

Concentration Polarisation in Polymer Electrolytes

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Introduction

Insufficient transport properties may cause concentration polarisation to occur in the electrolyte of lithium-polymer batteries, limiting the battery discharge performance, especially if solid polymer electrolytes (SPE) are used [1]. The transport properties of an SPE-system was previously studied [2], resulting in a characterisation method, determined transport properties and a numerical model describing the ion transport.

In this study, following the previous, the ion transport was investigated using an *in situ* spectroscopic method [3]. The salt concentration profile, $C_s(x,t)$, evolving during a galvanostatic polarisation and a following open circuit relaxation, was monitored. The experimental results were compared with the results of the transport model.

Experimental

The electrolyte consisted of a statistical co-polymer of ethylene- and propylene oxide ($M_w \approx 12000$ g/mole) with LiTFSI salt corresponding to 0.81 M, i.e. O:Li ratio 25. The electrolyte was placed in a Teflon cell, covered with a glass plate, with lithium metal working (WE) and counter electrodes (CE), according to fig. 1. The cell was secured to the sample table of a confocal microscope (Olympus BX40) attached to a RAMAN spectrometer (Dilor Labram). RAMAN-spectra could be measured, one point at a time, in a stepwise-sequence, starting close to the WE and moving outwards with 20 μm steps. A Perkin-Elmer PAR 263A was used to galvanostatically (± 0.5 A/m²) polarise the cell during one hour followed by an open circuit relaxation. $C_s(x)$ was determined [3] from the RAMAN spectra recorded during the polarisation and relaxation.

Model

The macroscopic mathematical model, implemented numerically, is based on concentrated electrolyte theory and employs concentration dependent parameters. The model and the parameters used are described in detail in ref. 2. In this study the model of case 3 was used.

Results

To establish a calibration curve RAMAN spectra for samples with different salt concentrations were recorded. A linear relation between the normalised RAMAN response and the TFSI concentration was obtained from 0.1 to 1.5 M.

The concentration polarisation in the electrolyte was investigated for both oxidising and reducing currents. $C_s(x,t)$ could be calculated from the spectra recorded at different times. It was observed that C_s at the WE surface dropped rapidly from 0.81 to 0.55 M after one hour reduction at 0.5 A/m². Interestingly, the concentration change at the electrode was larger when an oxidising current was applied, then C_s changed from 0.81 to about 1.2 M. This observation is in line with previous results, showing that the transport properties experience strong

concentration dependence.

The results were compared with simulations using the model. The model showed good agreement, as depicted in fig. 2, when the parameters previously determined were used. This means that the model can be used to accurately predict the behaviour of the electrochemical behaviour of the electrolyte.

Confocal RAMAN-spectroscopy proved to be a powerful tool to study the behaviour of an SPE *in situ*. It complements electrochemical studies. With some modifications to the model it may be used to describe gel electrolytes. Then a similar methodology could be employed to study such.

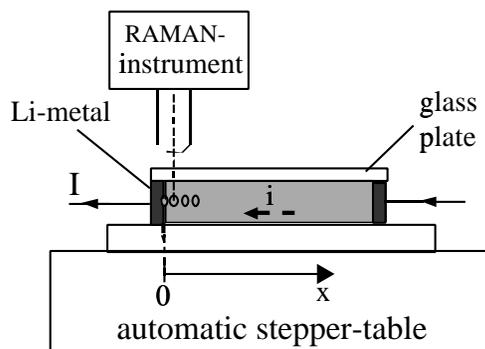


Figure 1. Experimental setup for polarisation experiments with RAMAN spectroscopy measurements.

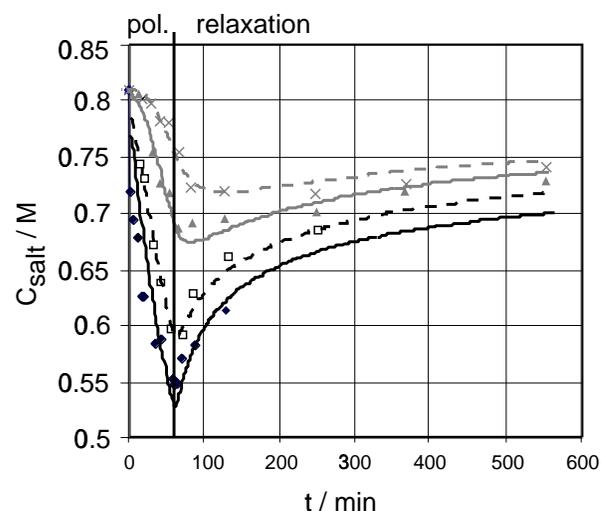


Figure 2. $C_s(x,t)$ determined from RAMAN-spectra (symbols) and simulations (lines) at different distances from the WE: 0 μm (\blacklozenge ; —), 20 μm (\bullet ; - -), 40 μm (\blacktriangle ; - · -), 60 μm (\times ; - -).

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References

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