Autolab Application Note BAT06

Determination of the MacMullin number

Keywords

Battery, separator, MacMullin number, conductivity, electrolyte, Metrohm Autolab, Autolab RHD Microcell HC, EIS, electrochemical impedance spectroscopy.

Introduction

The main components of a battery are the positive and negative electrodes, together with the electrolyte. While both ionic and electronic conductivities take place at the electrodes, the electrolyte provides only the ionic conductivity.

The most common electrolytes are in the liquid state. Therefore, they cannot be employed without a solid supporting material, which provides physical separation between the electrodes, necessary to avoid short circuits.

A typical separator is composed of a porous sheet of a polymeric material. Before assembling the battery, the separator is soaked with the electrolyte. The polymeric structure provides the physical separation between the electrodes, while the pores allow the electrolyte to be in contact with both electrodes, providing the desired ionic conductivity.

However, the separator limits the performances of the electrolyte. The resistivity of the electrolyte inside the pores is higher than the resistivity of the free electrolyte, because of the mass transfer limitation inside the pores. Battery separators are therefore designed to allow a sufficient ion conductivity, i.e., a relatively low resistivity.

A valuable way to compare battery separators is to monitor the difference between the resistivity of the separator soaked in the electrolyte, ρ_{sep}, and the resistivity of the free electrolyte ρ_{el}. The ratio of these two values is the MacMullin number N_M, shown in Equation 1

$$N_M = \frac{\rho_{sep}}{\rho_{el}} \qquad 1$$

Or, in terms of conductivity,

$$N_M = \frac{\sigma_{el}}{\sigma_{sep}} \qquad 2$$

(Conductivity being the inverse of resistivity).

In order to calculate the MacMullin number, the resistance of the electrolyte R_{el} and the resistance of the soaked separator R_{sep} are determined by electrochemical impedance spectroscopy (EIS). Then, the resistivity values of both the free electrolyte ρ_{el} and the soaked separator ρ_{sep} are calculated multiplying the resistance values by the geometric factors of the cells.

In the following section, a description of the setup used to measure the conductivity values is described.

Experimental Setup

In order to determine the resistivity values for the MacMullin number, EIS measurements are carried out, together with the fitting of data. In this way, the resistance values for the free electrolyte and for the soaked separator are measured, multiplied by the geometric factor of the cells, and the desired resistivity values are calculated.

In both cases, a Metrohm-Autolab PGSTAT204 is used (Figure 1), equipped with a FRA32M module, necessary for the EIS analysis.

Figure 1 – The Metrohm-Autolab PGSTAT204, with the FRA32M module.

The Autolab RHD Microcell HC setup, shown in Figure 2 is used, to control the temperature. The Autolab RHD Microcell HC setup is composed of a cell holder, equipped with a Peltier element, and a temperature controller programmable through the NOVA software.

Figure 2 - The Autolab RHD Microcell HC setup, composed of a cell stand (left-hand side), and the temperature controller (right-hand side).

The cell holder can host a variety of cells, for different applications. For measuring the resistivity of the free electrolyte, a TSC1600 closed cell is chosen, Figure 3-A, equipped with a platinum container of 1.6 mL of volume. For measuring the resistivity of the soaked separator, a TSC SW closed cell is preferred, Figure 3-B, with a two plane parallel flat disk electrodes.

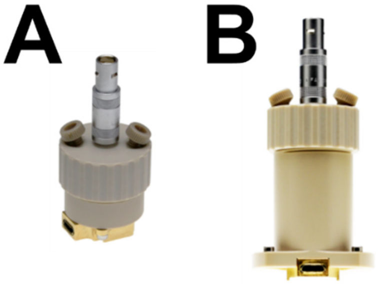

Figure 3 - the TSC1600 closed cell (A), and the TSC SW closed cell (B).

As electrolyte, a Metrohm 3M KCl solution (6.2308.020) is used.

Regarding the free electrolyte measurement, the cell is filled up with approximately 1.6 mL of electrolyte and closed.

As separator, a Whatman qualitative filter paper, grade 1, CAS 1001090, with 180 μm of thickness and 11 μm of pore size is chosen. A disk of the filter paper with the same diameter (11.7 mm) as the disk electrodes of the TSC SW closed cell is cut, and soaked with the above-mentioned electrolyte.

The geometric factors

The determination of the geometric factor of the cells is a preliminary issue to tackle.

The geometric factor of the TSC SW closed cell, K_{SW}, is calculated merely by the dimension of the cell, dividing the distance between the plates (same as the thickness of the separator), by the area of the sample. This results in a geometric factor of $K_{SW} = 1.68\mathrm{E}-4$ cm^{-1}.

On the other hand, it is not trivial to calculate the geometric factor K_{1600} of the TSC1600 closed cell.

A useful approach is to measure the resistance R_{st} of a conductivity standard, with tabulated conductivity values σ_{st}, and then calculate the geometric factor K_{1600}, with the aid of Equation 3.

$$K_{1600} = R_{st} \cdot \sigma_{st} \qquad 3$$

An EIS measurement is performed, and the fit of the data gives the desired resistance of the standards R_{st}.

For the above measurement, the Metrohm conductivity standard (6.2324.010) is employed, with a conductivity of $\sigma_{st} = 100$ μS cm^{-1}, at 25 °C.

The TSC 1600 closed is filled up with the conductivity standard and, once the cell is closed and connected to the holder, the temperature is set at 25 °C. Afterwards, an EIS measurement with a two-electrode configuration is performed. A data fitting with a $[R_{st}Q_{dl}]$ equivalent circuit shown a value of R_{st} = 661 Ω. From Equation 3, K_{1600} = 15.13 cm^{-1} is calculated.

The procedure

As previously mentioned, an EIS measurement at open circuit potential (OCP) with a two-electrode configuration is used. In both cases of free electrolyte and soaked separator, the measurements begin after a temperature of 25 °C is reached. Then, frequencies from 1 kHz to 10 Hz are applied, with an amplitude of 10 mV, at a rate of 10 frequencies per decade.

After each EIS measurement, a fit of the data is performed, using an $[RQ_{dl}]$ equivalent circuit, where $R = R_{el}$, the resistance of the bare electrolyte, and $R = R_{sep}$ the resistance of the soaked separator, and Q_{dl} is the constant-phase element modeling the double layer.

The value of interest, in both cases, is the resistance R. This, divided by the geometric factor K (cm^{-1}) of the cell, gives the desired resistivity ρ_{el} and ρ_{sep}, as shown in Equation 4. K_{1600} and K_{SW} are the geometric factors for the TSC 1600 closed and the TSC SW closed cells, respectively.

$$\begin{aligned}\rho_{el}\,(\Omega\cdot cm) &= \frac{R_{el}}{K_{1600}}\\ \rho_{sep}(\Omega\cdot cm) &= \frac{R_{sep}}{K_{SW}}\end{aligned}\tag{4}$$

Results and Discussion

In Figure 4 and Figure 5, the Nyquist plots of the free electrolyte and soaked separator, are shown respectively. In both Figures, the dots are referring to the data points, while the line shows the fitted results.

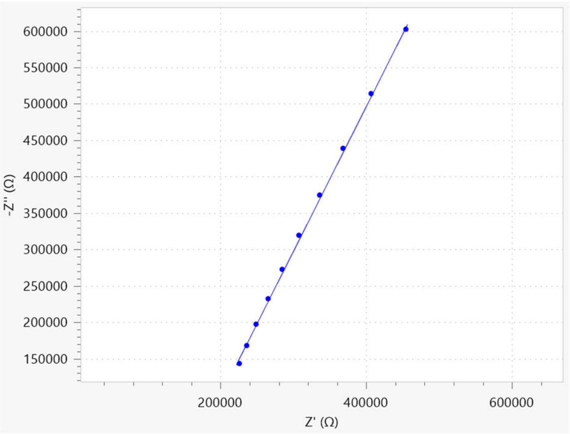

Figure 4 - Nyquist plot of the free electrolyte solution. The dots are referring to the data points, the solid line is the fitted result.

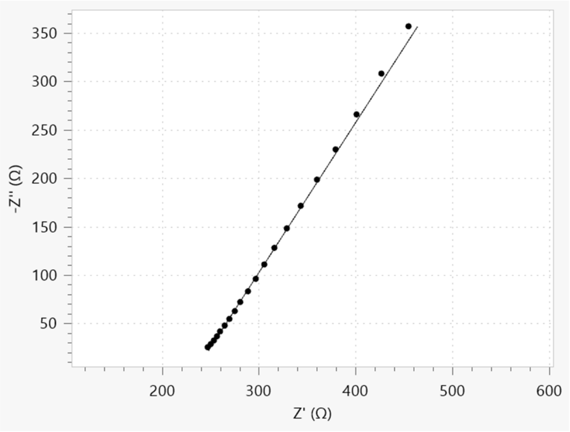

Figure 5 - Nyquist plot of the soaked separator. The dots are referring to the data points, while the solid line is the fitted result.

From the fitted results, the resistance values are extracted; R_{el} = 139 kΩ for the free electrolyte and R_{sep} = 233.35 Ω for the soaked separator. Using Equation 4, the resistivity values are calculated and listed in Table 1, together with the cell constants and the conductivity values.

Table 1 - Resistance R, resistivity ρ and conductivity σ values for the free electrolyte and the soaked separator. Also the respective cell constants K are listed.

	R (Ω)	K (cm^{-1})	ρ (Ω·cm)	σ (S·cm^{-1})
Free electrolyte (TSC 1600 closed)	1.39E5	15.13	9.92E3	1.01E-4
Soaked separator (TSC SW closed)	233.35	1.68E-4	1.39E6	7.18E-7

From the values of the resistivity and from Equation 1, the MacMullin number is calculated, resulting in $N_M = 140$. This value can be interpreted as following: the resistivity of the electrolyte coupled with such a separator is 140 times higher than the resistivity of the free electrolyte. Alternatively, the separator limits the conductivity of the free electrolyte by a factor of 140.

Conclusions

The MacMullin number is a parameter used to determine the quality of a separator, in terms of ionic conductivity, when soaked with an electrolyte. The MacMullin number can be calculated, using the results of data fitting of two EIS experiments and the geometric factors of the measurement cells. In this application note, a commercial electrolyte is employed, together with a porous filter, used as a separator. The resulting MacMullin number shows that the resistivity of an electrolyte wetting a separator is much higher than the resistivity of the free electrolyte.

Date

04 January 2017