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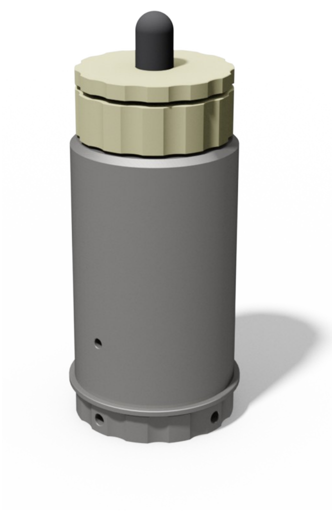
Application note

Pressure-dependent determination of the ionic resistance of solid ion conductors



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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 will vary a lot like a recently published joint study has shown.[6] It demonstrates that the resulting conductivity values for the same set of samples strongly depend on the used experimental conditions and procedures.

In this application note, we show how critical especially a precisely and accurately tracked and (re)-adjusted force for the investigation of solid ion conductors really is. An ideal application for the CompreDrive by rhd instruments!

Experimental

a) Chemicals

For our investigations an air-sensitive sulfur-based solid ion conductor was used, similar in composition to the one examined in [5]. The sample was 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 H test system (rhd instruments GmbH & Co. KG) was used. The CompreDrive, the heater 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.

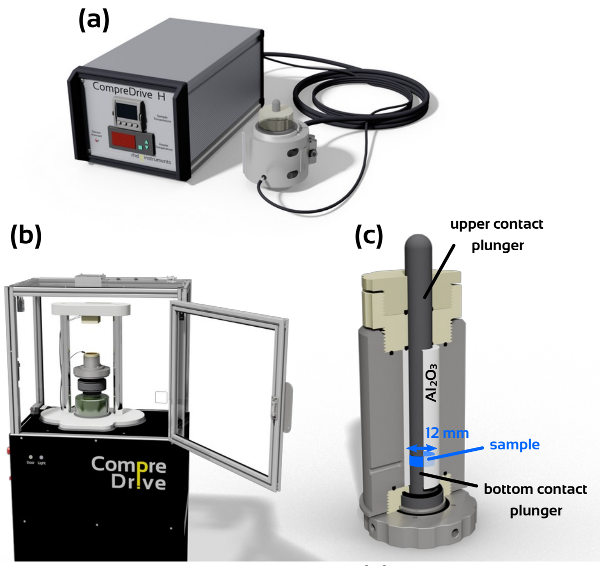

Figure 1: Representation of the **(a)** heater unit (H-Option for CompreDrive), **(b)** CompreDrive system and **(c)** used measuring cell CompreCell 12C.

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 (Ø 12 mm).

The powder-like solid ion conductor was filled into the CompreCell under inert gas atmosphere inside a glove box (MBraun). The cell was sealed with full assembly of the cell body.

A PGStat304N 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 ramp was applied, that was synchronized with the impedance analyser to measure impedance spectra at stable sample pressures. Communication between NOVA 2.1.4 and the CompreDrive H for force and temperature control was done by CompreDriveControl with an implemented DLL file in NOVA 2.1.4.

The sample temperature was checked by a Pt100-sensor plugged into the CompreCell 12C and adjusted by a heater unit (±0.2 °C). The applied force was constantly measured and adjusted by the closed-loop control as long as required.

Impedance analysis was done by the RelaxIS 3 software suite (developed and powered by rhd instruments GmbH & Co. KG).

c) Measurement parameters

The measurement procedure was compiled and run in interconnection of NOVA 2.1.4 and CompreDriveControl.

The impedance measurements were performed with a frequency range of 100 kHz to 0.1 Hz and an amplitude of $V_{AC,rms} = 100$ mV. The temperature was set to 30 °C and was actively controlled during the measurement to ensure reproducible thermal conditions.

Step	Action to be performed
1	Assembling of CompreCell 12C inside a glove box, filling with sample.
2	Inserting CompreCell 12C into the CompreDrive, connecting temperature sensor.
3	Setting temperature to 30 °C and waiting until temperature is stable.
4	Setting force to first value and waiting until force value becomes stable.
5	Getting actual applied force and temperature value and performing impedance spectrum.
6	After finishing step 5 repeat steps 4 & 5 for every chosen stack force value.

Results

The plot of stack pressure in dependence of time **Figure 2** clearly demonstrates how fast a stable and defined pressure can be realised with this setup.

The stack pressures p_{st} are calculated by dividing the applied stack force F_{ap} through the active sample area A, given by the diameter of the inner plunger ($A = 1.131$ cm²) as shown below.

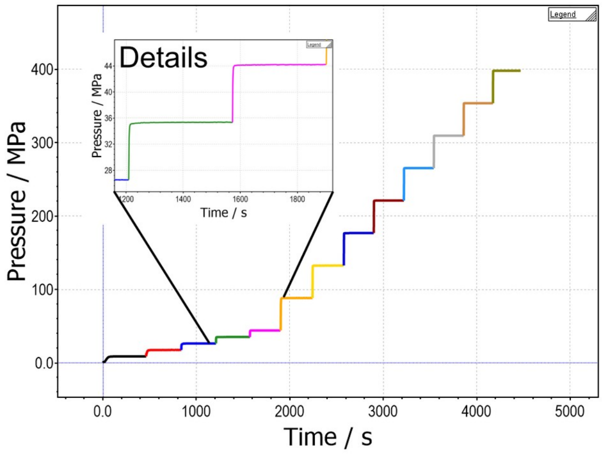

Figure 2: Stack pressure in dependence of time for the chosen, automated procedure. Stable pressure conditions are achieved within approximately 400 s, saving valuable time.

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

In **Figure 3** some exemplary impedance spectra are shown for different stack pressures.

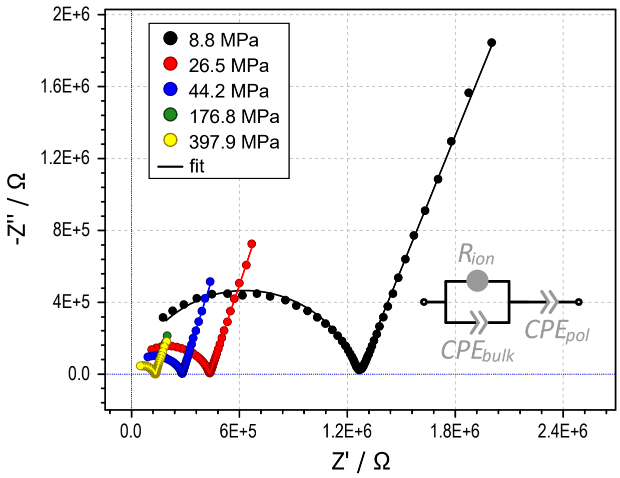

Figure 3: Nyquist plots and fits of exemplary impedance spectra of the used solid ion conductor in dependence of the applied pressure. Only at actively re-adjusted stack pressures above 180 MPa reproducible impedance behaviour is observed.

The spectra were fitted with the equivalent circuit shown as inset in **Figure 3**. The parallel R_{ion}/CPE_{bulk}-element represent the total ionic resistance as well the materials capacitance (grain and grain-boundary processes cannot be separated at 30 °C), while CPE_{pol} was used to describe the low-frequency electrode polarization.

Plotting the total ionic resistance R_{ion} of the sample in dependence of the applied stack pressure results in **Figure 4**, indicating that a constant R_{ion} is only achieved for high stack pressures above 180 MPa, ensuring proper interfacial contact.

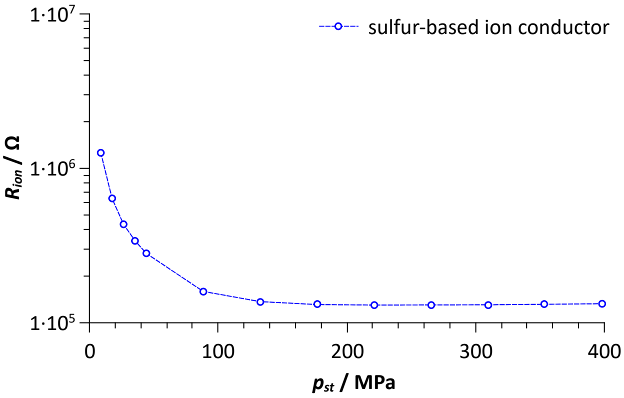

Figure 4: Total ionic resistance R_{ion} of the sample in dependence of the applied stack pressure. The ionic resistance is highly dependent on the applied stack pressure, especially for values below 180 MPa.

It furthermore shows that without active force regulation and readjustment, the ionic resistance could spread about magnitudes and cannot be determined reproducibly.

While in this case it seems that the ionic resistance shows no crucial dependence on the stack pressure exceeding values of 180 MPa, it has to be clarified, that this effect is highly specific for the used material. It cannot be predicted and might be even more pronounced for other materials.

Summary

The work clearly demonstrated the necessity of active force control during electrochemical measurements of solid ion conductors to enable reproducible measuring conditons. It furthermore shows, that:

a) in some cases, relatively high stack pressures (exceeding 180 MPa) are needed to ensure proper interfacial contact of particles.

b) setting insufficient stack pressures will result in far too high resistance values.

c) without active re-adjustment of the pressure (i.e. decreasing pressure over time) the resulting resistance value might not be stable and vary over time, in extreme over several magnitudes.

d) the CompreDrive setup enables reproducible, automated measurements and helps researchers to save valuable time, thereby speeding up the research activities significantly.

Acknowledgement

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