

Application Area: Batteries

Determination of the binary diffusion coefficient of a battery electrolyte

Keywords

Batteries, electrolytes, MacMullin number, separator, binary diffusion coefficient, tortuosity

Introduction

To understand battery systems, simulation tools are often employed. For a high level of accuracy and reliability, these tools need accurate values for the relevant physico-chemical parameters of the involved materials. 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 polarization (GPP) method, elaborated by Ehrl and Landesfeind et al.^{1,2} and Hou et al.³.

Experimental Setup

a) Chemicals

As liquid binary lithium ion battery electrolyte, 1 mol/L LiPF₆ (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 in high purity was used to prepare the counter and working electrodes. 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 prior to assemble the measuring cell. All chemicals were 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 the schematic drawing in Figure 1.

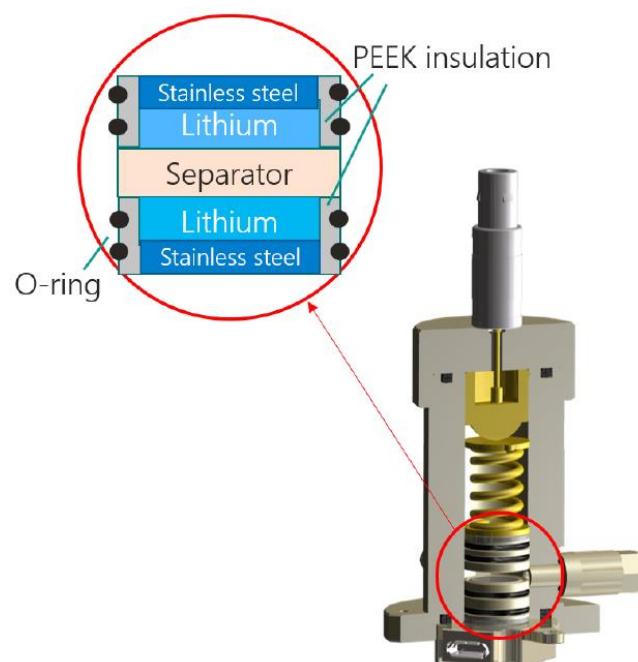


Figure 1 – Illustration of the TSC Battery Advanced measuring cell. Metallic lithium was used for both working and counter electrodes. A porous polyethylene separator soaked with 1 mol/L LiPF₆ solution in EC:DMC 1:1 (v:v) was placed between the electrodes.

Metallic lithium was used for both working and counter electrodes. The active electrode area was 1.13 cm². The PE separator soaked with electrolyte solution was placed between the lithium electrodes.

The sample temperature was controlled by the Microcell HC Setup using the 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 kept constant at 20 °C.

A Metrohm Autolab PGSTAT204 equipped with a FRA32M module was used for electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) experiments. For data acquisition, the NOVA software was used. The control of the Microcell HC temperature unit is integrated in NOVA.

c) Measurement parameters

As a first step, an impedance spectrum for frequencies ranging from 100 kHz down to 1 Hz, with 20 frequencies per decade, was measured by an AC voltage amplitude of 1 mV root mean square (RMS).

The next step consisted in a galvanostatic pulse polarization (GPP). Here, alternating positive and negative current pulses of 150 μ A, corresponding to a current density of $\approx 133 \mu\text{A}/\text{cm}^2$, were applied to the sample for a duration of 15 min, followed by an open circuit potential (OCP) measurement for 3.5 h in each case. The steps are listed in Table 1.

Table 1 – Experimental steps for the used procedure.

Experimental step	Method
1	Set temperature, 1800 s hold time for temperature equilibration
2	EIS measurement with $V_{AC}(\text{RMS}) = 1 \text{ mV}$ and $100 \text{ kHz} < f < 1 \text{ Hz}$, 20 frequencies per decade
3	GPP with $+150 \mu\text{A}$ for 900 s
4	OCP measurement for 10800 s, data recorded every 1 s
5	GPP with $-150 \mu\text{A}$ for 900 s
6	OCP measurement for 10800 s, data recorded every 1 s

Results and Discussion

By fitting a trend line the impedance spectrum, the resistance for bulk ion transport through the porous separator network R_{bulk} can be determined to be 63.3Ω , (Figure 2).

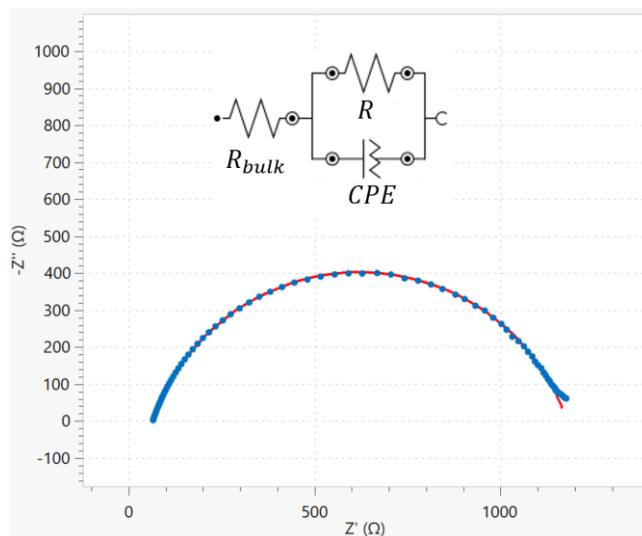


Figure 2 - Impedance spectrum measured for frequencies ranging from 100 kHz to 1 Hz using an AC voltage amplitude of 1 mV (RMS).

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 arrangement of a resistor R and a constant phase element CPE, $R \parallel \text{CPE}$, representing the solid electrolyte interface (SEI) properties as well as the charge transfer at the lithium-SEI interface was chosen. Splitting the $R \parallel \text{CPE}$ element as 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, given by the separator thickness and the active electrode area $A_{electrode}$:

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

Dividing the conductivity of the “free” electrolyte solution (9.9 mS/cm at 20 °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 AN-BAT-006 Determination of the MacMullin number⁵):

$$N_M = \frac{\sigma_{electrolyte}}{\sigma_{separator}} \quad 2$$

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

$$\tau_{separator} = N_M \cdot \epsilon_{separator} \quad 3$$

The resulting tortuosity is $\tau_{separator} = 4.2$, 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 values of the OCP, measured after a negative galvanostatic current pulse are plotted (blue dots in Figure 3).

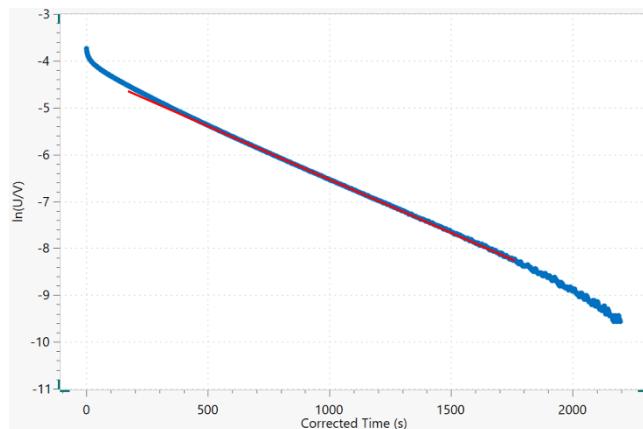


Figure 3 - Absolute values of OCP measured AT 20 °C (blue dots) after the current interrupt, plotted semi-logarithmically versus time. In red, the regression line is shown.

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 mol/L at a temperature of 20 °C^{1,2}:

$$D_{\pm}(T, c) = \frac{d^2_{separator}}{\pi^2} \cdot m_{ln} \cdot \tau_{separator} \quad 4$$

Here, a slope m_{ln} of 0.0023 s⁻¹ can be determined (red line in Figure 3).

Inserting that value into Equation 4 results in a binary diffusion coefficient of 2.5E – 6 cm²/s.

Conclusions

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 LiPF₆ solution in EC:DMC 1:1 (v:v) at 20 °C was determined to be 2.5E – 6 cm²/s which is very close to the value determined by Landesfeind et al. for a quite similar electrolyte solution².

Acknowledgement

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References

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- [5] AN-BAT-006 ‘Determination of the MacMullin number’, <https://www.metrohm.com/en/applications/AN-BAT-006>

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AN-BAT-009

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.