Application Note

Characterizing All-Solid-State Batteries Using Solartron Analytical EnergyLab XM Instrument

Application Note: 2025

1. Introduction

All-Solid-State Batteries (ASSBs) have emerged as a revolutionary advancement in energy storage systems. By replacing liquid electrolytes with solid-state electrolytes, ASSBs offer enhanced safety, higher energy density, and improved cycle life, making them ideal for applications like electric vehicles (EVs) and portable electronics.

A key challenge in ASSB development lies in accurately characterizing the solid electrolyte/electrode interfaces, ionic conductivity, and overall battery performance. The Solartron Analytical EnergyLab XM instrument provides industry-leading precision for electrochemical impedance spectroscopy (EIS), DC techniques, and materials analysis, enabling researchers to address these challenges effectively.

Challenges in ASSB Research:

1. Interface Characterization: Solid-state interfaces often introduce resistance and interfacial instability.
2. Low Ionic Conductivity: Many solid electrolytes suffer from reduced ionic conductivity compared to liquid electrolytes.
3. Material Compatibility: Assessing electrode/electrolyte compatibility over prolonged cycles.
4. Measurement Precision: Accurate measurement of high impedance across solid-state materials is critical.

To overcome these hurdles, advanced electrochemical techniques, such as Electrochemical Impedance Spectroscopy (EIS), Galvanostatic Cycling, and Pulse Testing using highly sensitive instruments capable of providing high-quality results, are essential.

2. Electrochemical Techniques for ASSB Research

2.1 Electrochemical Impedance Spectroscopy (EIS)

Purpose: EIS is used to analyze the resistive and capacitive behavior of SSEs and ASSB interfaces.

Application:

- Assess ionic conductivity of SSE materials.
- Identify interfacial resistances between electrodes and electrolytes.
- Monitor the evolution of resistance during cycling and thermal changes.

©Copyright 2024 AMETEK, Inc. All Rights Reserved

2.2 Galvanostatic Charge-Discharge Cycling

Purpose: Evaluate ASSB performance metrics such as capacity, cycle life, and energy efficiency.

Application:

- Quantify the effects of solid electrolyte thickness and electrode-SSE interfaces.
- Analyze capacity retention over prolonged cycling.
- Determine Coulombic efficiency.

2.3 DC Polarization Methods

Purpose: Determine the ionic conductivity and transport properties in solid electrolytes.

Application:

- Steady-state DC methods help extract transference numbers, such as Chronoamperometry to separate ionic and electronic contributions. It can also help to evaluate single-ion vs. multi-ion conductors for SSE materials.
- Cyclic voltammetry can help assess the redox potentials and guide the potential window of the cell operation.
- Potentiostatic Intermittent Titration Technique (PITT) and Galvanostatic Intermittent Titration Technique (GITT) to study diffusion processes.

2.4 Pulse Testing

Purpose: Assess battery response to dynamic load conditions in ASSBs.

Application:

- Measure short-term impedance changes during pulse current applications.
- Evaluate the impact of interfacial behavior under pulse conditions.
- Optimize the high-power capability of ASSBs.

3. Case Studies

3.1 Carrier transition from Li atoms to Li vacancies in ASSBs

Lu and co-workers studied the ion-migration mechanism in a lithium alloy anode to quantify Li kinetic evolution and transition from the alloying reaction to the metal deposition in an ASSB and identified that there is a carrier transition from Li atoms to Li vacancies during lithiation processes.

©Copyright 2024 AMETEK, Inc. All Rights Reserved

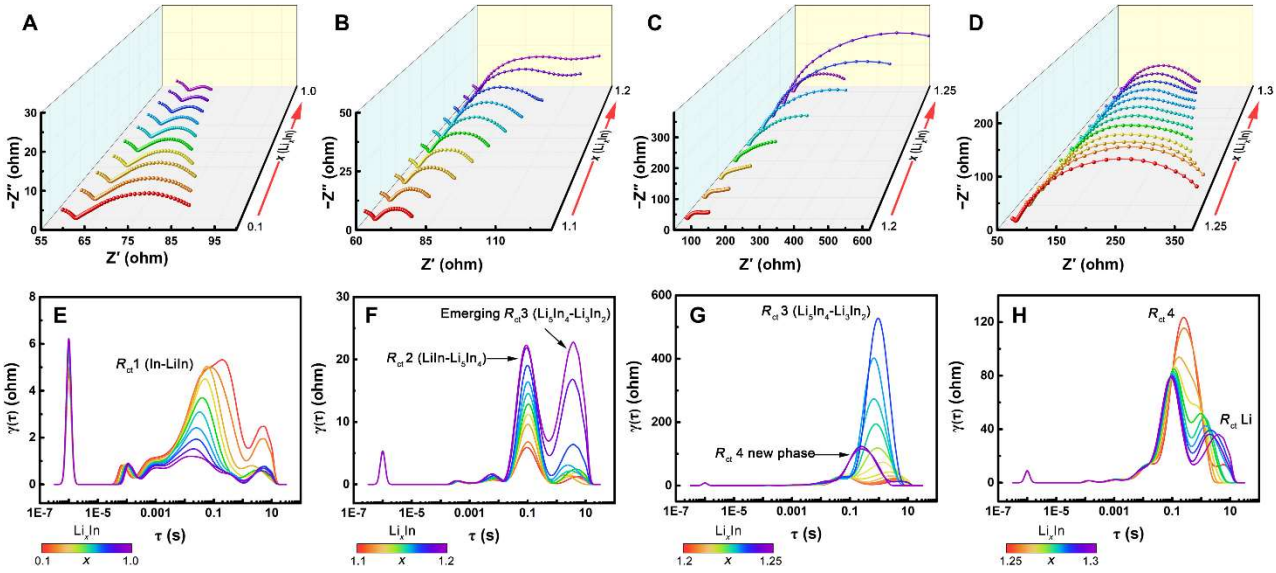


Figure 1. Li kinetic evolutions in Li-In during continuous lithiation processes. GEIS on LixIn of (A) 0 < x < 1, (B) 1.1 < x < 1.2, (C) 1.2 < x < 1.25, and (D) 1.25 < x < 1.3, respectively. (E to H) Corresponding DRT transformation of GEIS results in (A) to (D) to unravel the charge transfer evolution.[5.1]

The drastic changes in electrochemical features are linked to Li kinetic evolution, revealed via in situ GEIS with DRT analysis (Figure 1, using EnergyLab XM). EIS shows an incomplete semicircle for SSE grain boundaries and a full semicircle for Li-In electrodes and interfaces. Based on the comprehensive study conducted on different types of lithium alloys, authors concluded that Li alloys exhibit three charging stages with distinct rate-determining steps:

- Stable alloying: At low Li content (x < 1), low charge transfer impedance enables rapid Li^0 diffusion (~10^{-10} cm^2/s) with Li atoms as carriers.
- Charge transfer-limited: Between 1 < x < 1.25, charge transfer dominates, increasing overpotential (>300 mV) and transitioning from alloying to metal precipitation.
- Li^0 diffusion-limited: At x > 1.25, Li^0 diffusion slows (<10^{-12} cm^2/s), potential drops to 0 V, causing Li accumulation, interface failure, and Li vacancies as carriers.

3.2 Void formation behaviors in ASSBs

In another study, Lu and co-workers uncovered the interfacial void evolution principles in solid-state batteries, built a solid-state void nucleation and growth model, and made an analogy with the bubble formation in liquid phases, which affords fresh insights on understanding and designing solid-solid interfaces for ASSBs.

©Copyright 2024 AMETEK, Inc. All Rights Reserved

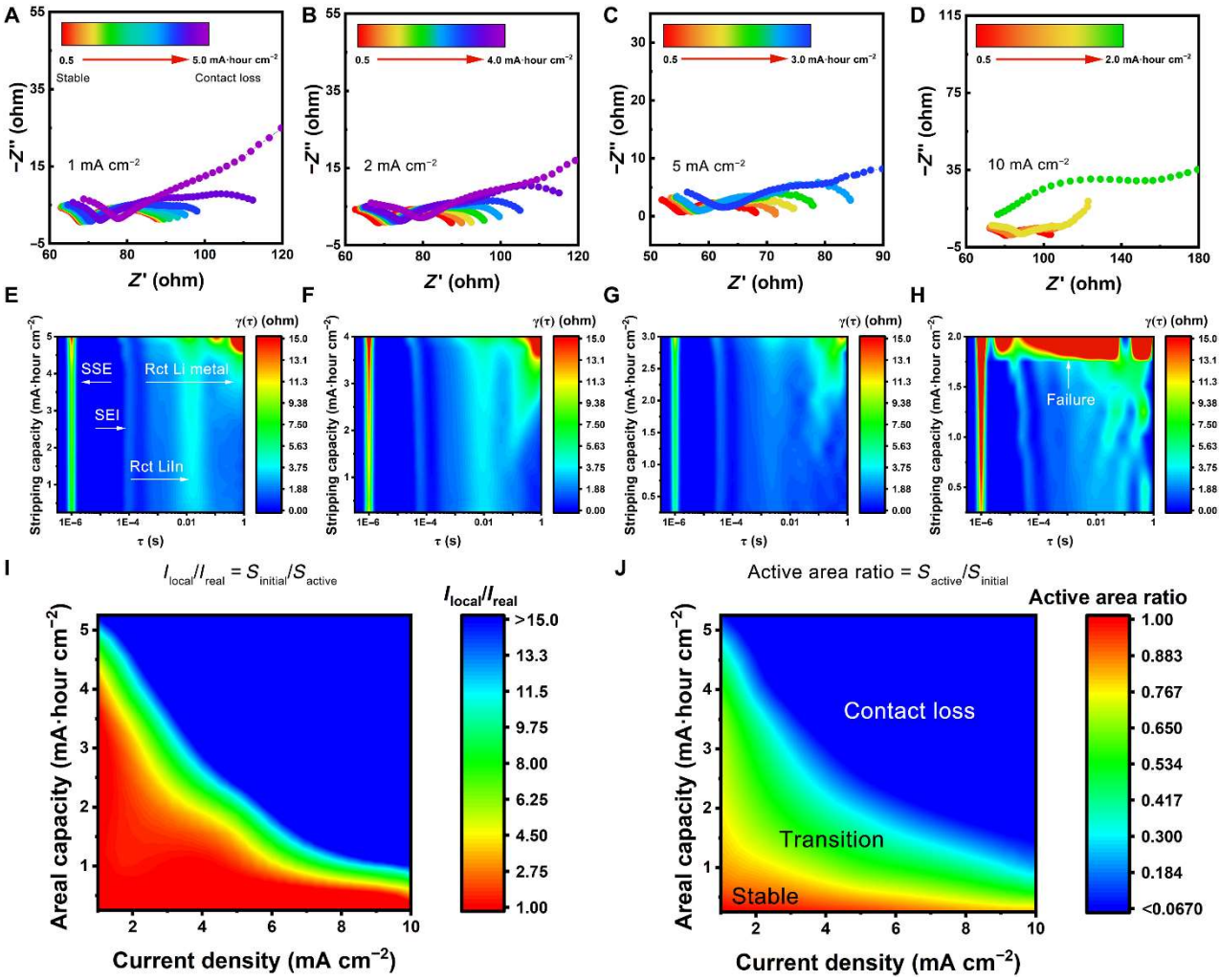


Figure 2. GEIS evaluation for Li half batteries during Li stripping process. The EIS recorded at the current density of (A) 1 mA cm^{-2}, (B) 2 mA cm^{-2}, (C) 5 mA cm^{-2}, and (D) 10 mA cm^{-2}. Corresponding DRT results (E–H) reveal charge transfer impedance (R_{ct}) Contour diagrams (I) and (J) display the areal capacity–current density phase transition for local current density and active contact area, respectively.[5,2]

The DRT of GEIS results (Fig. 2, A–D) acquired using EnergyLab XM are shown in Fig. 2, E–H, where each relaxation time τ represents a specific electrochemical process. Grain boundary impedance (R_{GB}) evolves with increasing Li stripping but remains stable at high frequencies (>10^5 Hz) and high stripping capacities (>5 mAh cm^{-2}). This stability prevents contact loss due to void accumulation. Thus, R_{GB} is independent of dynamic processes and effectively interprets anodic contact loss from the reduced active area.

In summary, Li void formation is a major cause of failure in solid-state batteries. This study links electrochemical performance with microscopic morphology, showing that current density controls void nucleation and growth, with contact loss proportional to i^2Void evolution progresses from 0D nucleation to 3D extension, driven by void injection and Li diffusion. To overcome void-related issues, improving void diffusivity, reducing polarization, and designing Li frameworks with optimized porosity can enhance SSLMB reliability.

4. Conclusion

©Copyright 2024 AMETEK, Inc. All Rights Reserved

The development of all-solid-state batteries requires an in-depth understanding of material properties, interfacial phenomena, and dynamic performance. Electrochemical techniques such as EIS, Galvanostatic Cycling, and Pulse Testing, enabled by tools like the AMETEK Solartron Analytical EnergyLab XM are indispensable for addressing challenges in ASSB research.

By combining advanced electrochemical methods with material characterization, researchers can unlock the full potential of ASSBs, paving the way for next-generation energy storage systems.

5. Reference

5.1 Yang Lu et al., The carrier transition from Li atoms to Li vacancies in solid-state lithium alloy anodes. Science Advances 7, eabi5520(2021). DOI:10.1126/sciadv.abi5520

5.2 Yang Lu et al., The void formation behaviors in working solid-state Li metal batteries. Science Advances 8, eadd0510(2022). DOI:10.1126/sciadv.add0510

©Copyright 2024 AMETEK, Inc. All Rights Reserved