



Application note

Three-Electrode All-Solid-State Battery Cycling



Introduction

As the solid-state battery field matures and more attention is turned to detailed characterization of interfaces and individual redox processes, the need for a suitable reference electrode (RE) system emerges, in order to enable three-electrode measurements [1, 2, 3]. While the use of standardized REs is well-established in electrochemical experiments with liquid electrolytes, it is very uncommon in the field of solid-state batteries. Two-electrode measurements are fundamentally limited since the observed response is always a combination of both electrodes. For example, without a RE it is not possible to access the individual anode and cathode potentials in full cell cycling tests, and electrochemical impedance spectra are difficult to interpret due to overlapping features from processes at both electrodes.

A three-electrode version of the CompreCell, an air-tight, high-pressure, solid-state battery measurement cell, was recently commercially released [4]. In this application note we demonstrate the characterization of a cell with a $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC) cathode, graphite anode, $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) electrolyte, and a lithium metal RE. Three-electrode charge/discharge cycling as well as electrochemical impedance spectroscopy (EIS) is shown.

Experimental

The three-electrode all-solid-state battery stack was assembled in a CompreCell 12

DP-3e cell (see figure on title page, rhd instruments GmbH & Co. KG): First, a gold-plated tungsten wire (25 μm \varnothing , Goodfellow) was used as the basis for the RE [1], and was inserted into the sleeve (12 mm inner \varnothing). 2×142 mg LPSCI (125 mg/cm^2 , Ampcera Argyrodite, MSE Supplies) was added to both sides of the wire and pre-compressed at 10 kN. 11.4 mg NMC composite (6.6 $\text{mg}_{\text{NMC}}/\text{cm}^2$; 65% NMC622 (BASF), 32% LPSCI, 3% C65 (Timcal)) and 8.9 mg graphite composite (5.4 $\text{mg}_{\text{Gr}}/\text{cm}^2$; 68% natural graphite (918-II, MTR), 32% LPSCI) were added to either side of the electrolyte pellet, and contacted directly by the tungsten carbide pistons (**Figure 1**). The assembly and pre-compression were done in an argon-filled glove box. Once sealed, the can be operated under ambient conditions.

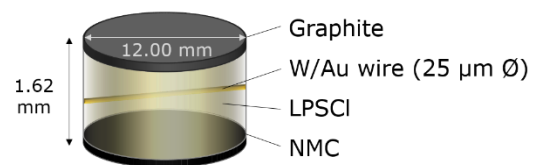


Figure 1. Sketch of the materials inside the three-electrode cell.

The cell temperature was controlled by a Huber Unistat 405 circulator (Peter Huber Kältemaschinenbau SE) and the pressure applied by a CompreDrive press (rhd instruments GmbH & Co. KG) using CompreDriveControl 1.14 (rhd instruments GmbH & Co. KG). A pressure of 100 MPa was applied for three minutes to compact the cell stack, and the measurements were performed at 20 °C and 10 MPa unless otherwise stated. The pellet thickness after compression was 1.62 mm. In the

CompreDrive, the pressure is dynamically regulated with a force sensor feedback loop controlling a servo motor. The pressure was thus kept constant even during the sample swelling and shrinking during cell cycling.

The lithium RE was created *in situ* by lithiating the W/Au wire [1] using the NMC cathode as a lithium source. A 5 μA constant current (CC) was passed for 30 min, plating a thin layer of lithium on the wire. A Biologic SP-200 potentiostat/galvanostat controlled by EC-Lab 11.43 (Biologic) was used for charge and discharge at a CC of either C/20 or C/10, which for the charge step was followed by a constant voltage (CV) stage where the full cell potential was held constant (C/50 or C/20 cutoff, respectively). Individual potential limits versus the Li RE were set separately for the anode (0.01 – 2.00 V) and cathode (3.00 – 4.20 V). Additionally, a 0.00 V limit was enforced for the anode during the CV stage. Galvanostatic EIS was performed using either a Biologic SP-200 or a Novocontrol NEISYS impedance analyzer (100 μA rms amplitude). 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 the Edelweiss software (rhd instruments GmbH & Co. KG).

Results and Discussion

A gold-plated tungsten wire is a good basis for a solid-state RE, as shown recently by Hertle *et al.* [1]. The tungsten core provides mechanical stability, enabling the use of

very thin wires, minimizing the obstruction of ions. The gold layer can be lithiated *in situ* to form either a pseudo-reference or a true RE through the formation of a mixed phase system. The separate alloying stages are visible as potential plateaus during the lithiation process (Figure 2). The potential profile was sloping since the NMC cathode was used as RE and counter electrode (CE) and experiences a shift in potential. The lithiation process was allowed to proceed into the plating region, creating a RE whose potential was stable for several days.

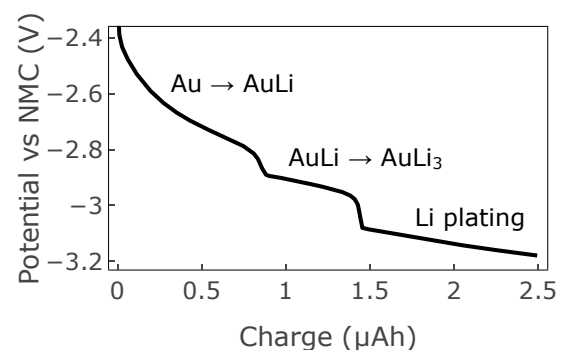


Figure 2. Potential of the W/Au wire during its *in situ* lithiation.

In this three-electrode system, the individual potentials of the NMC cathode and the graphite anode can be recorded during cycling, as shown in Figure 3. This allows a more detailed investigation of the redox processes occurring at both electrodes. The cathode and anode contributions to cell polarization are accessible, e.g. during the relaxation after the discharge step. Another benefit is that individual potential limits can be set for the cathode and anode, ensuring that neither electrode reach undesired potentials, which might otherwise lead to e.g. graphite lithium plating or NMC overcharging.

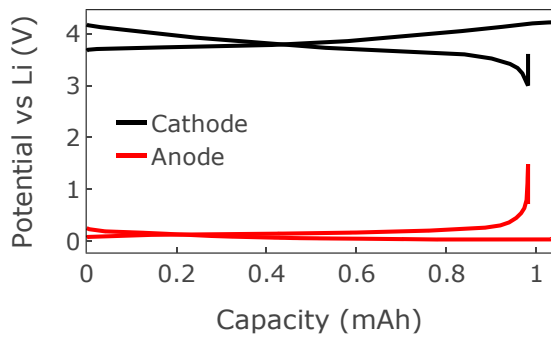


Figure 3. Charge/discharge curves at $C/20$ for the NMC cathode (black, WE vs RE) and graphite anode (red, CE vs RE).

At $C/20$, the electrode capacities were rather well matched, as both electrode potentials were close to their respective cutoffs at the end of charge and discharge (Figure 3). At higher C-rates, however, the graphite anode became limiting, and quickly reached its cutoff potential during charge (Figure 4). The NMC cathode thus only experienced shallow cycling, as it could not be fully utilized. Thanks to the individual potential limits, the charge step was stopped even though the cell potential was only about 3.7 V, avoiding lithium plating on the anode and premature cell failure. A RE can thus be helpful in finding the root cause of cell performance issues.

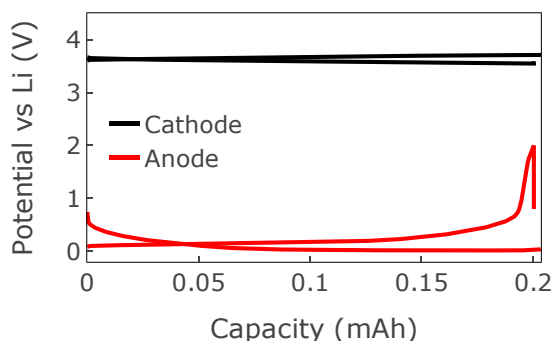
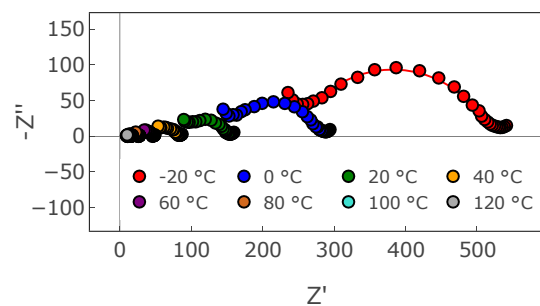
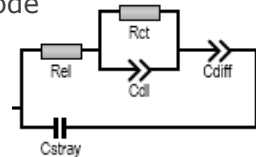


Figure 4. Charge/discharge curves at $C/10$.

With a three-electrode setup in the CompreDrive, EIS spectra for each electrode can easily be obtained as a function of e.g. temperature, pressure, or state of charge (SOC). Here, the temperature control was automated to obtain individual cathode and anode spectra between $-20\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$ (Figure 5). The NMC impedance was measured between the working electrode (WE) and the RE, while the graphite impedance was simultaneously measured between the CE and RE.

a) Cathode



b) Anode

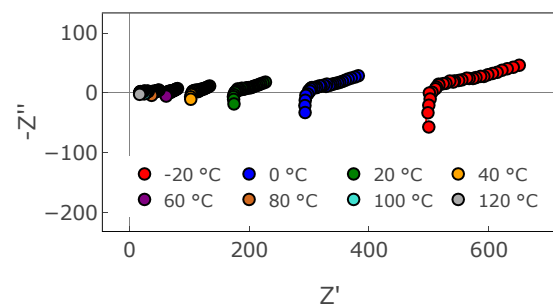
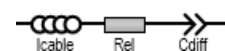


Figure 5. EIS spectra of a) the NMC cathode (WE vs RE) and b) the graphite anode (CE vs RE) at different temperatures (50% SOC, 10 kHz – 100 mHz, SP-200). Lines indicate equivalent circuits fits.

The equivalent circuits shown in **Figure 5** were used to extract the electrolyte resistance (R_{el}), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) for the cathode. In addition, a stray capacitance between the WE and RE (C_{stray}) was observed at high frequencies, as well as solid state diffusion (C_{diff}) at low frequencies. Further experiments would be necessary to prove the origin of C_{stray} , which could in principle arise either from external sources (cables, input terminals, etc.) or the sample itself (grain boundaries, composite pores, etc.). For the anode spectra (**Figure 5b**), C_{stray} was not observed, and the high frequency domain was instead dominated by the cable inductance (L_{cable}). Moreover, the graphite R_{ct} was too low to be observed at 50% SOC, while it was prominent at 0% SOC (**Figure 6**).

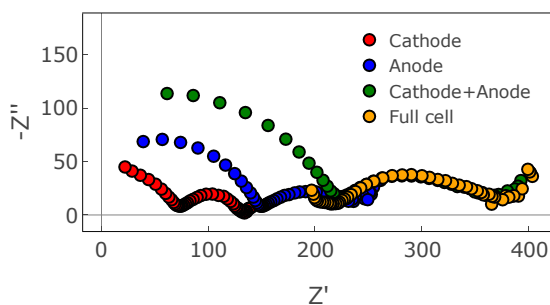


Figure 6. EIS spectra (WE vs RE) of the NMC cathode (red), the graphite anode (blue), the full cell (amber), and the sum of the individual electrode spectra (green) (20 °C, 0% SOC, 2 MHz – 100 mHz, NEISYS).

As shown in **Figure 6**, the full cell spectrum can also be reconstructed from the individual electrode spectra. The cathode (red) and anode (blue) spectra were recorded in three-electrode mode with the

respective electrode as WE, while the full cell spectrum (amber) was recorded in two-electrode mode. Shown in green is the sum of the cathode and anode spectra, which completely overlaps the full cell spectrum except at the highest frequencies (>100 kHz) where the difference in the physical cell connections lead to a different inductive contribution.

Summary

The three-electrode CompreCell allows for detailed characterization of all-solid-state battery cells by including a reference electrode in the form of a wire incorporated in the solid electrolyte layer. The individual potentials of each electrode can be separately monitored in e.g. cycling or impedance experiments, which is crucial to deconvolute the behavior of the two electrodes. At the same time, the CompreDrive setup provides actively controlled pressure and temperature of the air-tight cell, leading to optimal measurement conditions without unwanted external influence on the results.

An NMC | LPSCI | Graphite cell cycled in three-electrode mode was found to have evenly matched electrode capacities at C/20, but the graphite anode was limiting at higher currents. Three-electrode EIS spectra revealed the separate charge transfer processes on the cathode and anode, allowing the temperature dependent evaluation of parameters such as R_{el} , R_{ct} , and C_{dl} . The spectra were in good agreement with separate measurements performed in two-electrode mode.

Acknowledgements

The development of the CompreCell 12PEEK-DP-3e cell used for this application note is part of a subproject related to the project REFA (Grant No. 03EI6055+03EE6055A), funded by the Federal Ministry of Economic Affairs and Climate Action as part of the 7. Energieforschungsprogramm, which is highly appreciated. REFA is a joint research project with the two partners rhd instruments GmbH & Co. KG and Helmholtz Institute Ulm (HIU), associated with the Karlsruhe Institute of Technology (KIT). We thank our project partners Dr. Alberto Varzi, Dr. Dominic Bresser, and Mr. Mervyn Soans at HIU for providing materials as well as for the valuable and inspiring discussions.

Supported by:



Federal Ministry
for Economic Affairs
and Climate Action

on the basis of a decision
by the German Bundestag

Literature

- [1] J. Hertle, F. Walther, B. Mogwitz, S. Schröder, X. Wu, F. H. Richter and J. Janek, "Miniaturization of Reference Electrodes for Solid-State Lithium-Ion Batteries," *Journal of The*

Electrochemical Society, vol. 170, p. 040519, 2023.

- [2] Y. J. Nam, K. H. Park, D. Y. Oh, W. H. An and Y. S. Jung, "Diagnosis of failure modes for all-solid-state Li-ion batteries enabled by three-electrode cells," *Journal of Materials Chemistry A*, vol. 6, p. 14867–14875, 2018.

- [3] C. Sedlmeier, R. Schuster, C. Schramm and H. A. Gasteiger, "A Micro-Reference Electrode for Electrode-Resolved Impedance and Potential Measurements in All-Solid-State Battery Pouch Cells and Its Application to the Study of Indium-Lithium Anodes," *Journal of The Electrochemical Society*, vol. 170, p. 030536, 2023.

- [4] rhd instruments GmbH & Co. KG, "CompreCell 12 DP-3e," December 2023. [Online]. Available: <https://rhd-instruments.de/en/products/cells/comprecell-12-dp-3e>.