Application note

Finding the Critical Current Density
of a Solid Ion Conductor

Introduction

Lithium dendrites constitute a severe issue that affects solid (as well as liquid) electrolytes. Nevertheless, solid electrolytes have a number of promising properties that could lead to improved performance and safety of lithium ion batteries. Garnet type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolytes are particularly good ionic conductors, with room temperature conductivities approaching 1 mS/cm [1]. A high ionic conductivity does however not necessarily mean that a high direct current, which is needed for high power battery (dis)charge, can be safely applied. This is partly because lithium dendrites will start to form at some critical current density, eventually causing a short-circuit through the electrolyte layer [1, 2]. Determining this critical current density is therefore a crucial step in characterizing a solid-state battery electrolyte. In this application note, we measure the critical current density of two LLZO samples with different amorphous content under precise temperature and pressure control.

Experimental

Two samples of garnet-type Ta-doped LLZO were produced by Schott AG via a melting route, as described in detail elsewhere [2]. One sample ("*Low AM*") had a negligible amount of amorphous phase (0.1 %m/m), while the other ("*High AM*") had a high amorphous content (4.4 %m/m). Lithium foil (6 mm Ø) was applied to both sides of a polished LLZO pellet (1 mm thickness, 8.4 mm Ø) and heated at 190 °C to improve contact of the Li|LLZO interface, before applying copper foil as current collectors [2]. The pellet was loaded into an air tight CompreCell 12C measurement cell (rhd instruments GmbH & Co. KG, shown in **Figure 1**) and taken out of the glove box for the measurements.
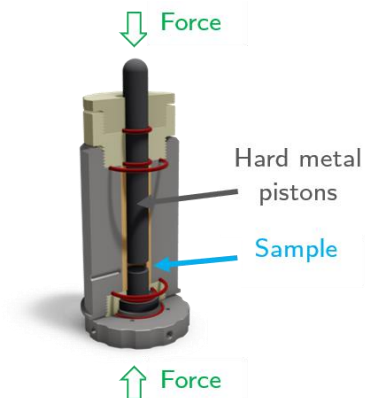

Figure 1. Intersection of the CompreCell, showing the pistons inside the cell housing.

In the CompreCell, the sample and pistons are surrounded by a ceramic (Al_2O_3) sleeve (12 mm inner Ø) inserted into a stainless-steel housing. The cell was equipped with a heating/cooling fluid mantle connected to a Presto A40 circulator (Julabo GmbH) and placed in a CompreDrive press (rhd instruments GmbH & Co. KG), which can be seen in the title page figure. CompreDriveControl 1.11 (rhd instruments GmbH & Co. KG) was used for temperature and pressure control. The cells were subjected to a pressure of 11 MPa, which was dynamically regulated with a force sensor feedback loop controlling a servo motor. The pressure was thus kept constant even during the shrinking/growing of the sample during the stripping/plating tests.

A Metrohm Autolab PGSTAT302N equipped with a FRA32-module, controlled through the NOVA 2.1 software, was used for all electrochemical measurements. Galvanostatic lithium stripping/plating experiments were carried out at 60 °C, starting at a current density of 0.05 mA/cm² and increasing step-wise by 0.05 mA/cm² up to a maximum of 2.0 mA/cm². Each current step was held for 30 minutes before applying a negative current for 30 minutes, and then proceeding to the next current density, as shown in blue in **Figure** 2. Electrochemical impedance spectroscopy (EIS) was performed at 25 °C before and after the stripping/plating tests, from 1 MHz to 10 Hz, with an amplitude of 10 mV rms. The figures in this application note were created using the Edelweiss software (rhd instruments GmbH & Co. KG).

Results and Discussion

The results of the galvanostatic lithium stripping/plating experiments can be seen in **Figure** 2. In general, the current/potential relationship followed Ohm's law, *i.e.* the samples exhibited mostly resistive behaviour. At the higher current densities, however, the potential had a slight slope rather than a stable plateau, due to lithium mass transport limitations. At some point, there was a sharp breakdown of the potential due to the short-circuit of the cell as lithium dendrites grew through the electrolyte. The critical current density was evaluated at the point of this breakdown, and was

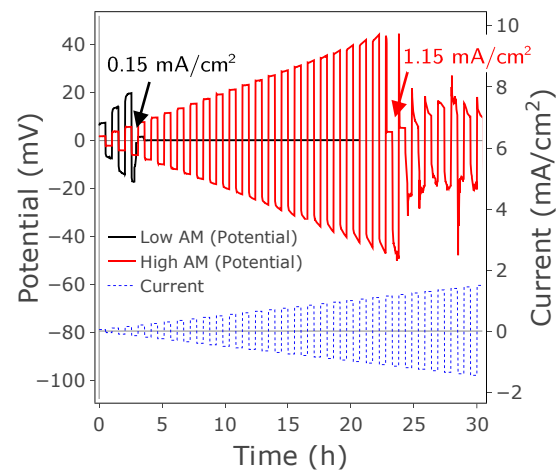0.15 mA/cm² and 1.15 mA/cm² for the Low AM and High AM samples, respectively.

Figure 2. Galvanostatic lithium stripping/ plating experiments. Potential of LLZO with a low (black) and high (red) amorphous content, respectively (left y-axis), and the applied current density (dotted blue line, right y-axis).

EIS carried out before and after the stripping/plating tests confirmed the formed short-circuit. While the pristine cells (squares in **Figure** 3) exhibited a series resistance of several hundred ohms, after having passed the critical current density, they had purely resistive spectra with very low resistance (<30 Ω, circles).
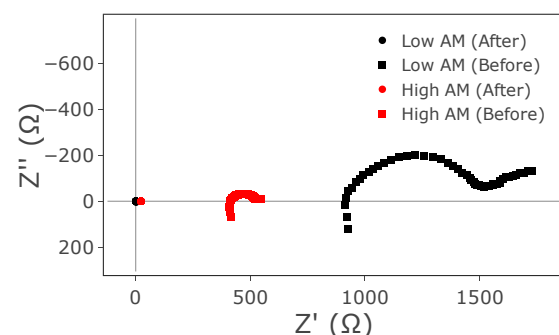

Figure 3. EIS spectra of the two LLZO samples with a low (black) and high (red) amorphous content, respectively, both before (squares) and after (circles) the stripping/plating tests.

The critical current density describes the limit below which the growth of lithium dendrites is negligible, and which can therefore safely be used in devices such as batteries. While the details of dendrite growth vary between different solid electrolyte types, it is understood to progress along the following general steps: Lithium metal can nucleate at inhomogeneities at the electrode|electrolyte interface, such as voids and grain boundaries. Poor interfacial contact can worsen the situation by creating an uneven current distribution, which is concentrated in a few spots where the electrolyte makes proper contact with the electrode. The accumulation of Li^0 at the nucleation sites creates mechanical stress which fractures the electrolyte, creating pathways for lithium dendrite growth. The presence of an amorphous phase in the LLZO samples tested herein increased the critical current density drastically, attributed to the fact that the amorphous phase can fill voids and grain boundaries [2]. This leads to a more uniform current distribution (preventing nucleation through high local current densities), as well as to a more compact and mechanically stronger microstructure (suppressing dendrite growth throughout the material) [2].

Summary

The critical current density of two LLZO samples with different amorphous content were determined by galvanostatic lithium stripping/plating. The sample with a high amorphous content had a much higher critical current density (1.15 mA/cm^2) compared to the sample with negligible amorphous content (0.15 mA/cm^2). Above the critical current density, lithium dendrites formed in the electrolyte, forming a short-circuit in the cell, which was confirmed by impedance spectroscopy. The critical current density was hence improved by the inclusion of an amorphous phase that occupies voids and grain boundaries in the structure, suppressing the formation and propagation of lithium dendrites.

Acknowledgements

Literature

[1] C. Wang, K. Fu, S. P. Kammampata, D. W. McOwen, A. J. Samson, L. Zhang, G. T. Hitz, A. M. Nolan, E. D. Wachsman, Y. Mo, V. Thangadurai and L. Hu, "Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries," *Chemical Reviews,* vol. 120, no. 10, pp. 4257-4300, 2020.

[2] N. Hoinkis, J. Schuhmacher, T. Fuchs, S. Leukel, C. Loho, A. Roters, F. H. Richter and J. Janek, "Amorphous Phase Induced Lithium Dendrite Suppression in Glass-Ceramic Garnet-Type Solid Electrolytes," *ACS Applied Materials & Interfaces,* vol. 15, no. 23, pp. 28692-28704, 2023.

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