://doi.org/10.1016/j.jpamate.2024.100181>.
- [11] C. Guhl, P. Kehne, Q. Ma, F. Tietz, P. Komissinskiy, W. Jaegermann, R. Hausbrand, Interfaces in solid-state sodium-ion batteries: NaCoO₂ thin films on solid electrolyte substrates, *Electrochim. Acta* 268 (2018) 226–233, <https://doi.org/10.1016/j.electacta.2018.02.109>.
- [12] C. Zhao, L. Liu, X. Qi, Y. Lu, F. Wu, J. Zhao, Y. Yu, Y.-S. Hu, L. Chen, Solid-state sodium batteries, *Adv. Energy Mater.* 8 (2018) 1703012, <https://doi.org/10.1002/aenm.201703012>.
- [13] X. Xiang, C. Du, R. Zhao, Z. Zhao, X. Ji, D. Liu, Z. Li, H. Wang, Y. Zhang, Y. Zhao, et al., Enhancing ion transport and suppressing electron conduction: a hybrid interlayer for stable garnet-based solid-state batteries, *Adv. Funct. Mater.* 35 (2025) 2426002, <https://doi.org/10.1002/adfm.202426002>.
- [14] J. Yang, H. Xu, J. Wu, Z. Gao, F. Hu, Y. Wei, Y. Li, D. Liu, Z. Li, Y. Huang, Improving Na/Na₃Zr₂Si₂PO₁₂ interface via SnO₂/Sn film for high-performance solid-state sodium metal batteries, *Small Methods* 5 (2021) e2100339, <https://doi.org/10.1002/smid.202100339>.
- [15] G. Deysher, Y.-T. Chen, B. Sayahpour, S.W.-H. Lin, S.-Y. Ham, P. Ridley, A. Cronk, E.A. Wu, D.H.S. Tan, J.-M. Doux, et al., Evaluating electrolyte-anode interface stability in sodium all-solid-state batteries, *ACS Appl. Mater. Interfaces* 14 (2022) 47706–47715, <https://doi.org/10.1021/acsami.2c12759>.
- [16] M. Moorthy, B. Moorthy, B.K. Ganesan, A. Saha, S. Yu, D.-H. Kim, S. Hong, S. Park, K. Kang, R. Thangavel, et al., A series of hybrid multifunctional interfaces as artificial SEI layer for realizing dendrite free, and long-life sodium metal anodes, *Adv. Funct. Mater.* (2023) 2300135, <https://doi.org/10.1002/adfm.202300135>.

- [17] X. Lv, F. Tang, Y. Yao, C. Xu, D. Chen, L. Liu, Y. Feng, X. Rui, Y. Yu, Sodium–gallium alloy layer for fast and reversible sodium deposition, *SusMat* 2 (2022) 699–707, <https://doi.org/10.1002/sus2.97>.
- [18] L.E. Goodwin, P. Till, M. Bhardwaj, N. Nazer, P. Adelhelm, F. Tietz, W.G. Zeier, F. H. Richter, J. Janek, Protective NaSICON interlayer between a sodium–tin alloy anode and sulfide-based solid electrolytes for all-solid-state sodium batteries, *ACS Appl. Mater. Interfaces* (2023), <https://doi.org/10.1021/acsami.3c09256>.
- [19] W. Kong, Z. Jiang, Y. Liu, Q. Han, L.-X. Ding, S. Wang, H. Wang, Stabilizing $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [Li metal anode interface in solid-state batteries by kevlar aramid nanofiber-based protective coating, *Adv. Funct. Mater.* (2023) 2306748, <https://doi.org/10.1002/adfm.202306748>.
- [20] L. Duchène, A. Remhof, H. Hagemann, C. Battaglia, Status and prospects of hydroborate electrolytes for all-solid-state batteries, *Energy Storage Mater.* 25 (2020) 782–794, <https://doi.org/10.1016/j.ensm.2019.08.032>.
- [21] Y. Li, Z. Wang, C. Sun, S. Liu, Y. Dou, X. Yuan, H. Jin, Y. Zhao, Na-K interlayer driven Na-NASICON solid-state batteries, *Adv. Funct. Mater.* 35 (2025) 2425995, <https://doi.org/10.1002/adfm.202425995>.
- [22] D. Kitsche, Y. Tang, H. Hemmelmann, F. Walther, M. Bianchini, A. Kondrakov, J. Janek, T. Brezesinski, Atomic layer deposition derived zirconia coatings on Ni-rich cathodes in solid-state batteries: correlation between surface constitution and cycling performance, *Small Sci.* 3 (2023) 2200073, <https://doi.org/10.1002/smssc.202200073>.
- [23] Y. Liu, Q. Sun, Y. Zhao, B. Wang, P. Kaghazchi, K.R. Adair, R. Li, C. Zhang, J. Liu, L.-Y. Kuo, et al., Stabilizing the interface of NASICON solid electrolyte against Li metal with atomic layer deposition, *ACS Appl. Mater. Interfaces* 10 (2018) 31240–31248, <https://doi.org/10.1021/acsami.8b06366>.
- [24] S. Lobe, A. Bauer, S. Uhlenbruck, D. Fattakhova-Rohlfing, Physical vapor deposition in solid-state battery development: from materials to devices, *Adv. Sci.* 8 (2021) e2002044, <https://doi.org/10.1002/adv.202002044>.
- [25] M. Xu, J. Yu, Y. Song, R. Ran, W. Wang, Z. Shao, Advances in ceramic thin films fabricated by pulsed laser deposition for intermediate-temperature solid oxide fuel cells, *Energy Fuels* 34 (2020) 10568–10582, <https://doi.org/10.1021/acs.energyfuels.0c02338>.
- [26] Q. Guo, X. Wang, M. Fu, X. Yu, J. Chen, D. Wang, C. Dong, Z. Mao, The effect of polished surface microstructure of ceramic electrolyte on solid-state sodium metal batteries, *Ceram. Int.* (2023), <https://doi.org/10.1016/j.ceramint.2023.08.195>.
- [27] X. Wang, J. Chen, D. Wang, Z. Mao, Improving the alkali metal electrode/inorganic solid electrolyte contact via room-temperature ultrasound solid welding, *Nat. Commun.* 12 (2021) 7109, <https://doi.org/10.1038/s41467-021-27473-4>.
- [28] J. Akedo, Aerosol deposition of ceramic thick films at room temperature: densification mechanism of ceramic layers, *J. Am. Ceram. Soc.* 89 (2006) 1834–1839, <https://doi.org/10.1111/j.1551-2916.2006.01030.x>.
- [29] M. Sozak, S. Knies, M. Bianchini, R. Moos, Room temperature fabrication of Binder-free $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ high-loading electrode films via the powder aerosol deposition method, *Batter. Supercaps* 9 (2026) e202500902, <https://doi.org/10.1002/batt.202500902>.
- [30] J. Akedo, Aerosol deposition method for fabrication of nano crystal ceramic layer, *MSF* 449–452 (2004) 43–48, <https://doi.org/10.4028/www.scientific.net/MSF.449-452.43>.
- [31] D. Hanft, J. Exner, M. Schubert, T. Stöcker, P. Fuierer, R. Moos, An overview of the aerosol deposition method: process fundamentals and new trends in materials applications, *J. Ceram. Sci. Technol.* 6 (2015) 147–182, <https://doi.org/10.4416/JCST2015-00018>.
- [32] T. Nazareus, Y. Sun, J. Exner, J. Kita, R. Moos, Powder aerosol deposition as a method to produce garnet-type solid ceramic electrolytes: a study on electrochemical film properties and industrial applications, *Energy Technol.* 9 (2021) 2100211, <https://doi.org/10.1002/ente.202100211>.
- [33] M. Sozak, T. Nazareus, J. Exner, J. Kita, R. Moos, Room temperature manufacture of dense NASICON solid electrolyte films for all-solid-state-sodium batteries, *J. Mater. Sci.* 58 (2023) 10108–10119, <https://doi.org/10.1007/s10853-023-08642-w>.
- [34] Z. Gao, J. Yang, H. Yuan, H. Fu, Y. Li, Y. Li, T. Ferber, C. Gohl, H. Sun, W. Jaegermann, et al., Stabilizing $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}/\text{Na}$ interfacial performance by introducing a clean and Na-Deficient surface, *Chem. Mater.* 32 (2020) 3970–3979, <https://doi.org/10.1021/acs.chemmater.0c00474>.
- [35] M. Guin, S. Indris, M. Kaus, H. Ehrenberg, F. Tietz, O. Guillon, Stability of NASICON materials against water and CO_2 uptake, *Solid State Ionics* 302 (2017) 102–106, <https://doi.org/10.1016/j.ssi.2016.11.006>.
- [36] J. Exner, T. Nazareus, D. Hanft, J. Kita, R. Moos, What happens during thermal post-treatment of powder aerosol deposited functional ceramic films? Explanations based on an experiment-enhanced literature survey, *Adv. Mater.* 32 (2020) 1908104, <https://doi.org/10.1002/adma.201908104>.
- [37] F. Kalyk, L. Pescara, M. Drüschler, N.M. Vargas-Barbosa, Toward robust ionic conductivity determination of sulfide-based solid electrolytes for solid-state batteries, *Adv. Funct. Mater.* (2025) e09479, <https://doi.org/10.1002/adfm.202509479>.
- [38] EL-CELL | EL-Cell GmbH, PAT-cell | cableless 3-electrode battery test cell, Verfügbar unter, [https://www.el-cell.com/products/test-cells/standard-test-cells/pat-cell/\(Aufgerufenam, 2016. \(Accessed 18 September 2025\)\)](https://www.el-cell.com/products/test-cells/standard-test-cells/pat-cell/(Aufgerufenam, 2016. (Accessed 18 September 2025))).
- [39] Y. Li, Z. Sun, C. Sun, H. Jin, Y. Zhao, Exploring the origin of ZrO_2 phase in $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ceramic electrolyte, *Ceram. Int.* 49 (2023) 3094–3098, <https://doi.org/10.1016/j.ceramint.2022.11.084>.
- [40] A. Jalilian-Khakhshour, C.O. Phillips, L. Jackson, T.O. Dunlop, S. Margadonna, D. Deganello, Solid-state synthesis of NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) using nanoparticle precursors for optimisation of ionic conductivity, *J. Mater. Sci.* 55 (2020) 2291–2302, <https://doi.org/10.1007/s10853-019-04162-8>.
- [41] R. Fuentes, Reaction of NASICON with water, *Solid State Ionics* 139 (2001) 309–314, [https://doi.org/10.1016/S0167-2738\(01\)00683-X](https://doi.org/10.1016/S0167-2738(01)00683-X).
- [42] I.-S. Jang, W. Go, B.-Y. Song, H. Park, Y.C. Kang, J. Chun, Improving ionic conductivity of von-alpen-type NASICON ceramic electrolytes via magnesium doping, *J. Adv. Ceram.* (2023), <https://doi.org/10.26599/JAC.2023.9220738>.
- [43] P. Vadhva, J. Hu, M.J. Johnson, R. Stocker, M. Braglia, D.J.L. Brett, A.J.E. Rettie, Electrochemical impedance spectroscopy for all-solid-state batteries: theory, methods and future outlook, *Chemelectrochem* 8 (2021) 1930–1947, <https://doi.org/10.1002/celc.202100108>.
- [44] K. Lee, E. Kazyak, M.J. Wang, N.P. Dasgupta, J. Sakamoto, Analyzing void formation and rewetting of thin in situ-formed Li anodes on LLZO, *Joule* 6 (2022) 2547–2565, <https://doi.org/10.1016/j.joule.2022.09.009>.
- [45] T. Krauskopf, H. Hartmann, W.G. Zeier, J. Janek, Toward a fundamental understanding of the lithium metal anode in solid-state Batteries-An Electrochemo-Mechanical study on the garnet-type solid electrolyte $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, *ACS Appl. Mater. Interfaces* 11 (2019) 14463–14477, <https://doi.org/10.1021/acsami.9b02537>.
- [46] T. Fuchs, C.G. Haslam, F.H. Richter, J. Sakamoto, J. Janek, Evaluating the use of critical current density tests of symmetric lithium transference cells with solid electrolytes, *Adv. Energy Mater.* (2023) 2302383, <https://doi.org/10.1002/aenm.202302383>.
- [47] Y. Lu, C.-Z. Zhao, H. Yuan, X.-B. Cheng, J.-Q. Huang, Q. Zhang, Critical current density in solid-state lithium metal batteries: mechanism, influences, and strategies, *Adv. Funct. Mater.* 31 (2021) 2009925, <https://doi.org/10.1002/adfm.202009925>.
- [48] L. Zhang, Y. Dai, C. Li, Y. Dang, R. Zheng, Z. Wang, Y. Wang, Y. Cui, H. Arandiyán, Z. Shao, et al., Recent advances in electrochemical impedance spectroscopy for solid-state batteries, *Energy Storage Mater.* (2024) 103378, <https://doi.org/10.1016/j.ensm.2024.103378>.
- [49] R.J.-Y. Park, C.M. Eschler, C.D. Fincher, A.F. Badel, P. Guan, M. Pharr, B. W. Sheldon, W.C. Carter, V. Viswanathan, Y.-M. Chiang, Semi-solid alkali metal electrodes enabling high critical current densities in solid electrolyte batteries, *Nat. Energy* 6 (2021) 314–322, <https://doi.org/10.1038/s41560-021-00786-w>.
- [50] S. Wang, H. Xu, W. Li, A. Dolocan, A. Manthiram, Interfacial chemistry in solid-state batteries: formation of interphase and its consequences, *J. Am. Chem. Soc.* 140 (2018) 250–257, <https://doi.org/10.1021/jacs.7b09531>.
- [51] D.-W. Lee, H.-J. Kim, Y.-H. Kim, Y.-H. Yun, S.-M. Nam, Growth process of $\alpha\text{-Al}_2\text{O}_3$ ceramic films on metal substrates fabricated at room temperature by aerosol deposition, *J. Am. Ceram. Soc.* 94 (2011) 3131–3138, <https://doi.org/10.1111/j.1551-2916.2011.04493.x>.
- [52] J. Exner, M. Schubert, D. Hanft, J. Kita, R. Moos, How to treat powders for the room temperature aerosol deposition method to avoid porous, low strength ceramic films, *J. Eur. Ceram. Soc.* 39 (2019) 592–600, <https://doi.org/10.1016/j.jeurceramsoc.2018.08.008>.
- [53] R. Sreedharan, M. Mohan, S. Saini, A. Roy, K. Bhattacharjee, Intermediate Cu-O-Si phase in the $\text{Cu-SiO}_2/\text{Si}(111)$ system: growth, elemental, and electrical studies, *ACS Omega* 6 (2021) 23826–23836, <https://doi.org/10.1021/acsomega.1c02646>.
- [54] J.A. Torres-Ochoa, D. Cabrera-German, O. Cortazar-Martinez, M. Bravo-Sanchez, G. Gomez-Sosa, A. Herrera-Gomez, Peak-fitting of Cu 2p photoemission spectra in Cu^0 , Cu^{1+} , and Cu^{2+} oxides: a method for discriminating Cu^0 from Cu^{1+} , *Appl. Surf. Sci.* 622 (2023) 156960 <https://doi.org/10.1016/j.apsusc.2023.156960>.
- [55] A.C. Lazanas, M.I. Prodromidis, Electrochemical Impedance Spectroscopy-A tutorial, *ACS Meas. Sci. Au* 3 (2023) 162–193, <https://doi.org/10.1021/acsmesuresciau.2c00070>.
- [56] A.R.C. Bredar, A.L. Chown, A.R. Burton, B.H. Farnum, Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications, *ACS Appl. Energy Mater.* 3 (2020) 66–98, <https://doi.org/10.1021/acsaem.9b01965>.
- [57] J. Kasemchainan, S. Zekoll, D. Spencer Jolly, Z. Ning, G.O. Hartley, J. Marrow, P. G. Bruce, Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells, *Nat. Mater.* 18 (2019) 1105–1111, <https://doi.org/10.1038/s41563-019-0438-9>.
- [58] P. Verma, P. Maire, P. Novák, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta* 55 (2010) 6332–6341, <https://doi.org/10.1016/j.electacta.2010.05.072>.
- [59] T. Krauskopf, B. Mogwitz, H. Hartmann, D.K. Singh, W.G. Zeier, J. Janek, The fast charge transfer kinetics of the lithium metal anode on the garnet-type solid electrolyte $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, *Adv. Energy Mater.* 10 (2020) 2000945, <https://doi.org/10.1002/aenm.202000945>.
- [60] Z. Yang, L. Chen, H. Jiang, X. Liang, J. Wei, Z. Xie, B. Tang, Z. Zhou, SnF_2 -induced highly current-tolerant solid electrolytes for solid-state sodium batteries, *Adv. Funct. Mater.* 33 (2023) 2306558, <https://doi.org/10.1002/adfm.202306558>.
- [61] Z. Yan, Symmetric cells as an analytical tool for battery research: Assembly, operation, and data analysis strategies, *J. Electrochem. Soc.* 170 (2023) 20521, <https://doi.org/10.1149/1945-7111/acaf42>.