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Application note

Determination of the temperature-dependent conductivity of a lithium-ion battery electrolyte by means of EIS

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Introduction

To understand battery systems, simulation tools are often employed. For a high level of accuracy and reliability, these tools need accurate values of relevant physico-chemical parameters of the materials being involved. In case of binary electrolyte solutions, at least four different concentration- and temperature-dependent transport parameters are required: the (ionic) conductivity $\sigma_{DC}(T,c)$, the binary diffusion coefficient $D_{\pm}(T,c)$, the transference number $t_{+}(T,c)$, and the thermodynamic factor $f_{\pm}(T,c)$. In previous application notes, we showed how to determine transference numbers [1] and the binary diffusion coefficient [2].

In this application note, we demonstrate how to determine the temperature-dependent ion-conductivity of a binary lithium-ion battery electrolyte solution by means of (electrochemical) impedance spectroscopy (EIS).

Experimental

a) *Chemicals*

As liquid lithium-ion battery electrolyte, a 2 mol/l $LiPF_6$ (lithium hexafluorophosphate) solution in a 1:1 (v:v) mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate) was purchased from Sigma-Aldrich Chemie GmbH and was used without any further purification. After receipt, the electrolyte solution has been stored and handled inside of an argon filled glove box (M. Braun Inertgas-Systeme GmbH).

b) *Sample preparation & measuring setup*

For electrochemical measurements, a TSC 1600 closed GC measuring cell (= TSC 1600 closed measuring cell with glassy carbon electrode cap) in combination with a Microcell HC setup (rhd instruments GmbH & Co. KG) was used. The cell constant K_{cell} of that measuring cell was determined to be 1.3 cm^{-1} in a separate experiment using a reference standard (HI70030C, from Hanna Instruments) [3]. The design of the TSC 1600 closed GC measuring cell is shown in Figure 1.

Inside of the glovebox, 1.0 mL sample solution was filled into the test cell, and the sealed test cell was then transferred to the test station outside of the glovebox.

To connect the test cell to the measuring device and to adjust the sample temperature, a Microcell HC setup was used. The temperature adjustment was done by Peltier element technique. The temperature accuracy of this setup is 0.1 °C with regard to the sensor position in the measuring cell base unit.

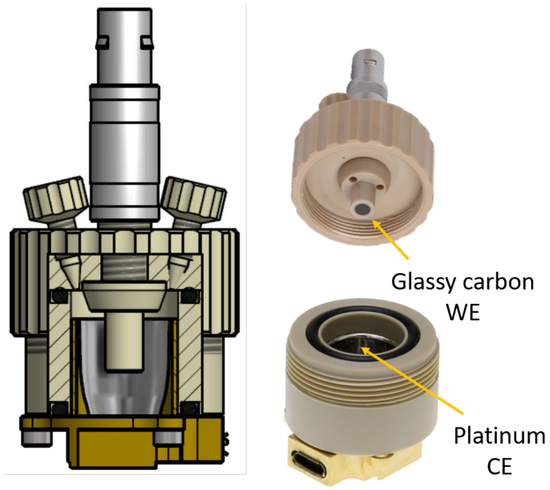

Figure 1: Schematic drawing of the TSC 1600 closed GC test cell. A platinum crucible serves as one electrode and as sample container, while as the other electrode, glassy carbon (GC) press-fitted in PEEK was used. Since the electrode in the cap is exchangeable, also other materials like platinum or gold could be used. For the determination of the electrolyte's conductivity, the choice of the electrode material is not relevant.

A PGStat204 potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for EIS measurements. For data acquisition, the NOVA 2.1.4 software was used. The control of the Microcell HC temperature unit is integrated in NOVA and therefore enables a convenient and user-friendly way to build experimental procedures including an automated adjustment of the sample's temperature.

Impedance data was evaluated by means of the RelaxIS 3® software suite (rhd instruments GmbH & Co. KG).

c) *Measurement parameters*

Impedance spectra were recorded for frequencies ranging from 1 MHz down to 1 Hz (20 frequencies per decade) with an AC voltage amplitude of 10 mV (rms) at several sample temperatures ranging from -20 °C to +60 °C with intervals of 5 °C. At each temperature, a hold time of 1800 s was chosen after reaching the temperature setpoint before starting the EIS experiment to ensure that the system is thermally equilibrated.

The single steps of the experimental procedure are listed in the following table.

Experimental step no.	Action to be performed
1	Determination of the cell constant using a reference standard, e.g. HI70030C, by means of a separate EIS experiment. Hint: Multiplying the determined bulk resistance value and the conductivity value at that specific temperature given by the manufacturer of the reference standard, directly provides you with the cell constant K_{cell}.
2	Adjustment of the temperature, and application of 1800 s hold time for ensuring temperature equilibration.
3	EIS measurement with V_{ac}(rms) = 10 mV and f = 1 MHz ... 1 Hz (20 frequencies per decade).
4	Repetition of no. 2+3 for all sample temperatures.

Results

The resulting temperature-dependent impedance spectra are shown in figure 2 as Bode plots (= log-log-plot of the real part of the impedance, *Z*′, against the measuring frequency, *f*).

At all temperatures, the impedance behavior for frequencies ranging from 1 MHz down to more or less 10 kHz is dominated by the migration of ions in the bulk of the electrolyte. That becomes visible in the Bode plots depicted in figure 2 as a broad plateau, whereby the plateau value is given as the bulk resistance for ion movement. With increasing temperature, the plateau value steadily decreases, indicating an increasing conductivity of the lithium-ion battery electrolyte, as expected in case of ionic conductivity.

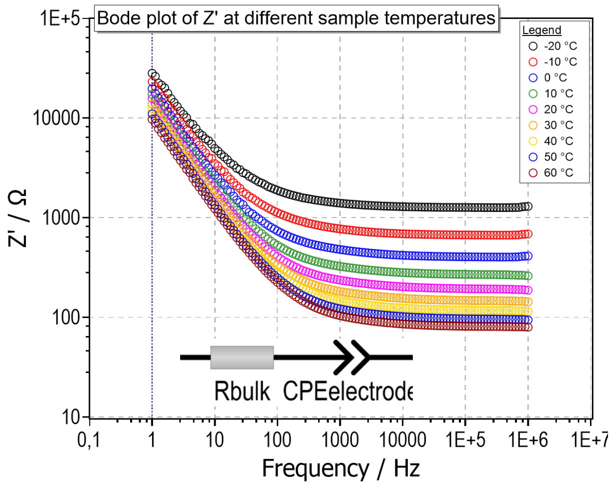

Figure 2: Impedance spectra at different sample temperatures (see legend) measured for frequencies ranging from 1 MHz to 1 Hz using an AC voltage amplitude of 10 mV (rms). An equivalent circuit consisting of an Ohmic resistor in series to a constant phase element was chosen for evaluating the measured impedance data.

For lower frequencies, an increase of the real part of the impedance is observed which is caused by the electrode polarization.

To fit the impedance spectra, a relatively simple equivalent circuit was chosen consisting of an Ohmic resistor connected in series to a constant phase element (*CPE*). Thereby, the Ohmic resistor represents the bulk resistance, R_{bulk}, and the *CPE* the electrode polarization, which shows a slightly non-ideal capacitive behavior.

In a next step, the conductivity σ_{DC} of the electrolyte can be caculated by multiplying the inverse bulk resistance, R_{bulk}, with the cell constant K_{cell}:

$$\sigma_{DC} = \frac{K_{cell}}{R_{bulk}}$$

The resulting mean values for the bulk resistance R_{bulk} calculated from three separate experiments (standard deviation lower than 2% in each case) are summarized in the following table. The mean ion conductivities were calculated from the mean bulk resistance values.

T / °C	$\langle R_{bulk} \rangle$ / Ω	$\langle \sigma_{DC} \rangle$ / mS/cm
-20	1238.8	1.0
-15	902.8	1.4
-10	673.9	1.9
-5	519.2	2.5
0	410.7	3.2
+5	333.3	3.9
+10	275.8	4.7
+15	232.5	5.6
+20	199.0	6.5
+25	173.0	7.5
+30	152.5	8.5
+35	135.9	9.6
+40	121.8	10.7
+45	110.0	11.8
+50	100.0	13.0
+55	91.6	14.2
+60	84.4	15.4

The determined temperature dependent ion conductivity values fit very well to literature values for similar systems (e.g. solution of $LiPF_6$ in EC:DMC 1:1 (w:w), [4]).

In figure 3, the natural logarithm of the conductivity in S/cm is plotted against the inverse temperature in Kelvin multiplied by a factor of 1000 (Arrhenius-plot).

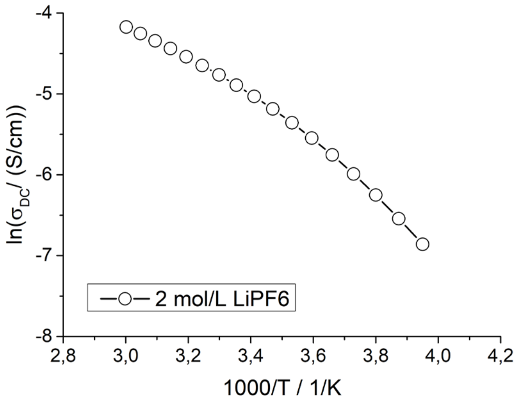

Figure 3: Arrhenius-plot of the calculated temperature-dependent ion-conductivity of the chosen lithium ion battery electrolyte, based on the bulk resistance values determined by means of EIS.

The temperature-dependence of the ion-conductivity shows a clear curvature which is typical for most liquid and polymeric electrolyte solutions and can be well-described by the so-called Vogel-Fulcher-Tamman equation (VFT equation):

$$\sigma_{DC}(T) = \sigma_0 \cdot exp\left(-\frac{B}{T - T_0}\right)$$

σ_0, B, and T_0 are empirical parameters whereby T_0 is often called 'Vogel temperature' and is related to the glass transition temperature determined by differential scanning calorimetry (DSC) in case of 'fragile' systems like e.g. ionic liquids and polymer electrolytes.

For the chosen electrolyte, the resulting fit values are: $\sigma_0 = 0.186$ S/cm, $B = 75.2$ K, $T_0 = 259$ K. They can be used as empirical parameter values for comparing electrolytes with different compositions.

Summary

In this application note, we showed how to use a turn-key system consisting of the Microcell HC setup, the TSC 1600 closed GC measuring cell, the measuring device PGStat204, and the powerful RelaxIS 3® software suite to determine the temperature-dependent ion-conductivity of a liquid lithium-ion battery electrolyte by means of EIS. The values determined by us here fit are in accordance with values which can be found in literature sources [4]. We also demonstrated how to further evaluate the temperature-dependence of the determined conductivity values based on the VFT equation.

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For more information, please contact us:

Literature

[1] M. Drüschler, B. Huber, 'Determination of the lithium ion transference number of a battery electrolyte by VLF-EIS', application note created by rhd instruments GmbH & Co. KG, downloadable via https://rhd-instruments.de/en/support/downloads.

[2] M. Drüschler, B. Huber, 'Determination of the binary diffusion coefficient of a battery electrolyte', application note created by rhd instruments GmbH & Co. KG, downloadable via https://rhd-instruments.de/en/support/downloads.

[3] Autolab Application Note EC10 "Automated Measurement of Temperature Dependent Ion-Conductivity".

[4] J. Landesfeind, H.A. Gasteiger, Temperature and Concentration Dependence of the Ionic Transport Properties fo Lithium-Ion Battery Electrolytes, J. Electrochem. Soc. 166 (14) A3079-A3097 (2019).