

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

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

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

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

A plot of $\text{Log}(Y')$ versus $\text{Log}(\omega)$ for the equivalent circuit of Figure 1 is shown in Figure 3, where ω is the measurement frequency.

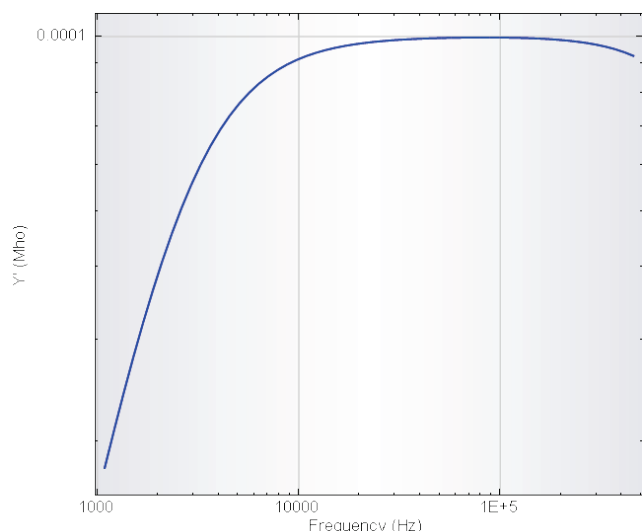


Figure 3 – Bode plot of the Y' for the equivalent circuit shown in Figure 1

At the high frequency limit, the $\text{Log}(Y')$ values decrease with increasing frequency. This is caused by the cable inductance. At slightly lower frequencies the curve is parallel to the $\text{Log}(\omega)$ axis. This part is governed by bulk ion transport and $\text{Log}(Y')$ is identical to σ_{DC}/K_{Cell} , where K_{Cell} is the cell constant which is accessible via an EIS measurement of an applicable conductivity standard.

At lower frequencies, the charging of the interfacial capacitance is observable which causes a decrease of the $\text{Log}(Y')$ values.

After fitting the recorded data to the equivalent circuit depicted 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} :

$$\sigma_{DC} = \frac{1}{R_{Bulk}} K_{Cell}$$

However, there exist additional experimental issues which have to be considered.

1. σ_{DC} shows a significant temperature dependence which can often be described by an empirical Vogel-Fulcher-Tamman approach, in which A , B and T_g are fitting parameters:

$$\sigma_{DC} = A \cdot \exp\left(-\frac{B}{T - T_g}\right)$$

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.

2. Most modern electrolytes are volatile. Leak-tight sample compartments, which allow for measurements within a broad temperature range, are needed.

3. Although the EIS experiments are fast since only the high frequency impedance has to be recorded, the data analysis might take a lot of time. Hence, an online analysis of the measured EIS data is highly welcome.

Experimental setup

The combination of the measurement setup *Microcell HC* (made by *RHD instruments*) with a Metrohm Autolab potentiostat/galvanostat instrument, as shown in Figure 4, provides a temperature-controlled electrochemical measurement system for volatile samples.

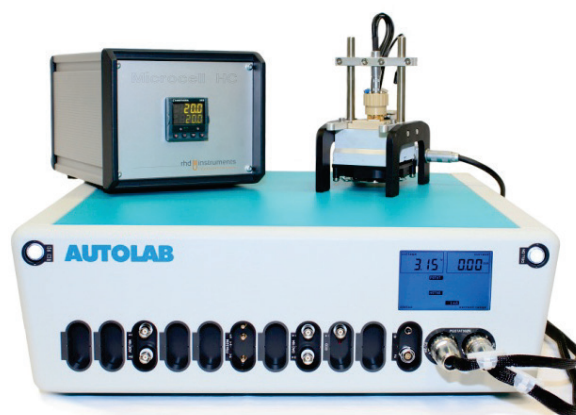


Figure 4 – The Microcell HC combined with the PGSTAT302N/FRA32M

The cell is fitted with a glass-sealed platinum wire working electrode and a platinum crucible counter electrode. These electrodes are connected to the Autolab. Figure 5 shows an overview of the electrochemical cell and the cell holder.

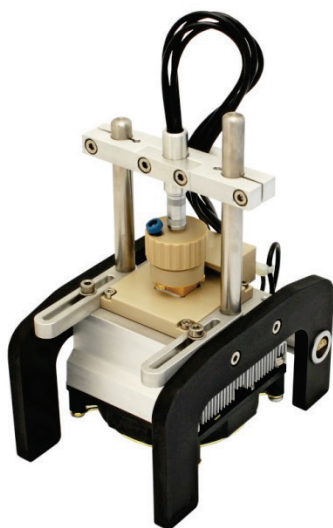


Figure 5 – Overview of the cell holder and the electrochemical cell

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

A task-specific dynamic link library (DLL) called *hcDLL*, which has been created for the NOVA software, allows for temperature controlled EIS measurements with automated data evaluation and presentation.

Through the dedicated interface, the RHD instruments offers the following unique advantages:

- Possibility to define a temperature range (in this application note: from 0°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 1.0 mol/L LiPF₆ solution in ethylene carbonate/dimethyl carbonate 1:1). For determination of the K_{Cell} value, an aqueous KCl standard (Metrohm) has been used.

Experimental measurements

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). The recorded data is subjected to an online fitting procedure using a serial *LRQ* equivalent circuit, as shown in Figure 1. Impedance spectra are measured for temperatures ranging from 0 °C to 60 °C in steps of 5 °C.

The measurement sequence contains three consecutive steps:

- Determination of K_{Cell}
- Verification of K_{Cell} and equivalent circuit
- Sample measurement

These steps are included in the *hcDLL ACM* (for *Automated Conductivity Measurement*). Starting the NOVA procedure, the DLL is initialised and the communication with the temperature controller is enabled. The measurement conditions and parameters can be specified, as shown in Figure 6.

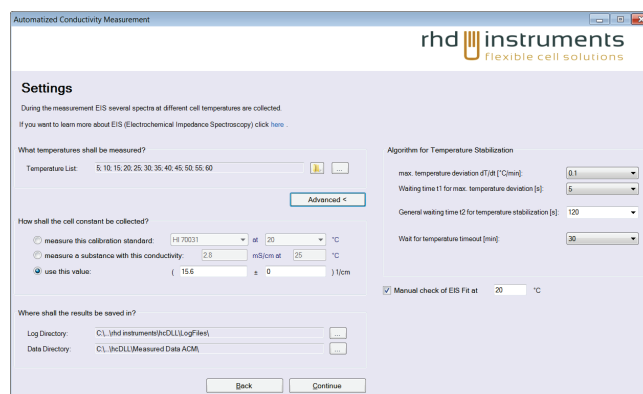


Figure 6 – The dialog window used to specify the measurement settings

The measurement temperatures as well as the temperature stability values can also be specified. The dialog window allows the value of K_{Cell} to be specified, if this value is already known, or to specify with which standard this value should be measured. In the measurements shown in this application note, the K_{Cell} was set to 15.6 cm⁻¹.

Once the measurements starts for the verification of K_{Cell} , NOVA will provide the Bode plots of Y' , the phase ϕ and $|Z|$, the Nyquist plot and a plot of the time dependence of the AC-current and AC-voltage or a Lissajous-plot.

When the measurement is finished, a window presents the Nyquist plot, the Bode plot and the $\log(Y')$ versus $\log(\omega)$ plot as well as the obtained σ_{DC} and offers the possibility to compare this value with values taken from literature whereby the underlying data base can easily be extended (see Figure 7).

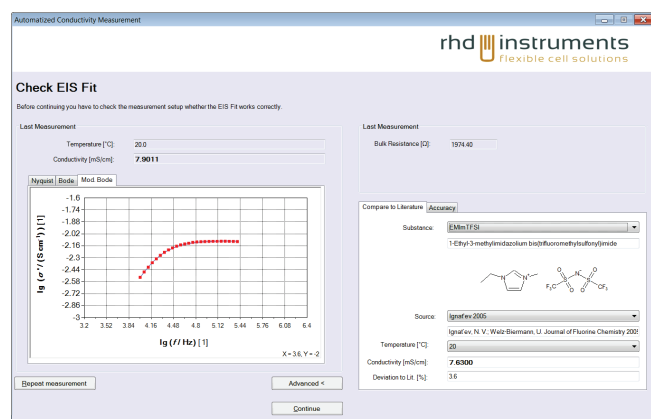


Figure 7 – Results of the verification of the K_{Cell} and the validity of the chosen equivalent circuit

After verifying the validity of K_{Cell} and the chosen equivalent circuit, the EIS measurement of the sample within the chosen temperature range is carried out. During the measurement, the same plots are shown in NOVA.

An additional window, generated by *hcDLL*, shows the temperature dependence in an Arrhenius-plot of σ_{DC} , which is updated during the measurement. This additional plot is embedded in the NOVA window as shown in Figure 8.

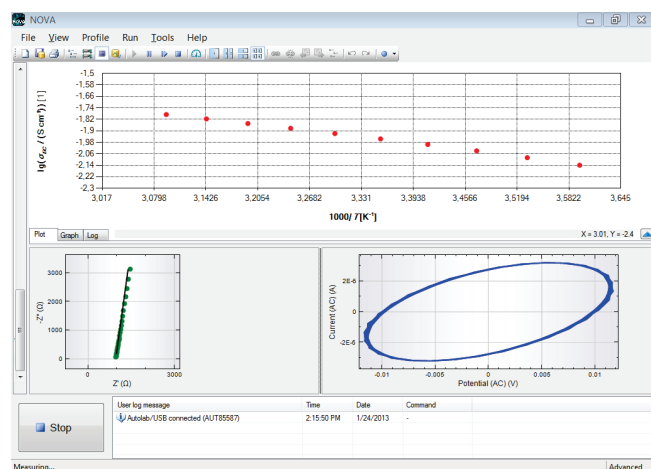


Figure 8 – Example of the Arrhenius-plot of σ_{DC}

During the measurement, log-files as well as result files are created in the ASCII-format.

Conclusions

The combination of the *Microcell HC* setup (from RHD instruments) with a Metrohm Autolab potentiostat/galvanostat fitted with the FRA32M module allows for an automatic determination of temperature dependent σ_{DC} values. This convenient combination offers the possibility to significantly reduce the time consumed by carrying out measurements and analysing the recorded data. Furthermore, user related errors can be avoided by providing an assistant leading through the measurement procedure.

More information on RHD products can be found on the RHD website (<http://www.rhd-instruments.de/>).

Date

1 August 2013