Application note

Programmed current derivative chronopotentiometry as a measure for Lithium-ion battery electrolyte performance

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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, one of the required transport parameters is the transference number t_+ which is a function of the electrolyte concentration as well as the temperature. The transference number can be determined by different methods [1-3]. However, significant deviations between the results of different methods applied to the identical electrolyte solution are usually found and some methods require the combination of intermediary results from separate experiments which leads to large statistical errors [2,3].

In this application note, we show how to use a quite simple, semi-empirical approach to measure the lithium mobility in a binary electrolyte solution, the so-called programmed current derivative chronopotentiometry [4,5,7].

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. To reproducibly and accurately adjust the lithium-lithium disctance, spacer-rings made of polyether etherketone (PEEK) were used (produced by and available from rhd instruments GmbH & Co. KG). 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, determined by the inner opening of the ring-like PEEK spacer, was 0.5 cm^2. A ring-like PEEK spacer with a thickness of 8 mm and a diameter of 8 mm for the inner-opening was placed between the lithium electrodes to adjust the lithium-lithium distance. After assembly of the cell, a hold time of at least 2 hours was chosen before starting the experiment since it was found that thereby the reproducibility level was improved.

The sample temperature was conrolled 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 set to +20 °C.

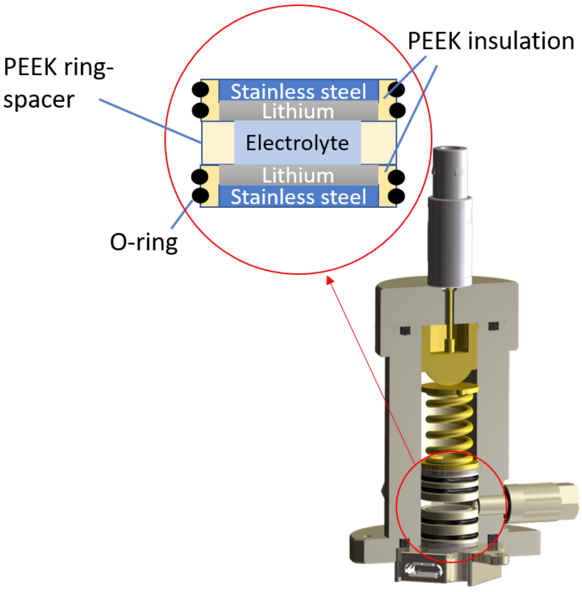

Figure 1: Schematic drawing of the TSC battery advanced measuring cell. As working and counter electrode, metallic lithium was used. A spacer-ring made of PEEK with a thickness of 8 mm and inner opening diameter of 8 mm was placed between the electrodes.

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.

c) *Measurement parameters*

First, the sample temperature is adjusted to 20 °C and a hold time of 3600 s is chosen to enable the system to reach a thermal equilibrium.

A current *I* that increases linear with time *t* with a rate of $v = 60\ \mu A/s$ is imposed to the test cell while the potential difference between working and counter electrode is measured. The cut-off limit is set to 10 V.

Experimental Step	Method
1	Wait for 7200 s after assembly of the test cell before starting the experiment.
2	Set temperature to 20 °C, apply 3600 s hold time for temperature equilibration.
3	Perform a linear stair case voltammetry experiment with start current = 0 A and stop current = 0.1 A and scan rate = 60 µA/s in steps of 15 µA while applying a cut-off limit of 10 V.

Results

An examplary *E* vs. *I* curve is shown in figure 2. For the selected electrolyte solution, a limiting current of 33 mA was determined which can be used as a measure for the lithium ion mobility at the given temperature, see discussion below figure 2.

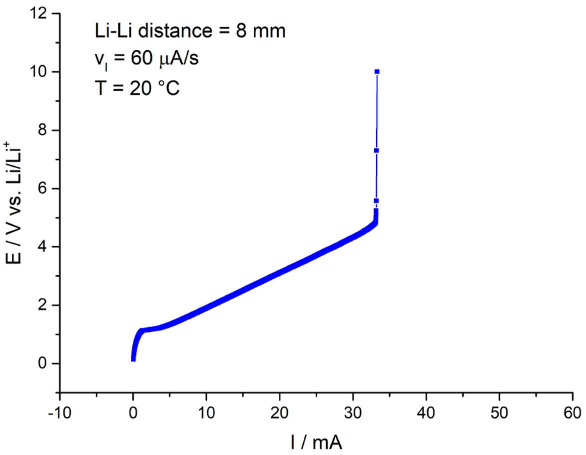

Figure 2: *E* vs. *I* for a programmed current derivative chronopotentiometry experiment applied to a lithium-electrolyte-lithium setup with a inter-lithium distance of 8 mm, a lithium surface area of 0.5 cm^2 and a scan rate of 60 µA/s.

The very first part of the curve is dominated by polarization (double layer charging) and SEI-related processes, which is followed by a linear part dominated by bulk ion transport.

The slope of the the linear part (here: 116 Ω) can be used to estimate the bulk ion conductivity by taking into account the electrode area and lithium-lithium distance for calculating the geometrical cell constant (here: 1.59 cm^{-1}). The resulting value is 9.9 mS/cm (@ 20 °C) which is in very good agreement with literature values and the values given by the manufacturer.

Finally, above a certain applied current limit I_{max} (here: 33 mA) the voltage increases drastically. The concentration of lithium-ions at the lithium electrode surface drops to zero since the flux of lithium ions to the surface is insufficient to accept all of the electrons being forced across the electrode-solution interface [6]. I_{max} therefore corresponds to the maximum accessible lithium ion flux under the applied current conditions [4]. It is important to note that this assumption is only valid if other effects like lithium plating/ dissolution are not rate-determining [4].

At identical conditions regarding the lithium-lithium distance, the exposed lithium electrode surface, the temperature, and the scan rate, one can take the measured current limit I_{max} value as a qualitative measure for the expected performance of the investigated electrolyte solution in lithium-ion cells. To compare the expected performance of different electrolyte solutions, the resulting I_{max} values can be compared.

Summary

In this application note, we showed how to apply a quite simple empirical method to qualitatively predict the performance of lithium ion battery electrolytes. This method does not effort highly sophisticated, long-term experiments and can be carried out very quickly [4].

Acknowledgement

The results presented here are part of the project LiMES funded by the Federal Ministry for Economic Affairs and Energy as part of the 7. Energieforschungsprogramm which is highly appreciated.

LiMES is a joint research project with the two partners rhd instruments GmbH & Co. KG and Karlsruhe Institute of Technology (KIT). We thank our project partners Dr. Andreas Hofmann and Ingo Reuter from KIT for the fruitful collaboration and valuable as well as inspiring input.

Supported by:

Federal Ministry
for Economic Affairs
and Energy

on the basis of a decision
by the German Bundestag

The PCDC procedure described in this application note is protected by a German patent [7].

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