Application Area: Batteries

Determination of the Lithium Ion Transference Number of a Battery Electrolyte by VLF-EIS

Keywords

Lithium ion batteries, transference number, electrochemical impedance spectroscopy, 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 $t_{+}(T,c)$, 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 electrochemical impedance spectroscopy (VLF-EIS) method elaborated by Wohde, Balabajew, and Roling[1].

Experimental Setup

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 Metrohm Autolab

Microcell HC setup was used. The design of the measuring cell is shown as schematic drawing in Figure 1.
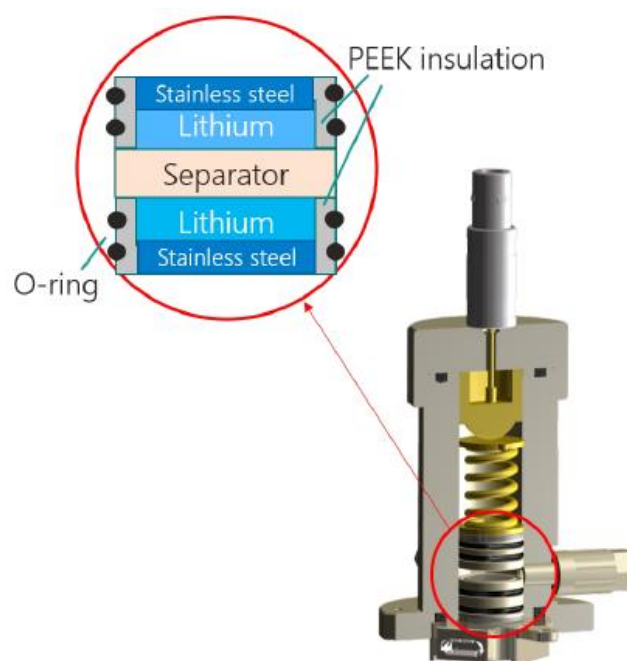

Figure 1 – Schematic drawing of the TSC battery advanced measuring cell. As working and counter electrode, metallic lithium was used. A porous polyethylene separator soaked with 1 mol/L LiPF$_6$ solution in EC:DMC 1:1 (v:v) was placed between the electrodes.

Metallic lithium was used as working and counter electrode. The active electrode area was 1.13 cm^2. The PE separator soaked with electrolyte 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 °C with regard to the sensor position in the measuring cell base unit. For the experiments presented here, the temperature was varied between -10 °C and +50 °C.

A Metrohm Autolab PGSTAT204 potentiostat/galvanostat equipped with a FRA32M module was used for EIS experiments (Figure 2).

Figure 2 – The Metrohm Autolab PGSTAT204, equipped with the FRA32M module.

For data acquisition, the NOVA 2 software was used. NOVA 2 software controls both Autolab potentiostat and Microcell HC for electrochemical measurement and temperature control respectively.

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

c) Measurement parameters

In the first step, consecutive EIS measurements with an AC voltage amplitude of 1 mV root mean square (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 more than 72 h. For the very-low-frequency electrochemical impedance spectroscopy (VLF-EIS) experiments, impedance spectra for frequencies ranging from 100 kHz down to 10 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 Setup	Method
1	Set temperature to 20 °C, apply 900 s hold time for temperature equilibration.
2	Perform EIS measurements with V_{AC}(RMS) = 1 mV and f = 1000 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 = 1000 kHz … 10 mHz (10 frequencies per decade).
4	Set 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 = 1000 kHz … 10 mHz (10 frequencies per decade).
6	Repeat steps 4 and 5 for the next temperatures.

Results and Discussion

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 resistor – constant phase element (R-CPE) representing the secondary electrolytic interface (SEI) and the charge transfer (CT) contributions to a combined $R_{interface}$-CPE element (Figure 3). 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.
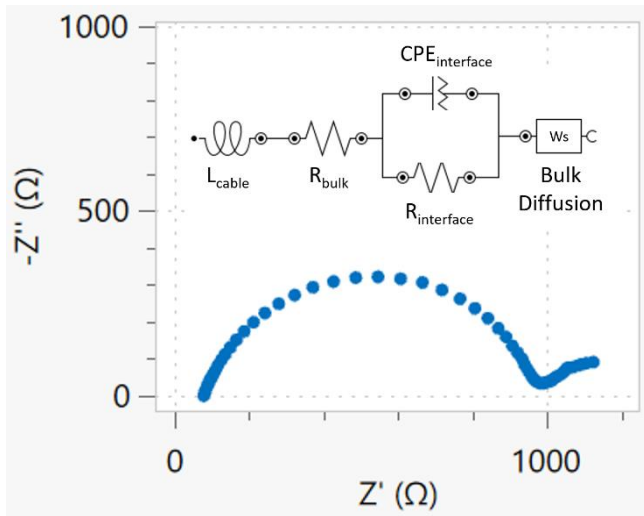
Figure 3 - Impedance spectrum measured at 20 °C for frequencies ranging from 100 kHz to 10 mHz using an AC voltage amplitude of 1 mV (RMS).

The diffusion impedance dominates the low frequency behavior. It is caused by the formation of a diffusion layer across the bulk of the electrolye solution and it is described by a Warburg short element *Ws*. Here *R$_{diffusion}$* denotes the diffusion resistance, τ the characteristic time for establishing the stationary diffusion profile across the electrolyte and α is the exponent to take into account the non-ideality[1]:

$$Z_{W_s}(\Omega) = R_{diffusion} \cdot \frac{\tanh[(j\omega\tau)^\alpha]}{(j\omega\tau)^\alpha} \qquad 1$$

In figure 3, the VLF-EIS spectra measured at 10 °C (black dots), 20 °C (red dots), 30 °C (blue dots), and 40 °C (green dots) are shown together in one plot.
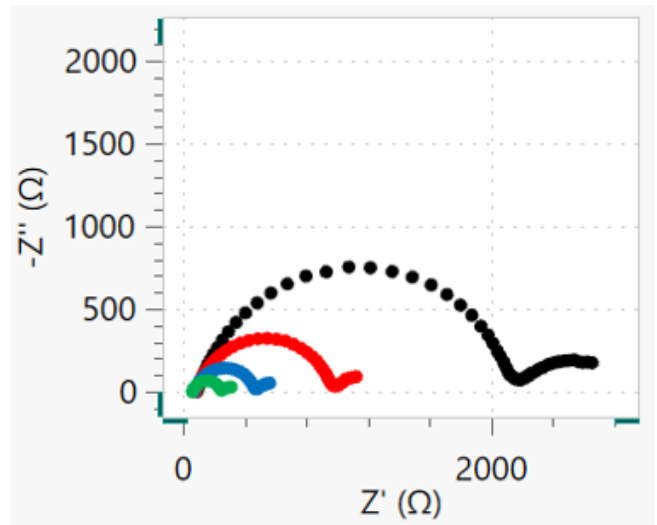

Figure 4 - Impedance spectra measured at 10 °C (black dots), 20 °C (red dots), 30 °C (blue dots), and 40 °C (green dots) for frequencies ranging from 100 kHz to 10 mHz using an AC voltage amplitude of 1 mV (RMS).

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 W$_s$ (R$_{diffusion}$).

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

T (°C)	R$_{bulk}$ (Ω)	R$_{interface}$ (Ω)	R$_{diffusion}$ (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$_{diffusion}$, the lithium ion transference number can be calculated:

$$t_{Li^+}^{current} = \frac{R_{bulk}}{R_{bulk} + R_{diffusion}} \qquad 2$$

The resulting transference numbers are plotted as a function of temperature in Figure 5.
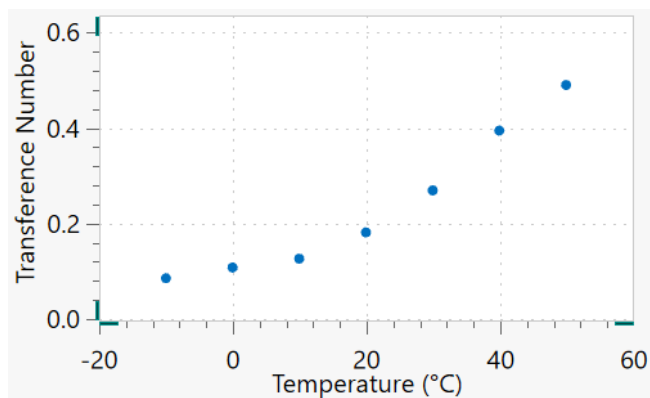

Figure 5 - lithium ion transference numbers as a function of sample temperature.

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 below room temperature and increases significantly with higher temperatures. However, the goal of this 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 analysts.

Conclusions

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].

Acknowledgments

References

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

[2] J. Landesfeind, H.A. Gasteiger, J. Electrochem. Soc., 166 (14) A3079-A3097 (2019).

[3] T. Hou, C.W. Monroe, Electrochimica Acta 332 135085 (2020).

Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.