In-temperature ionic conductivity measurements with the Autolab Microcell HC setup

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 σ_{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).

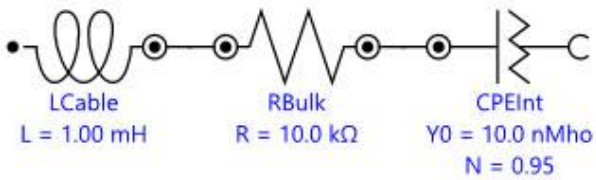

Figure 1. Equivalent circuit describing the interface between a good ion conductor and an inert electrode

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).

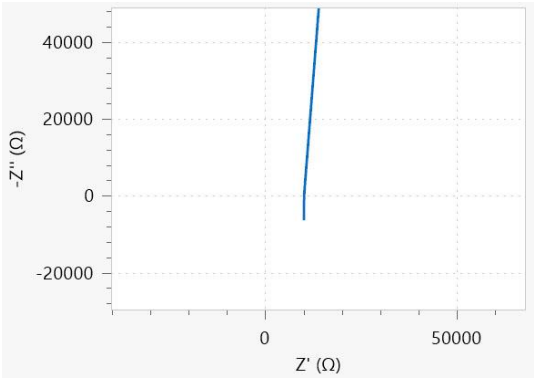

Figure 2. Nyquist plot corresponding to the equivalent circuit shown in Figure 1.

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:

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

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

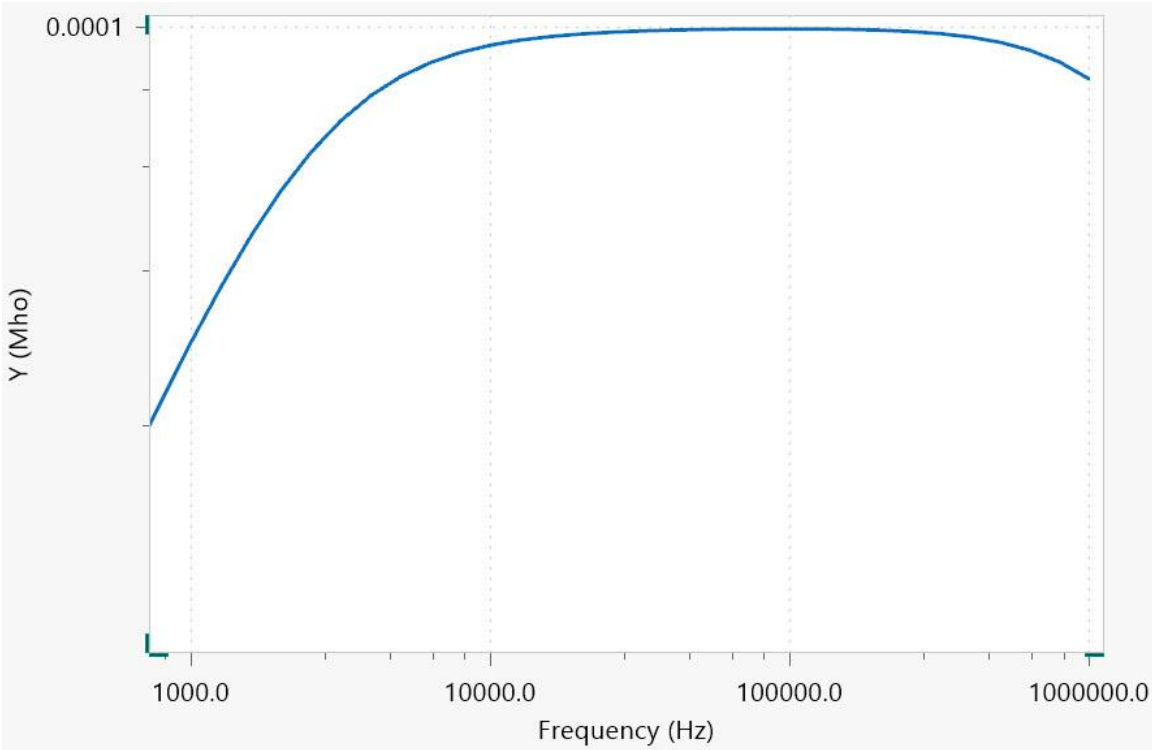

Figure 3. Bode plot of for the equivalent circuit shown in Figure 1

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:

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

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

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.

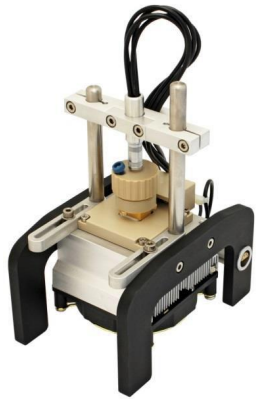

Figure 5. Overview of the cell holder and the electrochemical cell

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.

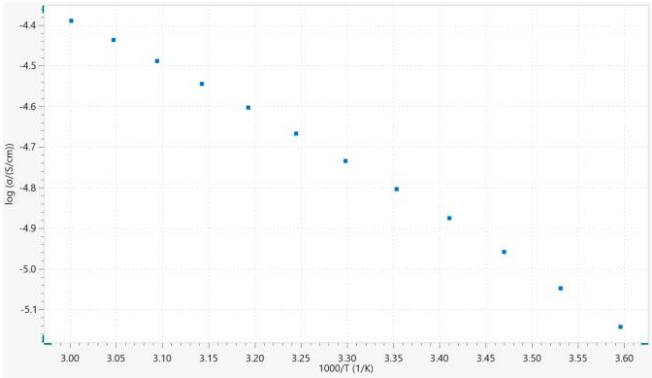

Figure 6. The Arrhenius plot of the conductivity.

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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Autolab PGSTAT204

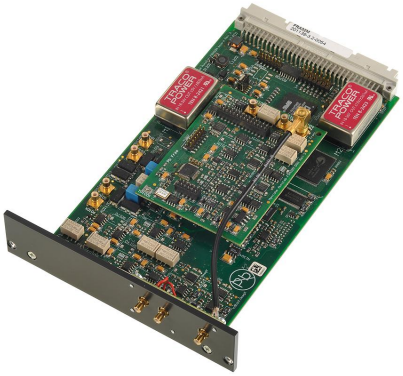
Le PGSTAT204 associe faible encombrement et conception modulaire. Cet appareil comprend un potentiostat/galvanostat de base avec une tension disponible de 20 V et une intensité maximum de 400 mA ou 10 A en association avec le BOOSTER10A. Le potentiostat peut évoluer à tout moment au moyen d'un module complémentaire, comme le module de spectroscopie d'impédance électrochimique (SIE) FRA32M.

Le PGSTAT204 est un appareil d'un prix abordable qui trouve toujours une place dans le laboratoire. Il dispose d'entrées et de sorties analogiques et numériques pour controler les accessoires Autolab et les appareils externes. Le PGSTAT204 comprend un intégrateur analogique intégré. Associé au logiciel performant NOVA, il peut etre utilisé pour la plupart des techniques d'électrochimie standard.

Autolab PGSTAT302N

Ce potentiostat/galvanostat haut de gamme pour courant élevé, avec une tension disponible de 30 V et une bande passante de 1 MHz, associé à notre module FRA32M, est spécialement concu pour la spectroscopie d'impédance électrochimique.

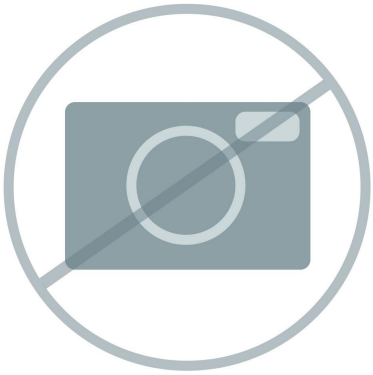
Le PGSTAT302N est le successeur du très populaire PGSTAT30. L'intensité maximale est de 2 A, la gamme d'intensité peut etre étendue à 20 A avec le BOOSTER20A, la résolution de l'intensité est de 30 fA pour une gamme d'intensité de 10 nA.



Module de spectroscopie d'impédance électrochimique

Le FRA32M fournit les moyens de réaliser des mesures d'impédance et d'impédance électrochimique en association avec l'Autolab. Ce module permet à la fois de réaliser des mesures d'impédance potentiostatiques et galvanostatiques sur une large gamme de fréquences allant de 10 µHz à 32 MHz (avec une limitation à 1 MHz en combinaison avec l'Autolab PGSTAT). Outre la SIE classique, le logiciel NOVA permet aussi aux utilisateurs de moduler d'autres signaux extérieurs tels que la vitesse de rotation d'une électrode à disque tournante ou la fréquence d'une source lumineuse en vue de réaliser une spectroscopie d'impédance électro-hydrodynamique ou photomodulée.

Le module FRA32M est fourni avec un logiciel puissant d'adaptation et de simulation pour l'analyse des données d'impédance.



Logiciel avancé pour la recherche électrochimique

NOVA est le progiciel concu pour le controle de tous les instruments Autolab avec interface USB.

Concu par des électrochimistes pour des électrochimistes, NOVA apporte plus de puissance et plus de flexibilité à votre potentiostat/galvanostat Autolab en intégrant plus de deux décennies d'expérience utilisateur et la toute dernière technologie logicielle .NET.

NOVA propose les fonctionnalités inédites suivantes :

- Un éditeur de procédures performant et flexible
- Une vue d'ensemble claire des données pertinentes en temps réel
- Des outils d'analyse de données et de tracés puissants
- Controle intégré des périphériques externes comme les instruments LQH Metrohm