



Quantitative separation of thermal and electrochemical contributions in nonlinear EIS measurements

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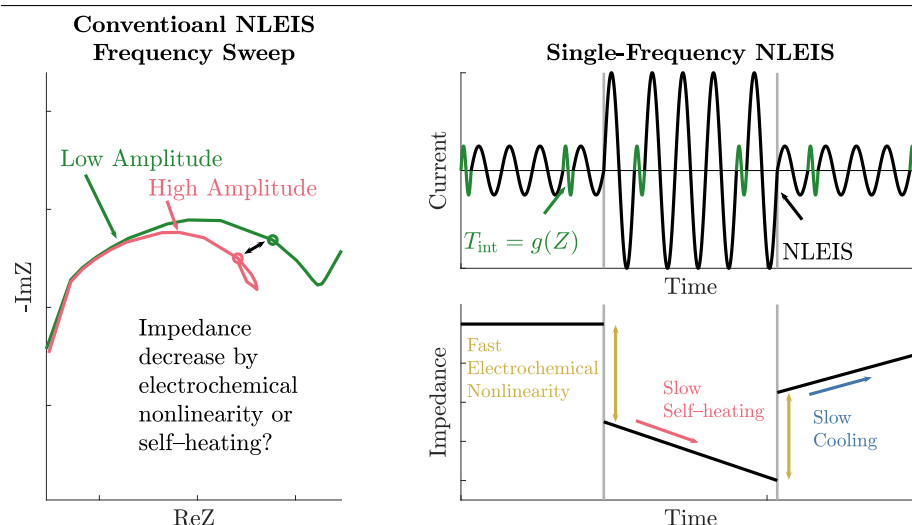
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HIGHLIGHTS

- Electrochemical nonlinearity responds fast to excitation.
- Thermal effects evolve gradually on the thermal time constant.
- Nonlinear response is temperature-dependent and most pronounced at low temperatures.
- Linear response up to 280 mV challenges conventional 20 mV criterion.

GRAPHICAL ABSTRACT



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ABSTRACT

Impedance decrease during high-current excitation as in Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) can arise from electrochemical nonlinearity, self-heating, or both. We developed two measurement protocols separating these contributions by exploiting distinct time scales: electrochemical nonlinearity responds quickly, while self-heating evolves slowly. The first protocol extends NLEIS frequency sweeps with auxiliary 1 kHz measurements for continuous internal temperature tracking via impedance phase. The second protocol employs single-frequency measurements with alternating excitation amplitudes, enabling direct observation of fast versus slow impedance changes. Experiments on a 3.5 Ah cylindrical lithium nickel manganese cobalt oxide (NMC) cell quantify contributions: at 5 °C and 10 Hz, impedance decrease is entirely electrochemical at 0.57C, while at 2.57C, temperature dependence contributes 15% and electrochemical nonlinearity 85%. At 25 °C, the cell remained linear. The widely-adopted 20 mV linearity criterion may be too strict: we observed linear behavior up to 280 mV, 14 times the threshold.

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Nomenclature**Acronyms**

CPE	Constant Phase Element
ECM	Equivalent Circuit Model
EIS	Electrochemical Impedance Spectroscopy
KK	Kramers–Kronig
NFRA	Nonlinear Frequency Response Analysis
NLEIS	Nonlinear Electrochemical Impedance Spectroscopy
NMC	Lithium Nickel Manganese Cobalt Oxide
OCV	Open Circuit Voltage
RMS	Root Mean Square
SoC	State of Charge
SoH	State of Health
THD	Total Harmonic Distortion

Variables

$\arg Z$	Impedance phase ($^{\circ}$)
β	Warburg exponent
Δt	Transition time (s)
ΔT	Temperature change (K)
$\Delta \text{Re}Z_{\text{II} \rightarrow \text{III}}$	Real impedance change at step transition during single-frequency NLEIS (Ω)
$\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$	Real impedance change at step transition during single-frequency NLEIS (Ω)
η_{ct}	Voltage drop across charge-transfer resistance (V)
f_{SF}	NLEIS excitation frequency (Hz)
Γ	Distortion amplification factor
γ	Warburg phase parameter
$\text{Im}Z$	Imaginary part of impedance (Ω)
ω	Angular frequency (rad s^{-1})
R_{ct}	Charge-transfer resistance (Ω)
$\text{Re}Z$	Real part of impedance (Ω)
σ	Warburg coefficient (Ω/s^{β})
$S_{Z,T}$	Sensitivity of impedance feature with respect to temperature
THD	Total harmonic distortion (%)
T_{int}	Internal cell temperature ($^{\circ}\text{C}$)
$ V_1 $	First harmonic magnitude of cell voltage response (V)
$ V_2 $	Second harmonic magnitude of cell voltage response (V)
$ V_3 $	Third harmonic magnitude of cell voltage response (V)
c	Specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
E_a	Activation energy (kJ mol^{-1})
f	Frequency (Hz)
I	RMS current (A)
i_{exc}	Excitation current (A and C-rate)
i_{req}	Current required to produce ΔT in Δt (A)
j	Imaginary unit
L_0	Inductance (H)

m	Mass (kg)
n	Constant phase element exponent
Q	Cell capacity (Ah)
Q_{th}	Thermal energy (J)
Q_{dl}	Constant phase element coefficient (F/s^{1-n})
R_{gas}	Gas constant ($\text{J K}^{-1} \text{mol}$)
R_0	Ohmic resistance (Ω)
R_{th}	Thermal resistance (K W^{-1})
T	Temperature ($^{\circ}\text{C}$)
Z_{W}	Warburg impedance (Ω)

charge-transfer kinetics and diffusion, depend nonlinearly on state variables such as concentration, temperature, and potential [1–4]. Despite this fundamental nonlinearity, Electrochemical Impedance Spectroscopy (EIS), a technique based on linear system theory, is widely used for battery characterization and state estimation [5–8].

Impedance, defined as the frequency-dependent ratio of voltage response to current excitation, is mathematically valid only when the battery is operated within its linear regime. To satisfy this linearity requirement, the EIS excitation current must be sufficiently small that the voltage response remains proportional to the applied excitation. This small-signal approximation linearizes the nonlinear characteristics around a specific operating point, capturing only linear dynamics while systematically discarding information about higher-order nonlinear behavior. However, the boundary between linear and nonlinear regimes remains poorly defined, creating challenges for experimental design and data interpretation. Potentially valuable information encoded in the nonlinear electrochemical response might be systematically overlooked, limiting our ability to fully characterize battery behavior.

The most widely-adopted linearity criterion in battery research specifies a maximum peak cell voltage response of 20 mV [9–16]. Alternative approaches for assessing linearity include Lissajous plots, Kramers–Kronig (KK) relations, and distortion analysis of the cell voltage response. Lissajous plots provide qualitative assessment by plotting excitation current versus voltage response in the time domain; linear systems produce perfect ellipses, while nonlinear behavior manifests as distorted ellipses [10,17]. The KK relations, which mathematically connect the real and imaginary components of impedance for linear, causal, and stable systems, enable validation by comparing measured spectra with KK-transformed data [18–21]. Randomly distributed residuals with zero mean indicate linear system behavior. However, both Lissajous plots and KK tests lack standardized quantitative thresholds for systematic comparison.

A quantitative metric is the Total Harmonic Distortion (THD), defined as the ratio of the Root Mean Square (RMS) magnitude of higher harmonics to the first harmonic magnitude:

$$\text{THD} = \frac{\sqrt{\sum_{n=2}^N |Y_n|^2}}{|Y_1|} \cdot 100\%, \quad (1)$$

where Y_n represents the magnitude of the n -th harmonic and N is the highest harmonic considered. A THD below 1% of the cell voltage response has been proposed as a linearity threshold [9,10].

A critical limitation of THD, when monitoring only response signal distortion, is its sensitivity to nonlinearities from any source, not exclusively from electrochemical processes in the cell. For example, amplifier nonlinearity can introduce harmonics in the excitation signal that are indistinguishable from electrochemical harmonics without proper verification [17].

1. Introduction

Batteries exhibit inherently nonlinear current–voltage characteristics due to electrochemical processes. These processes, including

Nonlinear Electrochemical Impedance Spectroscopy (NLEIS)

When excitation amplitudes exceed linear regime thresholds, batteries exhibit nonlinear behavior characterized by harmonic distortion in the voltage response. Measurement techniques that operate in this regime and exploit nonlinear characteristics are collectively termed Nonlinear Frequency Response Analysis (NFRA) or Nonlinear Electrochemical Impedance Spectroscopy (NLEIS). When specifically targeting second-harmonic responses, the term 2nd-NLEIS is used [1, 9,22]. Throughout this study, we use NLEIS to include all nonlinear impedance techniques.

A characteristic feature of NLEIS is the decrease in impedance magnitude with increasing excitation amplitude, particularly in the frequency range associated with charge-transfer processes [15,23–27]. Two distinct mechanisms can contribute to this amplitude-dependent impedance decrease. First, intrinsic electrochemical nonlinearity arises from the nonlinear relationship between current and overpotential described by the Butler–Volmer equation. At sufficiently high currents, overpotential saturates and no longer scales linearly with current, effectively decreasing the charge-transfer resistance R_{ct} . Second, self-heating effects occur because Joule heating (proportional to the square of current amplitude) increases internal cell temperature, which in turn decreases impedance [28,29].

Physics-based modeling frameworks have demonstrated fundamental relationships between electrochemical parameters and nonlinear responses [1–4]. These models typically incorporate charge-transfer nonlinearity, diffusion nonlinearity, and open circuit voltage nonlinearity [1–4,15,26,30–37]. However, only Zhu et al. modeled thermal effects [26], limiting the ability to distinguish electrochemical nonlinearity from self-heating in most modeling frameworks.

The relative contributions of electrochemical nonlinearity versus self-heating to the observed impedance decrease in experimental studies remain controversial, with different studies reaching contradictory conclusions. Huang et al. observed up to 66% decrease in R_{ct} for a commercial 1 Ah cell at -10°C when increasing excitation amplitude from 0.01 to $0.7C_{RMS}$ [24]. With measured temperature changes below 1.5 K, they attributed the impedance decrease primarily to charge-transfer nonlinearity. Similarly, Zhu et al. reported 70% decrease in R_{ct} for an 8 Ah prismatic cell at -20°C when excitation increased from 0.1 to $1.4C_{RMS}$, observing surface temperature increases of 1.4 K [26]. They too concluded that self-heating contributions were negligible compared to electrochemical nonlinearity.

In contrast, Andre et al. attributed impedance decrease in a 6.5 Ah cylindrical cell at -30°C primarily to self-heating, despite measuring only 0.4 K surface temperature increase at $0.11C_{RMS}$ [27]. They argued that inhomogeneous temperature distributions result in significantly higher internal temperatures than surface measurements indicate.

This disagreement highlights a critical methodological limitation: surface temperature measurements inadequately characterize internal thermal states during NLEIS. Substantial temperature gradients exist between cell core and surface, as well as across different surface locations, during operation [38–48]. The resulting ambiguity in mechanism attribution undermines the physical interpretation of NLEIS data and limits the technique's utility for quantitative battery characterization. Without methods to track internal temperature evolution during high-amplitude impedance measurements, impedance decrease cannot be unambiguously attributed to electrochemical nonlinearity, thermal effects, or their coupled interaction.

Knowledge gap and motivation for this study

Our literature analysis reveals a significant knowledge gap that limits the interpretation and comparability of NLEIS for battery characterization:

The relative contributions of electrochemical nonlinearity versus thermally-induced to observed impedance decrease during NLEIS remain unclear. Contradictory conclusions in literature stem from a fundamental methodological limitation: surface temperature measurements inadequately characterize internal thermal states during high-amplitude excitation. Without methods to track internal temperature evolution during NLEIS, impedance decrease cannot be unambiguously attributed to electrochemical nonlinearity, thermal effects, or their coupled interaction. No previous study has combined internal temperature measurements with NLEIS to separate these contributions experimentally.

To address this knowledge gap, we present two complementary experimental protocols (Section 2) enabling separation and quantification of electrochemical nonlinearity and thermally-induced effects during NLEIS. By combining EIS-based internal temperature estimation with systematic NLEIS characterization, we provide unambiguous attribution of impedance decrease with current amplitude. Furthermore, we establish signal validation procedures to distinguish electrochemical nonlinearities from instrumental artifacts. Based on our experimental results (Section 4), we develop practical recommendations for high-quality impedance measurements that maximize signal-to-noise ratio while ensuring valid linear system identification.

2. Methods

To quantify and separate electrochemical nonlinearity from thermally-induced effects during NLEIS, we developed two complementary experimental protocols. Both methods exploit the distinct time scales of these phenomena: electrochemical nonlinearity responds quickly to applied excitation, whereas self-heating evolves slowly according to the cell's thermal time constant. For cylindrical 18650 cells, thermal time constants in the range of several minutes have been reported [49–52], enabling temporal separation of these contributions. By monitoring impedance evolution over time while simultaneously tracking internal cell temperature, we can decouple these two effects.

2.1. Modified NLEIS sweep with internal cell temperature tracking

The first method extends conventional EIS frequency sweeps with additional auxiliary measurements to continuously track internal cell temperature evolution during high-amplitude excitation.

In conventional EIS measurements, excitation frequency is typically swept monotonically from high to low frequencies. Cumulative Joule heating progressively increases the internal cell temperature T_{int} , particularly at low frequencies, where longer measurement times and higher impedance magnitudes result in greater energy dissipation. Since both self-heating and nonlinear electrochemical effects decrease impedance magnitude, their contributions cannot be separated without additional information.

Our intermittent protocol addresses this limitation by performing auxiliary impedance measurements at 1 kHz throughout the frequency sweep using low-amplitude excitation to ensure linear cell response. Fig. 1(a) illustrates the measurement sequence, showing a segment of the excitation current (top) and the complete measurement frequency schedule (bottom) with 141 s measurement duration.

We exploit the temperature sensitivity of impedance phase at 1 kHz for internal temperature estimation [28]. The change in internal cell temperature ΔT_{int} is calculated from the change in negative impedance phase $\Delta -\arg Z$ according to:

$$\Delta T_{int} = \frac{\Delta -\arg Z}{S_{-\arg Z,T}}, \quad (2)$$

where $S_{-\arg Z,T}$ is the temperature sensitivity coefficient of the negative impedance phase in $^\circ\text{K}^{-1}$, determined through prior calibration measurements across the operating temperature range.

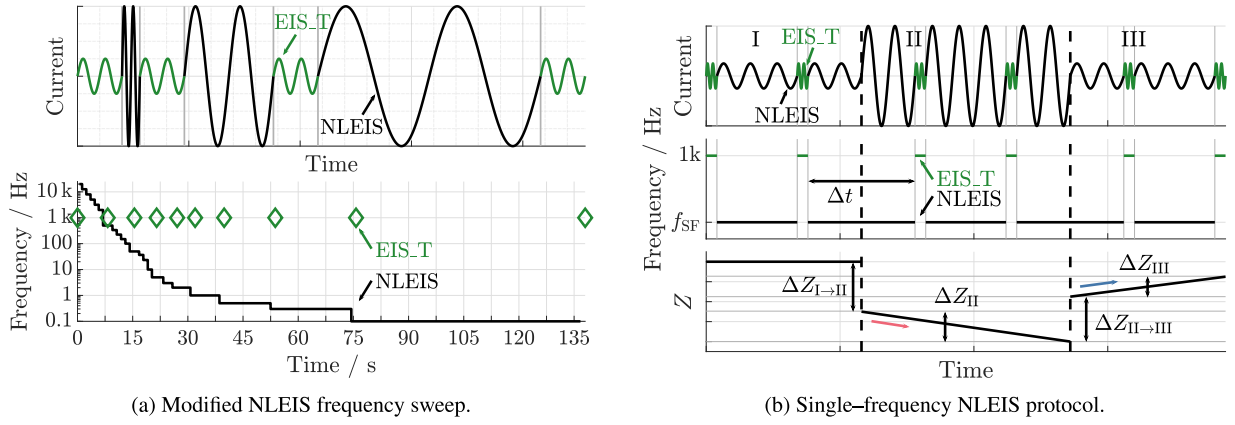


Fig. 1. Schematic illustration of proposed Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) measurement methods for separating electrochemical from thermal nonlinearities based on their distinct temporal signatures. **(a)** Modified NLEIS frequency sweep (NLEIS) with intermittent auxiliary frequency measurements (EIS.T) enabling internal cell temperature estimation via impedance phase. **(b)** Single-frequency NLEIS protocol: the cell is sequentially excited with low (Step I), high (Step II), and low (Step III) amplitude at a single frequency. Periodic auxiliary Electrochemical Impedance Spectroscopy (EIS) measurements track internal cell temperature evolution. Electrochemical nonlinearity produces fast impedance change $\Delta Z_{I \rightarrow II}$ and $\Delta Z_{II \rightarrow III}$ upon amplitude switching between steps, while self-heating causes slow impedance decrease ΔZ_{II} during sustained high-amplitude excitation (Step II) and slow impedance increase ΔZ_{III} during passive cooling (Step III). Comparing these temporal patterns enables quantitative separation of the two contributions. The transition time Δt denotes the interval between the last auxiliary measurement in Step I and the first in Step II.

To distinguish electrochemical nonlinearity from instrumental artifacts, we analyze harmonic distortion in both the excitation current THD_I and the cell voltage response THD_V as defined in Eq. (1) [17]. We introduce the distortion amplification factor Γ as the ratio of voltage to current THD :

$$\Gamma = \frac{\text{THD}_V}{\text{THD}_I}. \quad (3)$$

This metric enables distinction between two regimes: (1) linear behavior (ideally $\Gamma \approx 1$), where the cell preserves the harmonic content of the excitation signal; and (2) nonlinear behavior ($\Gamma \gg 1$), where the cell generates additional harmonic distortion beyond the excitation, indicating electrochemical nonlinearity. We complement this analysis by examining the first three individual harmonic magnitudes $|V_1|$, $|V_2|$, and $|V_3|$ to verify that harmonic patterns align with theoretical predictions and experimental studies for specific electrochemical processes.

The impedance change during NLEIS comprises two components:

$$\Delta \text{Re}Z = \Delta \text{Re}Z_{\text{NL}} + \Delta \text{Re}Z_{\text{th}}, \quad (4)$$

where $\Delta \text{Re}Z_{\text{NL}}$ represents electrochemical nonlinearity and $\Delta \text{Re}Z_{\text{th}}$ represents thermal effects. Our single-frequency NLEIS protocol, presented in the following section, enables experimental quantification of the nonlinear contribution $\Delta \text{Re}Z_{\text{NL}}$.

2.2. Single-frequency NLEIS protocol

The second method directly observes temporal impedance evolution at a single frequency during alternating low- and high-amplitude excitation, enabling separation of fast nonlinear electrochemical effects from slow thermal effects. This protocol adapts heating current methodologies previously developed for cold-start performance enhancement and thermal model parameterization [49–56], applying them specifically to distinguish nonlinear electrochemical behavior from thermal effects.

The measurement comprises three sequential steps with continuous impedance monitoring at a single frequency f_{SF} :

- Step I: Low-amplitude excitation for 2.3 min
- Step II: High-amplitude excitation for 2.3 min to induce both nonlinear and thermal effects due to self-heating
- Step III: Return to low-amplitude excitation for 4.5 min to observe thermal relaxation

Auxiliary 1 kHz impedance measurements using low-amplitude excitation are performed intermittently throughout all steps and immediately before and after amplitude transition (I→II and II→III) to track internal cell temperature evolution via Eq. (2). Fig. 1(b) schematically illustrates the complete sequence, showing excitation amplitude evolution (top), measurement frequency schedule (middle), and expected impedance evolution (bottom).

The distinct timescales of electrochemical nonlinearity and thermal effects enable their separation. Fast changes at step change indicate nonlinear electrochemical behavior. We expect the impedance to decrease at transition I→II and increase at transition II→III, reflecting amplitude-dependent electrochemical kinetics. Slow changes within steps indicate thermal effects: we expect the impedance to decrease progressively during Step II (heating) and increase during Step III (cooling) according to the cell's thermal time constant.

To probe frequency-dependent nonlinearity, we selected excitation current frequencies f_{SF} spanning the characteristic frequency range of the Nyquist semicircle. From the measured impedance evolution $\text{Re}Z$, we extract four characteristic parameters:

- $\Delta \text{Re}Z_{I \rightarrow II}$: Fast impedance change upon amplitude increase (Step I to Step II)
- $\Delta \text{Re}Z_{II \rightarrow III}$: Fast impedance change upon amplitude decrease (Step II to Step III)
- $\Delta \text{Re}Z_{II}$: Slow impedance change during Step II
- $\Delta \text{Re}Z_{III}$: Slow impedance change during Step III

We attribute $\Delta \text{Re}Z_{I \rightarrow II}$ and $\Delta \text{Re}Z_{II \rightarrow III}$ to amplitude-dependent nonlinear electrochemical effects, while $\Delta \text{Re}Z_{II}$ and $\Delta \text{Re}Z_{III}$ reflect self-heating and passive cooling, respectively. The auxiliary 1 kHz measurements provide internal cell temperature tracking, enabling validation of these attributions.

To verify that fast impedance changes arise from electrochemical nonlinearity rather than rapid heating, we perform a plausibility check. Two consecutive impedance points are separated by $\Delta t = 3.9$ s. If the fast impedance change were caused solely by a temperature change, the required ΔT follows from:

$$\Delta T_{\text{Re}Z} = \frac{\Delta \text{Re}Z}{S_{\text{Re}Z,T}} = \frac{\Delta \text{Re}Z_{I \rightarrow II/II \rightarrow III}}{S_{\text{Re}Z,T}}, \quad (5)$$

where $S_{\text{Re}Z,T}$ is the temperature sensitivity of the real part of impedance in ΩK^{-1} . Assuming no heat dissipation to the environment during Δt ,

Table 1
Equivalent Circuit Model (ECM) parameters of Eq. (8).

Parameter		Unit
R_0	Ohmic resistance	Ω
L_0	Inductance	H
R_{ct}	Charge-transfer resistance	Ω
Q_{dl}	Constant Phase Element (CPE) coefficient	F/s^{1-n}
n	CPE exponent	–
σ	Warburg coefficient	Ω/s^β
β	Warburg exponent	–
γ	Warburg phase parameter	–

the thermal energy required to produce ΔT_{ReZ} is

$$Q_{th} = mc\Delta T_{ReZ}, \quad (6)$$

where m is the cell mass in kg and c is specific heat capacity in $J\,kg^{-1}\,K^{-1}$. Equating the Joule heating power $I^2 R_{ReZ}$ with the energy balance over Δt gives the excitation current that would be required to produce ΔT_{ReZ} thermally [26]:

$$i_{req} = \sqrt{2 \frac{mc}{R_{ReZ}} \frac{\Delta T_{ReZ}}{\Delta t}}. \quad (7)$$

If i_{req} exceeds the actual excitation current, a purely thermal origin of the fast impedance change can be ruled out.

2.3. Data validation and Equivalent Circuit Model (ECM) fitting

All impedance spectra were validated using KK relations. We employed the linear KK test implementation by Schönleber et al. [19] via the Python package `impedance.py` (version 1.4.1) [57], executed in Python 3.11.0.

To estimate charge-transfer resistance R_{ct} , we fitted measured data to a five-element Equivalent Circuit Model (ECM) representing dominant physical processes in our frequency range (100 mHz to 20 kHz):

$$\hat{Z}_{ECM}(\omega) = R_0 + j\omega L_0 + \frac{R_{ct}}{1 + (j\omega)^n Q_{dl} R_{ct}} + Z_W, \quad (8)$$

where the components represent:

- R_0 : Ohmic resistance
- L_0 : High-frequency inductive effects
- R_{ct} : Charge-transfer resistance
- Q_{dl} : Constant Phase Element (CPE) modeling double-layer capacitance [58,59]
- Z_W : Warburg impedance representing diffusion

The Warburg impedance employs a modified semi-infinite diffusion formulation [60]:

$$Z_W = \frac{\sigma}{\omega^\beta} (\gamma - j), \quad (9)$$

where σ is the Warburg coefficient, β and γ are dimensionless fitting parameters, j is the imaginary unit, and $\omega = 2\pi f$ is the angular frequency. All model parameters are summarized in Table 1.

Parameters were estimated by minimizing the sum of squared residuals between measured impedance $Z(\omega)$ and model impedance $\hat{Z}_{ECM}(\omega)$ for both real and imaginary components using MATLAB's `nlinfit` function [61,62] with 1×10^{-6} coefficient tolerance. Initial parameter values were estimated from Nyquist plot features, with particular attention to R_0 determination due to its strong influence on convergence. The fitting frequency range was selectively limited to regions where the chosen model adequately describes measured impedance behavior.

3. Experimental

We characterized the impedance behavior of a cylindrical 3.5 Ah lithium-ion cell (MOLICEL INR18650-M35A [63], designated as Cell

A) with lithium nickel manganese cobalt oxide (NMC) positive electrode and graphite/silicon blend (GSi) negative electrode active material. For measurement setup validation, we employed an aluminum reference cylindrical with 18650 geometry (Cell R).

All electrochemical measurements were performed using a Bio-Logic VMP-300 electrochemical workstation [64]. Temperature was controlled using a Vötsch VTS 7011-5 environmental chamber providing indirect ambient temperature regulation. Cells were contacted using a FEINMETALL cylindrical cell adapter with four-wire sensing configuration and integrated Type K thermocouples [65,66]. Throughout each experiment, the negative and positive terminal temperatures were continuously measured using a PicoLog TC-08 data logger [67] with 2 Hz sampling rate. Complete cell specifications and experimental parameters are summarized in Table 2.

Prior to impedance characterization, Cell A underwent five stabilization cycles at 35 °C following the manufacturer-specified protocol: constant current–constant voltage (CC–CV) charging and constant current (CC) discharging to ensure stationary conditions.

Our experimental procedure comprised three complementary measurements: (1) temperature-dependent impedance characterization, (2) NLEIS sweeps, and (3) single-frequency NLEIS. Before each measurement, a consistent cell state was established using a standardized conditioning protocol. First, the cell underwent thermal equilibration at 35 °C for 3 h. Second, the cell was fully discharged at the standard current rate $I_{d/ch}$ to the cut-off voltage, yielding discharge capacity Q_{dis} , followed by 15 min relaxation. Third, the cell was charged to 50% SoC (capacity Q_{ch}) at the standard current rate using CC protocol. Fourth, the cell was allowed to relax for 12 h to establish electrochemical equilibrium. Finally, a verification EIS measurement was performed to confirm the cell state did not change before proceeding with experiments.

SoC stability was verified by comparing charge and discharge capacities before and after each experiment:

$$4Q = Q_{dis} - Q_{ch}. \quad (10)$$

3.1. Temperature sensitivity of impedance

Temperature-dependent impedance characterization was performed to determine the sensitivity coefficients required for internal temperature estimation during subsequent NLEIS measurements. The experimental sequence consisted of three steps: First, each target temperature was established with 3 h stabilization time to ensure thermal equilibrium throughout the cell. Second, EIS was performed using low-amplitude excitation (ensuring linear response) spanning 20 kHz to 100 mHz, with measurement parameters detailed in Table 2. Third, upon completing the impedance measurement, the temperature was adjusted to the next target value and the sequence repeated. Measurements progressed through decreasing temperatures (30 °C, 27.5 °C, 25 °C, 10 °C, 7.5 °C and 5 °C), beginning at the highest temperature.

Impedance sensitivity coefficients with respect to temperature, $S_{Z,T}$, were calculated by linear interpolation within two distinct temperature ranges: the low-temperature range (5 °C to 10 °C) yielding S_{Z,T_1} , and the high-temperature range (25 °C to 30 °C) yielding S_{Z,T_2} . These coefficients enable internal temperature estimation via Eq. (2) using impedance phase changes at 1 kHz.

3.2. NLEIS sweep

Modified NLEIS sweeps incorporating internal cell temperature tracking were performed at 25 °C and 5 °C. Each measurement sequence consisted of three steps: First, the target temperature was established with 3 h stabilization time to ensure thermal equilibrium throughout the cell. Second, progressive NLEIS sweeps were performed with systematically increasing excitation current amplitudes (0.14, 0.57, 1.43 and 2.57C), proceeding from lowest to highest amplitude. Between

Table 2

Specifications and experimental parameters for MOLICEL INR18650-M35A [63] (Cell A) and aluminum reference cylinder (Cell R). **Cell A:** 3.5 Ah nominal capacity Q , graphite/silicon blend (GSI) negative and lithium nickel manganese cobalt oxide (NMC) positive electrode active materials, 48 g mass m , 1.75 Ah charge capacity Q_{ch} at 50% State of Charge (SoC), 3.72 V Open Circuit Voltage (OCV) at 50% SoC, 0.49C standard discharge/charge current rate $I_{d/ch}$, and 32 m Ω charge-transfer resistance R_{ct} at 5 °C. **Cell R:** aluminum cylinder (18650 geometry) with 2.18 m Ω resistance for instrumentation validation. Electrochemical Impedance Spectroscopy (EIS) measurements: performed at six temperatures (5 °C, 7.5 °C, 10 °C, 25 °C, 27.5 °C and 30 °C) spanning 20 kHz to 100 mHz with at least four points per decade, using low-amplitude excitation currents i_{exc} of 0.06 and 0.14C to ensure linear response. Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) measurements: conducted at 5 °C and 25 °C with systematically increased excitation currents (0.14, 0.57, 1.43 and 2.57C) over the same frequency range for sweep measurements, and at discrete single frequencies f_{SF} of (950 Hz, 100 Hz, and 10 Hz) spanning the Nyquist semicircle. **Instrumentation:** BioLogic VMP-300 potentiostat [64], Vötsch VTS 7011-5 environmental chamber, FEINMETALL cell adapter with four-wire sensing and Type K thermocouples [65,66], PicoLog TC-08 temperature data logger [67].

Cell	Q Ah	Neg/Pos	m kg	Q_{ch} Ah	OCV V	$I_{d/ch}$ C-rate	R_{ct} at 5 °C m Ω	EIS i_{exc} C-rate	NLEIS Sweep/Single-Frequency T °C	i_{exc} C-rate	f_{SF} Hz
A ^a	3.5	GSI/NMC	0.048	1.75	3.72	0.49	32	0.06, 0.14	5, 25	0.14, 0.57, 1.43, 2.57	10, 100, 950
R ^r	–	–	–	–	–	–	2.18 [†]	–	5, 25	0.5, 2, 5, 9 ^{††}	10, 100, 950

^a MOLICEL INR18650-M35A

^r Aluminum reference cylinder (18650 geometry) for measurement setup characterization; [†]: resistance; ^{††}: current in A

consecutive sweeps, the cell was allowed to relax for 30 min at 25 °C or 60 min at 5 °C. Third, upon completing all amplitude variations at one temperature, measurements progressed to the next temperature, beginning with 25 °C.

Each frequency sweep covered 20 kHz to 100 mHz with at least four measurement points per decade. Auxiliary 1 kHz measurements, with an approximate measurement time of 1.2 s, were interspersed throughout the sweep to enable continuous internal cell temperature estimation, as illustrated in Fig. 1(a). Each impedance value represents the average of three consecutive periods, which provides a balance between measurement accuracy and temporal resolution. The total measurement duration per complete frequency sweep was 141 s.

3.3. Single-frequency NLEIS

Single-frequency NLEIS measurements were conducted at three characteristic frequencies (950 Hz, 100 Hz, and 10 Hz) spanning the Nyquist semicircle, at temperatures of 25 °C and 5 °C. The experimental protocol consisted of three sequential steps: First, the target temperature was established with 3 h stabilization time to ensure thermal equilibrium throughout the cell. Second, sinusoidal excitation currents were applied systematically at each frequency–amplitude combination detailed in Table 2. Measurements progressed from the highest frequency (950 Hz) to the lowest (10 Hz). At each frequency, excitation current amplitude was increased sequentially from 0.14C to 2.57C. Consistent with the NLEIS sweep measurements, the impedance was determined from three consecutive periods. Relaxation periods of 30 min (25 °C) or 60 min (5 °C) were imposed between measurements. Third, upon completing all frequency–amplitude combinations at one temperature, measurements progressed to the next temperature, beginning with 25 °C.

4. Results and discussion

This section presents experimental results from impedance-temperature sensitivity analysis, NLEIS sweeps, and single-frequency NLEIS experiments. Results are presented primarily for the nonlinear frequency range of Cell A. Detailed results for the linear frequency range and for Cell R for measurement setup characterization are provided in Sections S1 and S2 of the supplementary material linked in Appendix A. Our experimental data, along with postprocessing scripts, are available as a dataset [68].

The temperature sensitivities of the negative impedance phase and the real part of the impedance are summarized in Table 3. The notation S_{Z,T_1} indicates the impedance sensitivity in the temperature range 5 °C to 10 °C, while S_{Z,T_2} corresponds to 25 °C to 30 °C. The negative impedance phase sensitivities $S_{-argZ,T}$ of the auxiliary measurement at 1 kHz are -0.21 °K⁻¹ and -0.19 °K⁻¹, respectively. The sensitivity of the real part of the impedance decreases with increasing frequency and temperature.

Table 3

Impedance sensitivities with respect to temperature of the negative impedance phase $S_{-argZ,T}$ and the real part of the impedance $S_{ReZ,T}$ of Cell A (see Table 2 for detailed specifications) for different frequencies f . T_1 indicates the temperature range from 5 °C to 10 °C and T_2 from 25 °C to 30 °C. The sensitivities decrease with increasing frequency and temperature.

f Hz	S_{-argZ,T_1} °K ⁻¹	S_{-argZ,T_2} °K ⁻¹	S_{ReZ,T_1} m Ω K ⁻¹	S_{ReZ,T_2} m Ω K ⁻¹
10 ³	−0.21	−0.19	–	–
9.5 × 10 ²	–	–	−0.087	−0.029
10 ²	–	–	−0.26	−0.25
10 ¹	–	–	−1.5	−0.38
10 ⁻¹	–	–	−2.2	−0.37

4.1. NLEIS sweep

Fig. 2 presents Nyquist plots at 5 °C and 25 °C measured with excitation current amplitudes ranging from 0.14 to 2.57C. At 25 °C, impedance dependence on excitation amplitude is minimal, becoming noticeable only below 10 Hz. At 5 °C, however, amplitude-dependent impedance decrease is substantially more pronounced. Above 1.43C, the characteristic diffusion tail at low frequencies overlaps as the Nyquist curve bends toward lower impedance values rather than extending to higher values.

The maximum impedance deviation in real part between linear and high-amplitude excitation occurs at 0.1 Hz, reaching -1.2 m Ω and -10.6 m Ω at 25 °C and 5 °C, respectively, for 2.57C excitation. For the imaginary impedance component, the largest deviation occurs at 20 kHz, increasing from 1.24 m Ω at 0.57C to 3.41 m Ω at 2.57C. A small but systematic impedance increase at frequencies higher than 500 Hz with increasing excitation amplitude is also visible in the real part of the impedance. We discuss this effect in more detail at the end of Section 4.2.

The increase in the imaginary part of impedance above 2 kHz originates from inductive effects in the measurement setup rather than electrochemical processes. This attribution is confirmed by measurements on the aluminum reference cylinder (Cell R), which exhibits identical inductive behavior (see Section S2 of the supplementary material). Fitting the NLEIS sweep data measured at 9 A excitation to a series resistor–inductor model (Eq. (8), retaining only R_0 and L_0) using BioLogic ZFit [69] yields a resistance of 2.2 m Ω and inductance of 48 nH, characteristic of the measurement setup rather than the cell.

Fig. 3 provides detailed frequency-domain analysis, showing impedance alongside distortion amplification factor I and temperature change ΔT . The left column represents 25 °C data, while the right column shows 5 °C results. The THD and the first three voltage harmonics are shown in Fig. S1 of the supplementary material.

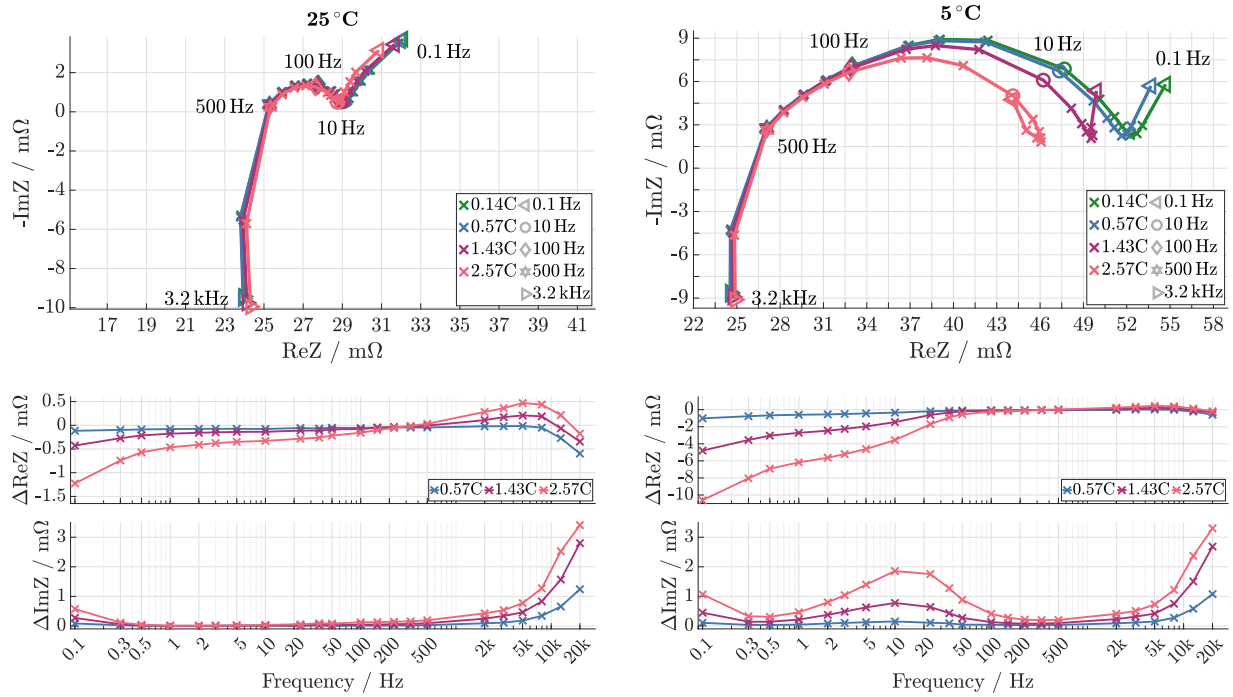


Fig. 2. **Top:** Nyquist curves of Cell A for different excitation current amplitudes: 0.5 A, 2 A, 5 A, and 9 A corresponding to 0.14, 0.57, 1.43, and 2.57C, respectively. The data in the **left** plot were measured at 25°C while the **right** plot shows the results for 5°C. For frequencies below 100 Hz, the impedance depends on the excitation current amplitude at both temperatures. However, at 5°C the effect is more pronounced. The real part of the impedance at 0.1 Hz decreases by 10.6 mΩ from 54.7 mΩ at 0.14C to 44.1 mΩ at 2.57C. In contrast, at 25°C, the difference is only 1.2 mΩ. Starting from 1.43C, the typical diffusion tail at low frequencies overlaps, as the Nyquist curve bends toward lower impedance values instead of higher. **Bottom:** Difference of the real $\Delta\text{Re}Z$ and imaginary $\Delta\text{Im}Z$ parts of the impedance referenced to the Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) measurement with the lowest excitation current amplitude (0.14C).

At 25°C, the cell operates within its linear regime across all excitation current amplitudes as Γ remains below three.

Since the cell behaves linearly, amplitude-dependent impedance changes must result from self-heating. Temperature measurements show increases of 2.8 K and 3.0 K at the positive and negative terminals, respectively, with the estimated internal temperature rising 3.4 K for 2.57C excitation. This agrees well with the calculated temperature change of 3.2 K using the maximum impedance change $\Delta\text{Re}Z_{\text{max}}$ (Fig. 2) and thermal sensitivity coefficient $S_{\text{Re}Z, T_2}$ (Table 3) via Eq. (5).

The internal cell temperature T_{int} estimated via impedance phase corresponds to the mean internal cell temperature [48,70], whereas temperatures measured at the positive and negative terminals reflect primarily terminal temperatures due to their direct thermal contact with the thermocouples.

During NLEIS sweeps, terminal temperatures increase more rapidly at the beginning and remain higher than or equal to T_{int} throughout most of the measurement, except in the low-frequency range. When the sweep reaches the 5 kHz measurement point after approximately 5 s, both terminal temperatures increase by approximately 0.5 K. This observation aligns with the manufacturer's specification that contact probe temperatures increase up to 1.5 K when carrying 9 A currents [66].

We verified this temperature rise using thermal imaging with a FLIR E85 camera [71]. Applying a sinusoidal current with 9 A peak amplitude at 950 Hz, we measured a sudden temperature increase of 0.5 K at the negative terminal, reaching 1.5 K after 10 s. This confirms that Joule heating in the contact probes and at the probe-terminal interface increases terminal temperature under high excitation currents and may consequently heat the entire cell.

The voltage THD (Fig. S1) remains below 0.22% for frequencies below 500 Hz. Notably, the highest THD and Γ values occur at the smallest excitation current, likely because higher harmonics are indistinguishable from the noise floor. At higher excitations, the first harmonic

increases while higher harmonics remain near the instrument's noise floor, reducing the calculated THD.

The elevated distortion at low current amplitudes in the kilohertz range (2.7% at 20 kHz) originates from excitation current distortion (1.2% at 20 kHz versus 0.1% at lower frequencies). Examining voltage response distortion alone might suggest electrochemical nonlinearity; however, Γ remaining constant across frequencies confirms instrumental rather than electrochemical origin.

Despite linear operation, the 1st voltage harmonic reaches 280 mV at 0.1 Hz, 14 times the conventional 20 mV linearity criterion. The 2nd and 3rd voltage harmonics remain below 100 μV in the low-frequency range.

At 5°C, Γ below 100 Hz increases with excitation current amplitude, reaching 15.3 at 2 Hz, indicating nonlinear behavior. The THD exhibits a similar trend, reaching a maximum of 1.7% at 2 Hz. The first voltage harmonic peaks at 417 mV, while the third harmonic reaches 7 mV at 2 Hz. Excitation of the 3rd harmonic has been attributed to charge-transfer kinetics [1,2,4].

Using Eq. (5), with $S_{\text{Re}Z, T_1} = -1.5 \text{ m}\Omega \text{ K}^{-1}$ (Table 3) and $\Delta\text{Re}Z = -3.56 \text{ m}\Omega$ at 10 Hz (value extracted from Fig. 2), we predict a temperature increase of 2.4 K. However, the measured terminal temperature increases are only 1 K, approximately two-fifths of the predicted value. Since thermal effects alone cannot explain the resulting impedance decrease of 3.56 mΩ at 10 Hz, electrochemical nonlinearity must contribute.

Below 2 Hz, THD, Γ , and $|V_3|$ decrease, indicating more linear behavior as temperature rises by 3.4 K, 3.9 K, and 5.2 K at the positive terminal, negative terminal, and T_{int} , respectively. At this point, both self-heating and nonlinear effects contribute to impedance decrease and cannot be unambiguously separated or quantified. Our proposed single-frequency NLEIS protocol (see Section 2.2) addresses this limitation by decoupling these contributions.

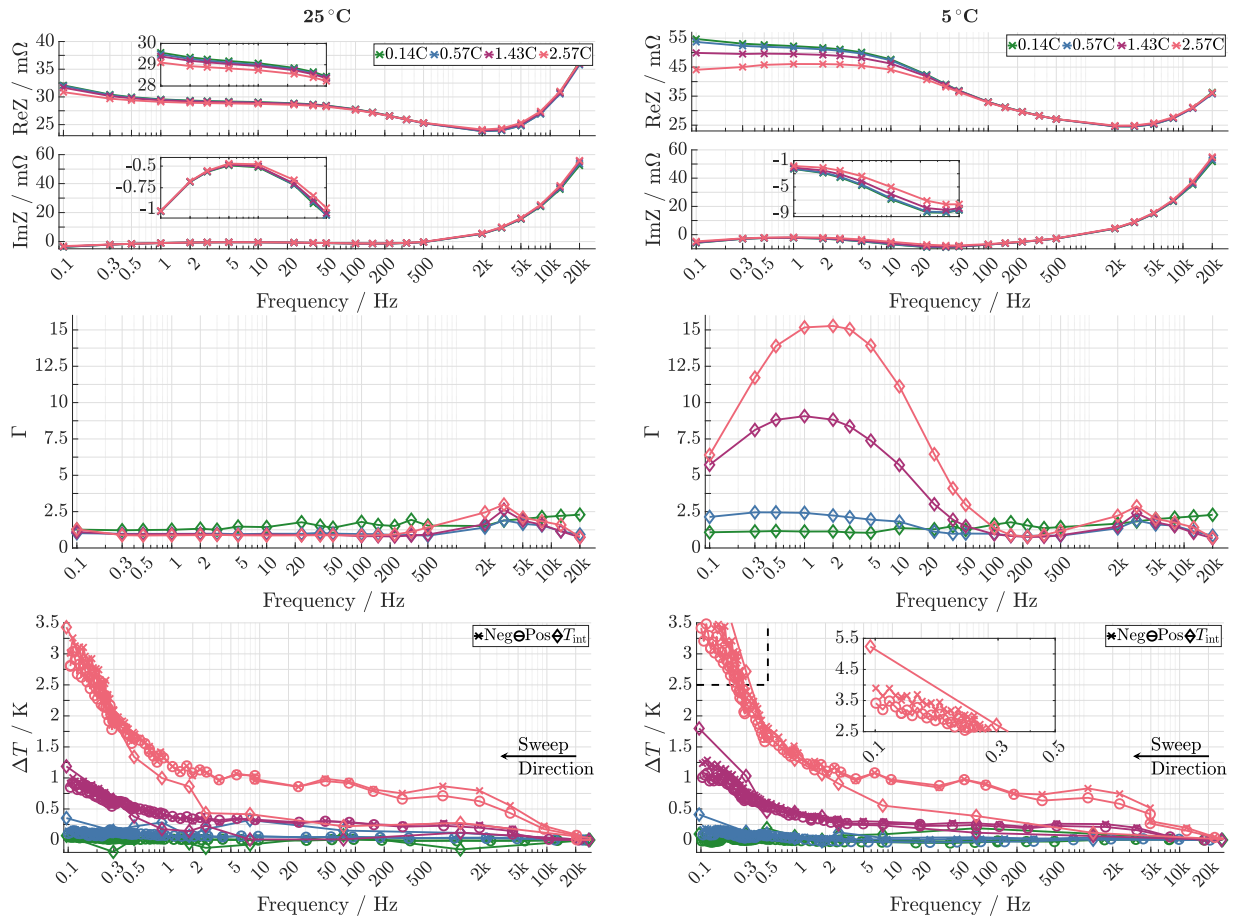


Fig. 3. Measurement results of Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) sweep experiments for Cell A at 25°C (left) and 5°C (right) for different excitation current amplitudes: 0.5 A, 2 A, 5 A, and 9 A corresponding to 0.14, 0.57, 1.43, and 2.57C, respectively. The top panel shows the real part of the impedance $\text{Re}Z$ and the imaginary part of the impedance $\text{Im}Z$ for the measured frequency range from 20 kHz to 0.1 Hz. The distortion amplification factor Γ (defined in Eq. (3)), is plotted as a function of frequency as well. The temperature change ΔT during the frequency sweep from 20 kHz to 0.1 Hz is measured with thermocouples at the positive (Pos) and negative (Neg) terminals. The internal cell temperature T_{int} is estimated via the impedance phase at 1 kHz. At 25°C, the cell operates within its linear regime ($\Gamma < 2.5$), while at 5°C below 100 Hz the cell shows nonlinear behavior. Both nonlinear and thermal effects decrease the impedance. The Total Harmonic Distortion (THD) and the first three voltage harmonics are shown in Fig. S1 of the supplementary material linked in [Appendix A](#).

The continuous temperature increase during NLEIS sweeps introduces an inherent time-variance that violates a fundamental assumption of impedance spectroscopy: the system operating point should remain constant throughout measurement. During our sweeps progressing from 20 kHz to 100 mHz, each frequency point is measured at a different cell temperature due to cumulative self-heating. This creates two distinct time-variance effects: (1) inter-frequency variance, where high-frequency impedance measured at the sweep beginning (cooler state) cannot be directly compared with low-frequency impedance measured at the sweep end (heated state), and (2) intra-frequency variance, where the cell temperature changes during individual low-frequency measurements. For example, the 100 mHz measurement with duration of approximately 60 s experiences an internal temperature increase of approximately 2.5 K, meaning the impedance value recorded represents an average over this temperature range rather than a single thermal state. In contrast, the 1 kHz measurement, with a duration of approximately 1.2 s, is significantly faster than the thermal time constants and can therefore be considered stationary.

In summary, our NLEIS results agree well with literature findings: (1) nonlinearity intensifies at lower excitation frequencies, and (2) reduced temperatures enhance nonlinear responses [3,9,11–16,22–27,30–37,72–83]. Nonlinear effects were only observed at 5°C for frequencies below 100 Hz and excitation current amplitudes larger than 0.6C.

However, in contrast to previous studies [24,26,27] that attributed impedance decrease predominantly to a single mechanism, our results indicate that both self-heating and electrochemical nonlinearity contribute. The quantitative separation and analysis of these contributions are presented in Section 4.2 using our single-frequency NLEIS protocol defined in Section 2.2.

Linearity criterion evaluation

The top and middle row of Fig. 4 examine the conventional 20 mV linearity criterion, introduced in Section 1, by plotting the first $|V_1|$ and third harmonics $|V_3|$ of voltage response and THD versus excitation current at 10 Hz for 25°C (left) and 5°C (right).

The first harmonic scales linearly with excitation current, as indicated by fitted linear functions for both temperatures. As previously discussed, the cell responds linearly to all excitation amplitudes at 25°C, even though the cell voltage response is 13 times larger than the 20 mV linearity criterion (260 mV at 2.57C; THD below 0.17%).

At 5°C, the cell voltage response to 1.42C is slightly lower at 234 mV but exhibits a THD of 0.64%, which is 3.8 times larger. Nonlinearity was confirmed by $\Gamma = 5.7$, and the real part of the impedance decreased by 3.7% compared to linear (0.14C) excitation. Even though THD appears low and remains below the proposed 1% threshold [9,10], the cell exhibits significant nonlinear behavior and impedance change.

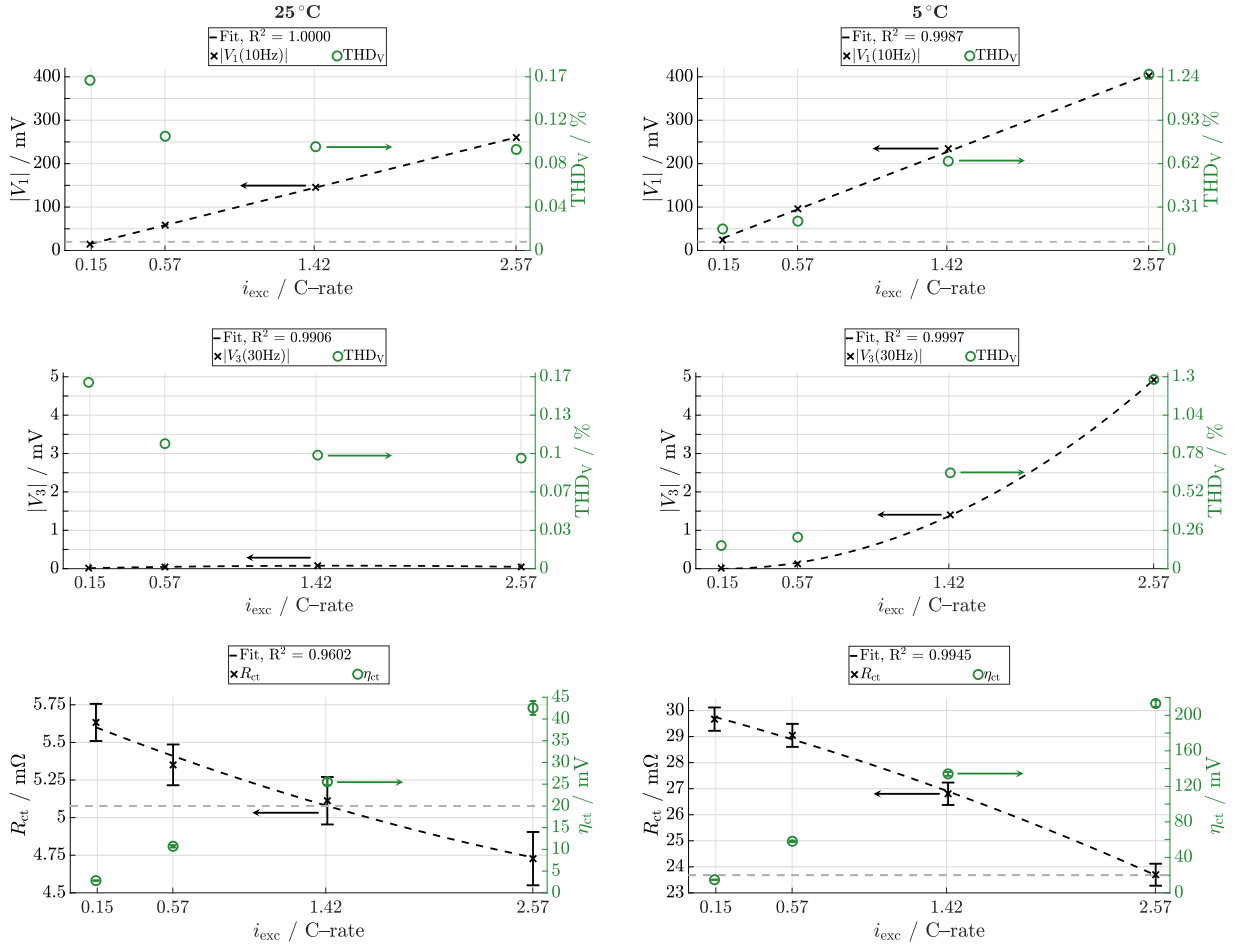


Fig. 4. Top and Middle: First $|V_1|$ and third harmonics $|V_3|$ of voltage response and Total Harmonic Distortion (THD) versus excitation current i_{exc} at 10Hz from Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) sweep in Fig. 3. The left column shows measurement results at 25°C, while the right column shows results at 5°C. The first harmonic scales linearly with excitation current, as indicated by fitted linear functions ($|V_1| = p_1 i_{exc} + p_0$) for both temperatures. The fit parameters are: $p_1 = 101$ mV, $p_0 = 0.5$ mV at 25°C and $p_1 = 155$ mV, $p_0 = 6.1$ mV at 5°C. Although THD remains below 1%, the cell voltage response is up to 13 times larger than the 20 mV linearity criterion (260 mV). The third harmonic at 5°C scales quadratically with excitation current, described by $|V_3| = p_2 i_{exc}^2 + p_1 i_{exc} + p_0$ with fitted parameters $p_2 = 0.83$ mV, $p_1 = -0.23$ mV, and $p_0 = 0.01$ mV. Bottom: Charge-transfer resistance R_{ct} decreases with increasing excitation current i_{exc} (see also Table 4). The relationship follows $R_{ct} = p_2 i_{exc}^2 + p_1 i_{exc} + p_0$ with fitted parameters $p_2 = 0.05$ mΩ, $p_1 = -0.48$ mΩ, $p_0 = 5.7$ mΩ at 25°C and $p_2 = -0.24$ mΩ, $p_1 = -1.84$ mΩ, $p_0 = 30$ mΩ at 5°C. The theoretical voltage drop across R_{ct} is calculated as $\eta_{ct} = R_{ct} \cdot i_{exc}$. Even under linear conditions at 25°C, η_{ct} reaches $43 \text{ mV} \pm 1.6 \text{ mV}$ at maximum excitation, twice the 20 mV linearity criterion. Error bars indicate standard deviation of the fit. R_{ct} was estimated from the Equivalent Circuit Model (ECM) fitting procedure defined in Section 2.3. ECM fitting results as Nyquist plots and residuals between measured impedance and fitted impedance model are shown in Fig. S2 of the supplementary material.

The bottom row of Fig. 4 shows charge-transfer resistance R_{ct} from ECM fitting and the theoretical voltage drop across R_{ct} :

$$\eta_{ct} = R_{ct} \cdot i_{exc} \quad (11)$$

The error bars indicate the standard deviation of the estimate. Even at 25°C, η_{ct} reaches $43 \text{ mV} \pm 1.6 \text{ mV}$ at maximum excitation, twice the 20 mV criterion. At 5°C, R_{ct} decreases quadratically with current amplitude by 20% when increasing excitation from 0.14C to 2.57C, even though THD remained below 1.75% throughout the NLEIS sweep. This suggests that thermal effects contribute to the observed R_{ct} decrease alongside electrochemical nonlinearity. The change in charge-transfer resistance between linear and high-amplitude excitations ΔR_{ct} is summarized in Table 4. ECM fitting results as Nyquist plots and residuals between measured impedance and fitted impedance model are shown in Fig. S2 of the supplementary material.

These results demonstrate that the 20 mV criterion may be too strict for linearity assessment and may lead to suboptimal measurement quality due to unnecessarily low excitation amplitudes.

The residuals of the Lin-KK test defined in Section 2.3 together with THD of the cell voltage response and distortion amplification factor F

Table 4

ΔR_{ct} defined as the difference between charge-transfer resistance R_{ct} for linear excitation (0.14C) and high-amplitude excitation currents i_{exc} . The values in percentage are normalized to R_{ct} for linear excitation. Charge-transfer resistance decreases with increasing excitation current; this is also visualized in Fig. 4. R_{ct} was estimated from the Equivalent Circuit Model (ECM) fitting procedure defined in Section 2.3. ECM fitting results as Nyquist plots and residuals between measured impedance and fitted impedance model are shown in Fig. S2 of the supplementary material.

i_{exc} C-rate	25°C		5°C	
	ΔR_{ct} mΩ	%	ΔR_{ct} mΩ	%
0.57	0.28	5	0.62	2.1
1.43	0.52	9.2	2.87	9.7
2.57	0.91	16.1	5.97	20.1

are shown in Fig. 5. At 25°C for excitation current rates below 0.6C, the residuals appear random and remain below 0.04%. At 2.57C, the

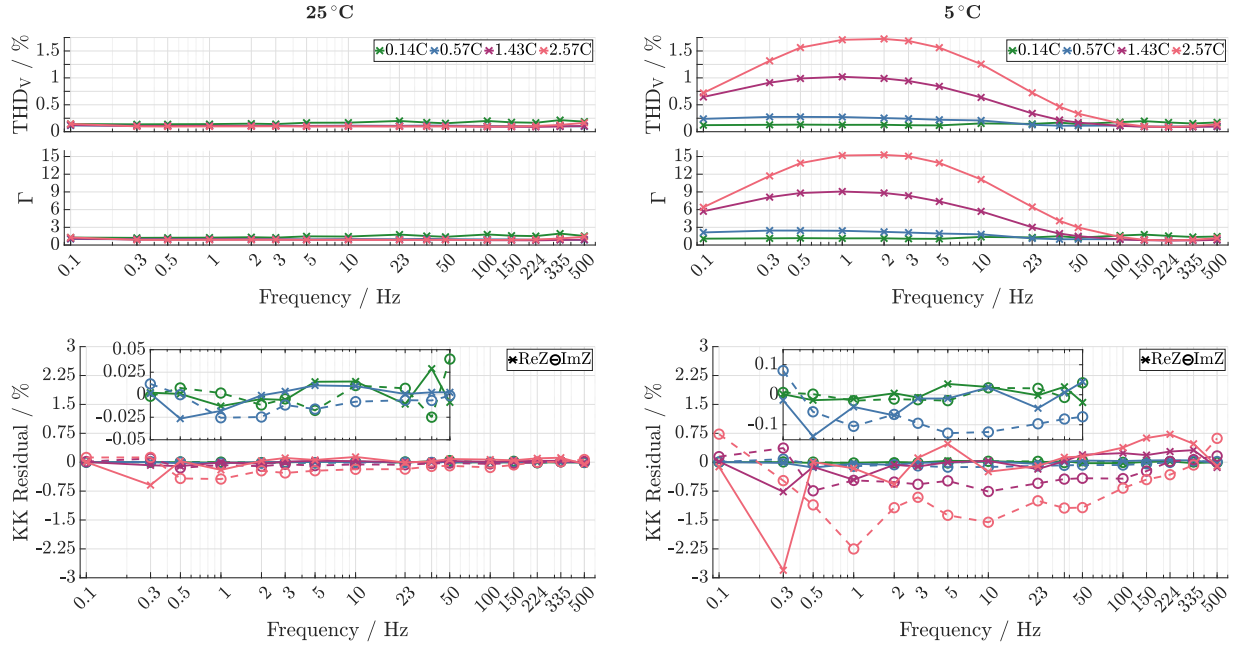


Fig. 5. Top: Total Harmonic Distortion (THD) of cell voltage response and distortion amplification factor Γ (defined in Eq. (3)) during Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) sweeps at 25 °C (left) and 5 °C (right) for different excitation current amplitudes: 0.5 A, 2 A, 5 A, and 9 A corresponding to 0.14, 0.57, 1.43, and 2.57C, respectively. At 25 °C, Cell A behaves linearly for all excitation currents, whereas at 5 °C, the cell exhibits nonlinear behavior for 1.43 and 2.57C. **Bottom:** Residuals of the Lin-Kramers-Kronig (KK) test defined in Section 2.3. Residuals remained below 2.8% for all measurements, indicating limited sensitivity of KK validation for detecting nonlinearity and time-variance.

residuals increase systematically for frequencies below 100 Hz, reaching up to 0.6% at 0.3 Hz.

At 5 °C, residuals for the same excitation currents are higher and shift systematically toward negative values, indicating a bias absent under linear conditions. During the NLEIS sweep with 1.43C, the cell exhibits nonlinear behavior ($\Gamma = 9$ at 1 Hz), and THD of the cell voltage response reaches 1% at 1 Hz. However, Lin-KK residuals remain below 0.77%. Their distribution is not centered around zero, indicating systematic error caused by nonlinear and time-variant behavior.

KK residuals remained below 2.8% for all measurements, regardless of excitation amplitude or observed harmonic distortion. Notably, measurements exhibiting clear amplitude-dependent impedance, Γ values up to 15, and THD up to 1.7% still produced KK residuals comparable to those from low-amplitude measurements, indicating limited sensitivity of KK validation for detecting nonlinearity and time-variance.

Temperature effects and Arrhenius behavior

This section estimates the contribution of thermal effects to impedance decrease using a simplified analytical approach [24,26]. Charge-transfer resistance exhibits typical Arrhenius temperature dependence:

$$R_{ct} = R_{ct,0} \exp\left(-\frac{E_a}{R_{gas}T}\right), \quad (12)$$

where E_a is the activation energy and R_{gas} is the universal gas constant. Our estimated R_{ct} agrees well with this prediction, as indicated by the corresponding fits in Fig. 6 (top). Using a lumped thermal model with Joule heating and thermal resistance R_{th} , we estimate temperature increases as:

$$\Delta T = ReZ \cdot I^2 \cdot R_{th}, \quad (13)$$

where I is the RMS current. For cylindrical 18650 cells, thermal resistance ranges from 0.36 K W⁻¹ to 0.46 K W⁻¹ for ambient temperatures from 13 °C to 42 °C [84].

Incorporating thermal effects into the Arrhenius equation yields:

$$\hat{R}_{ct} = R_{ct,0} \exp\left[-\frac{E_a}{R_{gas}(T_0 + ReZ \cdot I^2 \cdot R_{th})}\right], \quad (14)$$

where T_0 is the initial temperature. The estimates are shown in the bottom panel of Fig. 6 for 5 °C. For ReZ, we used the time-weighted average during the NLEIS sweep and $R_{th} = 0.4$ K W⁻¹.

Interestingly, this thermal-only model produces second-order polynomial behavior identical to the experimentally fitted R_{ct} versus current relationship (see Fig. 4), despite the latter containing both thermal and nonlinear contributions. This similarity demonstrates the difficulty in distinguishing these mechanisms without additional experimental approaches.

4.2. Single-frequency NLEIS

The Nyquist curves of Cell A at 5 °C and 25 °C are shown in Fig. 2. The impedance values closest to the single-frequency NLEIS frequencies ($f_{SF} = 10; 100; 950$ Hz) are indicated. For both temperatures, they correspond to the low-, medium-, and high-frequency parts of the charge-transfer semicircle.

Fig. 7 presents experimental results for Cell A at $f_{SF} = 10$ Hz, showing ReZ evolution, temperature change ΔT , and Γ across three steps: Step I (low-amplitude excitation), Step II (high-amplitude excitation), and Step III (return to low-amplitude excitation). The THD and the first three voltage harmonics are shown in Fig. S3 of the supplementary material.

The left column of Fig. 7 presents results at 25 °C. During Step I, the cell is excited with a 10 Hz sinusoidal current with 0.14C peak amplitude. The cell maintains constant impedance and temperature, with Γ below 2.5 and THD below 0.3%, indicating linear behavior. Transitioning to Step II decreases ReZ: $\Delta ReZ_{I \rightarrow II} = 120 \mu\Omega$ for the 0.14 to 2.57C transition, small relative to the absolute value of 29 m Ω . The Step II $\rightarrow$ III transition shows comparable impedance recovery: $\Delta ReZ_{II \rightarrow III} = 122 \mu\Omega$. The higher the excitation current, the larger the fast impedance change.

During Step II, continued heating decreases impedance by $\Delta ReZ_{II} = 1.16$ m Ω , with temperature increases of 2.67 K, 2.98 K, and 2.9 K at the positive terminal, negative terminal, and estimated internal cell

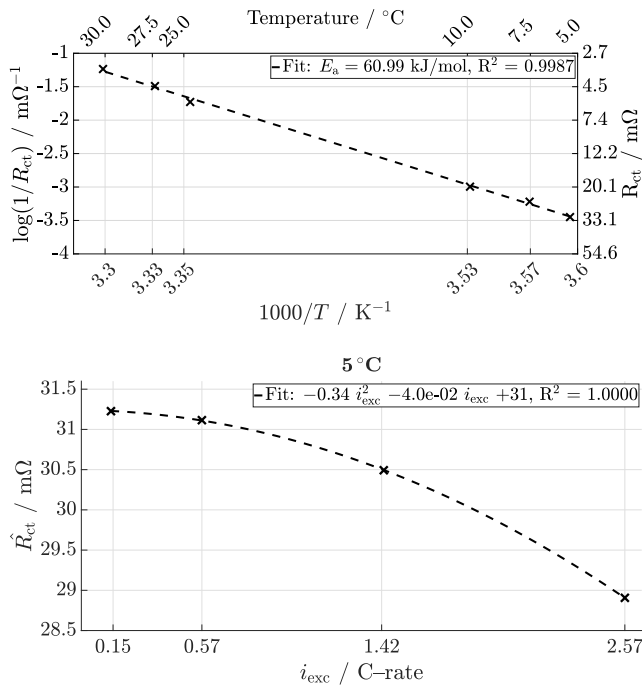


Fig. 6. **Top:** Arrhenius plot of charge-transfer resistance R_{ct} . R_{ct} was estimated from the Equivalent Circuit Model (ECM) fitting procedure defined in Section 2.3. ECM fitting results as Nyquist plots and residuals between measured impedance and fitted impedance model are shown in Fig. S2 of the supplementary material. **Bottom:** Calculated charge-transfer resistance $\hat{R}_{ct}$ with Joule heating incorporated into Arrhenius equation (Eq. (14)). $\hat{R}_{ct}$ decreases quadratically with increasing excitation current i_{exc} . This thermal-only model produces identical behavior to the experimentally fitted R_{ct} versus current relationship (see Fig. 4), despite the latter containing both thermal and nonlinear contributions. This similarity demonstrates the difficulty in distinguishing these mechanisms without additional experimental approaches.

temperature, respectively. Passive cooling in Step III increases the impedance by $\Delta \text{Re}Z_{III} = 0.48 \text{ m}\Omega$.

We attribute the lower absolute Γ and THD values and reduced noise in both values during Step II compared to Step I and III to higher signal-to-noise ratios due to higher excitation current and consequently larger cell voltage response.

The maximum cell voltage response of 262 mV at 2.57C coincides with the measurement results of the NLEIS sweep in Fig. S1. Second $|V_2|$ and third harmonics $|V_3|$ remain below $150 \mu\text{V}$ throughout the entire measurement.

Similar impedance and temperature behavior occurs at 5°C (right column of Fig. 7 and Fig. S3), but with more pronounced changes. Nonlinear behavior in Step II is confirmed by Γ exceeding 10, THD = 1.25%, and third harmonic magnitudes above 5 mV at 2.57C. During Step I and III, Γ indicates linear cell behavior, confirming the fast nature of nonlinearity.

The small periodic oscillations in Γ and voltage THD during the first f_{SF} measurement arise from incomplete settling following the previous 1 kHz measurement: the first of the three averaged periods is influenced by the cell's response to the prior excitation before reaching quasi-steady-state. This transient effect introduces minor distortion but remains negligible in magnitude. It can be further mitigated by introducing a settling delay between consecutive measurements or averaging additional periods, though this represents a trade-off between measurement accuracy and temporal resolution.

As shown in the previous section, nonlinear effects are less pronounced at higher frequencies. Results for excitation frequencies of 100 Hz and 950 Hz are provided in Section S1.2 of the supplementary material.

The four impedance parameters extracted from the measured impedance evolution $\text{Re}Z(f, t)$, namely $\Delta \text{Re}Z_{I \rightarrow II}$, $\Delta \text{Re}Z_{II \rightarrow III}$, $\Delta \text{Re}Z_{II}$, and $\Delta \text{Re}Z_{III}$ (defined in Section 2.2), and the temperature increase of the estimated internal cell temperature during Step II $\Delta T_{int, II}$ are summarized in Table 5. The lower the temperature, the lower the excitation frequency f_{SF} , and the higher the excitation current i_{exc} , the more pronounced the changes in impedance and temperature.

To test whether $\Delta \text{Re}Z_{I \rightarrow II}$ and $\Delta \text{Re}Z_{II \rightarrow III}$ resulted solely from thermal effects, we calculated the temperature change required to produce these impedance changes using Eq. (5). We then determined the excitation current i_{req} needed to generate this temperature change within $\Delta t = 3.9 \text{ s}$ under adiabatic conditions using Eq. (7). The specific heat capacity c was assumed to be $950 \text{ J kg}^{-1} \text{ K}^{-1}$ based on literature values [84–87]. For $\text{Re}Z$, we used the mean value during Step I or the mean of the first five samples during Step III.

The calculated required current rates exceeded the actual applied current rates by factors of 2.3 to 4.7 (Table 6). This discrepancy indicates that thermal effects alone cannot account for the observed fast impedance changes, pointing to significant nonlinear contributions.

Combining NLEIS sweep and single-frequency NLEIS results, we quantify thermal and nonlinear contributions during NLEIS using Eq. (4):

$$\Delta \text{Re}Z_{th} = \Delta \text{Re}Z - \Delta \text{Re}Z_{NL}, \quad (15)$$

where $\Delta \text{Re}Z$ is the difference in the real part of the impedance between linear and nonlinear EIS excitation current amplitude from NLEIS sweep experiments, and $\Delta \text{Re}Z_{NL}$ is the fast nonlinear contribution from single-frequency NLEIS experiments.

From the equation above, we can calculate the thermal contribution $\Delta \text{Re}Z_{th}$ to the overall impedance decrease. We chose to analyze the 10 Hz frequency point in the NLEIS frequency sweep. This point is reached 20 s after the start of the frequency sweep. Therefore, we expect negligible influence on the cell operating point and small temperature changes that do not alter the nonlinear behavior of the cell, allowing us to use $\Delta \text{Re}Z_{NL}$ from the $f_{SF} = 10 \text{ Hz}$ experiment.

The total impedance change $\Delta \text{Re}Z$ along with nonlinear $\Delta \text{Re}Z_{NL}$ and thermal $\Delta \text{Re}Z_{th}$ contributions are plotted in Fig. 8 for the 10 Hz and 5°C case. Their dependence on excitation current can be described with second-degree polynomial functions, where all decrease with increasing excitation current, matching our predictions from $\hat{R}_{ct} = g(i_{exc})$ in Eq. (14).

In addition to the absolute impedance values, Table 7 also summarizes the percentage contributions of $\Delta \text{Re}Z_{NL}$ and $\Delta \text{Re}Z_{th}$. For low excitation currents, the nonlinear contribution dominates: for Cell A at 0.57°C , the entire change in $\text{Re}Z$ is attributed to nonlinearity. At higher current rates, this share declines and the self-heating contribution increases. For example, at 2.57°C , 14.5% of the impedance change ($0.52 \text{ m}\Omega$) stems from self-heating.

The difference between the charge and discharge capacity ΔQ before and after each experiment, defined in Eq. (10), was maximal for the single-frequency NLEIS experiment. The difference was 11 mAh, corresponding to 0.63% of the charge at the set SoC of 50%, indicating stable SoC throughout our experiments. The maximum impedance change at 35°C after charging to Q_{set} and 12 h relaxation from the first to the last experiment for both real and imaginary parts is less than $120 \mu\Omega$. These checkups indicate stable cell behavior during our experiments and no effects that might influence our interpretation of results.

High-frequency impedance anomaly

As shown in previous sections, nonlinear effects dominate below 100 Hz for Cell A at 5°C . The nonlinearity manifests as impedance decrease and distortion.

At 950 Hz, the real part of impedance increases at the transition from Step I to Step II, as shown in Fig. S7 of the supplementary material. However, $\Gamma < 2.5$ indicates linear cell behavior.

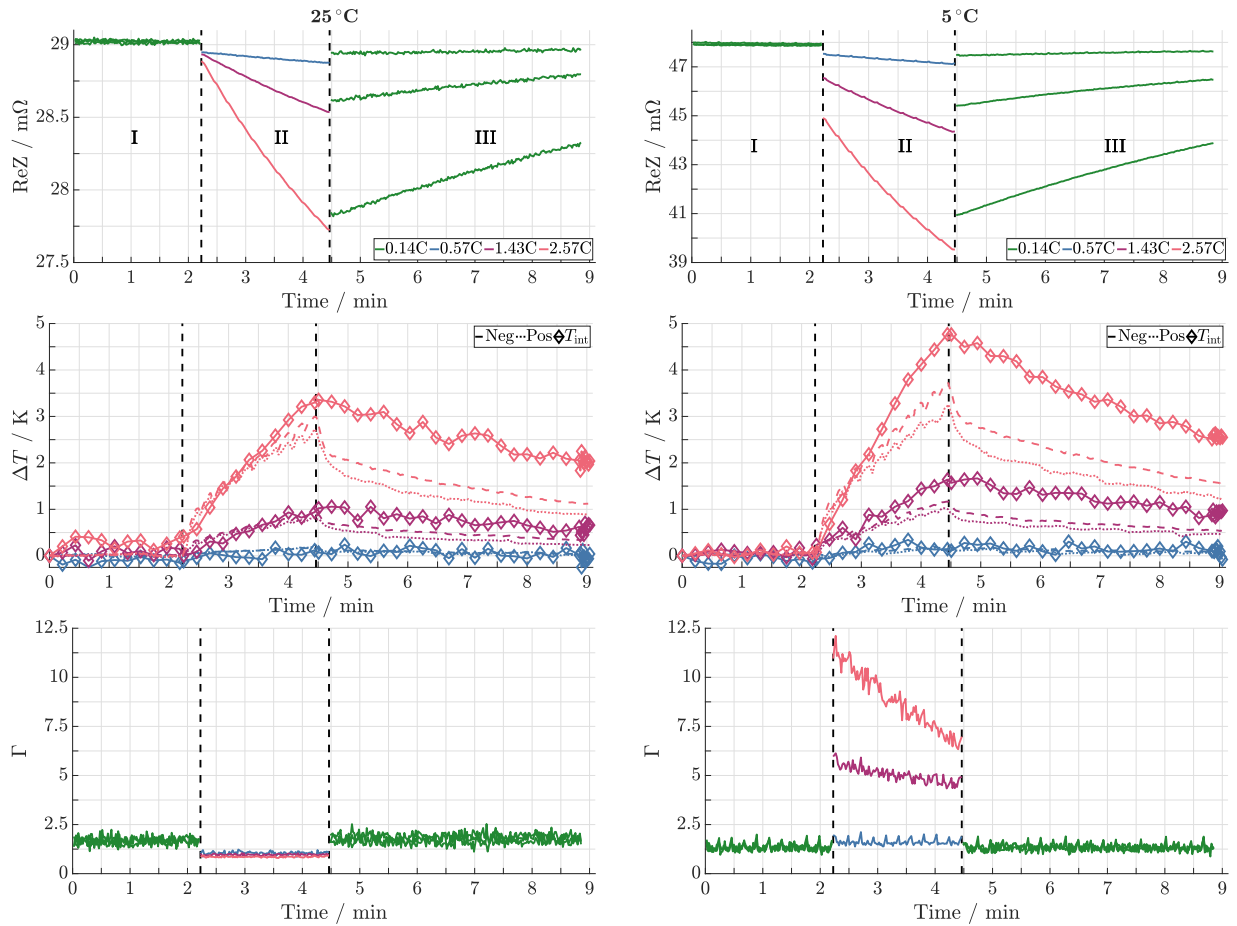


Fig. 7. Measurement results of single-frequency Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) protocol for Cell A at 25 °C (left) and 5 °C (right) for different excitation current amplitudes: 0.5 A, 2 A, 5 A, and 9 A corresponding to 0.14, 0.57, 1.43, and 2.57C, respectively. The excitation current frequency was 10 Hz. The measurement protocol, defined in Section 2.2, comprises three consecutive steps: Step I (low-amplitude excitation), Step II (high-amplitude excitation), and Step III (return to low-amplitude excitation). The top panels show real part of impedance ReZ evolution and temperature changes ΔT measured at negative (Neg) and positive (Pos) terminals and internal cell temperature T_{int} estimated via impedance phase at 1 kHz. The distortion amplification factor Γ (defined in Eq. (3)), is plotted over time as well. At 25 °C, the cell operates within its linear regime ($\Gamma < 2.5$), while at 5 °C the cell shows nonlinear behavior at step transitions characterized by fast increase of Γ and fast decrease of ReZ. The Total Harmonic Distortion (THD) of the excitation current I and the cell voltage response V , as well as the magnitudes of the first three harmonics $|V_1|$, $|V_2|$, and $|V_3|$, are shown in Fig. S3 of the supplementary material.

Table 5

Impedance parameters extracted from the measured impedance evolution during single-frequency Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) protocol defined in Section 2.2 at 5 °C and 25 °C. $\Delta \text{Re}Z$ represents changes in the real part of the impedance during step transitions ($\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$, $\Delta \text{Re}Z_{\text{II} \rightarrow \text{III}}$) or during steps ($\Delta \text{Re}Z_{\text{II}}$, $\Delta \text{Re}Z_{\text{III}}$). $\Delta T_{\text{int,II}}$ is the internal cell temperature increase during Step II estimated from impedance phase. The lower the temperature, the lower the excitation frequency f_{SF} , and the higher the excitation current i_{exc} , the more pronounced the changes in impedance and temperature.

i_{exc} C-rate	f_{SF} Hz	25 °C					5 °C				
		$\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ mΩ	$\Delta \text{Re}Z_{\text{II} \rightarrow \text{III}}$ mΩ	$\Delta \text{Re}Z_{\text{II}}$ mΩ	$\Delta \text{Re}Z_{\text{III}}$ mΩ	$\Delta T_{\text{int,II}}$ K	$\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ mΩ	$\Delta \text{Re}Z_{\text{II} \rightarrow \text{III}}$ mΩ	$\Delta \text{Re}Z_{\text{II}}$ mΩ	$\Delta \text{Re}Z_{\text{III}}$ mΩ	$\Delta T_{\text{int,II}}$ K
0.57	10	0.06	0.07	0.07	0.03	0.24	0.36	0.33	0.38	0.15	0.21
	100	0.04	0.05	0.04	0.01	0.12	0.08	0.07	0.06	0.03	0.28
	950	0.03	0.02	0.01	0.02	0.07	0.03	0.04	0.01	0.01	0.0
1.43	10	0.08	0.09	0.4	0.18	0.94	1.36	1.05	2.19	1.07	1.41
	100	0.05	0.06	0.25	0.10	1.12	0.09	0.1	0.33	0.13	1.29
	950	0.06	0.05	0.03	0.02	0.91	0.04	0.02	0.1	0.04	0.94
2.57	10	0.14	0.12	1.16	0.48	2.88	3.05	1.41	5.38	2.95	4.7
	100	0.07	0.06	0.73	0.31	3.13	0.14	0.15	1.03	0.45	3.84
	950	0.14	0.14	0.08	0.03	2.78	0.13	0.12	0.29	0.13	3.07

For more detailed analysis, we repeated the single-frequency NLEIS protocol at 25 °C with additional frequencies: 0.5 kHz, 2 kHz, and 5 kHz. Fig. S9 shows that $\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ increases linearly with increasing excitation current and frequency. However, when applying the same measurement protocol to Cell R (aluminum reference cylinder with 18650 geometry), no $\Delta \text{Re}Z$ dependence on excitation current or frequency was

observed. Therefore, we rule out effects caused by our measurement setup, including cell adapter, electrochemical workstation, and cabling, even though the load (resistor vs. battery) and operating voltage of the electrochemical workstation (0 V vs. 3.7 V) differ significantly.

Models accounting for electromagnetic effects inside cylindrical cells by considering their specific spiral-wound geometry might explain

Table 6

Required currents i_{req} to cause fast impedance changes $\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ and $\Delta \text{Re}Z_{\text{II} \rightarrow \text{III}}$ solely by thermal effects (Eq. (5) and Eq. (7)). The required current rates exceed actual applied current rates i_{exc} by factors of 2.3 to 4.7, indicating significant nonlinear contributions to fast impedance changes.

i_{exc} C-rate	5 °C $i_{\text{req, I} \rightarrow \text{II}}$ C-rate	$i_{\text{req, I} \rightarrow \text{II}}/i_{\text{exc}}$	$i_{\text{req, II} \rightarrow \text{III}}$ C-rate	$i_{\text{req, II} \rightarrow \text{III}}/i_{\text{exc}}$
0.57	2.69	4.7	2.69	4.7
1.43	5.52	3.9	4.95	3.5
2.57	8.2	3.2	5.94	2.3

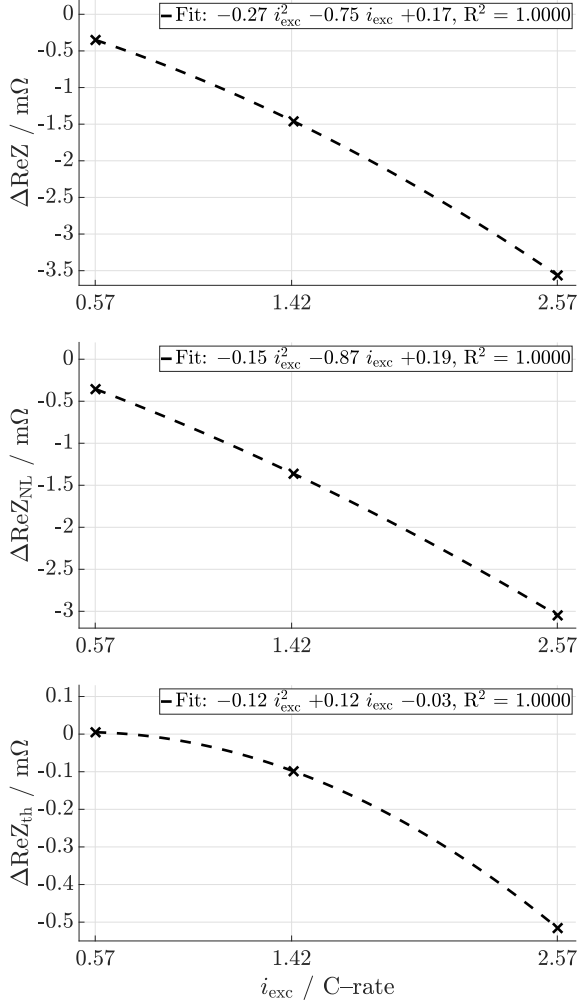


Fig. 8. Top: Change in real part of impedance $\Delta \text{Re}Z$ at 10 Hz at different excitation currents i_{exc} compared to linear excitation at 5 °C of Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) sweep experiments. **Middle:** Fast nonlinear impedance decrease $\Delta \text{Re}Z_{\text{NL}}$ measured in single-frequency NLEIS experiments defined in Section 2.2. $\Delta \text{Re}Z_{\text{NL}}$ corresponds to $\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ in Table 5. **Bottom:** Calculated thermal contribution $\Delta \text{Re}Z_{\text{th}}$ of the overall impedance decrease using Eq. (15). For low excitation currents, the nonlinear contribution dominates, whereas at higher current rates, this share declines and the self-heating contribution increases. Table 7 summarizes these findings.

frequency-dependent impedance changes [88–91]. However, influence on cell impedance by inductive coupling inside the cell has been reported to begin above 3 kHz [88,89]. Furthermore, the skin effect is only relevant at frequencies above at least 10 kHz [92]. Nevertheless, these electromagnetic effects fail to explain our measured current amplitude dependence of $\Delta \text{Re}Z$. This would only be possible if the coupling inductance increases linearly with excitation current.

Since the real part of impedance decreases during Step II, we can also rule out that the fast impedance increase is triggered by a positive temperature coefficient safety device or coating [93,94].

The observed linear scaling of $\Delta \text{Re}Z_{\text{I} \rightarrow \text{II}}$ with both excitation current and frequency in the high-frequency range currently lacks a conclusive physical explanation and warrants further investigation. Nevertheless, since this behavior is confined to frequencies above 100 Hz, well separated from the nonlinear regime, it does not affect the validity of the results presented below 100 Hz.

5. Conclusion

The widely-adopted 20 mV voltage response criterion, derived exclusively from single-electrode charge-transfer kinetics, might be too restrictive for practical linearity assessment of complete battery cells. Our results for a 3.5 Ah GSi/NMC cylindrical 18650 cell demonstrate linear cell behavior ($\Gamma < 2.5$, THD $< 0.22\%$) with voltage responses up to 280 mV, 14 times the conventional threshold. This discrepancy arises because the 20 mV criterion is derived analytically by linearizing the Butler–Volmer equation via first-order Taylor series expansion around the equilibrium potential and imposing an acceptable error threshold. This approach neglects ohmic, diffusion, and inductive contributions to total cell impedance. The distortion amplification factor Γ , defined as the ratio of voltage to current THD, provides a reliable linearity indicator that distinguishes electrochemical nonlinearity ($\Gamma \gg 1$) from linear behavior ($\Gamma < 3$).

Based on our experimental findings (Section 4), we propose the following guidelines for reproducible cell impedance characterization:

- (1) Monitor internal cell temperature during NLEIS measurements, enabling quantification of self-heating contributions.
- (2) Extend the 20 mV criterion by cell-specific, frequency-, and temperature-dependent linearity assessment using complementary validation metrics: (i) distortion amplification factor $\Gamma < 3$ as primary linearity indicator, (ii) systematic amplitude-dependence testing to verify impedance independence, (iii) harmonic content analysis to identify specific nonlinear processes, and (iv) Lin-KK validation as secondary check for data quality rather than sole linearity criterion.

We introduced two complementary NLEIS measurement protocols that quantitatively separate electrochemical nonlinearity from self-heating effects by exploiting their distinct time scales: electrochemical nonlinearity responds quickly to excitation amplitude changes, while self-heating evolves slowly according to the cell's thermal time constant. The first protocol extends conventional NLEIS sweeps with auxiliary 1 kHz measurements to track internal temperature evolution via impedance phase (Fig. 1(a)). The second protocol employs single-frequency NLEIS measurements with alternating low and high excitation amplitudes, enabling direct observation of fast versus slow impedance changes (Fig. 1(b)).

Impedance decrease during NLEIS results from both electrochemical nonlinearity and self-heating. Below 100 Hz at 25 °C, impedance changes are dominated by thermal effects, while at 5 °C, electrochemical nonlinearity becomes the primary contributor. These findings resolve previous contradictions in the literature by demonstrating that both mechanisms contribute simultaneously, with their relative importance depending on specific measurement conditions.

Future work should extend our proposed NLEIS protocols to different cell chemistries. The high-frequency impedance anomaly observed above 500 Hz (fast impedance increase with excitation amplitude) needs further investigation.

The protocols and insights presented here provide a systematic framework for physically-meaningful NLEIS measurements that reliably separate electrochemical nonlinearity from thermal effects. By resolving fundamental methodological limitations, this work enables exploitation of nonlinear electrochemical information for battery research.

Table 7

Changes in real part of impedance $\Delta \text{Re}Z$ at 10 Hz at different excitation currents i_{exc} compared to linear excitation at 5 °C of Nonlinear Electrochemical Impedance Spectroscopy (NLEIS) sweep experiments. The measured temperature change ΔT at negative (Neg) and positive (Pos) terminals and internal cell temperature T_{int} , estimated via impedance phase at 1 kHz, are summarized as well. $\Delta \text{Re}Z_{\text{NL}}$ is the fast nonlinear impedance decrease measured in single-frequency NLEIS experiments defined in Section 2.2. $\Delta \text{Re}Z_{\text{NL}}$ corresponds to $\Delta \text{Re}Z_{\text{I-II}}$ in Table 5. Using Eq. (15) we can quantify the thermal contribution $\Delta \text{Re}Z_{\text{th}}$ of the overall impedance decrease. For low excitation currents, the nonlinear contribution dominates: at 0.57C, the whole change of $\text{Re}Z$ is attributed to its nonlinearity. At higher current rates, this share declines and the self-heating contribution increases. This is visualized in Fig. 8.

i_{exc} C-rate	5 °C NLEIS Sweep					Single-frequency NLEIS			Eq. (15)		Eq. (5)
	f Hz	$\Delta \text{Re}Z$ mΩ	ΔT_{neg} K	ΔT_{pos} K	ΔT_{int} K	f_{SF} Hz	$\Delta \text{Re}Z_{\text{NL}}$ mΩ	%	$\Delta \text{Re}Z_{\text{th}}^{\dagger}$ mΩ	%	$\Delta T_{\text{Re}Z}^{\ddagger}$ K
0.57	10	0.35	0.0	0.0	0.0	10	0.36	101.4	0.0	−1.4	0.0
1.43	10	1.46	0.3	0.3	0.2	10	1.36	93.2	0.1	6.8	0.1
2.57	10	3.56	1.0	1.0	0.6	10	3.05	85.5	0.52	14.5	0.4

$^{\dagger} \Delta \text{Re}Z_{\text{th}} = \Delta \text{Re}Z - \Delta \text{Re}Z_{\text{NL}}$

$^{\ddagger} \Delta T_{\text{Re}Z} = \Delta \text{Re}Z_{\text{th}} / S_{\text{Re}Z, T_i}$

CRedit authorship contribution statement

Norbert Sailer: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Lukas Totschnig:** Validation, Methodology. **Christoph Steffan:** Writing – review & editing, Validation, Supervision. **Jan Philipp Schmidt:** Writing – review & editing, Validation, Supervision.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used Claude Sonnet 4.5 by Anthropic PBC, in order to improve the readability and language of the manuscript. After using these tools/services, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2026.240924>.

Data availability

All data used in this article are publicly available through a Mendeley Data repository at <https://doi.org/10.17632/djzsz28xft.1>.

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