Application Note AN-BAT-006

MacMullin数的测定

叠加方法

锂离子电池的一个重要部件是隔膜,用于物理分离正负电极。通常隔膜由聚合物材料制成。
为了测量隔膜的性能,引入了MacMullin数。MacMullin数为纯电解质的离子电导率与有隔膜电解质的离子电导率的比值。

本应用报告中,MacMullin数是通过叠加方法计算的。该方法包括对具有不同堆叠厚度的样品进行电化学阻抗谱测量,通过增加电池内隔膜的数量来实现。然后根据数据拟合计算离子电阻,并绘制出与电池中隔膜数量的关系图,斜率给出了MacMullin数。

INTRODUCTION

One important component of lithium ion batteries is the separator foil – a thin, electronically insulating, porous membrane that prevents the electrodes from being in direct contact with each other while being permeable to ionic current. To maintain a good lithium ion battery performance, the resistance of a separator foil filled with electrolyte should be low. Consequently, information about the effective ion conductivity of these systems is an important parameter for the performance of a separator material.

Usually, the focus is not on the effective ionic conductivity, but on another quantity: the so-called MacMullin number N_M [1]. The MacMullin number is the ratio of the ionic conductivity of the pure electrolyte $\sigma_{electrolyte}$ and ionic conductivity of the separator foil filled with electrolyte $\sigma_{separator}$ (Equation 1).

$$N_M = \frac{\sigma_{electrolyte}}{\sigma_{separator}} \qquad 1$$

Therefore, the MacMullin number is a quantity that describes the decrease of the effective conductivity by the presence of a separator foil. For lithium ion battery separators, often a value between 4 and 20 is found [1–3]. Theoretically, the MacMullin number is linked to the separator foil's porosity ε and tortuosity τ [2, 3].

EXPERIMENTAL

Chemicals

As electrolyte, a 1 mol/L $LiPF_6$ (lithium hexafluorophosphate) solution in a 1:1 ratio in volume mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate, purchased from Sigma-Aldrich / Merck KGaA) was used without any further purification. After receiving, the electrolyte was stored and handled inside of an argon-filled glove box. As battery separator material, a tri-layer separator based on polyethylene/polypropylene with a thickness of 21.5 µm was used.

Sample preparation and measuring setup

Circular specimens with a diameter of 12 mm were punched out from the separator foil. To ensure an optimal wetting, the specimens were stored for at least 24 hours in the electrolyte solution.

For the electrochemical measurements, a TSC battery standard cell (**Figure 1**) in combination with a Microcell HC setup was used.

As current collectors, two planar stainless steel disc electrodes (diameter 8 mm) press-fitted into a PEEK sleeve were used. The cell constant is the ratio of the electrode area A (cm^2) and its thickness l (cm), and it is measured in cm^{-1}. To calculate the cell constant, the area of the stainless steel electrodes and the separator thickness were measured, resulting in a cell constant value of 0.0043 cm^{-1}.

The cell constant, together with the resistance related to the bulk ion transport inside of the porous separator network R_{ion} (Ω), is used in the calculation of the conductivity σ (S cm^{-1}, **Equation 2**).

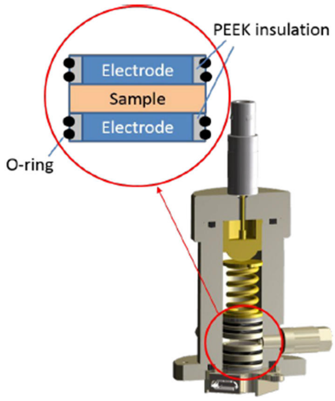

Figure 1. Schematic drawing of the measuring cell TSC battery standard. The separator foils filled with electrolyte were placed between the upper and lower electrode.

$$\sigma = \frac{1}{R_{ion}} \cdot \frac{l}{A} \qquad (2)$$

The contact pressure applied onto the electrolytesoaked separator foil stack inside of the TSC battery cell was adjusted to approximately 100 kPa using a gold-plated spring with a spring constant of 2.43 N mm^{-1}. At this contact pressure, no significant compression of the separator foil was found.

In the Microcell HC setup, the temperature is adjusted via a Peltier element, with an accessible temperature range of -40 ° C to +100 ° C. To accurately measure the temperature, a Pt100 temperature sensor is embedded in the base unit of the TSC battery cell, at a position very close to the sample. The accuracy of the temperature measurement is 0.1 ° C with respect to the sensor position inside of the base unit. For the determination of the MacMullin number, the temperature was adjusted to 20.0 ° C.

Because the TSC battery measuring cell is completely airtight, the experiments took place on the Microcell system outside of the glove box. For the impedance measurements, a Metrohm Autolab PGSTAT204 equipped with a FRA32M module was used. The communication with the temperature controller is integrated in the NOVA software enabling automated measuring routines.

Measurement parameters

The impedance measurements were performed at a frequency range of 1 MHz to 100 Hz with an amplitude of 10 mV.

Impedance measurements were taken on samples with different stack thickness, achieved by increasing the number of separators inside the cell.

After reaching the temperature set point of 20.0 ° C, a waiting time of 300 s was chosen to ensure for complete thermal equilibrium.

Table 1. Steps and relative actions per step.

Step	Action to be performed
1	Transferring the cell into the glove box and loading the cell with one specimen of the electrolyte-filled separator foil.
2	Taking the prepared cell out of the glove box and connecting it to the Microcell HC cell stand.
3	Connecting the measuring device (2-electrode configuration).
4	Setting the temperature to 20.0 ° C and waiting for 300 s.
5	Performing an impedance spectroscopy measurement.
6	After finishing step 5, repeating steps 1–5 by adding further specimens of the electrolyte-filled separator foil (one per loop) until a stack of five specimens is created.

RESULTS

The resulting impedance spectra for different stack thicknesses are shown in **Figure 2**.

At high frequencies, the impedance behavior 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 inside of the porous separator network. In absence of the inductive behavior at high frequencies, they would be identical. The increase at lower frequencies is then caused by electrode polarization.

As expected, increasing the stack thickness by adding further specimens of the electrolyte–soaked separator foil leads to a shift to higher values for the intersection point due to the higher bulk resistance value.

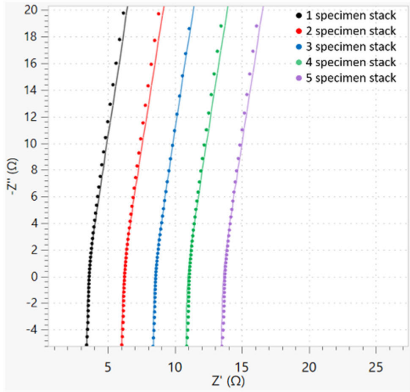

Figure 2. Impedance spectra of the soaked separator foils for different stack thicknesses. For a better visibility of the shift along the Z'-axis, the spectra were cut at 3 kHz. The points are the meas ured values and the lines represent the fit.

The spectra were fitted with the equivalent circuit shown in **Figure 3**.

The inductance l_{cable} takes into account the high frequency contributions by the electrical cables and connectors, the resistor R_{ion} represents the ion migration in the porous separator network, and the constant phase element CPE_{pol} describes the electrode polarization at low frequencies.

The resulting stack thickness-dependent values for R_{ion} are given in **Table 2**. The fit error of R_{ion} was lower than 0.4% in all cases.

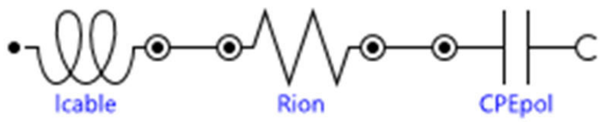

Figure 3. Equivalent circuit for fitting the impedance spectra.

Table 2. Ion migration resistance per sample number.

$N_{specimen}$	R_{ion}/Ω
1	3.38
2	5.98
3	8.34
4	10.78
5	13.43

A plot of these values shows a linear relationship, where the slope gives a value of 2.49 Ω for the ionic resistance change per added specimen ΔR_{ion} / $\Delta N_{specimen}$ (**Figure 4**).

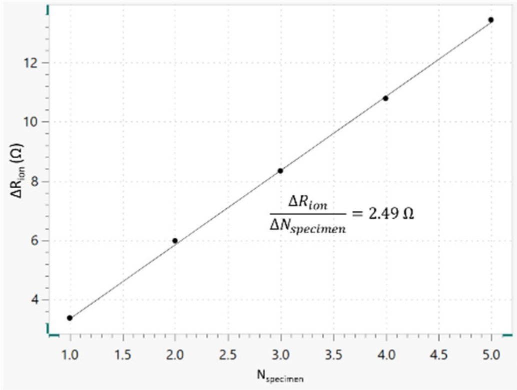

Figure 4. Plot of total ionic resistance value Rion in dependence of the number of separator specimens Nspecimen.

Taking into account the separator thickness d, the active area A of the stainless steel electrode, and the resistance per added specimen ΔR_{ion} / $\Delta N_{specimen}$, the corresponding ionic conductivity of the electrolyte-soaked separator $\sigma_{separator}$ can be calculated as shown in **Equation 3**.

$$\sigma_{separator} = \frac{1}{\Delta R_{ion}/\Delta N_{specimen}} \cdot \frac{d}{a} \qquad 3$$

Here, a value of $\sigma_{separator}$ = 1.7 mS cm^{-1} was measured at 20 ° C. The conductivity of the pure electrolyte solution at 20.0 ° C was determined to be $\sigma_{electrolyte}$ = 9.9 mS cm^{-1}.
Therefore, the MacMullin number was calculated to be N_M = 5.8 which lies within the typical range for such separators **[3]**.
It should be mentioned that Raccichini et al. found that the MacMullin number can be slightly dependent on the chosen electrolyte solution **[4]**, although Landesfeind et al. showed that there was no dependence of the MacMullin number on the electrolyte salt, solvent composition, or salt concentration for the samples chosen by them **[3]**. Therefore, further research has to be performed to shed more light on the influence of the electrolyte properties on the determined MacMullin number values for separator foil. Ideally, the MacMullin number should be determined by using the electrolyte that is used for the final application.

CONCLUSION

In this application note, the so-called stacking method is applied to determine the MacMullin number of separator foils. A Metrohm Autolab Microcell HC setup combined with a TSC battery standard cell is used, together with a typical lithiumion battery electrolyte as well as a typical separator material.

ACKNOWLEDGEMENT

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CONFIGURATION

Autolab PGSTAT204

PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。

PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。

TSC Battery Standard

TSC Battery 是一种封闭式测量池,用于组装 **半电池** 或 **全电池** 或 **带有活性物质和隔板的大容量电池** 。此外,它还适用于测量与板/板几何形状的金属电极接触的固体和凝胶状样品。

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