

Three-Electrode Testing for Solid-State Batteries: Separating Anode and Cathode Behavior

Why two-electrode cells hide the root cause of capacity fade, how a reference electrode works in a solid-state cell, and how to interpret the resulting impedance data.

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The Problem With Two-Electrode Cells

You run a solid-state cell for 80 cycles. Capacity drops from 180 mAh/g to 120 mAh/g. Impedance climbs from 40 $\Omega\cdot\text{cm}^2$ to 310 $\Omega\cdot\text{cm}^2$. Now answer this question: **which electrode failed?**

In a two-electrode configuration you cannot answer it. The cell voltage you measure is the difference between cathode potential and anode potential:

$$V_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

One number, two unknowns. A 250 $\Omega\cdot\text{cm}^2$ impedance rise could be:

- Lithium dendrites penetrating the separator layer at the anode
- A resistive interphase growing between the sulfide electrolyte and the NMC cathode
- Contact loss at the cathode composite from volume change during delithiation
- Any combination of the above

Each of these demands a completely different fix. Dendrite suppression means raising stack pressure or adding an interlayer. Cathode interphase growth means coating the active material (LiNbO_3 , Li_2ZrO_3). Contact loss means reformulating the composite or changing the pressing protocol. Guess wrong and you burn two months.

The three-electrode cell resolves this by adding a **reference electrode** — a third terminal that holds a stable, known potential and lets you measure each electrode independently against it.

How a Reference Electrode Works in a Solid-State Cell

The basic principle

A reference electrode is any electrode whose potential stays fixed regardless of the small currents flowing through the measurement circuit. In liquid systems this is straightforward — Ag/AgCl, saturated calomel, or a lithium wire immersed in electrolyte. In a solid-state cell, the reference must make ionic contact with the solid electrolyte without disturbing the main current path.

Once installed, your potentiostat measures three things simultaneously:

$V_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$ (what you saw before)

$V_{\text{working}} = E_{\text{cathode}} - E_{\text{reference}}$ (cathode alone)

$V_{\text{counter}} = E_{\text{anode}} - E_{\text{reference}}$ (anode alone)

Now the $250 \Omega\text{-cm}^2$ rise resolves into two numbers. If the cathode contributes $30 \Omega\text{-cm}^2$ and the anode contributes $220 \Omega\text{-cm}^2$, you have a lithium-metal problem, not a cathode problem.

Three practical implementations

1. Embedded lithium wire (most common)

A 50–100 μm lithium wire is placed at the mid-plane of the solid electrolyte layer during assembly, with one end exiting through a side port in the mold. Li/Li^+ is an excellent reference in solid-state systems — its potential is defined, stable, and needs no additional interface.

- **Pros:** Simple, cheap, thermodynamically well-defined (0 V vs Li/Li^+)
- **Cons:** The wire creates a small mechanical discontinuity in the electrolyte; under 300+ MPa it can extrude or short to an electrode if misplaced. Requires careful placement during assembly.

2. Side-contact ring

A thin metal ring (Li-coated Cu, or Li foil) contacts the outer circumference of the electrolyte pellet, away from the active stack.

- **Pros:** No discontinuity in the ion path; mechanically robust under high stack pressure
- **Cons:** Sits outside the primary current-flow region, so at high current density it can report a potential offset from the true mid-plane value. Best for low-rate studies ($< C/2$).

3. Micro-reference on the separator edge

A lithographically-defined Li dot or a thin Li/SE micro-cell bonded at the pellet edge.

- **Pros:** Minimal geometric perturbation, good for high-rate work
- **Cons:** Fabrication complexity; typically only used in specialized labs with cleanroom access.

For most research groups, **the embedded lithium wire is the right starting point** — it's what the majority of published three-electrode ASSB studies use.

Placement: The Detail That Decides Whether Your Data Is Real

This is the part most groups get wrong the first time.

A reference electrode reports the potential **at the point where it sits**. If it's off-center — say 80% of the way toward the cathode instead of at the mid-plane — it picks up part of the cathode's ohmic drop and attributes it to the anode. The result looks like clean data but is systematically wrong.

Rules for placement

Rule	Reason
Mid-plane, $\pm 10\%$ of electrolyte thickness	Symmetric ohmic split between the two half-cells
Radially outside the active stack footprint	Prevents the wire from carrying main-cell current
Electrically isolated from both current collectors	A short to either electrode makes all three measurements meaningless
Same Ar-glovebox handling as the rest of the cell	Li reacts with trace $\text{H}_2\text{O}/\text{O}_2$; a passivated reference drifts

Sanity check before you trust the data

After assembly, measure the open-circuit potential of each half:

- **E_anode vs reference** should read ~ 0 V if the anode is lithium metal. If it reads 0.3 V, your reference is contaminated or the wire is partly passivated.
- **E_cathode vs reference** should match the expected OCV of the cathode material (e.g. ~ 3.7 V for NMC811 at 50% SOC). A reading 200 mV off means the reference is misplaced or drifting.
- **Sum check:** $E_{\text{cathode}} - E_{\text{anode}}$ must equal the directly-measured V_{cell} to within 5 mV. If it doesn't, something is shorted.

Run this check on every cell. It takes 30 seconds and saves entire experimental campaigns.

Reading the Data: Four Diagnostic Patterns

Once you have clean three-electrode data, most failure modes reveal themselves as characteristic signatures.

Pattern 1 — Anode-dominated impedance growth

Signature: Anode half-cell impedance climbs steadily cycle-over-cycle; cathode stays flat.

Interpretation: Lithium-metal interface degradation. Either (a) SEI accumulation from electrolyte decomposition, or (b) contact loss from void formation during stripping.

Distinguishing between (a) and (b): Raise stack pressure by 50 MPa and re-measure. If impedance drops sharply, it was void formation (mechanical). If unchanged, it's chemical SEI growth.

Typical fixes: Higher stack pressure, Li-alloy interlayer (Mg, Ag), or a more reductively-stable electrolyte at the anode side.

Pattern 2 — Cathode-dominated impedance growth

Signature: Cathode half-cell impedance rises; anode is stable.

Interpretation: Cathode–electrolyte interphase (CEI) growth, typically from oxidative decomposition of the solid electrolyte at high cathode potential. Sulfides are particularly vulnerable above 2.5 V vs Li/Li⁺.

Confirming it: Cycle the same cell in a narrower voltage window (e.g. cut off at 4.0 V instead of 4.3 V). If the growth rate drops proportionally, it's oxidative.

Typical fixes: Coat the cathode active material (LiNbO₃, Li₂ZrO₃, Al₂O₃), or use a dual-layer electrolyte with an oxidatively-stable layer (e.g. halide) at the cathode.

Pattern 3 — Sudden anode potential excursion

Signature: Anode potential drops below 0 V vs Li/Li⁺ during charge, often abruptly.

Interpretation: Lithium plating exceeding the transport capability of the interface — the precursor to dendrite formation. This is the single most valuable measurement a three-electrode cell provides, because in a two-electrode cell it's completely invisible until the cell shorts.

Action: Reduce charge rate, raise temperature, or increase stack pressure. Map the onset current density as a function of temperature to find your safe operating window.

Pattern 4 — Both electrodes stable, capacity still fading

Signature: Neither half-cell impedance changes much, but capacity declines.

Interpretation: The loss is not interfacial. Likely candidates: active-material cracking in the cathode composite, loss of percolation in the carbon network, or lithium inventory loss to irreversible side reactions.

Next step: Post-mortem — cross-section SEM of the cathode composite, or ICP for lithium inventory. Three-electrode data has told you where *not* to look, which is still valuable.

Impedance Deconvolution: A Worked Example

Consider a Li | Li₆PS₅Cl | NMC811 cell after 100 cycles at 60 °C.

Two-electrode EIS gives a single semicircle plus tail, total 310 Ω·cm². You fit it with R_{bulk} + R_{interface} + Warburg and get R_{interface} = 265 Ω·cm². That number is the sum of both interfaces, and there's no honest way to split it.

Three-electrode EIS run at the same state:

Measurement	R _{bulk}	R _{interface}
Full cell	45 Ω·cm ²	265 Ω·cm ²
Cathode vs ref	22 Ω·cm ²	51 Ω·cm ²
Anode vs ref	23 Ω·cm ²	214 Ω·cm ²

The bulk resistance splits cleanly in half — expected, since the reference sits at the mid-plane. This is itself a validation that placement was correct.

The interface resistance splits 51 / 214. **81% of the interfacial loss is at the lithium anode.** Cathode coating work would have been almost entirely wasted effort; the correct intervention is on the anode side.

This single measurement redirects months of work.

Practical Considerations

Which cells justify a three-electrode mold?

Three-electrode assembly takes roughly 2× as long as two-electrode and has a higher failure rate (a misplaced reference wire means scrapping the cell). It is not the default choice for every experiment.

Use three-electrode when:

- You're diagnosing an unexplained capacity fade
- You're developing a new electrolyte and need to know its stability window against both electrodes
- You're optimizing charge protocols and need to see the anode plating threshold
- You're writing a paper where reviewers will ask "which electrode?"

Stick with two-electrode when:

- Running long-term cycling on an already-characterized system
- High-throughput composition screening (you want speed, not mechanism)
- Routine QC against a known baseline

A common workflow: screen in two-electrode, then build three or four three-electrode cells of the top candidate to understand *why* it works.

Temperature and reference stability

At elevated temperature, lithium creeps. A reference wire that sat cleanly at the mid-plane at 25 °C can migrate under 300 MPa at 80 °C. If you're running above 60 °C:

- Re-verify the OCV sanity check after thermal equilibration, not just at assembly
- Consider the side-contact ring geometry instead of an embedded wire
- Re-check the sum rule ($E_{\text{cathode}} - E_{\text{anode}} = V_{\text{cell}}$) at intervals during long runs

Common failure modes during assembly

What happens	Cause	Prevention
Reference reads open-circuit / noisy	Wire lost ionic contact	Press the wire gently into the electrolyte surface before the top layer goes on
All three potentials read the same	Wire shorted to an electrode	Keep the wire radially outside the stack footprint; check with a multimeter before pressing
Sum rule violated by >50 mV	Reference off-center or passivated	Re-scrape the Li wire in the glovebox immediately before placement
Reference drifts over hours	Trace moisture reacting with Li	Verify glovebox H ₂ O < 0.1 ppm; dry all components 24 h at 80 °C under vacuum

Summary

A two-electrode solid-state cell tells you *that* something failed. A three-electrode cell tells you *which electrode* and *by how much*. For mechanism work, that distinction is the difference between a targeted fix and months of guessing.

The key requirements:

1. **Reference at the electrolyte mid-plane**, radially outside the active stack
2. **Lithium metal** as the reference material (0 V vs Li/Li⁺, no additional interface)
3. **Sanity-check every cell** with the OCV sum rule before trusting any data
4. **Re-verify after thermal ramps** if operating above 60 °C

Our [three-electrode mold \(MOL1D100A\)](#) provides a dedicated side port for the reference lead, a PEEK core rated to 200 °C, and die-steel plungers stable to 5 T stack force — designed so that the reference wire can be positioned and held at the mid-plane without extruding under pressure.

For working-cavity sizes outside the standard $\varnothing 10$ mm, or for 1000 MPa configurations, contact business@labcorematerials.com — quotes returned within 48 hours.

Related reading: [Solid-State Battery Test Mold Selection and Usage Guide](#)

Enquiries: business@labcorematerials.com · labcorematerials.com

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