Application Note AN-EC-010

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).

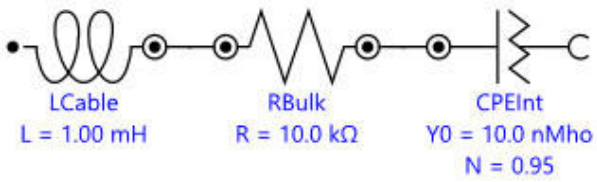


Figure 1. Equivalent circuit describing the interface between a good ion conductor and an inert electrode

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).

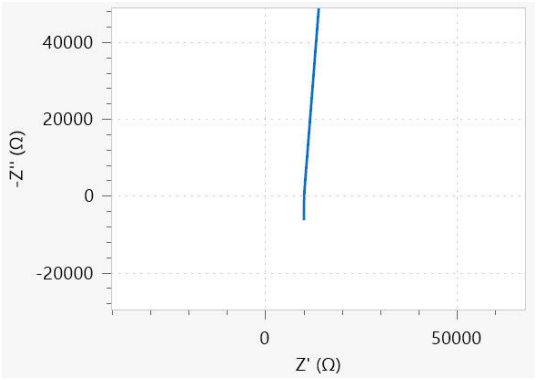


Figure 2. Nyquist plot corresponding to the equivalent circuit shown in Figure 1.

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.

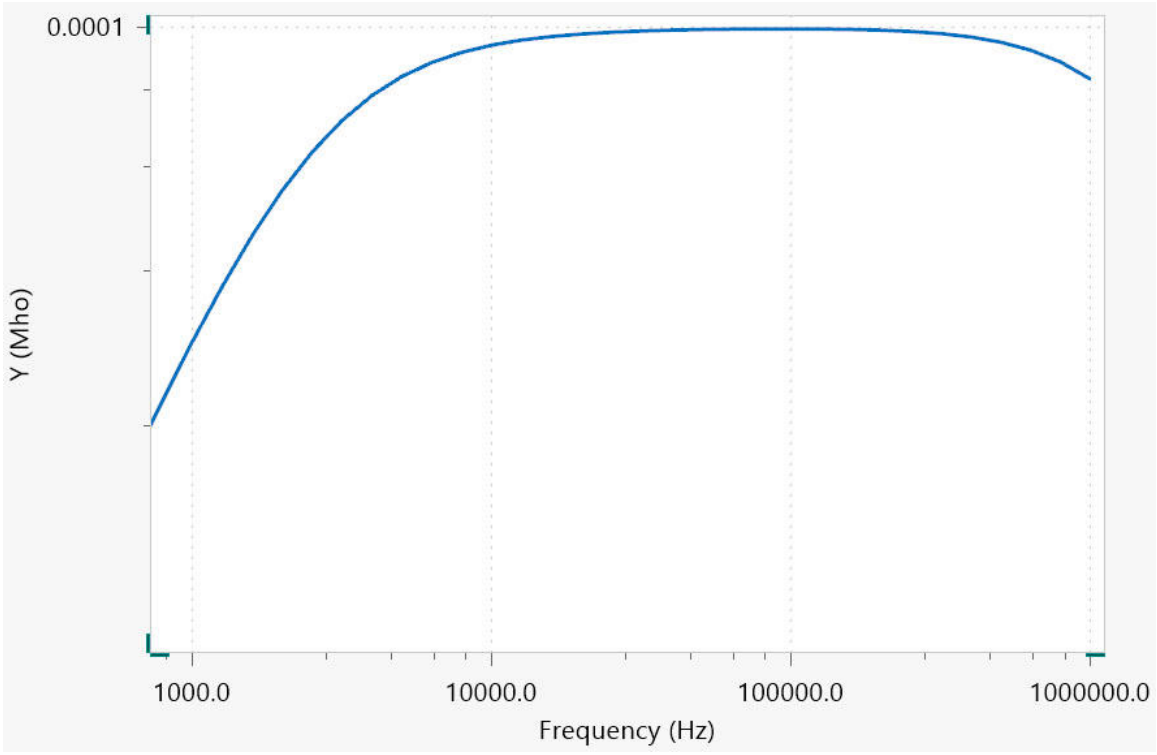


Figure 3. Bode plot of for the equivalent circuit shown in Figure 1

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:

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

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

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.

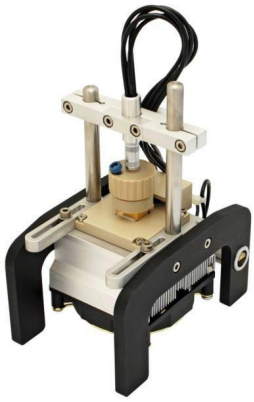


Figure 5. Overview of the cell holder and the electrochemical cell

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.

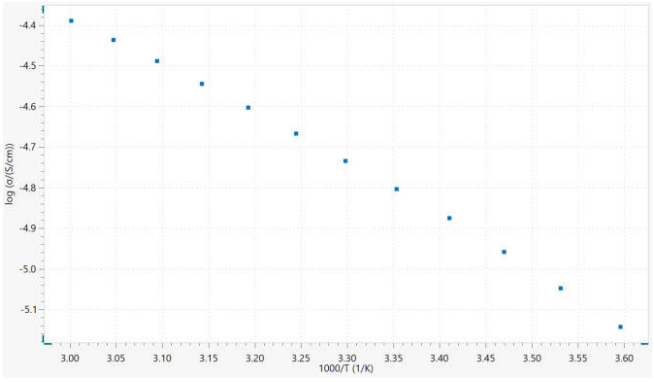


Figure 6. The Arrhenius plot of the conductivity.

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

The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

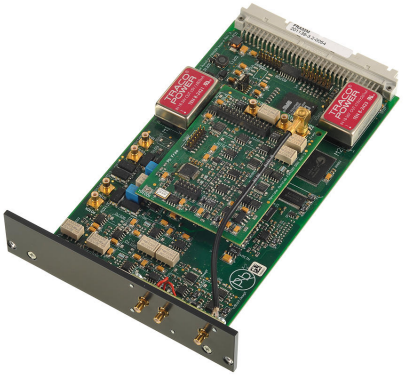
The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.



Autolab PGSTAT302N

This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.

The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.



Electrochemical impedance spectroscopy module

The FRA32M provides the means to perform impedance and electrochemical impedance measurements in combination with the Autolab. This module allows one to perform both potentiostatic and galvanostatic impedance measurements over a wide frequency range of 10 µHz to 32 MHz (limited to 1 MHz in combination with the Autolab PGSTAT). In addition to the classical EIS, the NOVA software also allows the users to modulate other outside signals such as rotation speed of a rotating disk electrode or the frequency of a light source to perform Electro-hydrodynamic or Photo-modulated impedance spectroscopy.

The FRA32M module comes with a powerful fit and simulation software for the analysis of impedance data.

Advanced software for electrochemical research

NOVA is the package designed to control all the Autolab instruments with USB interface.

Designed by electrochemists for electrochemists and integrating over two decades of user experience and the latest .NET software technology, NOVA brings more power and more flexibility to your Autolab potentiostat/galvanostat.

NOVA offers the following unique features:

- Powerful and flexible procedure editor
- Clear overview of relevant real-time data
- Powerful data analysis and plotting tools
- Integrated control for external devices like Metrohm Liquid Handling devices

Download the latest version of NOVA