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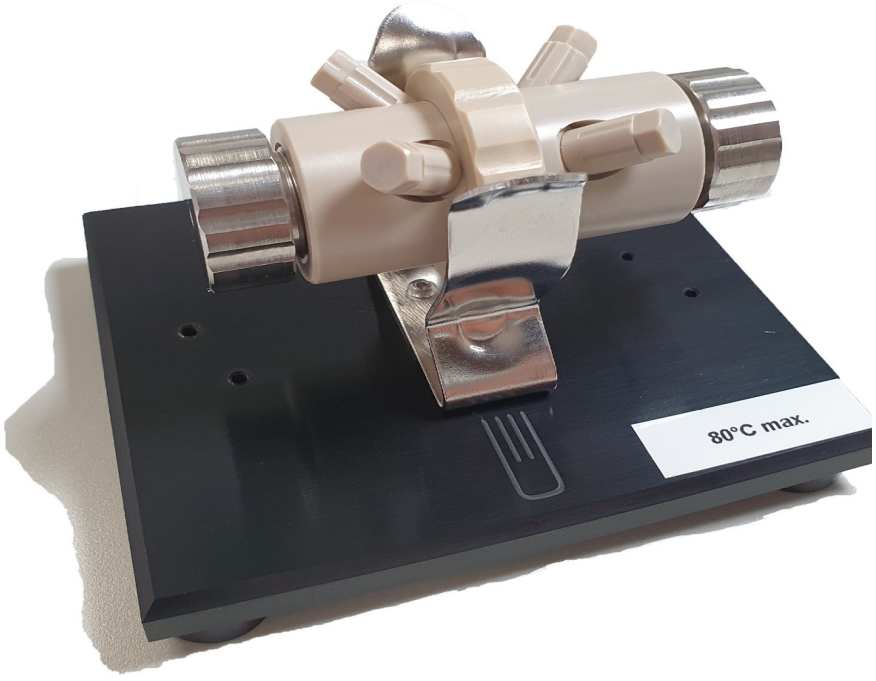
Application note

Determination of the temperature-dependent conductivity of lithium-ion battery electrolytes by a DC method



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Introduction

One important component of every electrochemical cell is the electrolyte solution. A measure for the ability of an electrolyte solution to conduct ionic current is its conductivity σ_{DC}. The conductivity can be measured by alternating current (ac) or direct current (dc) techniques. Usually, ac techniques such as electrochemical impedance spectroscopy are applied, because dc techniques often suffer from parasitic polarisation and also decomposition effects [2]. However, ac techniques tend to require relatively costly equipment and trained laboratory personnel. Therefore, the application of dc methods which are often easier to perform and to interpret would be preferable.

In this application note, we demonstrate how to determine the temperature-dependent conductivity of a typical lithium-ion battery electrolyte by means of a simple dc method. We use the test cell "TCE Cell One" for this purpose. This test cell has been developed by rhd instruments GmbH & Co. KG.

Experimental

a) Chemicals

As lithium-ion battery electrolyte, a 2 mol/l $LiPF_6$ (lithium hexafluorophosphate) solution in a 1:1 (v:v) mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate) was purchased from Sigma-Aldrich Chemie GmbH and was used without any further purification. Metallic lithium foil from Thermo Fisher (Kandel) GmbH in high purity was used. After receipt of the electrolyte solution as well as the lithium foil, they have been stored and handled inside of an argon filled glove box (M. Braun Inertgas-Systeme GmbH).

b) Sample preparation & measuring setup

For the electrochemical measurements, a TCE Cell One, see **Figure 1**, with a slightly modified inter-electrode distance was used (rhd instruments GmbH & Co. KG). This test cell enables the user to place two lithium electrodes in a well-defined distance from each other and to fill the space between them with liquid electrolyte.

The assembled TCE Cell One was transferred into a climate chamber of type "LabEvent" (Weiss Umwelttechnik GmbH) to adjust the sample temperature. The accuracy of the temperature is of the order of 0.5 °C.

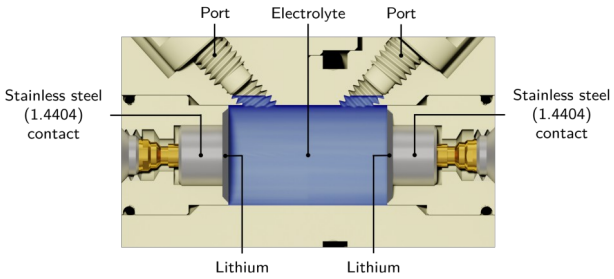

Figure 1: Schematic drawing of the test cell "TCE Cell One". Two metallic lithium electrodes are separated from each other by a compartment filled with liquid lithium ion battery electrolyte.

For the measurements, a Metrohm Autolab PGSTAT302N equipped with a FRA32-module was used. The communication with the climate chamber was integrated into the NOVA 2.1.5 software procedure by progamming a DLL. This allowed for performing automated measuring routines.

The recorded potential-current curves were evaluated and plotted by OriginPro 2022b (OriginLab Corp.).

c) Measurement parameters

The potential-current curves were recorded using the linear staircase voltammetry (LSV) command in NOVA 2.1.5. The current was increased starting at 0 A with a scan rate of 60 µA/s to 6 mA as stop current. The current step height was set to 15 µA. The potential was measured in the last quarter of the interval time (alpha value = 1). As potential cut-off limit, 9.5 V was used.

After reaching each temperature set point and before starting a LSV measurement, a waiting time of 1800 s was chosen to ensure for complete thermal equilibrium.

Step	Action to be performed
1	Cleaning and drying the parts of the test cell and transferring them into the glovebox.
2	Using the electrodes with punching edge (core metal: 1.4404 stainless steel) and punching out metallic lithium from the foil.
3	Assembling the test cell and using the lateral ports to fill the empty space between the electrodes with liquid electrolyte (approx. 1.3 ml).
3	Connecting the measuring device (2-electrode configuration with metallic lithium as working electrode and as counter electrode).
4	Starting the measurement procedure: Setting the first temperature ideally beginning with the lowest temperature and waiting for 1800 s. Measuring a potential-current curve using the LSV command. Repeating this step for each temperature.

Results

The resulting potential-current curves for temperatures from -20 °C to +60 °C are shown in **Figure 2.**

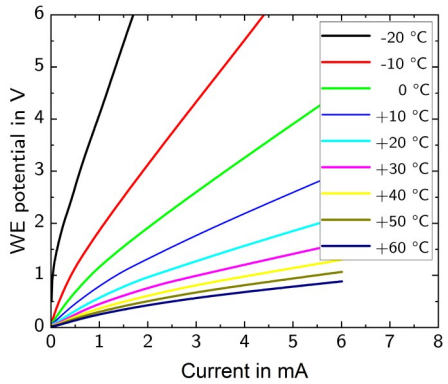

Figure 2: Potential-current curves at different temperatures recorded by means of LSV for 2 mol/l $LiPF_6$ in EC:DMC 1:1 (v:v) confined between two metallic lithium electrodes in the TCE Cell One.

For low currents, the resulting potential-current curves are non-linear. Here, interfacial processes (e.g. double layer formation, SEI formation, etc.) dominate. For currents higher than approx. 2 mA, the migration of ions through the bulk dominates and the potential-current curves become linear. The slopes give the temperature-dependent bulk resistance values. The determined values are in good agreement with the ones that could be determined using impedance spectroscopy for the bulk resistance.

Multiplying the reciprocal resistance values with the cell constant results in temperature-dependent conductivity values.

$$\sigma_{DC} = \frac{K_{cell}}{R_{bulk}}$$

The cell constant (K_{cell} = 1.78 cm^{-1}) was calculated by dividing the distance between the metallic lithium electrodes (here: 14 mm; standard value for TCE Cell One is 16 mm) by the area of one electrode (0.785 cm^2). Because of the reactivity of lithium metal, it was not possible to calibrate the test cell using an aqueous calibration standard.

The resulting values for the ion conductivity are listed in the table below ("DC-method") together with the values determined by impedance spectroscopy [1] ("AC-method").

T / °C	R_{bulk} / Ω	σ_{DC} / mS/cm DC-method	σ_{DC} / mS/cm AC-method
-20	2680,4	0.7	1.0
-10	1208,6	1.5	1.9
0	657,5	2.7	3.2
+10	417,4	4.3	4.7
+20	290,8	6.1	6.5
+30	212,7	8.3	8.5
+40	163,3	10.9	10.7
+50	132,5	13.5	13.0
+60	102,8	17.3	15.4

The determined temperature-dependent ion conductivity values fit very well with the values

determined for the same lithium ion battery electrolyte by applying electrochemical impedance spectroscopy [1]. Slight differences especially at very low and high temperatures could most likely be explained by the fact that the potential difference between the electrodes also contains contributions by the interface and not only by bulk ion transport.

In **Figure 3**, the Arrhenius-plot of the determined conductivity values is shown.

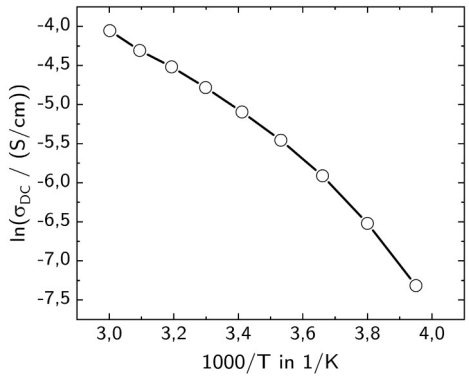

Figure 3: Arrhenius-plot of the determined temperature-dependent conductivity values of the chosen lithium ion battery electrolyte.

The Arrhenius-plot shows a pronounced curvature which is typical for many liquid and polymeric electrolytes. To fit the data, the Vogel-Fulcher-Tamman (VFT) equation can be applied, see [1].

Summary

In this application note, we have demonstrated how to determine temperature-dependent conductivity values for a typical lithium ion battery electrolyte. Instead of using an ac method like electrochemical impedance spectroscopy, we applied a very simple and easy-to-evaluate dc method based on linear scan voltammetry.

For doing so, the liquid battery electrolyte was placed between metallic lithium electrodes and a linearly increasing current was applied while the potential difference between the metallic lithium electrodes was measured. The slope of the resulting linear potential-current curve can be used to directly extract the bulk resistance value. From the bulk resistance, the conductivity value can then finally be calculated. This procedure was repeated for different temperatures ranging from -20 °C up to +60 °C.

The resulting temperature-dependent conductivity values are in accordance with values that can be determined using ac methods (electrochemical impedance spectroscopy [1]).

Acknowledgement

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Literature

[1] Application note "Determination of the temperature-dependent conductivity of a lithium-ion-battery electrolyte by means of EIS", rhd instruments GmbH & Co. KG, 2021.

[2] "Primary Standards and Standard Reference Materials for Electrolytic Conductivity", R. H. Jameel, Y. C. Wu, K. W. Pratt, National Institute of Standards and Technology Gaithersburg, MD 20899-8390