使用 Autolab Microcell HC 设置进行温度下离子电导率测量

One approach for improving the performance of energy storage devices (e.g., batteries and supercapacitors) is to enhance the ion conductivity (σ_{DC}, S cm^{-1}) of the electrolyte. The common method to obtain σ_{DC} is to perform electrochemical impedance spectroscopy (EIS) experiment at different temperatures using a 2-electrode setup. For routine measurements of a large number of samples, fast exchange of sample compartments or if an automatic sample analysis is desired this approach is very convenient as it reduces errors and saves time. Metrohm Autolab provides a measurement setup, the Autolab Microcell HC, which can be combined with an Autolab instrument with a FRA32M module allowing for an automatic determination of temperature dependent σ_{DC} values. In this application note, general information about the basics of σ_{DC} determination as well as an exemplary study of $\sigma_{DC}(T)$ for a typical Li-ion battery electrolyte are presented.

PRINCIPLES OF ION CONDUCTIVITY MEASUREMENTS

When a good liquid ion conductor is in contact with a blocking electrode, the recorded EIS data of most real systems can be described by a serial connection of an inductor (L_{Cable}) representing the inductance of the cables connecting the electrodes with the instrument, an ohmic resistor (R_{Bulk}) describing the resistance for bulk ion transport, and a constant phase element (CPE_{Int}), which takes into account a non-ideal capacitive behaviour of the interface. (see Figure 1).

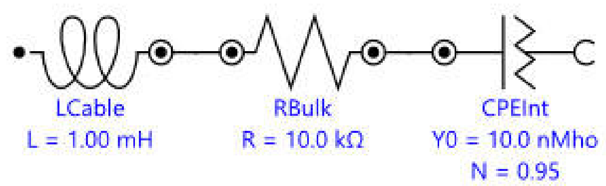

Figure 1. Equivalent circuit describing the interface between a good ion conductor and an inert electrode

It is a common procedure to analyse EIS data in the Nyquist plot. The equivalent circuit shown in Figure 1 leads to a slightly curved line due to the non-ideal capacitive behaviour of the interface, which intersects the Z' axis at R_{Bulk}, at high frequencies (see Figure 2).

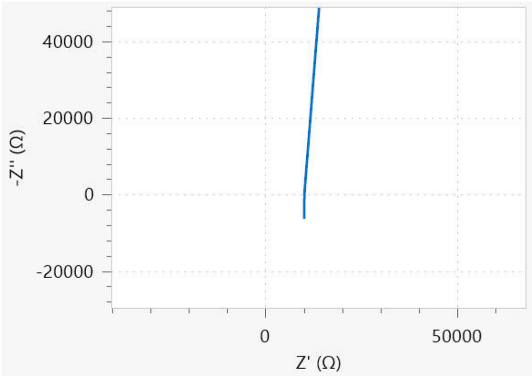

Figure 2. Nyquist plot corresponding to the equivalent circuit shown in Figure 1.

However, the Nyquist plot is not the best data representation for a proper analysis, because in a high frequency regime artefacts, either due to the cable's impedance or the presence of bulk impedance, lead to a second intercept with the real axis of the Nyquist plot. Therefore, care has to be taken to avoid misinterpretations concerning the R_{Bulk} value.

Instead of the Nyquist plot, a Bode plot of the modulus of the admittance, *Y* (in Siemens, *S* or *Mho*) should be preferred. The relationship between the impedance *Z* and the admittance are given by:

$$Y = \frac{1}{Z} = \frac{Z'}{|Z|^2} + j\frac{Z''}{|Z|^2} \qquad 1$$

Where the real (*Y'*) and imaginary (*Y''*) parts of the admittance are given by:

$$Y' = \frac{Z'}{|Z|^2} \qquad Y'' = \frac{Z''}{|Z|^2} \qquad 2$$

The Bode plot of the admittance modulus *Y* for the equivalent circuit of **Figure 1** is shown in **Figure 3**.

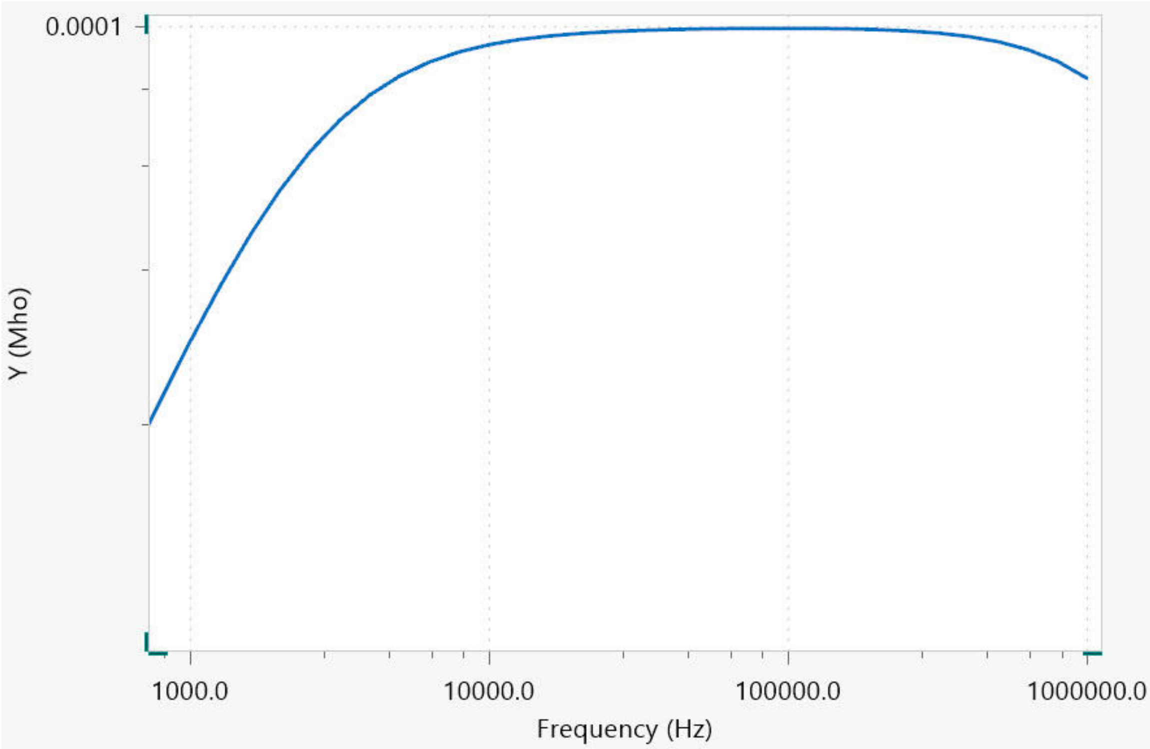

Figure 3. Bode plot of for the equivalent circuit shown in Figure 1

At high frequencies, the admittance values decrease with increasing frequency. This is caused by the inductance of the cables. At lower frequencies the curve is parallel to the frequency axis. This part is governed by bulk ion transport and the value of the admittance is identical to σ_{DC} / K_{Cell} . Here, K_{Cell} (cm^{1}) is the cell constant which can be calculated via an EIS measurement of an applicable conductivity standard, such as the Metrohm conductivity standard 100 µS/cm. At lower frequencies, the charging of the interfacial capacitance is observable which causes a decrease of the admittance values.

After fitting the recorded data to the equivalent circuit in **Figure 1**, the reciprocal of the obtained value for R_{Bulk} can be multiplied with the cell constant K_{Cell} to calculate σ_{DC}:

$$\sigma_{DC} = \frac{1}{R_{Bulk}} K_{Cell} \qquad (3)$$

However, there are additional experimental considerations. First of all σ_{DC} shows a significant temperature dependence which can often be described by an empirical Vogel-Fulcher-Tamman approach:

$$\sigma_{DC} = \sigma_0 exp\left(-\frac{A}{T - T_g}\right) \quad (4)$$

With σ_0, A and T_g the fitting parameters. Therefore, the sample temperature has to be controlled. Often, the temperature of the sample compartment is controlled via an external circulating bath, which is a relatively time-consuming procedure.

Secondly, most modern electrolytes are volatile and require leak-tight sample compartments, which allow for measurements within a broad temperature range.

Finally, although the EIS experiments are fast since only the high frequency impedance has to be recorded, the data analysis might be time consuming. An analysis tool for the measured EIS data like the Fit and Simulation Command found in NOVA is highly welcome.

EXPERIMENTAL SETUP

The combination of the measurement setup Autolab Microcell HC with a Metrohm Autolab potentiostat/galvanostat instrument equipped with a FRA32M module, as shown in **Figure 4**, provides a temperature-controlled electrochemical measurement system for volatile samples.

Figure 4. The Autolab Microcell HC combined with the Autolab PGSTAT204 and the FRA32M module

EXPERIMENTAL SETUP

The cell is fitted with a glass-sealed platinum wire working electrode and a platinum crucible counter electrode. The cell is then connected to a cell holder capable to control the temperature of the cell via a Peltier element, see Figure 5.

The cell holder is connected to the temperature controller, itself connected to the PC via a serial RS-232 interface, allowing for an automated temperature control.

Through the dedicated NOVA commands, the Autolab Microcell HC offers the following unique advantages:

- Possibility to define a temperature range (in this application note: from 5 ° C to 60 ° C).
- Possibility to define stability conditions (in this application note 0.5 ° C/min) as well as waiting time for maximum temperature deviation.
- Possibility to define a hold time after fulfilling the stability conditions.

For the measurements presented in this application note, the measurement cell is filled with 1.0 mL of 1 M $LiClO_4$ solution in ethylene carbonate/dimethyl carbonate 1:1. For the determination of the K_{Cell} value, the Metrohm conductivity standard 100 µS/cm (6.2324.010) has been used.

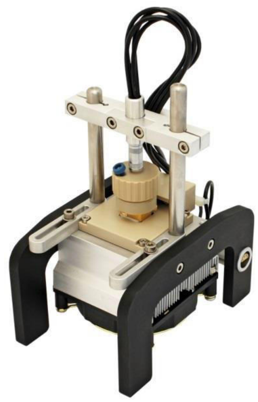

Figure 5. Overview of the cell holder and the electrochemical cell

RESULTS AND DISCUSSION

The impedance is sampled at open circuit potential within a frequency range from 250 kHz to 1 kHz applying an AC amplitude of 10 mV (RMS). Using the Fit and Simulation Command in NOVA, the recorded data are subjected to a fitting procedure using a serial *LRQ* equivalent circuit i, as shown in Figure 1. Impedance spectra are measured for temperatures ranging from 5 ° C to 60 ° C in steps of 5 ° C.

The measurement temperatures as well as the temperature stability values can also be specified. A message box allows the value of the cell constant K_{Cell} to be specified. In this application note, K_{Cell} is set to 15.6 cm^{-1}.

After inserting the K_{Cell} value, the EIS measurement of the sample within the chosen temperature range is carried out.

Once the measurements starts, NOVA shows the impedance Nyquist plot, the Bode plot of the impedance modulus *Z* and phase ϕ; the Bode plots of the admittance modulus *Y*, the plots of the time dependence of the AC-current and AC-voltage and the Lissajous plots, per frequency.

When the measurement is finished, the Arrhenius plot of the σ_{DC} conductivity is shown, Figure 6.

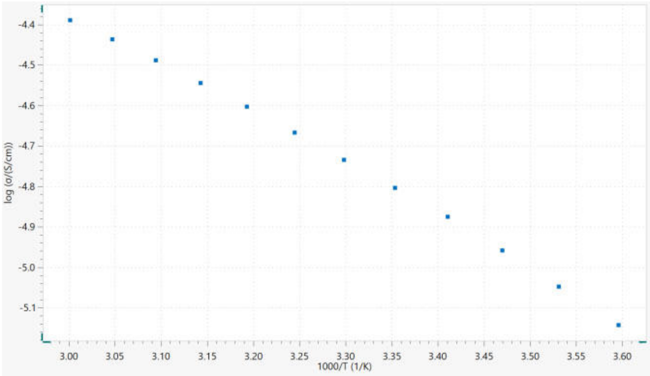

Figure 6. The Arrhenius plot of the conductivity.

According to **Figure 6**, the natural logarithm of the conductivity at 25 ° C (3.35 1000/K) is ≈ 4.8, resulting in a conductivity of 8.2 mS/cm, in accordance with literature data, 8.4 mS/cm[**1**].

CONCLUSIONS

The combination of the Autolab Microcell HC setup with the Metrohm Autolab potentiostat/galvanostat instruments fitted with the FRA32M module allows for an automatic determination of the temperature-dependent σ_{DC} values. This convenient combination offers the possibility to significantly reduce the time spent on performing measurements and analyzing the recorded data.

REFERENCES

1. Kang Xu, "Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries", Chemical Reviews, 2004, Vol. 104, No. 10.

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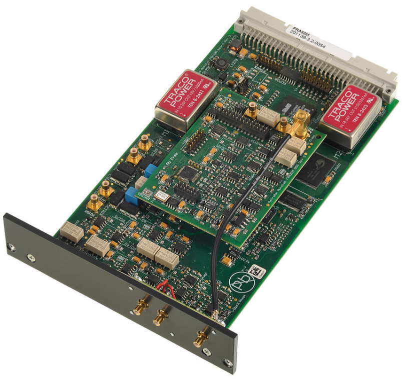
EXPERIMENTAL SETUP

Autolab PGSTAT204

PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。
PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。

Autolab PGSTAT302N

该恒电位仪/恒电流仪,具有 30 V 顺从电压,带宽为 1 MHz,可与我们的 FRA32M 模块联用,专门针对电化学阻抗谱而设计。
PGSTAT302N 是流行的 PGSTAT30 的后继款型。最大电流为 2 A,借助 BOOSTER20A 电流范围可扩展至 20 A,当电流范围为 10 nA 时电流分辨率为 30 fA。



FRA32M 提供了用于测量阻抗的工具,与 Autolab 联用可测量电化学阻抗。该模块允许在 10 μHz 至 32 MHz 的较宽频率范围中同时进行恒电位和恒电流阻抗测量(与 Autolab PGSTAT 联用极限为 1 MHz)。除了传统的 EIS 电化学阻抗谱之外,NOVA 软件还允许用户调节其它外部信号,诸如旋转圆盘电极的转速或光源频率,以测量电-流体或光调制阻抗谱。
FRA32M 模块带有功能强大的匹配和仿真软件,可分析阻抗数据。

Metrohm

NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

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- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

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