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Methodological Optimisation and Interpretation of Coulometric Titration Time Analysis

Matthew Richard Burton,^{*a,b} Yu Xia^a and Mauro Pasta^{*a,b}

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Coulometric titration time analysis (CTTA) has recently emerged as a powerful technique for quantifying the rate of solid electrolyte interphase (SEI) growth and elucidating the underlying mechanisms governing degradation in solid-state batteries with argyrodite solid electrolytes. However, subsequent studies employing metallic interlayers and variable stack pressures have revealed that CTTA results are highly sensitive to the effective contact area between the solid electrolyte and the current collector. In this work, we further explore CTTA as a SEI characterisation technique to gain more information on its strengths and weaknesses. The findings highlight key challenges when comparing results across samples and propose strategies to mitigate these effects. Moreover, this study contextualises CTTA within the broader suite of SEI characterisation techniques, offering guidance on its optimal implementation and interpretation.

Introduction

Solid-state batteries (SSBs) offer the potential for volumetric energy densities exceeding 1000 W h L^{-1} due to the use of lithium metal anodes.¹ There are two leading categories of solid electrolytes, oxides and sulfides. Oxide electrolytes exhibit relatively good stability against lithium metal but suffer from comparatively low ionic conductivity.² In contrast, sulfide solid electrolytes can exhibit ionic conductivities exceeding those of liquid electrolytes,² but are thermodynamically unstable against lithium metal.

Among sulfides, the argyrodite structure type electrolytes, namely $\text{Li}_6\text{PS}_5\text{Cl}$, are considered the leading candidates. However, $\text{Li}_6\text{PS}_5\text{Cl}$ have a theoretical reduction potential of 1.71 V vs. Li^+/Li .³ Such instability is not inherently detrimental if the resulting interphase is electronically insulating and sufficiently ionically conductive ($<10 \Omega \text{ cm}^{-2}$), such that cell impedance remains acceptable.^{4,5} In this case, a passivating solid electrolyte interphase (SEI) forms.⁶ Conversely, if the interphase is electronically conductive, continuous growth occurs, forming a mixed-conducting interphase (MCI).⁷

Early studies suggested that the interphase between $\text{Li}_6\text{PS}_5\text{Cl}$ and lithium was passivating and only a few nanometers thick, based on impedance analyses assuming Li_2S -dominated behaviour.⁸ This interpretation was later challenged, with reports of continuous interphase growth described by a Wagner-type diffusion-controlled model.^{4,9,10} Time-of-flight secondary ion mass spectrometry (ToF-SIMS) estimated interphase thicknesses on the order of hundreds of nanometers,¹¹ consistent with in situ X-ray photoelectron spectroscopy (XPS) measurements from our group.¹²

Coulometric titration time analysis (CTTA) has emerged as a powerful method to probe interphase growth kinetics.¹⁰ CTTA employs constant-current (CC) pulses followed by open-circuit periods (OCV), where voltage evolution during relaxation reflects lithium consumption by interphase formation (Figure 1a). The cumulative passed capacity enables quantification of growth kinetics. Impedance spectroscopy has further been integrated to monitor interphase resistance evolution.¹³

However, recent studies have revealed that CTTA is sensitive to stack pressure.^{14,15} Increased pressure correlates with higher apparent lithium consumption, attributed to changes in contact area between the solid electrolyte and current collector. Additionally, raising the working electrode potential, for example via alloy anodes, slows interphase growth.¹⁵

Our previous work demonstrated that depositing an interlayer directly onto the solid electrolyte, rather than onto the current collector, increased the electrochemically active surface area by 30× prior to lithiation.¹⁶ This resulted in accelerated lithium consumption during CTTA. While most interlayers exhibited similar behavior when operated within 50 mV of the lithium potential, Mg was shown to result in a slower rate due to a more stable SEI composition. Additionally, a Li_2O layer has been shown to slow interphase growth.¹³ This observation means SEI growth rate may not be as concerning for lithium excess configurations, where a native passivation layer exists.

In this work, we systematically evaluate the influence of electrochemically active surface area on CTTA. We quantify contact area effects using potentiostatic electrochemical impedance spectroscopy (PEIS), examine the impact of pressure and current collector configuration, and compare CTTA with alternative interphase characterization techniques. Finally, we define the conditions under which CTTA provides reliable kinetic information.

Methods

Cells were made using $\text{Li}_6\text{PS}_5\text{Cl}$ (Posco, D_{50} 5 μm). Pellets (10 mm diameter) were prepared by pressing powders at 400 MPa for 300 s using stainless steel pistons. Lithium counter electrodes (100 μm calendered foil) were then applied at 80 MPa for 30s. For two electrode cells, the cell housing was MACOR, for three electrode setups the cell housing was polyetheretherketone. For three electrode cells a ring of an InLi alloy that consisted of 75 at. % In and 25 at. % Li was used that surrounded the middle of the solid electrolyte pellet (Figure 2) as previously reported.¹³

All experiments were performed at 30 °C under Ar, with stack pressure maintained via a calibrated spring assembly. Electrochemical measurements were conducted using a BioLogic VMP3.

CTTA experiments employed a current of 12.25 μA , corresponding to a nominal current density of 15.6 $\mu\text{A cm}^{-2}$. Each current pulse lasted for 600 s.



PEIS measurements were conducted from 100 Hz to 50 mHz (10 points per decade, logarithmic spacing) with a 10 mV sinusoidal perturbation and 0.1 s stabilization time. To quantify relative contact area, PEIS was performed using stainless steel, Ni foil, and Ni sputtered current collectors under defined pressures.

Ni was deposited by radio frequency (RF) magnetron sputtering with a 50 mm diameter Ni target and a sputtering power of 50 W, using a MBraun MB EVAP PVD system inside an argon-filled glovebox. Base pressure before sputtering was 7×10^{-6} mbar, and the pressure during sputtering was 1×10^{-2} mbar. Pure Ar gas was used as the sputtering gas with a gas flow rate of 10 sccm. Prior to Ni deposition the target was sputtered for 10 minutes with the substrate shielded to remove any contamination.

Results and Discussion

Influence of Pressure on CTTA

Figure 1 shows data that is consistent with recent reports,^{14,15} where increasing stack pressure increases apparent lithium consumption during CTTA. Raising pressure from 3 MPa to 13 MPa increased the time required to reach the lithium potential by approximately 10× (Figure 1b), indicating an enhanced electrochemically active surface area. Over 400 h, total consumed capacity increased by only 1.2× (Figure 1c). This disparity indicates that time to plate and cumulative capacity do not scale proportionally.

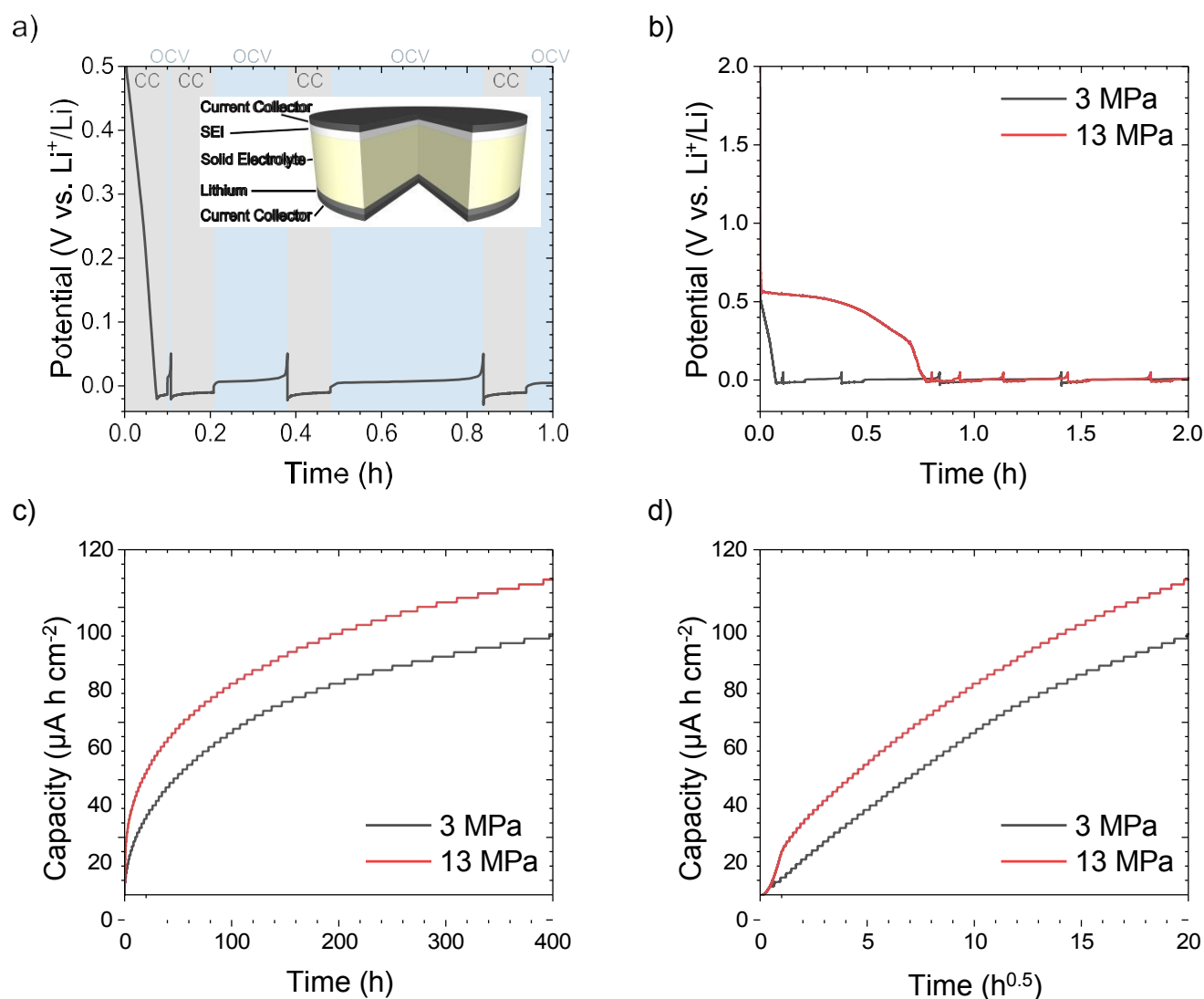


Figure 1 The effect of pressure on CTTA: **a)** illustration of CTTA operation, **b)** comparison of the initial CTTA profiles at different pressures, **c)** comparison of CTTA profiles over 400 hours with linear time and **d)** the square root of time.

PEIS measurements reveal that increasing pressure from 3 MPa to 13 MPa increases contact area by a factor of 2.6 (Figure 2). The contact area increase is deduced from the increase in the capacitance from the CPE element which results in a smaller tail being exhibited in the Nyquist plot.¹⁶ Enhanced contact arises from increased particle deformation at the current collector interface. However, because the absolute current was held constant, increasing the area reduced the effective current density. Thus, although the reactive area increased 2.6×, local lithium flux per unit area also decreased correspondingly. The combined effects result in the non-linear scaling of the CTTA response.



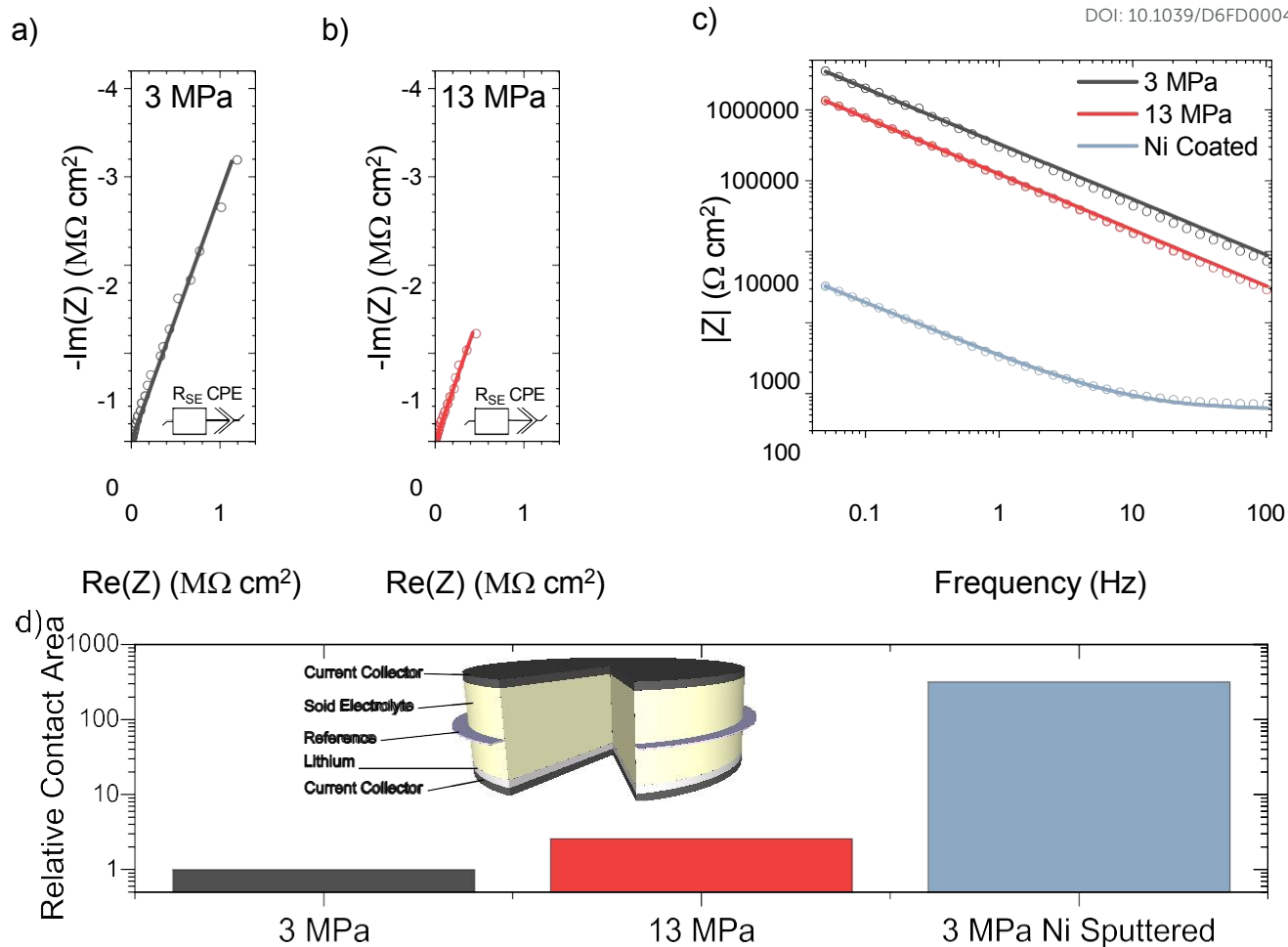


Figure 2 PEIS to determine the initial electrochemically active surface area: Nyquist plots (circles data, lines fits) with equivalent circuits of $\text{Li}_6\text{PS}_5\text{Cl}$ against stainless steel at **a)** 3 MPa and **b)** 13 MPa, **c)** comparison of Bode plots and **d)** comparison of relative surface areas with the Ni sputtered current collector normalised against PEIS conducted at 3 MPa with a Ni foil current collector.

Influence of Current Collector Configuration

Sputtering a 500 nm Ni layer directly onto $\text{Li}_6\text{PS}_5\text{Cl}$ dramatically increased electrochemically active surface area. PEIS indicates an increase exceeding 300× relative to planar contact (Figure 2), as deduced from the increase in capacitance. Despite this, the time to reach lithium potential increased by only 10× (Figure 3).

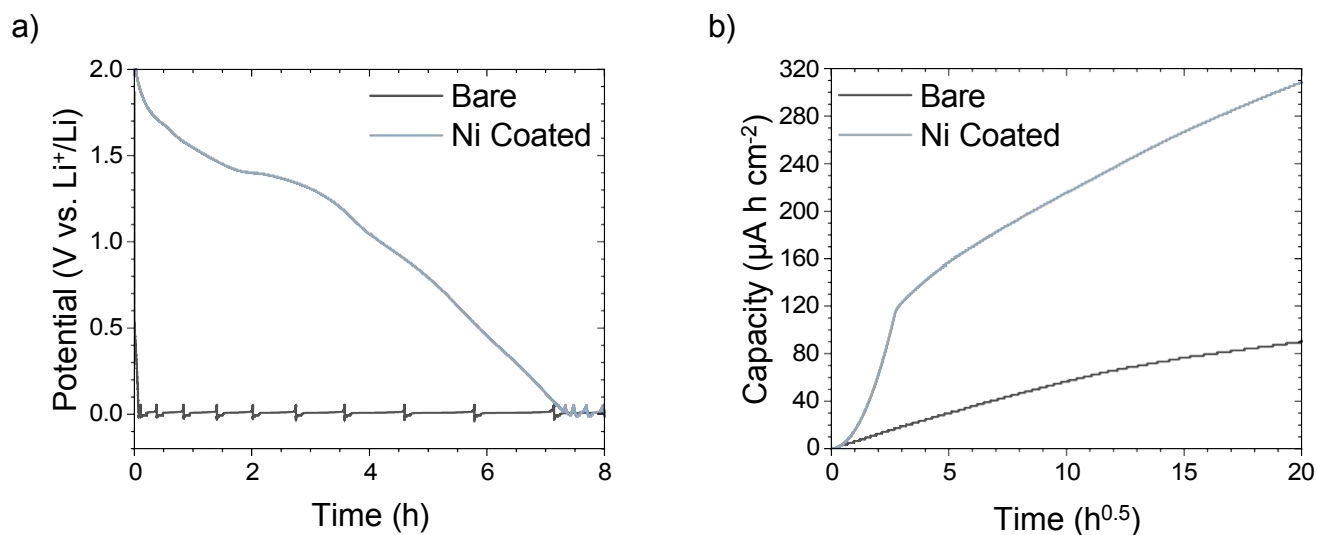


Figure 3 The effect of working electrode surface area on CTTA: **a)** comparison of the initial CTTA profiles, **b)** comparison of CTTA profiles over 400 hours with the square root of time.



The capacity required to reach the lithium potential was $115 \mu\text{Ah cm}^{-2}$, corresponding to an estimated interphase thickness $>1 \mu\text{m}$ if uniformly distributed.¹⁰ At this thickness, the interphase occupies a substantial fraction of the $\sim 5 \mu\text{m}$ particles, likely forming a connected layer. Once a continuous interphase forms, the geometric advantage of increased initial contact area diminishes, explaining the sub-linear scaling between area enhancement and CTTA response.

Mechanistic Interpretation

In the early stages of CTTA, larger contact area (Figure 4a-c, as deduced from PEIS) distributes current across a broader interface, producing thinner local interphases for a given capacity (Figure 4d-f). This is shown electrochemically by faster rates of initial capacity consumption. As growth proceeds, localized interphases coalesce into a continuous layer (Figure 4g-i). Once a connected SEI forms, differences in initial geometry become less dominant, resulting in lesser differences capacity consumption over time in the CTTA experiments. Nevertheless, variations in transport distance and local current density persist, maintaining measurable kinetic differences.

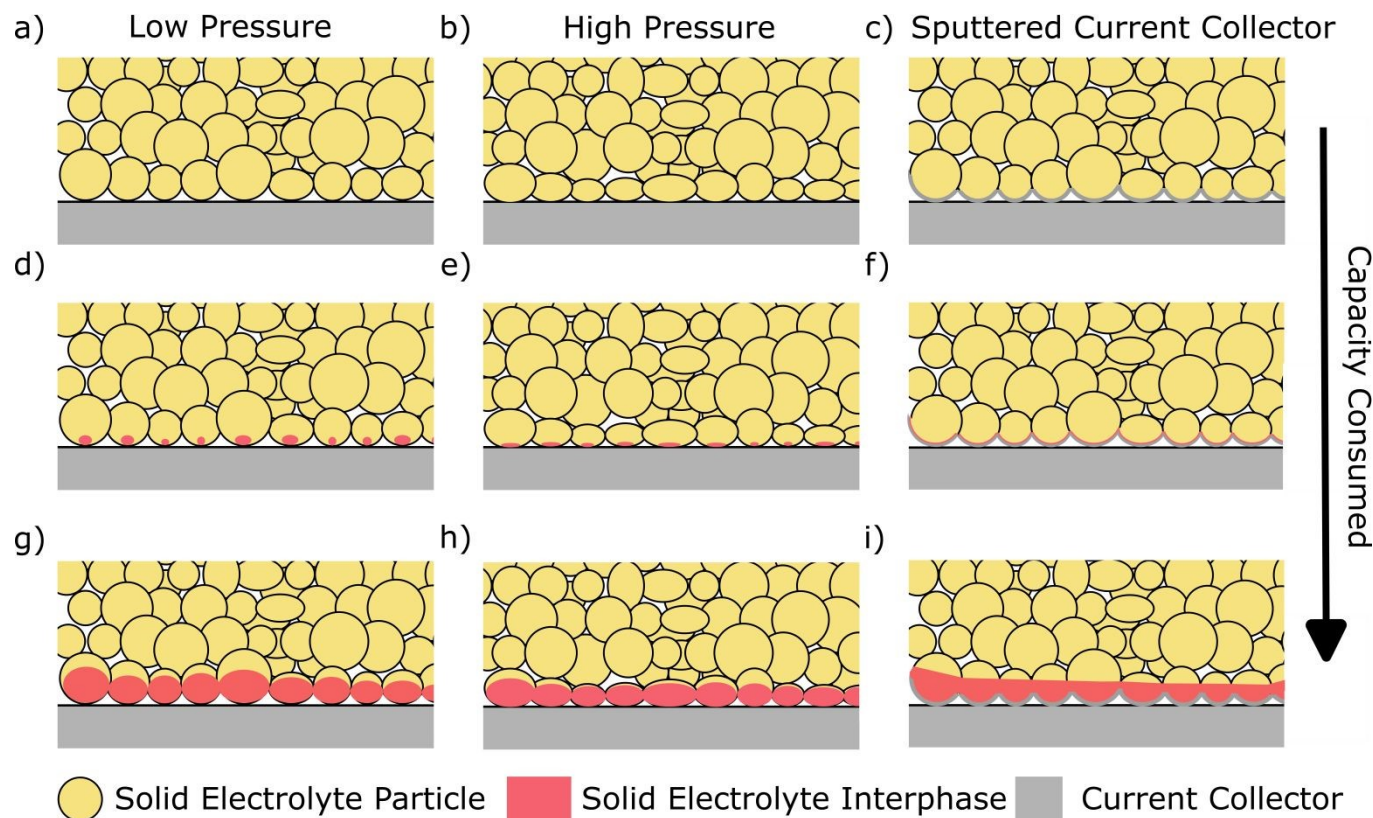


Figure 4 Schematic illustration of SEI growth at different pressures and current collector configurations during CTTA: **a-c**) highlighting the difference in contact areas between the solid electrolyte and the current collector, **d-f**) how the thickness of the SEI varies at the early stages of CTTA, **g-i**) localised SEI growth has turned into a connected SEI when sufficient capacity has passed.

These results demonstrate that the CTTA response is highly sensitive to electrochemically active surface area and does not scale linearly with it.

Comparison with Alternative Techniques

Virtual electrode plating XPS (VEP-XPS) removes macroscopic contact limitations by driving lithium plating through electron irradiation of the solid electrolyte surface.^{12,13} This configuration enables direct observation of interphase composition and chemical evolution. However, lithium deposited in the XPS chamber is exposed to residual gases, leading to parasitic reactions that complicate interpretation of intrinsic interphase kinetics.

ToF-SIMS provides depth-resolved chemical information and can reveal static compositional gradients across the interphase,^{11,15} but could struggle to capture an evolving gradient such as seen with phosphorus.¹³ Transmission electron microscopy offers high-resolution structural and thickness measurements.¹⁷ Nevertheless, both techniques are inherently destructive and provide post-mortem snapshots rather than time-resolved kinetic data. Furthermore, sample preparation may alter delicate interphase structures.

CTTA therefore occupies a distinct position among characterization tools: it enables operando quantification of lithium consumption over extended timescales under electrochemically relevant conditions. While sensitive to interfacial geometry, it remains uniquely capable of probing interphase growth kinetics when the contact area is carefully controlled and independently quantified.



The density of solid electrolytes is critical for suppressing dendrite formation,^{18,19} and practical SSBs will likely employ highly densified separators. Under such conditions, contact-area artifacts are minimized. For representative kinetic measurements, CTTA should therefore be conducted using fully densified solid electrolytes with well-defined interfacial contact.

Conclusions

We systematically evaluated the influence of electrochemically active surface area on CTTA measurements of interphase formation between Li₆PS₅Cl and lithium metal. Stack pressure and current collector configuration strongly affect the contact area, leading to substantial changes in apparent lithium consumption. The CTTA response does not scale linearly with area due to evolving current density distribution and interphase thickening.

Reliable kinetic analysis using CTTA requires a controlled and well-defined interfacial geometry, ideally employing fully densified solid electrolytes. When combined with complementary structural and compositional techniques, CTTA provides a robust framework for quantifying interphase growth in sulfide solid-state batteries.

Data availability

Data for this article, including PEIS and CTTA, are available at Zenodo at <https://doi.org/10.5281/zenodo.18862487>.

Author Contributions

M.B. and M.P. conceived the idea. M.B. performed all the experiments, with the exception of Ni sputtering which was performed by Y.X. M.B. wrote the manuscript, with input from all authors. M.P. supervised the design of the project and provided frequent input on the interpretation of all results.

Conflicts of interest

There are no conflicts to declare.

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^{0a} Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom; E-mail: Matthew.Burton@materials.ox.ac.uk, Mauro.Pasta@materials.ox.ac.uk

Matthew.Burton@materials.ox.ac.uk

^{0b} The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot OX11 0RA, United Kingdom.



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