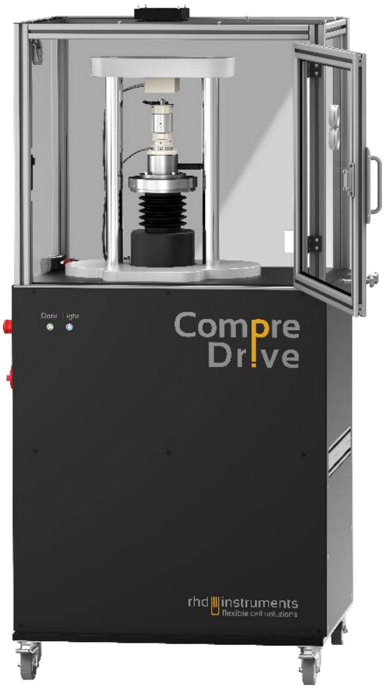
Application note

Solid-State Battery Characterization with OrigaFlex + CompreDrive



06/2026
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Introduction

Electrochemical experiments in solid-state electrolyte research can be challenging, since such cells are limited to thin layers that have to be pressed in order to keep the internal resistance sufficiently low. Including a reference electrode in solid-state cells is therefore difficult, and especially "true" reference electrodes, based on a mixed-valence redox couple, are rare in the solid-state electrolyte literature. Nevertheless, reference electrodes are crucial for separating the electrochemical contributions of the anode and cathode. In a recent publication, we described an easy way to fabricate and employ reference electrodes based on a thin wire coated with $Li_4Ti_5O_{12}$ / $Li_7Ti_5O_{12}$ (LTO) [1]. The potential of this reference electrode is stable for several months, as it is much less reducing than Li. This potential is also independent of the applied pressure, enabling the determination of the reaction volume of both anode and cathode individually [1].

In this application note, we demonstrate the characterization of a solid-state battery cell with a $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC) cathode, a lithium metal anode, and Li_6PS_5Cl (LPSCl) electrolyte with an incorporated LTO reference electrode. Charge/discharge cycling with *in situ* thickness monitoring, as well as electrochemical impedance spectroscopy (EIS), is shown. The measurements were performed under active pressure and temperature regulation, achieved with a CompreDrive setup in conjunction with an OrigaFlex potentiostat. Communication and synchronization between the potentiostat and temperature/pressure controller enabled correlation between data collected by the different instruments, as well as automation of measurement procedures.

Experimental

The all-solid-state battery under study was assembled in a CompreCell 12DP-3e cell [2], which has a 12 mm Ø sample cavity in a PEEK sleeve (**Figure 1**). The reference electrode, consisting of an LTO-coated Ni wire (100 µm Ø), was prepared as described earlier [1] and inserted into the sleeve.

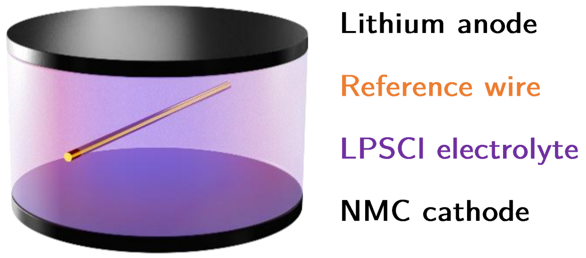

***Figure 1.** Sketch of the components comprising the three-electrode cell stack.*

LPSCl (Ampcera Argyrodite, $d_{50} \approx 1$ µm, MSE Supplies) was added to both sides of the reference wire (in total 200 mg/cm^2) and pressed into the sleeve by applying 100 MPa in a ComPrep [3] frame. NMC composite (11.6 mg; 6.7 mg$_{NMC}$/cm^2; 65% (m/m) NMC622 (BASF), 32% (m/m) LPSCl, 3% (m/m) C65 (Timcal)) was added to bottom side of the electrolyte pellet and pressed with 150 MPa. Finally, a lithium metal disk (11.9 mm Ø, 100 µm thickness) was added to the top side of the electrolyte and pressed with 100 MPa for 30 seconds. The active materials were contacted directly by tungsten carbide pistons (**Figure 1**). The assembly and pre-compression were done in an argon-filled glove box. Once sealed, the cells are air-tight and can be operated under ambient conditions.

The cell temperature and pressure were controlled by a CompreDrive [4] equipped with an HC-Addon [5]. An LVDT Distance Add-on [6, 7] was used for *in situ* sample thickness monitoring. All measurements were performed at 25 °C unless otherwise stated.

An OrigaFlex OGF$^+$500EIS potentiostat / galvanostat controlled by OrigaMaster 5 (Origalys) was used for all electrochemical measurements. The potentiostat was connected in four-electrode configuration to the CompreDrive using BNC cables (Ref2 <-> S; Wrk <-> WE; Ref <-> RE; Aux <-> CE). Ground was communicated through the BNC shields and was hence not connected separately. Furthermore, a bespoke serial cable was used to connect the OrigaFlex COM2 port to the CompreDrive digital I/O port for triggering. The potentials of both anode and cathode *vs* the reference electrode were recorded during charge/discharge cycling.

After applying 10 MPa to the cell, the open-circuit potential (OCP) was monitored for 12 hours before starting charge/discharge cycling with a constant current (CC) of C/10 (based on a nominal capacity of 276.5 mAh/g$_{\mathrm{NMC}}$) between 1.23 V and 2.63 V cathode potential *vs* LTO (2.8 V and 4.2 V, respectively, *vs* Li$^{0/+}$), which for the charge step was followed by a constant voltage stage (C/20 cutoff). Five cycles were performed with 30-minute OCP stages between the charge and discharge steps. EIS was performed at 5 MPa and 0% state of charge (SOC) with a peak amplitude of 10 mV at 2 kHz – 10 mHz. Finally, EIS was performed from -30 °C to 60 °C and back with 1-hour equilibration time at each temperature. This was automated by sending a trigger signal to the CompreDrive over the serial cable for each temperature setpoint. When the temperature was stable, a trigger signal was sent back to the OrigaFlex to begin an impedance measurement, before repeating for the next temperature setpoint.

The impedance data was evaluated by equivalent circuit fitting in RelaxIS 3.0 (rhd instruments GmbH & Co. KG), while Edelweiss 1.0 (rhd instruments GmbH & Co. KG) was used for data synchronization, data analysis and for creating the plots in this application note.

Results and Discussion

The separate potentials of the NMC cathode and lithium anode during charge/discharge cycling are shown in **Figure 2**. The lithium potential *vs* LTO stayed at -1.57 V ± 2 mV throughout, as expected for reversible lithium stripping and plating. The NMC cathode exhibited an initial discharge capacity of 93.7 mAh/g_{NMC}. The cell breathing could be clearly observed during the cycling (orange trace in **Figure 2**), and varied between 2 µm and 4 µm for the first five cycles. This is in line with the theoretical expansion and contraction of lithium stripping and plating ($V_m = 13.0$ cm^3/mol), which for this capacity corresponds to 3.0 µm [1].

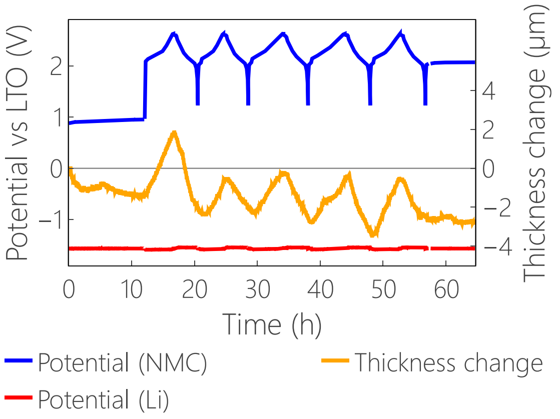

Figure 2. *Charge/discharge cycling of the NMC/Li cell with in situ thickness monitoring.*

Impedance spectra of the NMC cathode and lithium anode *versus* the LTO reference electrode are shown in **Figure 3**. The cathode spectrum features a flattened semicircle corresponding to the charge transfer (R_{ct}), followed by solid-state diffusion at low frequencies. The anode charge transfer was much smaller, exhibiting mostly ionic electrolyte resistance (R_{ion}). The sum of the two spectra (green) overlaps with the full cell spectrum (orange) as expected.

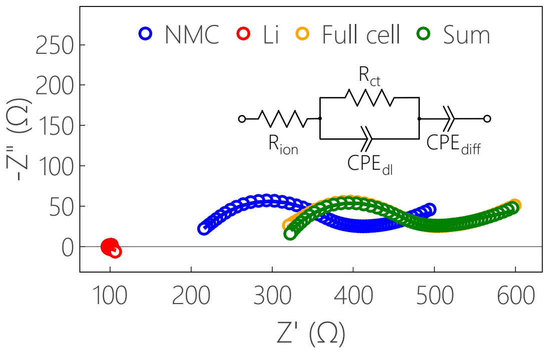

Figure 3. *Impedance spectra of the NMC cathode (blue) and lithium anode (red) versus the reference electrode, as well as their sum (green), and the full cell spectrum (i.e. cathode vs. anode, orange), at 25 °C, 0% SOC. Lines indicate fits to the equivalent circuit shown.*

To assess the activation energy, EIS spectra of the NMC cathode were recorded at different temperatures (**Figure 4**). Both R_{ct} and R_{ion} decreased with temperature according to the Arrhenius equation [7]. Hence, the activation energy for both the ion conduction in the solid electrolyte (0.19 eV, $r^2 = 0.995$) and the NMC charge transfer (0.27 eV, $r^2 = 0.995$) could be determined. Notably, higher activation energies have been reported for LPSCl in literature (0.34 – 0.46 eV [8]). This might be because of different synthesis conditions, which is known to have a large impact on the activation energy of solid electrolytes [9]. On the other hand, material properties such as porosity [10] and particle size distribution [11] are not expected to affect the activation energy, only the magnitude of the conductivity.

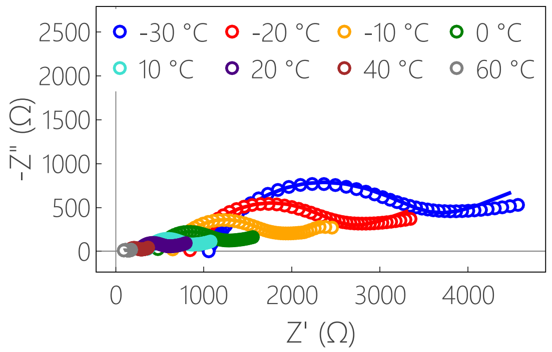

Figure 4. *Impedance spectra of the NMC cathode at varying temperature (heating sweep, 0% SOC). Lines indicate fits to the equivalent circuit shown in Figure 3.*

Summary

A three-electrode solid-state battery cell with an NMC cathode, a lithium metal anode, and LPSCl electrolyte, was characterized using an OrigaFlex potentiostat in conjunction with a CompreDrive pressure regulating setup. The incorporated LTO reference electrode was used to determine the individual electrode potentials during cycling, as well as to isolate the EIS responses of each electrode separately. This true reference electrode allowed for accurate and stable potential determination throughout the measurements. The charge transfer resistance of the NMC cathode and the LPSCl ionic resistance could be measured autonomously at a range of temperatures by means of digital I/O trigger signals sent between the CompreDrive and the OrigaFlex. This general way of digital triggering works with many different devices. Rather low activation energies for those two processes were determined in the case of these particular materials. Additionally, the thickness of the cell was monitored *in situ*, revealing a cell breathing of 2 – 4 µm during cycling. This originated predominantly from the stripping and plating of the lithium metal anode.

Acknowledgements

The study described in this application note was performed with the support of Firoozeh Faramarzi and Maxime Valay from the Origalys company (contact@origalys.com), who are greatly acknowledged for the many helpful discussions and for granting access to the OrigaFlex potentiostat.

We also express our gratitude to Dr. Mervyn Soans, Dr. Alberto Varzi, and Prof. Dr. Dominic Bresser (Helmholtz Institute Ulm, HIU) for providing the cathode composite and reference electrodes used in this work.

Literature

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