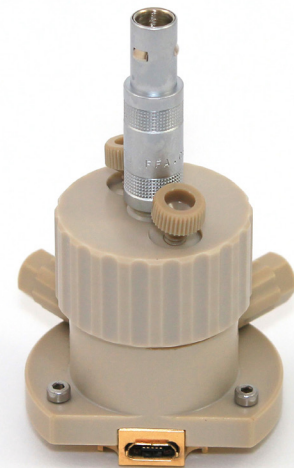


Application note

Investigation of the Solid Electrolyte Interphase Structure and Kinetics

- A combined approach by EIS and CV



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 LiPF_6 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 properties [1]. Complementary results from the experimental techniques 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.

Experimental

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 LiPF_6 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, if available, and lowest water content). All chemicals were stored and handled inside an Ar-filled glovebox. Also the cell assembly was done inside a glovebox, whereby the measurements of the prepared cell were performed outside of the glovebox.

b) Sample preparation & measuring setup

Prior to cell assembly, the GC sheet was freshly polished using diamond suspensions of different particle sizes starting with 3 μm go-

ing 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 LiPF_6 in 50/50 (vol/vol) EC/EMC was mixed with 1 mol/L LiPF_6 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.

For electrochemical measurements, a TSC surface measuring cell in combination with a Microcell HC setup has been used (rhd instruments). The design of the measuring cell is shown as a schematic drawing in Figure 1.

As working electrode the GC sheet was used, while elemental Li served as counter electrode and reference electrode, respectively. The active area of the working electrode is defined as 0.28 cm^2 by means of an EPDM o-ring with a diameter of 6 mm clamped onto the GC surface.

The sample temperature was controlled by the Microcell HC Setup using Peltier technique in combination with an Eurotherm control unit. The temperature accuracy of this setup is 0.1 $^\circ\text{C}$. For the experiments presented here, the temperature was kept constant at 25 $^\circ\text{C}$.

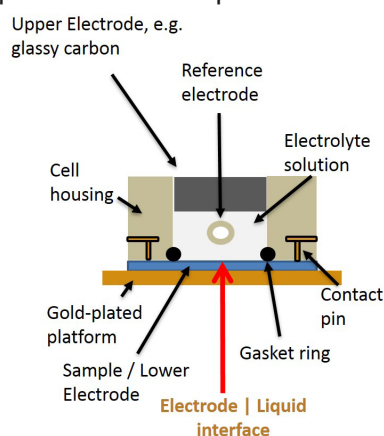


Figure 1: Schematic drawing of the TSC surface design. As sample / lower electrode (= working electrode), a GC sheet was used. Li was used as upper electrode (= counter electrode) and as reference electrode, respectively.

A Metrohm Multi-Channel potentiostat/galvanostat equipped with a FRA32-module

(Metrohm Autolab B.V.) was used for EIS and CV experiments. For data acquisition, the NOVA 2.1.4 software was used. The control of the sample's temperature is integrated in NOVA.

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

c) Measurement parameters

According to the information given in [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

Figure 2 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.

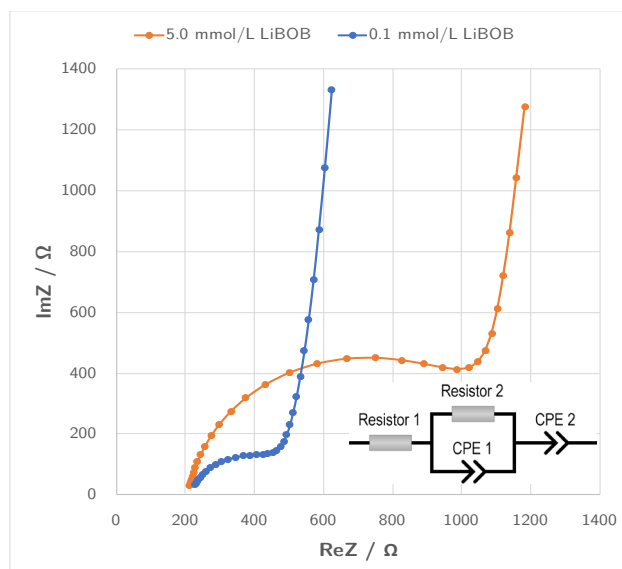


Figure 2: Impedance spectra taken 20 h after voltammetric SEI formation for 0.1 mmol/L and 5.0 mmol/L of LiBOB and a small amount of ferrocene dissolved in the electrolyte at an electrode potential of 3 V vs. Li/Li⁺.

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 R_2 - CPE_1 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 CPE_2 into account which is connected in series to the R_2 - CPE_1 element. For the complete equivalent circuit, see Figure 2. Here, the resistor R_1 has also to be considered which represents the contribution by bulk ion transport and causes the high-frequency offset on the ReZ 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} of the SEI can be calculated:

$$d_{SEI} = (\epsilon_0 \epsilon_r A) / C_{SEI}$$

ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity and A 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^+ ion transport separated by a solid-like backbone with slower Li^+ ion 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 3, CVs for LiBOB concentrations of 0.1 mmol/L and 5.0 mmol/L are depicted.

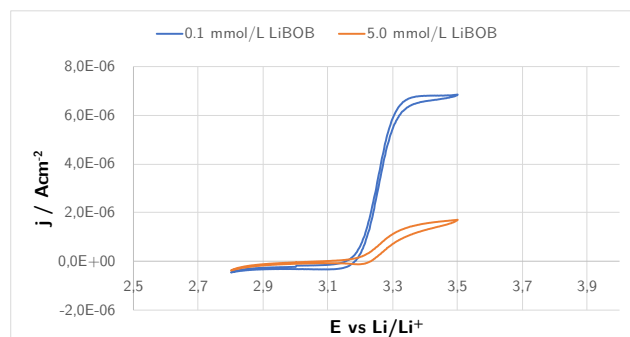


Figure 3: Cyclic voltammograms between 2.8 V and 3.5 V vs. Li/Li^+ in presence of Ferrocene for electrolytes containing 0.1 mmol/L LiBOB and 5.0 mmol/L LiBOB.

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 coef-

ficient $D_{\text{Fc,eff}}$ of ferrocene which is proportional to the diffusion-limited current $j_{\text{anod,limit}}$.

$$D_{\text{Fc,eff}} = (d_{\text{SEI}} j_{\text{anod,limit}}) / (F c_{\text{Fc,bulk}})$$

F is the Faraday constant and $c_{\text{Fc,bulk}}$ 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^+ ions (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 seems to be confirmed that Li^+ ions as well as Ferrocene molecules both tend to be transported via path ways through electrolyte-filled pores inside of the SEI.

Acknowledgement

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- [1] S. Kranz, T. Kranz, A. G. Jaegermann, B. Roling, *Journal of Power Sources* 418 (2019) 138-146.
- [2] K. Xu, *Chemical Reviews* 114 (2014) 11503-11618.
- [3] T. Kranz, S. Kranz, V. Miß, J. Schepp, B. Roling, *J. Electrochem. Soc.* 164 (2017) 3777-3784.