



# Application note

## Investigating the Pressure Dependent Ionic Conductivity of a Solid Electrolyte with the CompreFrame

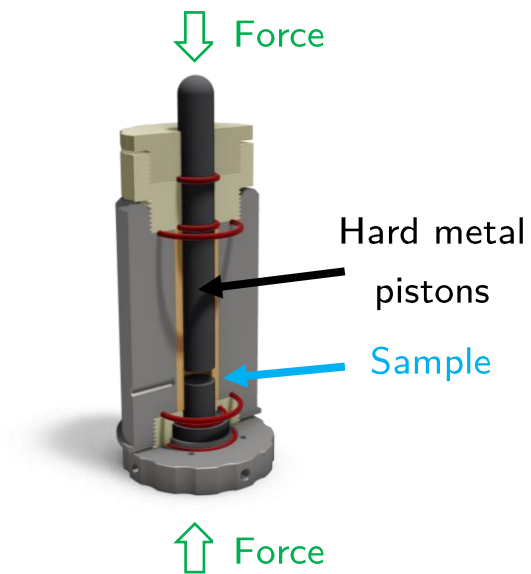


## Introduction

Solid electrolytes are expected to enable all-solid-state batteries with improved safety as well as energy and power density, and have therefore increasingly garnered interest in both academia and industry [1]. There are however many practical challenges in the characterization of solid electrolytes, related to e.g. sample preparation and measurement conditions. In a recent round-robin study, ionic conductivities measured for several inorganic solid electrolyte samples were found to vary by as much as one order of magnitude [2]. Parameters such as pelletization pressure, measurement temperature and measurement pressure will greatly affect the obtained results.

To address these issues, the *CompreDrive* system has previously been developed to allow for precise and active pressure control during electrochemical measurements [6]. As a more cost-efficient alternative, the use of the *CompreFrame* is described here, determining the pressure dependent ionic conductivity of an inorganic solid electrolyte. The pressure in the *CompreFrame* is applied uniaxially, is uniformly distributed over the sample surface, and is continuously monitored during the measurement. Unlike in the *CompreDrive*, however, there is no feedback control loop that actively controls the pressure. Rather, the pressure in the *CompreFrame* is manually adjusted, and a spring assembly ensures a stable pressure throughout the measurement. The same

sample cells and temperature control options as for the *CompreDrive* can be used with the *CompreFrame*, meaning that the sample temperature can be monitored, actively controlled and also automated.



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

## Experimental

A commercial sample of a solid electrolyte powder (141 mg, 125 mg/cm<sup>2</sup>) was loaded into an air tight *CompreCell* 12C measurement cell (rhd instruments GmbH & Co. KG, shown in **Figure 1**) inside an argon filled glove box. In this cell, the sample has a diameter of 12 mm and is contacted by two tungsten carbide pistons. The sample and pistons are surrounded by a ceramic (Al<sub>2</sub>O<sub>3</sub>) sleeve inserted into a stainless-steel housing. The sample was lightly compacted by pressing and twisting the pistons by hand, before the cell was sealed and taken out of the glove box. The powder sample height at this stage was

1.35 mm (calculated by measuring the total cell height and subtracting the height of the empty cell). The cell was equipped with a heating/cooling fluid mantle connected to a Huber Unistat 405 circulator (Peter Huber Kältemaschinenbau AG), placed in a CompreFrame pressure jig (rhd instruments GmbH & Co. KG), which can be seen in the title page figure. The force sensor (100 kN) was tared with the fluid jacket in place. CompreDriveControl 1.13 together with CompreFrameControl (rhd instruments GmbH & Co. KG) was used for temperature control, data logging, and generating the force/temperature figure for this application note.

A NEISYS Electrochemical Impedance Analyzer controlled by Detachem 1.19 (Novocontrol Technologies GmbH & Co. KG) was used for all electrochemical impedance spectroscopy (EIS) measurements. Initially a load/short calibration was performed with a 100  $\Omega$  resistor or a gold pellet, respectively, in a CompreCell 12C mounted in a CompreFrame. Potentiostatic impedance spectra were collected from 2 MHz to 1 Hz with an amplitude of 30 mV rms. Fitting of equivalent circuits and the Arrhenius equation was performed with RelaxIS 3 (rhd instruments GmbH & Co. KG), which was also used to create the EIS figures shown here.

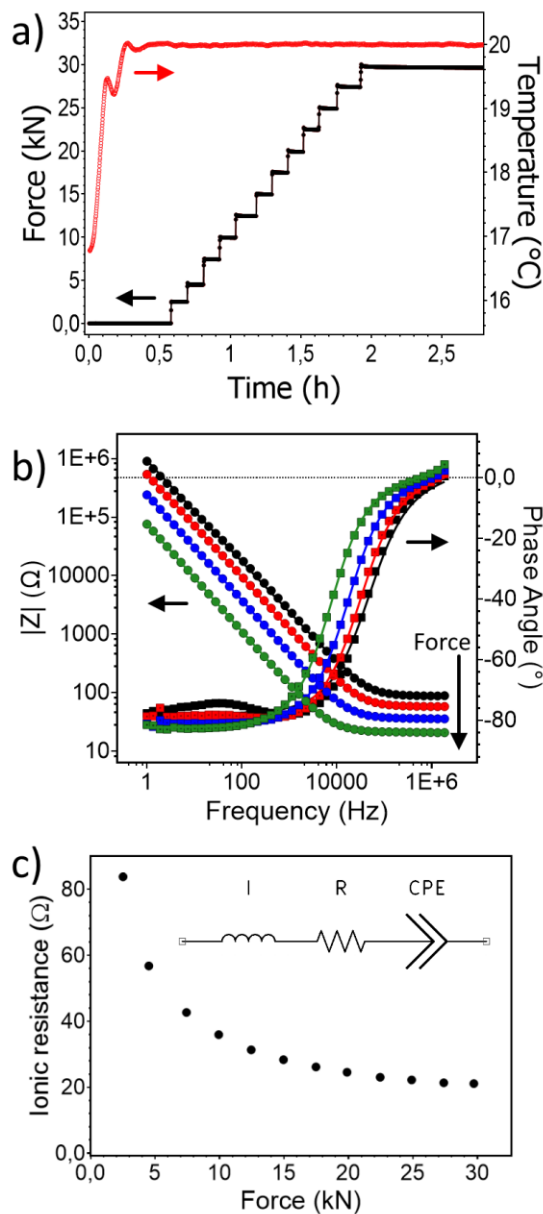
The cell temperature was allowed to stabilize at 20 °C before the force was increased in 2.5 kN steps up to 30 kN. At each force value, 0 V was applied to the cell for 5 minutes before recording an EIS

spectrum. For reference, the cell was also placed in a CompreDrive system (rhd) and subjected to a force of 20 kN (10 kN/min ramp speed). In this setup, EIS was measured at 20 °C as described above.

## Results

The force and temperature measured in the CompreFrame during the stepwise powder compaction is shown in **Figure 2a**. As can be seen in the Bode plot for the impedance measured at each force step (**Figure 2b**),  $|Z|$  exhibits a plateau at high frequencies, with a positive phase angle ( $\varphi$ ) due to cable inductance only at the very highest frequencies. At intermediate to low frequencies,  $|Z|$  and  $|\varphi|$  increases with decreasing frequency due to the blocking behaviour of the electrodes. Thus, the spectra can be modelled by a simple I-R-CPE equivalent circuit (**Figure 2c**), where I corresponds to the inductance and R to the ionic resistance ( $R_{ion}$ ) of the sample, while CPE is a constant phase element modelling the capacitive charging of the electrodes. Fitting the equivalent circuit elements to the spectra reveals the force dependent ionic resistance as shown in **Figure 2c**. At the lowest force (2.5 kN, 22 MPa), there is an additional feature at low frequencies (10 – 100 Hz) with a reduction in  $|\varphi|$  (black squares in **Figure 2b**). This could for example arise from grain boundary interfacial resistance, or from Maxwell-Wagner relaxation [4].

After the initial force ramp, the height of the pellet in the cell was 0.81 mm (calculated as described above). The



**Figure 2.** Force ramp of a CompreCell with a solid electrolyte sample in the CompreFrame. a) Measured force (black, left axis) and temperature (red, right axis). b) Bode plot of the impedance at 2.5 kN (black), 5 kN (red), 10 kN (blue), and 30 kN (green). Circles show  $|Z|$  on the left axis, and squares show  $\varphi$  on the right axis. Lines indicate equivalent circuit fits. c) Equivalent circuit fitted to the spectra and the resulting resistance values as a function of the applied force.

density of the pellet was thus  $1.54 \text{ g/cm}^3$  (cf.  $0.93 \text{ g/cm}^3$  for the powder before the force ramp), which is close to the theoretical density of  $1.64 \text{ g/cm}^3$ . Based on the calculated density, the porosity of the pellet after compaction at 30 kN (265 MPa) was 5.9%. The ionic resistance decreased with the applied force (Figure 2c), as a result of the compaction of the powder. At the highest applied force, the resistance value levelled off, as a fully compressed pelletized state at the theoretical density was approached. After this point, decreasing the force did not affect the resistance as strongly as during the compression stage. All subsequent measurements of the compressed pellet were done at a force of 20 kN (177 MPa).

The ionic conductivity ( $\sigma$ ) of the sample can be calculated as

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

where  $d$  and  $A$  is the thickness and cross section area, respectively, of the sample. The resistance in the pelletized state ( $19.42 \text{ } \Omega$  at 20 kN and  $20 \text{ } ^\circ\text{C}$ ) thus corresponds to  $3.69 \text{ mS/cm}$ . For reference, the conductivity as measured in a CompreDrive unit at 20 kN and  $20 \text{ } ^\circ\text{C}$  was  $3.64 \text{ mS/cm}$ . A more extensive comparison between results obtained in the Compredrive and CompreFrame will be available in a separate application note, along with evaluating the long-term force drift of the CompreFrame, and automated temperature dependent measurements in the CompreFrame.

## Summary

The pressure dependent electrochemical impedance behaviour was measured for an inorganic solid electrolyte using the CompreFrame pressure jig. The pressure was manually adjusted while the temperature was actively controlled and monitored. A plateau in the resistance was observed at the highest applied pressure of 265 MPa (30 kN), and the ionic conductivity closely matched that measured in the CompreDrive system (3.69 mS/cm vs 3.64 mS/cm at 20 kN and 20 °C).

Supported by:



Federal Ministry  
for Economic Affairs  
and Climate Action

on the basis of a decision  
by the German Bundestag

## Acknowledgements

The development of the CompreFrame used for this application note is part of a subproject related to the project REFA (Grant No. 03EI6055+03EE6055A), funded by the Federal Ministry of Economic Affairs and Climate Action as part of the 7. Energieforschungsprogramm, which is highly appreciated. REFA is a joint research project with the two partners rhd instruments GmbH & Co. KG and Helmholtz Institute Ulm (HIU). We thank

our project partners Dr. Alberto Varzi, Dr. Dominic Bresser, and Mr. Mervyn Soans at HIU for the fruitful collaboration as well as for the valuable and inspiring input.

## Literature

- [1] A. Banerjee, X. Wang, C. Fang, E. A. Wu and Y. S. Meng, "Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes," *Chemical Reviews*, vol. 120, no. 14, p. 6878–6933, 2020.
- [2] S. Ohno, T. Bernges and J. Buchheim, "How Certain Are the Reported Ionic Conductivities of Thiophosphate-Based Solid Electrolytes? An Interlaboratory Study," *ACS Energy Letters*, vol. 5, no. 3, pp. 910-915, 2020.
- [3] "Application note: Determination of the pressure- and temperature-dependent ionic conductivity of solid electrolytes," December 2020. [Online]. Available: [https://rhd-instruments.de/download/appnotes/application-note\\_conductivity%20of%20solid%20electrolytes.pdf](https://rhd-instruments.de/download/appnotes/application-note_conductivity%20of%20solid%20electrolytes.pdf).
- [4] M. Iwamoto, "Maxwell–Wagner Effect," in *Bhushan, B. (eds) Encyclopedia of Nanotechnology*, Dordrecht, Springer, 2012, p. 1276–1285.