



Application note

Determination of the
binary diffusion coefficient
of a lithium-ion battery electrolyte



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 binary diffusion coefficient of a commercial liquid binary lithium ion battery electrolyte based on a galvanostatic pulse method elaborated e.g. by Ehrl and Landesfeind et al. [1,2] and Hou et al. [3].

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. To ensure good wettability, the separator was stored in the electrolyte solution for 48 h before cell assembling. 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 electrolyte solution was placed between the lithium electrodes.

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 kept constant at 20 $^{\circ}\text{C}$.

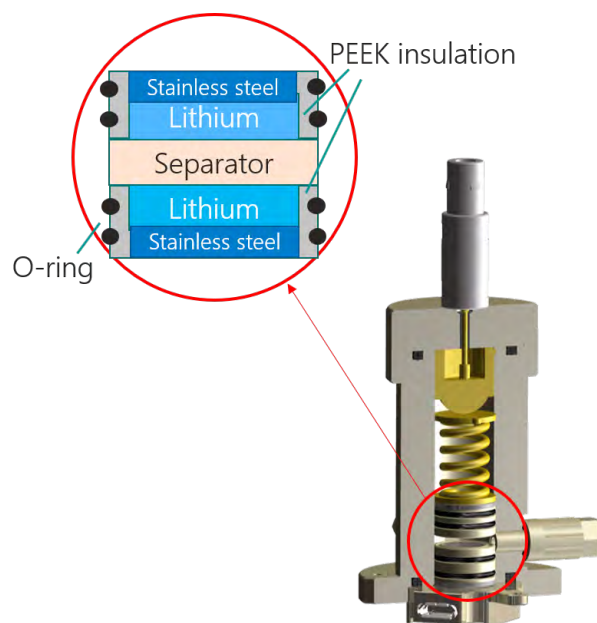


Figure 1: Schematic drawing of the TSC battery advanced measuring cell. As working and counter electrode, metallic lithium was used. A porous polyethylene separator soaked with 1 mol/L LiPF_6 solution in EC:DMC 1:1 (v:v) was placed between the electrodes.

A PGStat204 potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for EIS and time-domain 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

An impedance spectrum for frequencies ranging from 100 kHz down to 1 Hz (20 frequencies per decade) was measured with an AC voltage amplitude of 1 mV (rms). In a second step, alternating positive and negative pulse currents (GPP)

of 150 μA corresponding to a current density of $\sim 133 \mu\text{A}/\text{cm}^2$ were applied to the sample for a duration of 15 min, followed by an open circuit potential measurement for 3.5 h in each case.

Experimental step no.	Action to be performed
1	Setting temperature, 1800 s hold time for temperature equilibration
2	Performing EIS measurement with $V_{AC}(\text{rms}) = 1 \text{ mV}$ and $f = 100 \text{ kHz} \dots 1 \text{ Hz}$ (20 frequencies per decade)
3	Performing GPP experiment with $+150 \mu\text{A}$ for 900 s
4	Performing OCP measurement for 10800 s, record data every 1 s
5	Performing GPP experiment with $-150 \mu\text{A}$ for 900 s
6	Performing OCP measurement for 10800 s, record data every 1 s

Results

By fitting the impedance spectrum, the resistance for bulk ion transport through the porous separator network R_{bulk} can be determined to be 63.3Ω , see figure 2.

As equivalent circuit for analyzing the data, a serial connection of an Ohmic resistor R_{bulk} representing the ion transport through the porous separator network, and a parallel R - CPE element representing the solid electrolyte interface (SEI) properties as well as the charge transfer at the lithium-SEI interface was chosen. Splitting the R - CPE element as e.g. suggested by Wohde et al. [4] was not considered since that has a negative effect on the fit quality most likely caused by overlapping time constants for the processes taking place at the lithium-SEI interface and inside the SEI.

From R_{bulk} , the conductivity can be calculated taking into account the cell constant which is given by the separator thickness $d_{separator}$ and the active electrode area $A_{electrode}$:

$$K_{cell} = \frac{d_{separator}}{A_{electrode}} = \frac{0.05 \text{ cm}}{1.13 \text{ cm}^2} = 0.0442 \text{ cm}^{-1}$$

The conductivity of the electrolyte-soaked PE separator is $0.7 \text{ mS}/\text{cm}$:

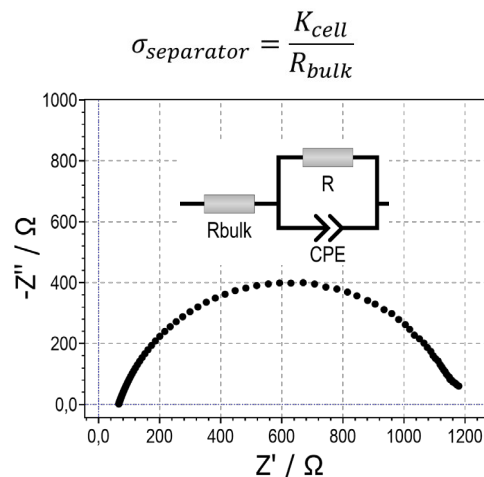


Figure 2: Impedance spectrum measured for frequencies ranging from 100 kHz to 1 Hz using an ac voltage amplitude of 1 mV (rms).

Dividing the conductivity of the “free” electrolyte solution ($9.9 \text{ mS}/\text{cm}$ @ $20 \text{ }^\circ\text{C}$) by the conductivity of the electrolyte-soaked separator foil, the so-called MacMullin number N_M can be calculated, see also our application note ‘Determination of the MacMullin number’ [5]:

$$N_M = \frac{\sigma_{electrolyte}}{\sigma_{separator}}$$

The resulting MacMullin number N_M for the chosen PE separator is 14.1. Since the porosity $\tau_{separator}$ of the separator material is known, the tortuosity $\tau_{separator}$ can be calculated as well:

$$\tau_{separator} = N_M \cdot \varepsilon_{separator}$$

The resulting tortuosity $\tau_{separator}$ is 4.2 which is slightly lower than the value determined by Landesfeind et al. [2] for the same material.

To determine the binary diffusion coefficient, the absolute OCP values measured after a negative galvanostatic current pulse are plotted semi-logarithmically versus time, see Figure 3.

At long times after the current interrupt, a linear relationship with slope m_{ln} is observed, which enables the calculation of the binary diffusion coefficient D_{\pm} for the given electrolyte concentration of $1 \text{ mol}/\text{L}$ at a temperature of $20 \text{ }^\circ\text{C}$ [1,2]:

$$D_{\pm}(T, c) = \frac{d_{\text{separator}}^2}{\pi^2} \cdot m_{\ln} \cdot \tau_{\text{separator}}$$

Here, a slope m_{\ln} of 0.0023 s^{-1} can be determined. Inserting that value into the formula results in a binary diffusion coefficient of $2.5 \times 10^{-6} \text{ cm}^2/\text{s}$.

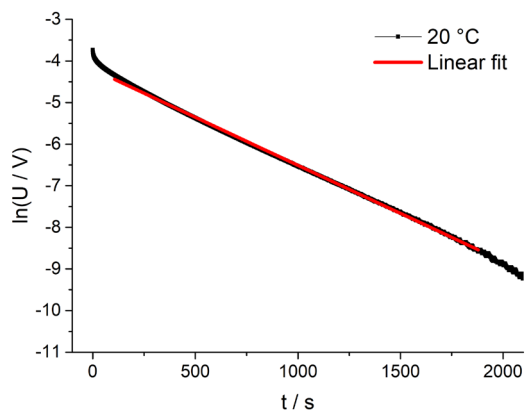


Figure 3: Absolute ocp values measured after the current interrupt plotted semi-logarithmically versus time. The curve is only shown for values t values from 0 s to 2000 s since at longer times, significant scattering due to the device limits regarding the voltage resolution is observed.

Summary

In this application note, we showed how to determine the MacMullin number of electrolyte-soaked separator foil, the tortuosity of that foil as well as finally the binary diffusion coefficient of the chosen binary liquid battery electrolyte.

The measured binary diffusion coefficient for 1 mol/L LiPF_6 solution in EC:DMC 1:1 (v:v) at $20 \text{ }^\circ\text{C}$ was determined to be $2.5 \times 10^{-6} \text{ cm}^2/\text{s}$ which is very close to the value determined by Landesfeind et al. for a quite similar electrolyte solution [2].

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For more information, please contact us:



Literature

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