



Application note

Distinguishing Bulk and Grain Boundary Conductivity in Solid Electrolytes



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Introduction

Accurate determination of the ionic conductivity of a solid electrolyte requires not only precise control of the measurement parameters (pressure, temperature, ...), but also knowledge about the state of the sample, such as the porosity. The influence of resistance across grain boundaries can lead to incorrect results when trying to determine the bulk conductivity [1]. From electrochemical impedance spectroscopy (EIS) alone, it is generally difficult to determine whether the observed resistance originates primarily from the bulk behavior, or from grain boundaries [2]. High-frequency semicircles are sometimes attributed to grain boundaries, but can also have many other origins, such as cell artefacts (stray capacitance), instrument artefacts (input capacitance), active material porosity, etc.

Yamakov *et al.* recently described a method to distinguish between ion conduction through the bulk of a solid electrolyte particle (σ_B) and ion conduction between particles, *i.e.* the grain boundary conductivity (σ_{GB}) [3]. This model states that the conductivity scales with the pelletization pressure P according to

$$\sigma \sim \left(P \cdot \frac{\rho_0}{\rho} \right)^\eta$$

where ρ is the sample density and ρ_0 is the theoretical bulk density at zero pressure. The η parameter can assume different values according to the kind of packing and whether the bulk or grain boundaries are limiting the ion conduction:

$$\eta_{HCP} = 2/3 \text{ for } \sigma_{GB} \ll \sigma_B$$

$$\eta_{HCP} = 1/3 \text{ for } \sigma_{GB} \gg \sigma_B$$

$$\eta_{RND} = 3/4 \text{ for } \sigma_{GB} \ll \sigma_B$$

$$\eta_{RND} = 1/2 \text{ for } \sigma_{GB} \gg \sigma_B$$

where 'HCP' refers to a hexagonally close packed system and 'RND' to randomly packed particles. For the case when $\sigma_{GB} \approx \sigma_B$, η is between the limits listed above. In order to quantitatively describe electrolyte particle packing, this elastic model would have to be extended to an elastoplastic model [3]. In fact, depending on whether the conductivity is measured 'in-die' (*i.e. in situ* while the pelletization pressure is still applied) or 'out-of-die' (*i.e.* after the pressure has been removed), plastic deformations may or may not have to be considered. The so-called Heckel plastic model identifies a logarithmic dependence between the pelletization pressure and the porosity measured at zero pressure [4]. For 'in-die' measurements, the linearity generally holds for intermediate compaction pressures, while deviations from linearity can be identified at lower pressures, where packing, rearrangement, and fragmentation dominate. At higher pressures, on the other hand, deviations can occur because of elastic deformations [4]. The models discussed here can be applied in the intermediate pressure region where plastic deformations dominate.

In this application note, we employ the model developed by Yamakov *et al.* [3] to differentiate between bulk and grain boundary conductivity, using the

CompreDrive system to automate the measurement in a single procedure.

Experimental

Three different sulfide-based electrolytes were studied here: $\text{Li}_6\text{PS}_5\text{Cl}$ ('LPSCI-1') and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ('LGPS') with particle size $<100\ \mu\text{m}$ (MSE Supplies), as well as a second source of $\text{Li}_6\text{PS}_5\text{Cl}$ ('LPSCI-2'). 100 mg/cm² of electrolyte powder was placed in a CompreCell 12PEEK DP measurement cell (rhd instruments GmbH & Co. KG, 12 mm sample \varnothing). The sample was contacted directly with hard metal pistons. Actively regulated pressure was applied by a CompreDrive (rhd instruments GmbH & Co. KG) under controlled temperature (25 °C). EIS was recorded *in situ* in the CompreDrive using a Biologic SP-240 potentiostat between 1 MHz and 100 Hz using an amplitude of 10 mV. The pressure dependent ionic resistance ($R(P)$) was evaluated by equivalent circuit fitting to the EIS data using RelaxIS 3 (rhd instruments GmbH & Co. KG), and the conductivity calculated according to

$$\sigma(P) = \frac{1}{R(P)} \cdot \frac{d(P)}{A}$$

where $d(P)$ and A are the sample thickness and cross section area, respectively. Note that the pressure dependence of both the sample thickness and resistance have to be taken into account, as they change significantly in the investigated range of 10 – 600 MPa (by 37% and 70%, respectively, starting from the powder form). To measure $\sigma(P)$ both 'in-die' and 'out-of-die' *in situ* in the CompreDrive, a

sawtooth-like pressure ramp was performed (**Figure 1**): After every pelletization step at successively higher pressures (red in **Figure 1**), the conductivity at 100 MPa (blue) and then 10 MPa (green) was measured, to find a dataset which could characterize the system in a condition as near as possible to 'out-of-die'. Therefore, without the need of preparing a fresh cell every time, we can study the system at 10 MPa, considered as 'close to zero pressure', and at 100 MPa, introduced since the electrolytes under study show the highest conductivity around this pressure.

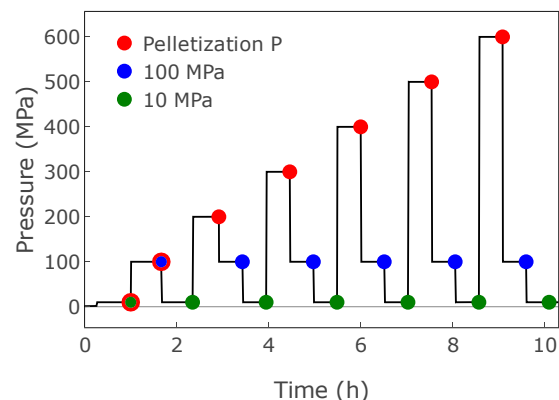


Figure 1: Pressure ramp with measured data shown in black. Colored dots indicate when EIS measurements were performed.

The pressure dependent sample thickness $d(P)$ was calculated from an *ex situ* measurement taken after the completed pressure ramp, and corrected by the CompreDrive motor position, as follows:

1. 10 – 650 MPa (5-minute equilibration time) was applied stepwise to the empty cell while recording the motor position, in order to estimate the deformation of the setup itself (CompreDrive + CompreCell) at each pressure. For the

most accurate results, this calibration should be performed shortly before each measurement.

2. The position was also recorded during the sawtooth-like pressure ramp in **Figure 1**, performed with the CompreCell filled with sample (30-minute equilibration time).
3. The final height of the empty and the filled cell were measured with a caliper in order to calculate the final pellet thickness d^{fin} as the difference in height between the filled and empty cell.

To account for the deformation of the sample as well as the whole setup under pressure, this *ex situ* value was corrected by the position change for the filled and empty cell at the corresponding pressure values, that is:

$$d(P) = (h_e(P) - h_e^{fin}) - (h_f(P) - h_f^{fin}) + d^{fin}$$

where h_e and h_f are the position values for the empty and filled cell, respectively, and h^{fin} is the final value measured at the end of the procedure. Note that a decreasing sample thickness $d(P)$ manifests as increasing position values $h(P)$.

The sample density was computed from the as obtained $d(P)$, the porosity was calculated as $1 - \rho/\rho_0$ ($\rho_0 = 1.64 \text{ g/cm}^3$ [3]). All figures in this application note were created with Edelweiss 0.0.1 (rhd instruments GmbH & Co. KG).

Results and Discussion

It is informative to look at the Heckel plot of the different solid electrolyte samples

(**Figure 2**: $-\ln(\text{porosity})$ vs. pelletization pressure), since it shows when rearrangement or elastic deformations take place, and compares the different degrees of compaction [4].

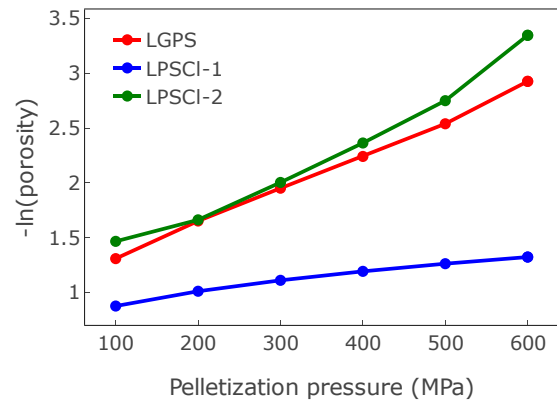


Figure 2: Heckel plots for the different electrolytes.

The recorded impedance spectra could be fitted with a blocking electrode equivalent circuit (**Figure 3**) for all the samples. The dependence of the resulting conductivity on the 'scaled pressure' ($P \cdot \frac{\rho_0}{\rho}$) is shown in **Figure 4**. To evaluate η , linear fitting was performed on the log-log curves in **Figure 4**, in the pressure ranges where both the data itself and the corresponding Heckel plot (**Figure 2**) was linear. This choice allows to exclude the low- and high-pressure regimes, potentially affected by particle rearrangement and elastic deformation, respectively. In particular the latter reduces the slope at high pressure (as seen in **Figure 4**) which would influence the fitting if included. The present study is therefore limited to the dataset at 100 MPa, where plastic deformations dominate [4]. The 10 MPa dataset has been excluded since it wasn't possible to

find reliable η values. In fact, attention must be paid to avoid effects of contact resistance or particle binding properties that come into play at too low pressures.

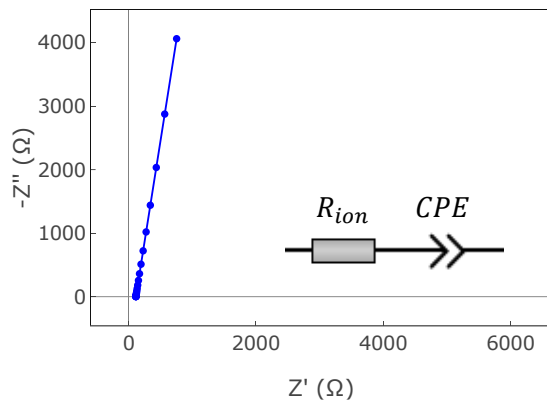


Figure 3: Illustrative impedance spectrum recorded at the first 100 MPa setpoint for LPSCI-2. Dots are experimental values and the solid line is the fit result for the shown equivalent circuit.

According to the results displayed in Table 1, $\eta \approx 1/2$ for LGPS, indicating that the grain boundaries are not limiting the ion conduction and that the observed conductivities can be attributed to the bulk, rather than the grain boundaries. LPSCI-2 displays the opposite behavior, with $\eta \approx 3/4$, i.e. the grain boundary conductivity is limiting, not the bulk. For LPSCI-1, the η between $1/2$ and $3/4$

indicates that the bulk and grain boundary conductivities are on the same order of magnitude. Compared to LPSCI-1, which has the highest conductivity of the three samples, and $\sigma_{GB} \approx \sigma_B$, LPSCI-2 is limited by a lower σ_{GB} , while LGPS is limited by a lower σ_B . The large difference between the two LPSCI samples is noteworthy, as the magnitude of the conductivity, its pressure dependence, and its origins all differ greatly (Figure 4). To achieve reproducibility in solid-state battery testing, the properties of the specific electrolyte samples must thus be individually characterized, and both the preparation and measurement conditions carefully controlled.

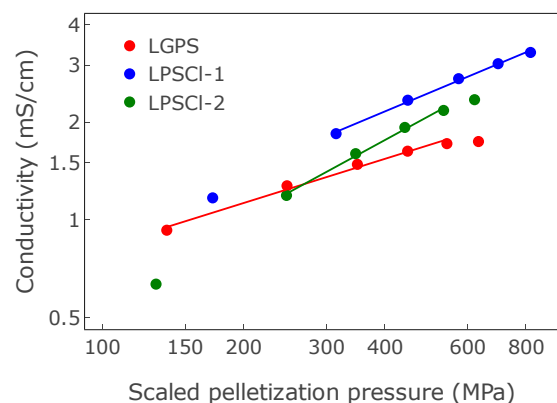


Figure 4: Conductivity measured at 100 MPa vs $P \cdot \rho_0 / \rho$ (log-log plot). Lines show the fits used to calculate η .

Table 1. Fitting parameter η (95% confidence interval) and the corresponding type of packing and conductivity contributions.

	η	Category	Packing	σ
LGPS	0.45 ± 0.03	$\eta \approx 1/2$	RND	$\sigma_{GB} \gg \sigma_B$
LPSCI-1	0.61 ± 0.02	$1/2 < \eta < 3/4$	RND	$\sigma_{GB} \approx \sigma_B$
LPSCI-2	0.79 ± 0.04	$\eta \approx 3/4$	RND	$\sigma_{GB} \ll \sigma_B$

Conclusions

The relationship between the pressure used for pelletization of electrolyte powders, the resulting sample density, and the ionic conductivity, was used to distinguish bulk and grain boundary conductivity, using a method developed by Yamakov *et al.* [3]. For the investigated LGPS sample, the grain boundaries were not limiting the ionic conductivity, enabling determination of the bulk conductivity by EIS. Two examined LPSCI samples from different sources exhibited higher conductivities than LGPS. For one LPSCI sample, the resistance across the grain boundaries was similar to that of the bulk, while for the other sample the grain boundary conductivity was much lower. The measured impedance thus does not originate only from the bulk conductivity, but contains a contribution from the grain boundaries. This highlights the need for precise pressure control during impedance measurements for accurate conductivity determination. Employing the CompreDrive system, the experiments necessary for this evaluation could be automated into one single procedure.

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