Application note

A Wire Ring Reference Electrode for Sintered Oxide Ceramic Solid-State Battery Samples

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Introduction

Three-electrode setups for testing solid-state battery cells are an important tool in research and development since they allow measuring the potentials of both anode and cathode with respect to a known reference. Nevertheless, incorporating a reference electrode in the solid electrolyte is challenging, especially if the electrolyte cannot be cold-pressed. For example, battery components based on $Li_7La_3Zr_2O_{12}$ (LLZO) solid-state electrolytes must typically be sintered at elevated temperatures, making the use of three-electrode setups difficult.

In this application note, we describe a wire-ring reference electrode that can be pressed against the sides of a pre-sintered electrolyte pellet to allow for a three-electrode configuration. The wire-ring used in this case was made from platinum, and lithium was plated in situ to form a stable, well-known reference potential. Cycling and electrochemical impedance spectroscopy (EIS) in three-electrode mode were performed on a fully inorganic all-solid-state cell consisting of a lithium metal anode, an LLZO separator, and a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) based composite cathode.

Experimental

The cells were manufactured based on the method previously published by C. Roitzheim et. al. [1]. A 3 mm thick pre-sintered LLZO pellet (11.5 mm Ø) was coated on one side with a composite cathode ink comprising NMC811, LLZO, and Li_3BO_3 (LBO). The cathode layer was approximately 100 µm thick and covered the whole pellet area. After sintering at 750 °C, Li-metal foil was attached to the other side of the LLZO pellet by pressing and melting (10 mm original Ø) to obtain a full cell.

The samples were contacted in a three-electrode configuration using a CompreCell 12 DP [2] (rhd instruments GmbH & Co. KG), which has a 12 mm Ø sample cavity and a selection of sleeves for different cell configurations. In this case, a two-part sleeve was used ("PEEK Sleeve Set for Wire Ring Reference"), allowing the use of a reference electrode in the form of a Pt wire (0.7 mm Ø) bent into a ring shape that can be pressed around the outside of the electrolyte, half-way between the anode and cathode (**Figure 1**). The anode and cathode were contacted directly by tungsten carbide pistons, which also apply pressure to the sample. The cell assembly was done in an argon-filled glove box. Once sealed, the cells are air-tight and can be operated under ambient conditions.

Figure 1. Sketch of the wire ring reference electrode clamped onto the cell stack.

The cell temperature and pressure were controlled by a CompreDrive [3] equipped with an HC-Addon (rhd instruments GmbH & Co. KG) [4]. All measurements were performed at 60 °C and 5 MPa unless otherwise stated. EIS was performed with a Novocontrol NEISYS impedance analyzer, while a Biologic SP-200 potentiostat / galvanostat was used for all other electrochemical measurements.

In order to plate lithium on the wire ring *in situ*, it was connected as the working electrode (WE), and the Li anode as counter electrode (CE). A constant current (CC) of -1 µA was first passed for 1 min in order to enable the lithium plating to nucleate without excessive overpotential. Then, -20 µA CC was applied for 1 h, after which the open-circuit potential (OCP) was monitored.

Charge/discharge cycling was performed in a standard three-electrode configuration, connecting the NMC cathode as WE, the Li anode as CE, and the Li wire ring as reference electrode. Charging and discharging was done with a CC of 40 µA between 3.0 V and 4.3 V cell voltage, which for the charge step was followed by a constant cell voltage stage (20 µA cutoff). EIS was performed with an rms amplitude of 10 mV from 2 MHz to 100 mHz. The impedance data was evaluated by equivalent circuit fitting in RelaxIS 3.0 (rhd instruments GmbH & Co. KG). The figures in this application note were created using Edelweiss 0.2 (rhd instruments GmbH & Co. KG).

Results and Discussion

While a bare Pt wire can act as a pseudo-reference electrode, *e.g.* for use in EIS, its potential does not remain stable for longer experiments. To stabilize the potential of the wire ring electrode, it was lithiated *in situ* (**Figure 2**), after which the potential was stable within 1 mV of the lithium anode potential. The charge passed corresponds to about 1 µm of ideally plated lithium (assuming approximately 0.25 mm contact width between the wire ring and the electrolyte).

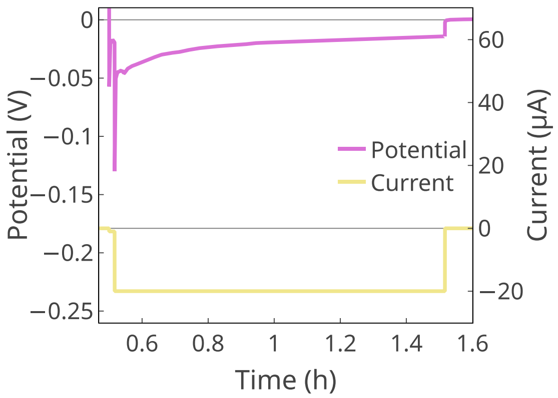

***Figure** 2. Lithium plating of the Pt wire ring electrode, forming a lithium metal reference electrode in situ.*

The lithiated reference electrode was stable enough to perform cycling in three-electrode mode over several days. As shown in **Figure 3**, the cell voltage could be separated into the contributions from the cathode and anode. The anode potential stayed within 10 mV of the lithium reference potential, exhibiting plateaus at ±5 mV on charge and discharge. Hence, the cell voltage was mainly determined by the cathode potential.

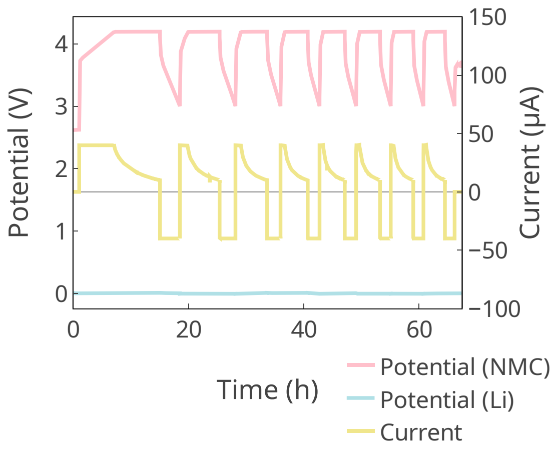

***Figure 3**. Charge/discharge cycling of a solid-state battery cell in three-electrode configuration.*

After cycling, three-electrode EIS revealed that the full cell impedance spectrum almost completely overlapped with the cathode spectrum (**Figure 4**, 0% state of charge). The cathode exhibited a flattened semicircle in the mid-frequency range (~10 kHz – 50 Hz), followed by diffusion-limited behavior at low frequencies. The semicircle had a resistance of 1.7 kΩ, which could originate either from the NMC charge transfer reaction or from a resistive surface layer. The lithium metal anode, on the other hand, had a much smaller charge transfer resistance (7.5 Ω), and was not diffusion limited at the lower frequencies. Thus, the lithium metal anode does not limit the performance of the cell, which rather depends on the ceramic NMC811 based composite cathode.

At high frequencies, the end of an almost ideal (*i.e.*, non-flattened) semicircle was visible in the CE spectrum. This originated from the ionic resistance of the electrolyte in parallel with the stray capacitance of the cell and/or the instrument [5]. It is not visible in the WE spectrum since the impedance is much higher.

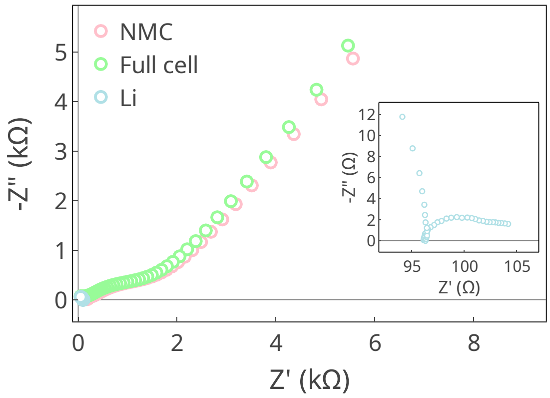

***Figure 4**. Three-electrode impedance spectra of the cycled cell in the discharged state. Lithium anode spectrum shown enlarged in the inset.*

The CE spectrum also exhibited a very small (0.2 Ω) loop around 2 kHz, which is an artefact present because the reference electrode is not placed perfectly halfway between the WE and CE. Shifting the reference electrode to either side caused the loop to become more pronounced (indicating that it was already placed almost in the center) since the reference electrode potential then had a bias towards one electrode.

The cell design of the CompreCell DP setup puts some limitations on the dimensions of compatible samples, such as the electrolyte thickness, which is recommended to be at least 2 mm, to accommodate the reference electrode without electrical contact to the WE or CE. Moreover, the electrolyte pellet diameter cannot exceed 12 mm, but must also not be too small (at least approximately 11.5 mm), to ensure proper contact with the wire ring electrode. In principle, a thicker wire could be used for smaller diameter samples, with the tradeoff that the electrolyte then needs to be thicker. In practice, since pellets typically shrink slightly upon sintering, a pre-sintering diameter of 12 mm usually results in compatible sample dimensions.

Summary

A wire ring reference electrode enabled electrochemical testing of a Li | LLZO | (NMC811/LLZO/LBO) solid-state battery cell in three-electrode configuration. The wire ring is pressed against the sides of the electrolyte in between the anode and cathode, and is hence compatible also with sintered electrolytes where the reference electrode cannot be incorporated by cold-pressing during fabrication. Lithium plating of the platinum wire ring lead to a stable potential for several days, making three-electrode cycling as well as low-frequency EIS possible.

The three-electrode measurements revealed that the lithium metal/LLZO interface at the anode is not limiting for the cell performance, having a charge-transfer resistance two orders of magnitude smaller than the NMC based composite cathode. This is also reflected in the fact that the anode potential did not deviate significantly from the lithium reference potential.

The inclusion of a reference electrode in the solid-state battery cell made it possible to gain deeper understanding of the contribution of each electrode to the full cell voltage and total cell resistance. This is crucial for improving the cell performance by systematic optimization of the electrodes and interfaces.

Literature

[1] C. Roitzheim, Y. J. Sohn, L.-Y. Kuo, G. Häuschen, M. Mann, D. Sebold, M. Finsterbusch, P. Kaghazchi, O. Guillon and D. Fattakhova-Rohlfing, "All-Solid-State Li Batteries with NCM–Garnet-Based Composite Cathodes: The Impact of NCM Composition on Material Compatibility," *ACS Applied Energy Materials*, vol. 5, no. 6, p. 6913–6926, 2022.

[2] rhd instruments GmbH & Co. KG, "CompreCell DP," October 2025. https://rhd-instruments.de/solutions-and-products/for-solid-state-batteries/comprecell-dp/.

[3] rhd instruments GmbH & Co. KG, "CompreDrive," October 2025. https://rhd-instruments.de/solutions-and-products/for-solid-state-batteries/compredrive/.

[4] rhd instruments GmbH & Co. KG, "HC-Addon," October 2025. https://rhd-instruments.de/solutions-and-products/for-solid-state-batteries/hc-addon/.

[5] C. Karlsson, "Application note: Three-Electrode All-Solid-State Battery Cycling," December 2023. https://rhd-instruments.de/magazine/three-electrode-all-solid-state-battery-cycling/.