

Application note

Determination of the pressure- and
temperature-dependent ionic
conductivity of solid electrolytes



Introduction

With further progress in improving lithium ion batteries, the focus of research has turned to alternative technologies (next-generation batteries), including all-solid-state-batteries (ASSB), since these systems have the potential to exceed current battery systems in terms of energy density as well as safety concerns.[1]

For commercial use of ASSBs, it is crucial to use highly ionic conductive solid electrolytes while simultaneously ensuring proper interfacial contact and stability. During the last years, very promising sulfur-based candidates have been synthesized and investigated, showing ionic conductivities in the range of 10 mS cm^{-1} at room temperature.[2]-[5]

Unfortunately, it is often neglected to ensure well-defined experimental conditions. Therefore, the resulting values might vary a lot, as it was demonstrated in a recently published joint study.[6] It was shown in an inter-laboratory round-robin test that the resulting conductivity values for the same set of samples (two of those were $\text{Li}_6\text{PS}_5\text{Cl} = \text{LPSCI}$ and $\text{Li}_6\text{PS}_5\text{I} = \text{LPSI}$) strongly depended on the chosen experimental conditions, devices and procedures. Hence, it would be optimal to have a single device, which enables for a proper sample pre-treatment and which is furthermore able to run such electrochemical investigations under well-defined and (re-)adjusted pressure and temperature conditions (heating and cooling) in a fully automatic way, to ensure reproducible results.

Given this background, in this application note we want to focus on conductivity measurements of the two solid ion conductors mentioned above by use of our CompreDrive HC system.

Experimental

a) Chemicals

For our investigations two air-sensitive sulfur-based solid ion conductors (LPSCI and LPSI) were used, provided by the working group of

Prof. Dr. Wolfgang Zeier (University of Münster), identical in composition to those examined in [6] (for sample preparation please see original publication). The samples were stored and handled under inert conditions (inert argon atmosphere inside of a glovebox).

b) Sample preparation & measuring setup

For the electrochemical measurements a CompreCell 12C in combination with the CompreDrive HC test system (rhd instruments GmbH & Co. KG) was used. The CompreDrive HC with external circulator unit and the cell design of the assembled CompreCell 12C are shown as rendered technical drawings in **Figure 1**. The inner insulating sleeve material of the CompreCell 12C is Al_2O_3 .

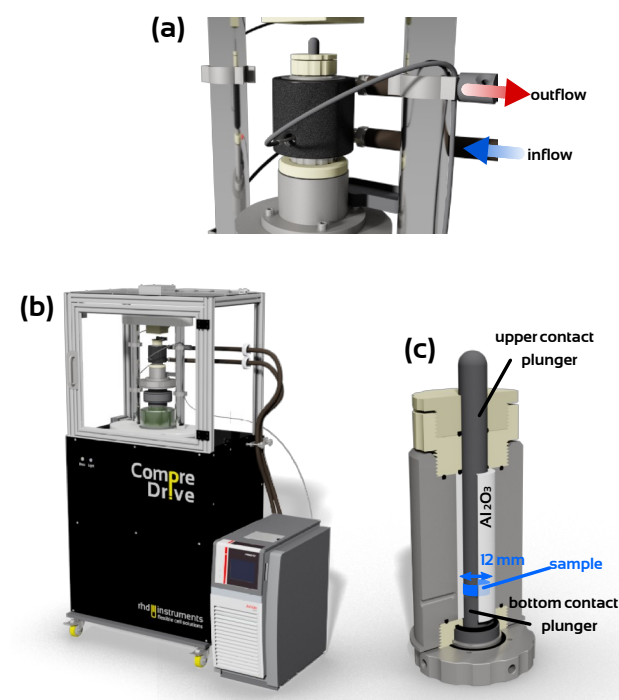


Figure 1: Representations of (a) CompreCell with assembled HC-fluid mantle, (b) CompreDrive HC system with external circulator, and (c) used measuring cell CompreCell 12C.

The impedance measurements were carried out in a 2-electrode setup, with the hard-metal plungers serving as electrodes with an active area of 1.131 cm^2 ($\varnothing 12 \text{ mm}$).

The powder-like solid ion conductor was filled into the CompreCell under inert-gas atmosphere inside a glove box (MBraun Inert-

gassysteme GmbH). The cell was sealed with full assembly of the cell body.

For measurements on LPSCI, a NEISYS measuring device (Novocontrol Technologies GmbH & CO. KG) was used controlled via the dedicated DetaChem 1.16 software.

In case of LPSI, a PGStat204 potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for EIS experiments. For data acquisition, the NOVA 2.1.4 software was used.

The CompreDrive was controlled with the CompreDriveControl software. An automated pressure- or temperature-ramp was applied, which was synchronized with the impedance analyser to measure impedance spectra at stable conditions.

Communication between DetaChem and the CompreDriveControl software was done using the “external application” function in DetaChem and “CompreDriveRemote” together with look-up tables for the desired pressure and temperature values.

Communication between NOVA 2.1.4 and the CompreDrive HC for force- and temperature-control was done by via an implemented DLL file in NOVA (part of CompreDriveRemote).

The sample temperature was measured by a Pt100-sensor plugged into the CompreCell 12C and adjusted by the circulating thermostat (Presto A40 from JULABO GmbH (± 0.1 °C)). The applied force was constantly measured and adjusted by the closed-loop control of the CompreDrive HC as long as required.

Impedance data analysis was done using the RelaxIS 3 software suite (rhd instruments GmbH & Co. KG).

c) Measurement parameters

The measurement procedure was compiled and run in interconnection of NOVA or DetaChem, respectively, and CompreDriveControl.

The impedance measurements were performed with a frequency range of 10 MHz to 0.1 Hz (Novocontrol) or 1 MHz to 0.1 Hz (Metrohm) with an amplitude of $V_{AC,rms} = 7.07$ mV. Dur-

ing the pressure ramps the temperature was set to 20 °C and was actively controlled during the measurement to ensure reproducible thermal conditions.

During the temperature-ramps the pressure was set to 500 MPa and was actively controlled during the measurement to ensure reproducible pressure conditions.

Pressure -ramp	
Step	Action to be performed for pressure-ramp
P1	Assembling of CompreCell 12C inside a glove box, filling with sample.
P2	Inserting CompreCell 12C into the CompreDrive, connecting temperature sensor.
P3	Setting temperature to 20 °C and waiting until temperature is stable.
P4	Setting force to first value and waiting until force value becomes stable.
P5	Getting actual applied force and temperature value and performing impedance spectroscopy experiment.
P6	After finishing step 5 repeat steps 4 & 5 for every chosen stack force value.
Temperature-ramp	
Step	Action to be performed for temperature-ramp
T1	Taking the prepared cell from the pressure-ramp experiment.
T2	Measuring height of the closed cell to get sample thickness after pressure-ramp.
T3	Setting pressure to 500 MPa and waiting until pressure is stable.
T4	Setting temperature value to first value and waiting until temperature becomes stable.
T5	Getting actual applied force and temperature value and performing impedance spectroscopy experiment.
T6	After finishing step 5, repeat steps 4 & 5 for every chosen temperature value.

Results

In **Figure 2** the plot of the stack-pressure as well as the temperature in dependence of time clearly demonstrates how fast stable and defined measurement conditions can be realised with this setup within only one, totally automated experiment.

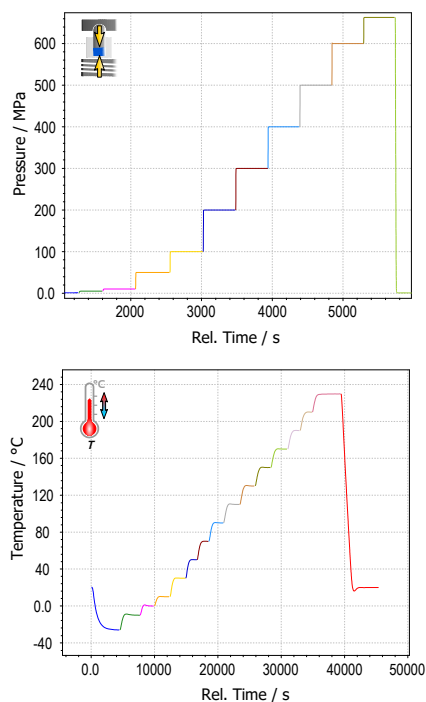


Figure 2: Stack-pressure and sample temperature in dependence of time for the chosen, automated procedure. For each step, stable pressure as well as temperature conditions are achieved within approximately 400 s and 2000 s, respectively - saving valuable time.

The stack-pressures p_{st} are calculated by dividing the applied stack-force F_{ap} by the active sample area A , given by the diameter of the inner plunger ($A = 1.131 \text{ cm}^2$), as shown below.

$$p_{st} = \frac{F_{ap}}{A}$$

The solid electrolytes were filled as powders into the CompreCell 12C and were compressed, while impedance measurements were carried out at 20 °C with increasing stack-pressures – to check for a proper consolidation of the sample at a constant and moderate temperature and for estimating, which pressure is

needed to ensure reproducible impedance spectra. These spectra are shown in **Figure 3**, indicating that a constant R_{ion} will only be achieved at a high stack-pressure above 400 MPa, ensuring proper interfacial contact.

Hence all temperature-dependent measurements were carried out at a constant stack-pressure of 500 MPa for both samples.

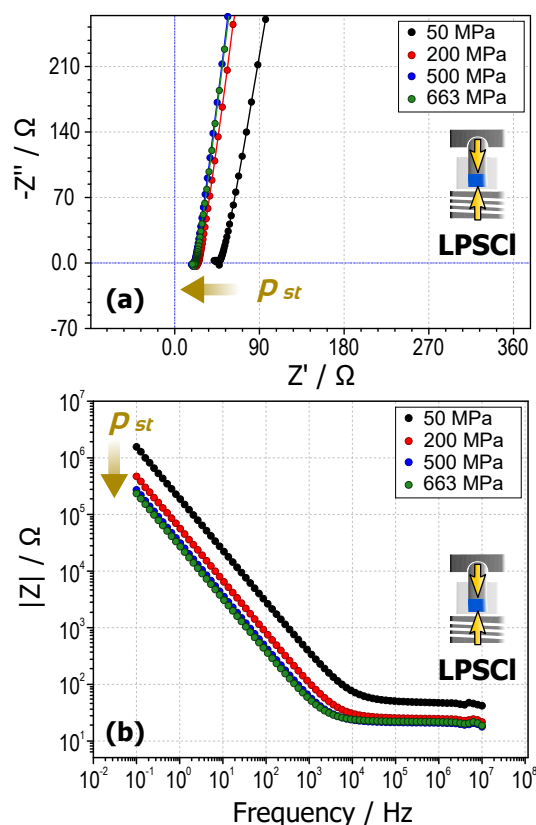


Figure 3: Impedance spectra of the LPSCI sample for increasing stack-pressures at 20 °C. Data shown in (a) Nyquist-plot, (b) Bode-plot.

The temperature-dependent measurements were conducted between -30 °C and 230 °C. Only at low temperatures and only in case of the less-conductive sample LPSI a semicircle is observed in the Nyquist plot within the chosen frequency range. Some representative spectra for the cooling steps are shown for both electrolytes in **Figure 4**.

In the case of increasing ionic conductivity, the semicircle shifts to higher frequencies and cannot be observed any more for the chosen frequency range. Therefore, the equivalent circuit for fitting the impedance spectra of the more

conductive sample LPSCI and for the LPSI sample at higher temperatures has to be adjusted.

The spectra were fitted with the equivalent circuits shown in **Figure 5**. The parallel R_{ion}/C_{bulk} -element represents the resistance to ion migration in the bulk material and the bulk capacitance (grain and grain-boundary processes cannot be separated here), while CPE_p was used to describe the low-frequency electrode polarization. Circuit (a) was used, if parts of the bulk semicircle were visible in the spectra, in the other cases circuit (b) was used.

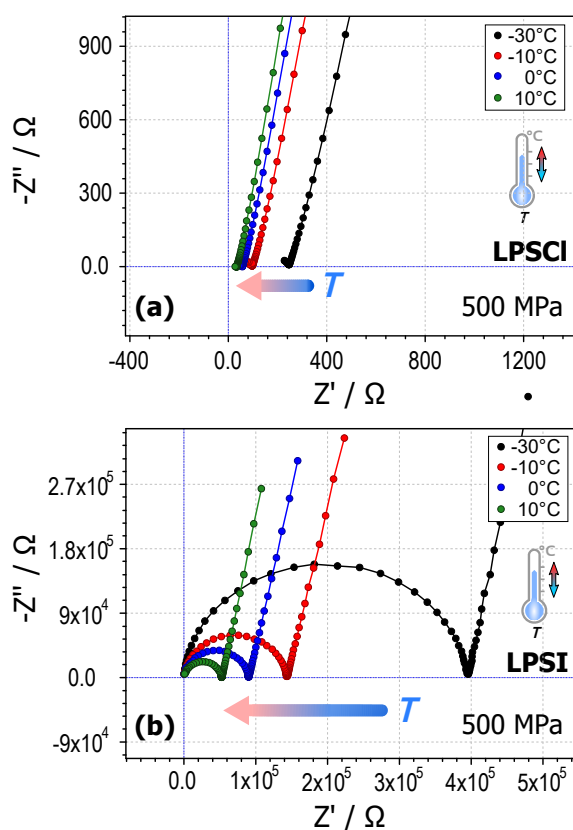


Figure 4: Temperature-dependent impedance spectra for $T < 20\text{ }^{\circ}\text{C}$ for (a) LPSCI and (b) LPSI ($p_{st} = 500\text{ MPa}$).

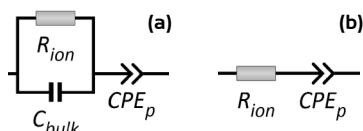


Figure 5: Equivalent circuits for fitting the impedance spectra.

From the fitted resistance values R_{ion} the corresponding ionic conductivities σ can be calculated as shown below.

$$\sigma = \frac{1}{R_{ion}} \cdot \frac{d}{A}$$

d represents the thickness of the compressed sample pellet, A stands for the contact area between the sample surface and electrode.

Linearised Arrhenius-plots of the temperature-dependent, calculated ionic conductivity values for LPSCI and LPSI were created using the RelaxIS 3 software ($p_{st} = 500\text{ MPa}$). Linear regression results in activation barriers for both solid electrolytes of $E_{A,LPSCI} = 0.364\text{ eV}$ and $E_{A,LPSI} = 0.398\text{ eV}$ (**Figure 6**). This result evaluation can be performed completely with RelaxIS 3.

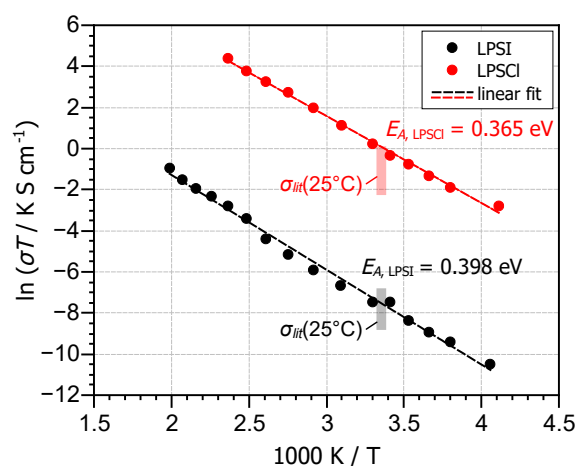


Figure 6: Arrhenius-plot and fit curves of the calculated ionic conductivity values for both samples LPSCI and LPSI ($p_{st} = 500\text{ MPa}$). Reported ranges for the values of the ionic conductivities at $25\text{ }^{\circ}\text{C}$ according to [6] are indicated.

Both the determined conductivities and the activation energies are in accordance to the values reported by Ohno *et al.* (see indications in **Figure 6** and following table).

sample	E_A / eV	$E_{A,lit} [6] / \text{eV}$
LPSCI	0.364	0.342 – 0.456
LPSI	0.398	0.393 – 0.433

Summary

In a former application note we already demonstrated the importance of active force-control for solid electrolytes in a reliable and robust way. In this application note we highlighted the importance of active force-control in combination of active temperature-control (heating & cooling) using the CompreDrive HC system for investigations of compressed solid ion conductors between -30 °C and 230 °C.

For our experiments, we chose the two solid electrolytes LPSCI and LPSI. The resulting temperature-dependent values for the ionic conductivities are in accordance with the reported values for samples of identical composition.

Being able to perform those experiments with a turn-key-system and with user-defined and automated procedures allows for three things at once: Saving valuable time, optimised user-friendliness and – most important – reproducible and robust measurement conditions and, hence, reliable and reproducible results

Acknowledgement

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