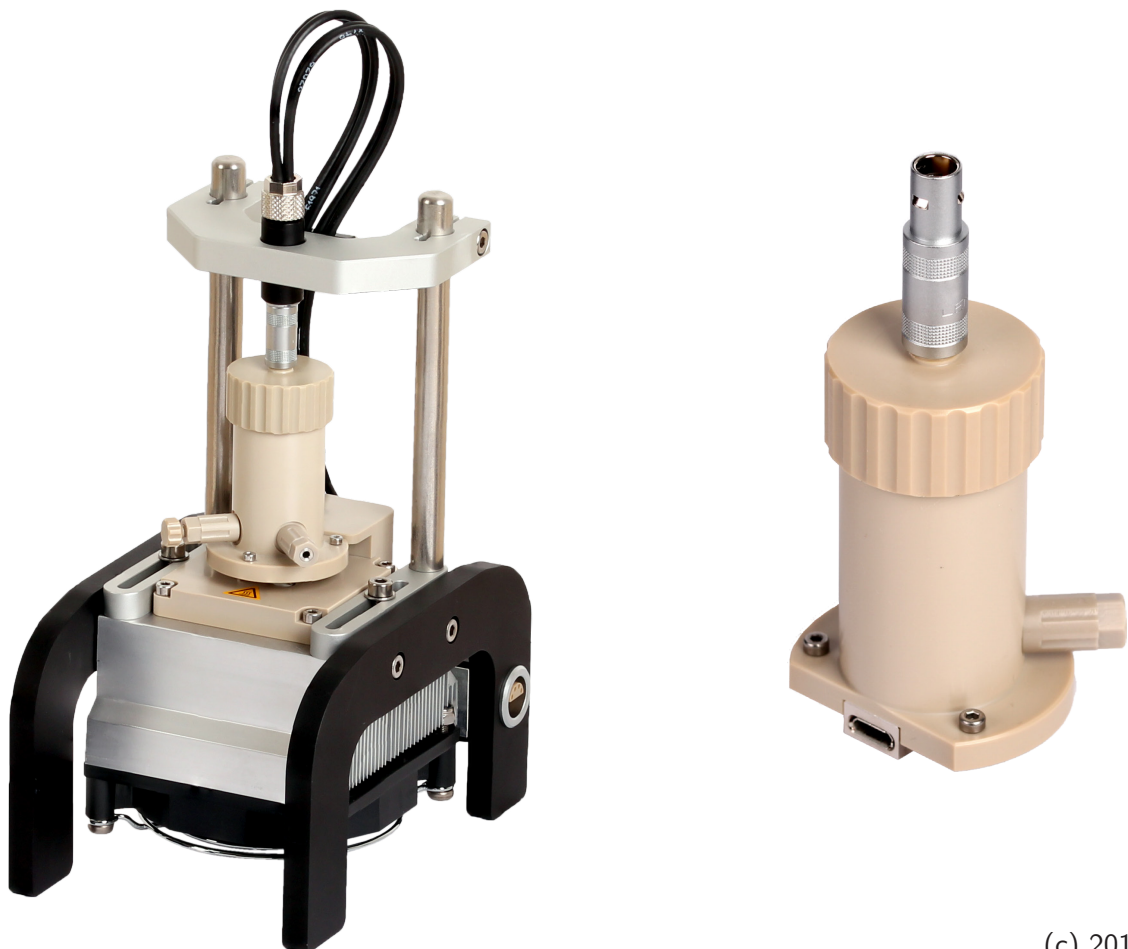


Application note

Determination of the
lithium ion transference number
of a battery electrolyte
by VLF-EIS



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 conductivity $\sigma(T,c)$, the binary diffusion coefficient $D_{\pm}(T,c)$, the transference number $t_{\pm}(T,c)$, and the thermodynamic factor $f_{\pm}(T,c)$.

In this application note, we demonstrate how to determine the lithium ion transference number of a commercial liquid binary lithium ion battery electrolyte based on the very elegant and one-step very-low-frequency impedance spectroscopy (VLF-EIS) method elaborated by Wohde, Balabjew, and Roling [1].

Experimental

a) Chemicals

As liquid binary lithium ion battery electrolyte, 1 mol/L LiPF_6 (lithium hexafluorophosphate) solution in EC (ethylene carbonate) : DMC (dimethyl carbonate) 1:1 (v:v) was purchased from Sigma-Aldrich Chemie GmbH and was used without any further purification. Metallic lithium foil from Rockwood Lithium GmbH (now part of Albemarle Corp.) in high purity was used for preparing the counter and working electrode. A porous polyethylene film (PE, Nitto Denko Corp., Sunmap® LC) with a thickness of 500 μm and 30% porosity was used as separator. All chemicals have 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 battery advanced measuring cell in combination with a Microcell HC setup (rhd instruments GmbH & Co. KG) was used. The design of the measuring cell is shown as schematic drawing in Figure 1.

As working and counter electrode, metallic lithium was used. The active electrode area was 1.13 cm^2 . The PE separator soaked with elec-

trolyte solution was placed between the lithium electrodes to reduce influences by convection. To ensure good wettability, the separator was stored in the electrolyte solution for 48 h before assembling the measuring cell.

The sample temperature was controlled by the Microcell HC Setup using Peltier technique. The temperature accuracy of this setup is 0.1 $^{\circ}\text{C}$ with regard to the sensor position in the measuring cell base unit. For the experiments presented here, the temperature was varied between -10 $^{\circ}\text{C}$ and +50 $^{\circ}\text{C}$.

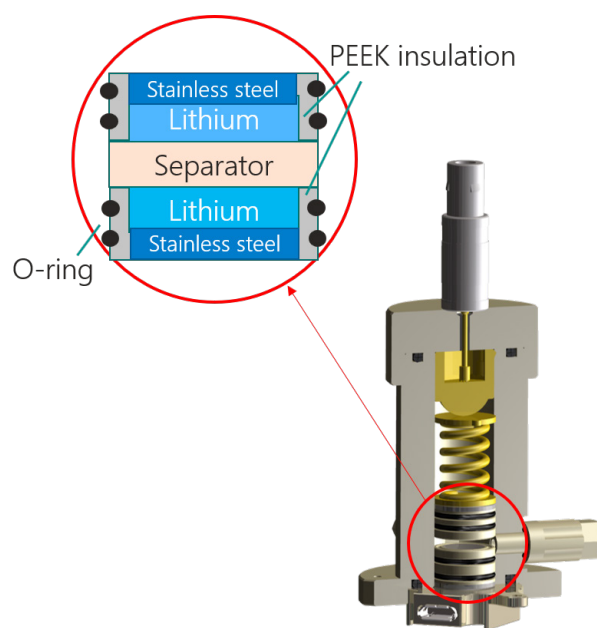


Figure 1: Schematic drawing of the TSC battery advanced measuring cell. As working and counter electrode, metallic lithium was used. A porous polyethylene separator soaked with 1 mol/L LiPF_6 solution in EC:DMC 1:1 (v:v) was placed between the electrodes.

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 control of the Microcell HC temperature unit is integrated in NOVA.

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

c) Measurement parameters

In a first step, consecutive EIS measurements with an ac voltage amplitude of 1 mV (rms) were performed in the frequency range from 100 kHz

to 1 Hz to make sure that the system and especially the lithium-electrolyte interface is stable which could take up to more than 72 h. For the VLF-EIS experiments, impedance spectra for frequencies ranging from 100 kHz down to 1 mHz (10 frequencies per decade) were measured with an ac voltage amplitude of 1 mV (rms). To ensure that the system is thermally equilibrated, a hold time of 900 s was chosen after reaching the temperature set-point before starting the VLF-EIS measurement.

Experimental Step	Method
1	Set temperature to 20 °C, apply 900 s hold time for temperature equilibration
2	Perform consecutive EIS measurements with V_{ac} (rms) = 1 mV and $f = 100$ kHz ... 1 Hz (10 frequencies per decade) until EIS response is stable
3	Carry out VLF-EIS measurement with V_{ac} (rms) = 1 mV and $f = 100$ kHz ... 1 mHz (10 frequencies per decade)
4	Set temperature to 30 °C, apply 900 s hold time for temperature equilibration
5	Carry out VLF-EIS measurement with V_{ac} (rms) = 1 mV and $f = 100$ kHz ... 1 mHz (10 frequencies per decade)
6	Repeat steps 4 + 5 for next temperatures

Results

The resulting VLF-EIS spectra can be described with the equivalent circuit proposed by Wohde and Roling [1].

The impedance response at high frequencies is dominated by the movement of ions through the electrolyte-soaked separator network and further serial resistance contributions like contact resistances, which is represented by the Ohmic resistor R_{bulk} .

At intermediate frequencies, the impedance response is governed by the contributions of the

solid electrolyte interface (SEI) between lithium and the electrolyte solution and the charge-transfer at the lithium electrode (CT). However, in contrast to Wohde and Roling [1], we merged the two R-CPE elements representing the SEI and the CT contributions to a combined $R_{interface}$ -CPE_{interface} element, see figure 2. Since the time constants for the SEI and the CT related processes were too similar, it was impossible to separate them in the equivalent circuit fit.

The diffusion impedance dominates the low frequency behavior. It is caused by the formation of a diffusion layer across the bulk of the electrolyte solution and it is described by a Warburg short element Ws . Here $R_{diffusion}$ denotes the diffusion resistance, and τ the characteristic time for establishing the stationary diffusion profile across the electrolyte [1]:

$$\hat{Z}_{Ws}(\omega) = R_{diffusion} \cdot \frac{\tanh[(j\omega\tau)^\alpha]}{(j\omega\tau)^\alpha}$$

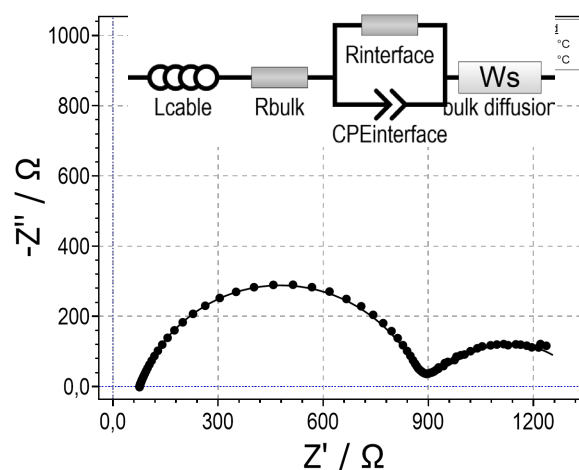


Figure 2: Impedance spectrum measured at 20 °C for frequencies ranging from 100 kHz to 1 mHz using an ac voltage amplitude of 1 mV (rms).

In figure 3, the VLF-EIS spectra measured at 10 °C, 20 °C, 30 °C and 40 °C are shown together in one plot. As expected, an increase of the sample temperature leads to significantly decreasing values for the bulk ion transport resistance R_{bulk} , the interfacial resistance $R_{interface}$, and the diffusion impedance Ws ($R_{diffusion}$).

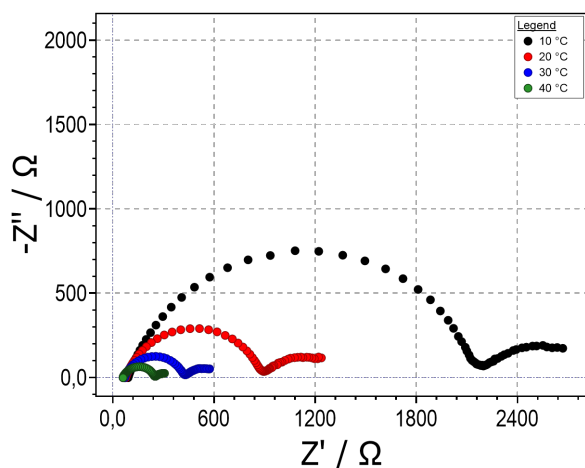


Figure 3: Impedance spectra measured at 10 °C, 20 °C, 30 °C, and 40 °C for frequencies ranging from 100 kHz to 1 MHz using an ac voltage amplitude of 1 mV (rms).

The parameter values resulting from the fit are given in the following table.

T [°C]	R_{bulk} [Ω]	$R_{\text{interface}}$ [Ω]	$R_{\text{diffusion}}$ [Ω]	τ [s]	α
-10	147	11551	1569	189	0,42
0	113	4823	934	155	0,41
+10	89	2053	615	142	0,40
+20	79	890	356	99	0,39
+30	69	397	187	66	0,37
+40	60	185	92	26	0,36
+50	50	84	52	14	0,33

From R_{bulk} and $R_{\text{diffusion}}$, the lithium ion transference number can be calculated:

$$t_{\text{Li}^+}^{\text{current}} = \frac{R_{\text{bulk}}}{R_{\text{bulk}} + R_{\text{diffusion}}}$$

The resulting transference numbers are plotted as a function of temperature in figure 4.

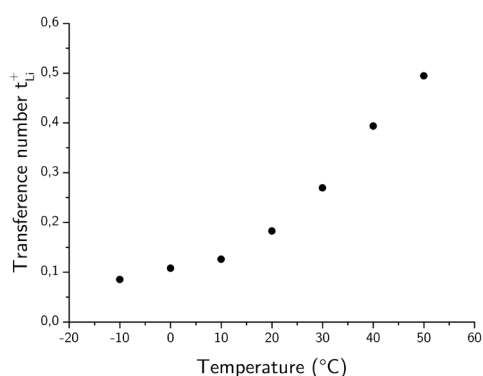


Figure 4: lithium ion transference numbers as a function of sample temperature.

T [°C]	Lithium-ion transference number
-10	0.09
0	0.11
+10	0.13
+20	0.18
+30	0.27
+40	0.39
+50	0.49

The lithium ion transference numbers determined here are comparable to those determined by Landesfeind and Gasteiger [2] and Hou and Monroe [3]. Interestingly, the lithium ion transference number is relatively low for temperatures lower than room temperature and increases significantly for higher temperatures. However, the goal of our application note is to show how to perform the experiment. To verify the results presented here, the experiment should be repeated several times by different experimenters.

Summary

In this application note, we showed how to determine the temperature-dependent lithium ion transference number of a commercial binary lithium ion battery electrolyte by applying the elegant VLF-EIS method proposed by Wohde and Roling [1]. The resulting values are close to the values determined for similar electrolyte systems using alternative approaches [2,3].

Acknowledgement

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Literature

- [1] F. Wohde, M. Balabajew, B. Roling, J. Electrochem. Soc. 163 (5) A714-A721 (2016).
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