

Application Area: Batteries

Investigation of the Solid Electrolyte Interface Structure and Kinetics

Keywords

Batteries, solid electrolyte interface, SEI, electrochemical impedance spectroscopy, EIS, cyclic voltammetry, CV, LiBOB, glassy carbon, GC.

Introduction

In a recent publication, Kranz et al. studied the structure of a model solid electrolyte interphase (SEI) forming on a planar glassy carbon electrode in contact with a typical organic battery electrolyte (1 M LiPF₆ in 3/3/4 EC/EMC/DMC) containing different amounts of lithium bis(oxalate)borate (LiBOB), which is often used as additive to improve the SEI stability [1]. Complementary results from the experimental techniques such as FIB-SEM, AFM, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV)-based redox probe experiments were combined to shed more light on the SEI structure as well as on the transport kinetics through the SEI.

This application note presents the experimental details and an overview of the most important findings from the EIS and CV experiment performed by Metrohm Autolab potentiostat combined with Metrohm Autolab RHD microcell HC.

Experimental Setup

a) Chemicals

The glassy carbon (GC) sheet was obtained from HTW Hochtemperatur-Werkstoffe GmbH, Germany (Sigradur-G®), Lithium foil from Rockwood Lithium GmbH (company acquired by Albemarle) and all chemicals for preparing the 1 mol/L LiPF₆ in 3/3/4 (vol/vol/vol) ethylene carbonate / ethyl methyl carbonate / dimethyl carbonate (EC/EMC/DMC) electrolyte as well as LiBOB were purchased from Sigma Aldrich Co. (battery grade). All chemicals were stored and handled inside an Ar-filled glovebox. Also the cell assembly was done inside a glovebox, whereas the measurements of the prepared cell were performed outside of the glovebox.

b) Measuring setup and sample preparation

A Metrohm Autolab multichannel potentiostat/galvanostat M204, equipped with a FRA32M module, was used for EIS and CV experiments. The Multi Autolab M204 can

accommodate up to 12 channels, or one module per channel, with a maximum of 6 channels and 6 modules. A typical example of Multi Autolab M204 equipped with 6 channels and 6 modules is shown in Figure 1.



Figure 1 - The Multichannel Autolab M204 potentiostat.

For electrochemical measurements, a TSC surface measuring cell in combination with an Autolab Microcell HC setup has been used. The design of the measuring cell is shown as a schematic drawing in Figure 2.

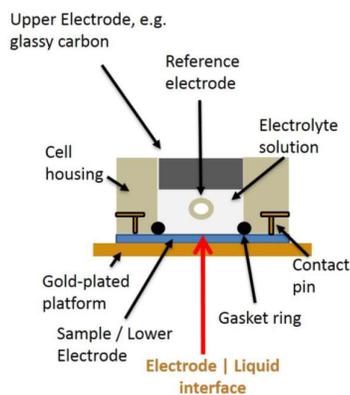


Figure 2 - Schematic drawing of the TSC surface design. Glassy carbon was used as a working electrode to form the SEI layer on its surface (lower electrode), and metallic lithium was used as both counter and reference electrodes (upper electrodes).

The sample temperature was controlled by the Autolab Microcell HC setup using a cell holder equipped with a Peltier element, in combination with a temperature control unit, Figure 3.



Figure 3 – The Metrohm Autolab Microcell HC setup. On the left, the cell holder, on the right, the temperature controller.

The temperature accuracy of this setup is 0.1 °C. For the experiments presented here, the temperature was kept constant at 25 °C.

For data acquisition, the NOVA 2 software was used. The control of the sample's temperature is integrated in NOVA.

Prior to cell assembly, the GC sheet was freshly polished using diamond suspensions of different particle sizes starting with 3 μm going down to 0.25 μm particle size. After the polishing procedure, the GC sheet was thoroughly cleaned with HPLC grade acetone. For preparation of the electrolyte, 1 mol/L LiPF₆ in 50/50 (vol/vol) EC/EMC was mixed with 1 mol/L LiPF₆ in DMC. LiBOB salt was added and dissolved in the final electrolyte to generate LiBOB concentrations of e.g., 0.5 mmol/L and 5 mmol/L.

As working electrode the GC sheet was used, while metallic lithium served as both counter electrode and reference electrode. The geometrical active area of the working electrode was set to 0.28 cm² by using an EPDM O-ring with a diameter of 6 mm clamped onto the GC surface.

c) Measurement parameters

According to the information given in reference [1], the experimental parameters were as follows: "The SEI formation was carried out by slow scan CV. [...] Three CV cycles between 3 V and 0.01 V vs. Li/Li⁺ with a scan rate of 0.5 mV/s were performed. Prior to SEI formation, an impedance spectrum at 3 V was taken in order to check if any resistive layer was observable on the GC. Before any EIS measurement, the cell was stabilized at 3 V for 10 min. The frequency was varied from 100 kHz to 0.3 Hz with an RMS AC voltage of 5 mV. [...] For the redox probe experiments, the electrolyte was exchanged inside the glovebox for a ferrocene-containing electrolyte. Subsequently, one cyclic voltammogram was taken per half-hours in a voltage range between 2.8 V and 3.5 V using a scan rate of 10 mV/s."

Results and Discussion

Figure 4 shows impedance spectra obtained 20 h after voltammetric SEI formation for electrolyte solutions with 0.1 mmol/L and 5.0 mmol/L of LiBOB and small amounts of dissolved ferrocene at an electrode potential of 3 V vs. Li/Li⁺. For the data representation, the Nyquist plot has been chosen, where the imaginary part of the impedance is plotted against the real part. In this representation, different processes contributing to the real part of the impedance can be distinguished. However, the measuring frequency is only implicitly contained.

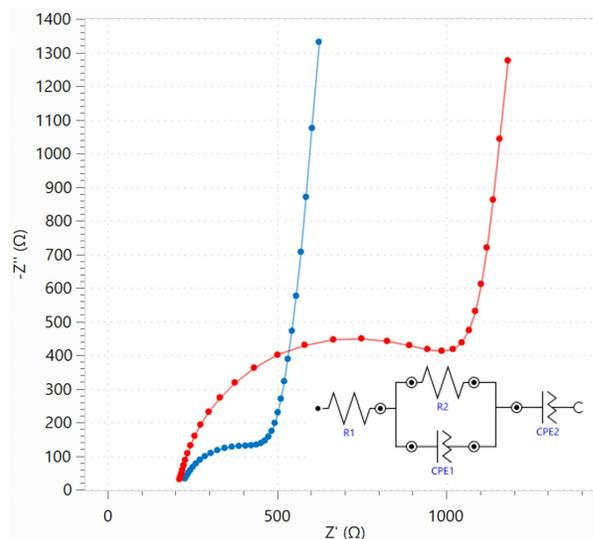


Figure 4 - Impedance spectra taken 20 h after voltammetric SEI formation for cell containing 0.1 mmol/L LiBOB (in blue) and the cell containing 5.0 mmol/L LiBOB (in red) at 3 V vs. Li/Li⁺. Also the equivalent circuit is shown.

At the high-frequency part, a semi-circle caused by the presence of a SEI is clearly visible. Fitting the semi-circle by a parallel R₂-CPE₁ element, one can extract the SEI resistance R_{SEI} and estimate the SEI capacitance C_{SEI}. For lower frequencies, a mainly capacitive increase due to electrode polarization is observable. This part can be fitted by taking another CPE₂ into account which is connected in series to the R₂-CPE₁ element. For the complete equivalent circuit, see Figure 4. Here, the resistor R₁ has also to be considered which represents the contribution by bulk ion transport and causes the high-frequency offset on the Z' axis. From the spectra, it is clearly visible that R_{SEI} is lower for a relatively low concentration of LiBOB and increases with increasing LiBOB concentration. This is well-known from literature, stating that LiBOB-based SEIs are more resistive [2].

Using the C_{SEI} values from the data fit together with estimated values for the relative permittivity ϵ_r , the thickness d_{SEI} (m) of the SEI can be calculated:

$$d_{SEI} = \frac{\epsilon_0 \epsilon_r A}{C_{SEI}} \quad 1$$

Where ϵ_0 ($= 8.85E - 12 F m^{-1}$) is the vacuum permittivity, ϵ_r is the relative permittivity and A (m) is the electrode area.

Depending on the chosen relative permittivity, the calculated thickness varies between 20 and 100 nm. However, compared with the values obtained by FIB-SEM and AFM experiments, the EIS-based values are smaller. Possible explanations for this are discussed by Kranz et al. One plausible explanation is that the SEI is not a dense layer but a porous network with liquid pathways with a faster, less-hindered Li^+ transport separated by a solid-like backbone with slower Li^+ transport kinetics [1].

Immediately after recording an impedance spectrum, a CV experiment was carried out in the WE potential range from 2.8 V to 3.6 V to use the ferrocene/ferrocenium redox couple (half-wave potential $E_{1/2} = 3.24$ V here) as a probe for the molecule transport through the SEI. In Figure 5, CVs for LiBOB concentrations of 0.1 mmol/L (blue line) and 5.0 mmol/L (red line) are depicted.

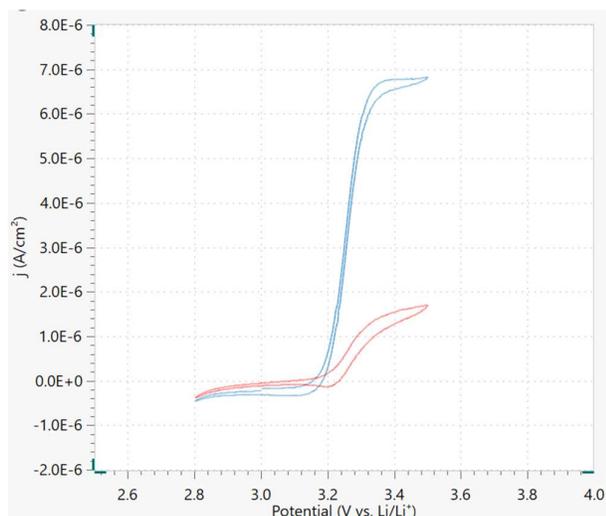


Figure 5 - Cyclic voltammograms between 2.8 V and 3.5 V vs. Li/Li^+ in presence of Ferrocene for electrolytes containing 0.1 mmol/L LiBOB (in blue) and 5.0 mmol/L LiBOB (in red).

The cyclic voltammograms are dominated by a diffusion-limited current at potentials more positive than the ferrocene half-wave potential, pointing to a diffusion-limited transport

process through the SEI layer. In case of the higher concentration of 5.0 mmol/L LiBOB, the diffusion-limited current is significantly reduced.

The resulting cyclic voltammograms can be used to estimate the effective diffusion coefficient $D_{Fc,eff}$ ($cm^2 s^{-1}$) of ferrocene which is proportional to the diffusion-limited current density $j_{anod,limit}$ ($A cm^{-2}$).

$$D_{Fc,eff} = \frac{d_{SEI} \cdot j_{anod,limit}}{F \cdot c_{Fc,bulk}} \quad 2$$

Where F ($= 96485 F m^{-1}$) is the Faraday constant and $c_{Fc,bulk}$ ($mol cm^{-3}$) is the bulk concentration of ferrocene.

Thus, the effective diffusion coefficient of the probe molecule Ferrocene decreases with increasing LiBOB concentration.

Another fundamental finding is that for each LiBOB concentration, the effective diffusion coefficients of Ferrocene (based on CV experiments) are very similar to the effective diffusion coefficients of the Li^+ (estimated from impedance results, for underlying theory see [3]) and that furthermore the effective diffusion coefficients of both species show a quite similar temporal evolution with growing SEI (not shown here, see [1]).

From this, it is likely that Li^+ as well as ferrocene molecules both tend to be transported via pathways through electrolyte-filled pores inside of the SEI.

Acknowledgements

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References

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local [Metrohm distributor](#). Additional instrument specification information can be found at www.metrohm.com/en/products/electrochemistry.