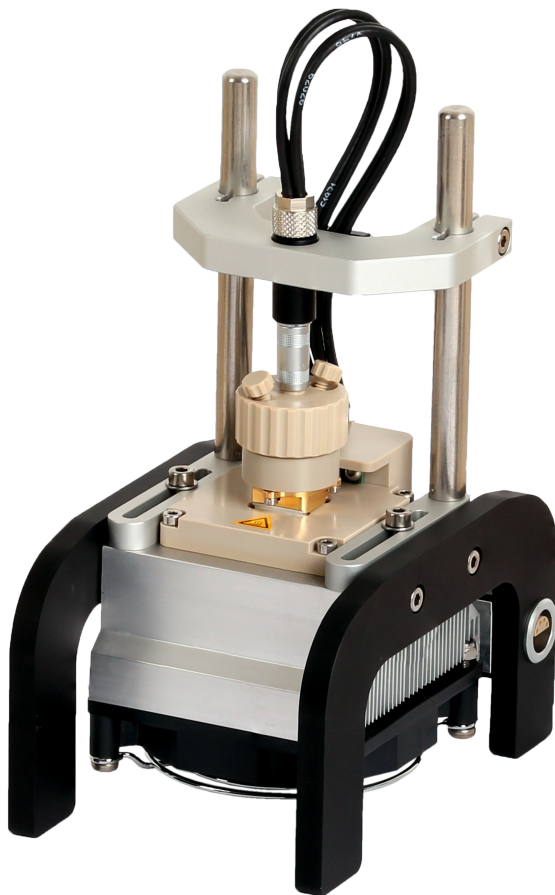


Application note

Determination of
the cell constant for
conductivity measurements



Introduction

One important component of every electrochemical cell is the electrolyte solution. A measure for the ability of an electrolyte solution to conduct electrical current is its conductivity $\sigma_{\text{electrolyte}}$. The conductivity can be measured by alternating current (ac) or direct current (dc) techniques. In case of ac measurements, electrochemical impedance spectroscopy is often applied [1].

The electrochemical test cells (“conductivity cells”) that are used for these measurements have to be calibrated initially using a calibration standard which is typically an aqueous potassium chloride solution [2]. The result of that calibration is the so-called cell constant K_{cell} which has the unit [1/cm]. The cell constant can be used to calculate the conductivity from bulk resistance values determined for other electrolyte solutions of unknown conductivity.

In this application note, we demonstrate how to determine K_{cell} for the test cell “TSC 1600 closed GC” which has been developed by rhd instruments GmbH & Co. KG for the determination of the conductivity of electrolyte solutions that are sensitive towards humidity and oxygen like lithium ion battery electrolytes.

Experimental

a) Chemicals

As calibration standard, the commercially available standard HI 70030P from Hanna Instruments based on an aqueous potassium chloride solution was used. The conductivity of this standard is 11.670 mS/cm at 20 °C which is of the same of magnitude like typical lithium ion battery electrolytes.

b) Sample preparation & measuring setup

For the electrochemical measurements, a [TSC 1600 closed GC test cell](#), see **Figure 1**, in combination with a [Microcell HC setup](#) (rhd instruments GmbH & Co. KG) was used.

In the Microcell HC setup, the temperature is adjusted via a Peltier element. The accessible temperature range is -40 °C to +100 °C. For measuring the temperature, a Pt100 temperature sensor is embedded in the socket of the TSC 1600 closed GC, at a position very close to the electrolyte solution. The accuracy of the temperature is 0.1 °C with regard to the sensor position inside of the base unit.

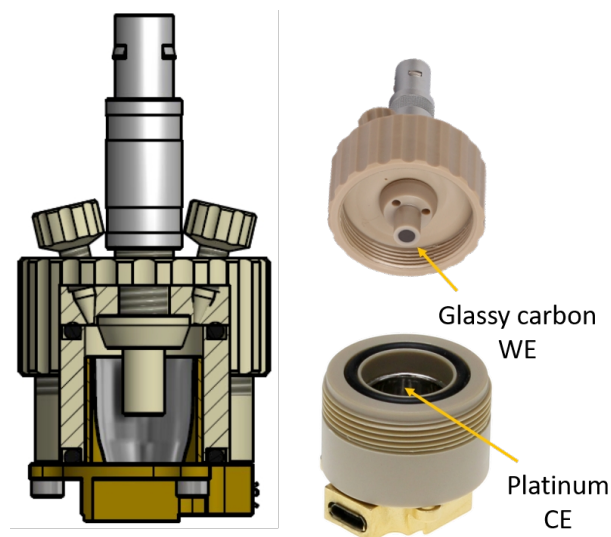


Figure 1: Schematic drawing of the measuring cell TSC 1600 closed GC. The glassy carbon electrode tip is part of the cap and used as working electrode in this experiment. The platinum crucible being part of the base unit serves as sample container and as counter electrode. Not shown here is the Pt100 temperature sensor which is embedded into the socket and enables the monitoring of the electrolyte solution temperature.

For the impedance measurements, a Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used. The communication with the temperature controller is integrated in the NOVA 2.1.5 software enabling automated measuring routines.

The recorded impedance data were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS 3 (rhd instruments GmbH & Co. KG).

c) Measurement parameters

The impedance measurements were performed at a frequency range of 1 MHz to 100 Hz with an amplitude of $V_{AC,rms} = 10.0$ mV.

After reaching the temperature set point of 20.0 °C, a waiting time of 1800 s was chosen to ensure for complete thermal equilibrium.

Step	Action to be performed
1	Clean the test cell and polish the electrodes.
2	Fill the conductivity standard solution HI 70030P into the test cell. A sample volume of 0.9 ml is used.
3	Connect the measuring device (2-electrode configuration with glassy carbon as working electrode and platinum as counter electrode).
4	Set the temperature to 20.0 °C and waiting for 1800 s.
5	Perform an impedance spectroscopy measurement.

Results

The resulting impedance spectrum is shown in **Figure 2**.

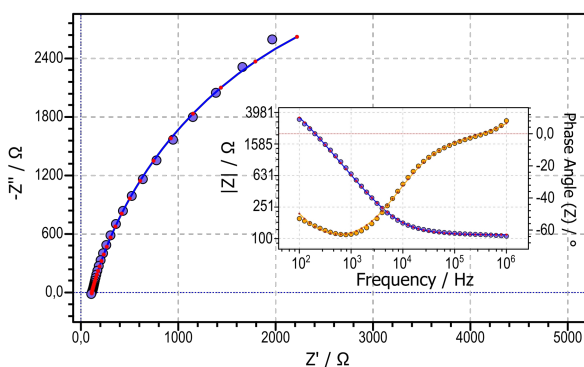


Figure 2: Impedance spectrum of the aqueous conductivity standard HI 70030P (Hanna Instruments), measured at 20 °C using the test cell TSC 1600 closed GC. The points are the recorded data, the line is the resulting fit to the equivalent circuit shown in **Figure 3**.

At high frequencies, the impedance behaviour is dominated by inductive effects caused by the connection cables. The intersection at the Z' -axis is close to the bulk resistance value for bulk ion transport. In absence of the inductive behaviour at high frequencies, they would be identical. The increase at lower frequencies is then caused by electrode polarization. Further-

more, contributions by a (partial) charge transfer reaction become visible at the lowest frequencies as the beginning of a large semi-circle in the Nyquist plot. This might either be caused by the interaction between the chloride anions and the carbon and platinum atoms by means of adsorption or the decomposition of impurities.

The spectrum was fitted with the equivalent circuit shown in **Figure 3**. The inductance L_{cable} takes the high frequency contributions by the connection cables into account, the resistor R_{ion} represents the ion migration in calibration standard's bulk volume, and the constant phase element CPE_{pol} describes the electrode polarization at low frequencies while R_{int} stands for contributions by charge transfer and ion adsorption.

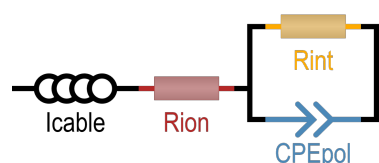


Figure 3: Equivalent circuit for fitting the impedance spectra.

The resulting value for R_{ion} is given in the following table. The fit error of R_{ion} was 0,5%.

$T / ^\circ\text{C}$	R_{ion} / Ω
20	111.09

The cell constant K_{cell} can be calculated by multiplying the determined value for the bulk resistance R_{ion} for the calibration standard at 20 °C with the known conductivity of this calibration standard at the same temperature:

$$K_{cell} = R_{ion} \cdot \sigma_{ion}$$

$$K_{cell} = 111.09 \, \Omega \cdot 11.67 \, \frac{\text{mS}}{\text{cm}} = 1.30 \, \frac{1}{\text{cm}}$$

A cell constant of $1.3 \frac{1}{\text{cm}}$ has been determined for the used test cell TSC 1600 closed GC. The cell constant can now be used for measurements of electrolyte solutions of unknown con-

ductivity to calculate conductivity values from measured bulk resistance values [1].

Some practical hints:

- Before starting the measurement, all cell parts should be thoroughly cleaned and the electrodes should be polished.
- For quality management purpose, the cell constant should be checked from time to time.
- Although we determined the cell constant in this application note only once, it is recommended to perform at least a three-fold measurement.
- Traceable, commercial cell constants are based on aqueous solutions of potassium chloride. However, once the conductivity of another electrolyte solution has been determined, this electrolyte solution can also be used as a calibration standard.
- Since the test cell parts expand or shrink with the sample temperature, the cell constant might show a slight dependence on the temperature.

Summary

In this application note, we demonstrated how to determine the cell constant for a conductivity test cell. We used a TSC 1600 closed GC test cell for this purpose and a commercial calibration standard based on an aqueous potassium chloride solution.

Acknowledgement

The results presented here are part of a sub-project related to the project LiMES funded by the Federal Ministry for Economic Affairs and Climate Action as part of the 7. Energieforschungsprogramm which is highly appreciated.

LiMES is a joint research project with the two partners rhd instruments GmbH & Co. KG and Karlsruhe Institute of Technology (KIT). We thank our project partners Dr. Andreas Hofmann and Ingo Reuter from KIT for the fruitful

collaboration as well as for the valuable and inspiring input.

Supported by:



on the basis of a decision
by the German Bundestag

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