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Electrochemical characterisation and modelling of the mass transport phenomena in $LiPF_6$–EC–EMC electrolyte

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ABSTRACT

The conductivity, the salt diffusion coefficient, the lithium-ion transport number and the thermodynamic factor of the salt and the solvent were reported for $LiPF_6$ in EC:EMC (3:7) at 25 °C and for concentrations between 0.2 and 2.0 mol/dm^3. The mass transport in the electrolyte was fully characterised by combining three types of electrochemical experiments; concentration cells, galvanostatic polarisation experiments and electrochemical impedance measurements with a mathematical description of the mass transport in the electrolyte. The apparent salt diffusion coefficient had a local maximum in the concentration range, while the viscosity-dependent salt diffusion coefficient decreased from 4.1×10^{-10} m^2/s at 0.2 mol/dm^3 to 4.4×10^{-11} m^2/s at 2.0 mol/dm^3. Both the thermodynamic factor and the conductivity varied strongly with the concentration. The conductivity had a maximum of 9.5 mS/cm at 1.0 mol/dm^3. The lithium-ion transport number with respect to the room decreased with increasing salt concentration, with a maximum of 0.37 at 0.2 mol/dm^3 in the concentration range. The Maxwell–Stefan diffusivities and the electrolyte potential drop in a lithium-ion battery at steady state were lastly calculated from the obtained transport properties. An analysis of the characterisation method was also done on the basis of the characterisation results.

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1. Introduction

Electrolytes with low lithium-ion transport numbers and salt diffusion coefficients cause large concentration polarisations during operation of Li-ion battery cells. This leads to poor high-rate performance, unwanted side reactions and ageing. It is therefore important to be able to characterise and model the transport phenomena in electrolytes under conditions relevant to cell operation. The accurate determination of mass transport and thermodynamic properties of the electrolyte is an important step in this work.

Transport properties and thermodynamic properties such as activity coefficients and partial molar volumes, are parameters that describe the transport phenomena in an electrolyte. The definition of the transport and thermodynamic properties must be connected with a mathematical description of the electrodiffusional transport process, which can be derived from for example irreversible thermodynamics [1]. Conventionally, conductivity and a set of diffusion coefficients and transport numbers are defined and used as transport property parameters, but other parameter sets are also possible, like Maxwell–Stefan diffusion coefficients, and friction/interaction parameters. With properly determined parameters it is possible to make a well-informed evaluation of the merits of a particular electrolyte, and to simulate the behaviour of a battery cell including time-dependent concentration and potential profiles in the electrolyte.

The number of independent parameters that are needed to describe the mass transport in a certain electrolyte is a function of the number of species. An electrolyte with n species need $n(n-1)/2$ transport properties. Thus, three transport properties, and in addition at least one thermodynamic property, are necessary for a salt with two ions dissolved in one solvent. For a salt with two ions dissolved in two solvents, six independent transport properties and at least four thermodynamic properties are necessary. The steep rise in the number of parameters with the number of species makes it impractical to characterise multi-solvent electrolytes, especially when the properties of the solvents are similar. In those cases, it is well motivated to describe the electrolyte as a salt dissolved in one solvent.

Lithium hexafluorophosphate dissolved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) is commonly used in liquid electrolyte Li-ion batteries. For example it is the chosen electrolyte for the Generation 2 battery technology for hybrid electric vehicles in the Freedom Car Programme (USA). The electrolyte

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has been studied in Li-ion cells by Zhang et al. [2]. They saw that SEI layers were formed on a $LiMn_2O_4$ cathode and a graphite anode, which is essential in Li-ion battery operation. The ionic conductivity of the electrolyte was studied by Ding et al. [3] over a range of compositions and temperatures. The conductivity was equal to 8.7 mS/cm at 1 M $LiPF_6$ at 25 °C and at a solvent composition of 3:7 EC:EMC. The self-diffusion coefficients of ^7Li and ^{19}F in the electrolyte have been measured by Capiglia et al. [4], from which they calculated the cation transport number. It was found to be 0.37 at low salt concentrations and at an EC:EMC ratio of 2:8, which implies that the majority of the current is carried by the hexafluorophosphate ion. However, no one has made a complete mass transport characterisation of this electrolyte.

There are numerous experimental methods that can be used to characterise the transport phenomena in electrodiffusion processes. Self-diffusion coefficients can be measured with pulsed-field gradient NMR. Concentration profiles in electrolytes can be studied with in-situ confocal Raman spectroscopy or NMR, while the individual velocities of the species in the electrolyte during passage of current can be studied with electrophoretic NMR. Examples of electrochemical methods that are used for characterising transport phenomena in electrolytes are; the Hittorf method, concentration cells, polarisation/relaxation methods and electrochemical impedance spectroscopy.

Electrochemical methods have the advantage that the experiments resemble the relevant processes occurring in a battery during use, and that the only instrumentation needed is a potentiostat. However, one has to deal with the fact that only the potential difference between two electrodes is measured, and not the concentration. This can be partly solved by relating the potential difference of the electrodes to concentration difference with concentration cell experiments.

In the literature mass transport characterisation of electrolytes using electrochemical methods has been described by several workers, see e.g. [5–10]. The salt diffusion coefficient is usually estimated from the relaxation of a concentration profile. This technique was originally applied with optical detection methods; Newman and Chapman [11] observed the concentration profiles in aqueous potassium chloride under conditions of restricted diffusion by Rayleigh interference optics. They concluded that the experiment yielded a well-defined, differential diffusion coefficient even in concentrated solutions. Ma et al. [5] developed this method to an electrochemical method by assuming that the quasi-electrostatic potential difference between two electrodes is proportional to the salt concentration difference when no current is passing through the cell. The concentration difference was created by galvanostatic polarisation for a predetermined time. By combining this experiment with a similar experiment under semi-infinite diffusion conditions, concentration cells and conductivity measurements a full set of thermodynamic and transport properties was determined for a sodium salt in poly(ethylene oxide).

Hafezi and Newman [6] analysed the semi-infinite galvanostatic polarisation method by measurements with aqueous silver nitrate solutions. They found that at very short times after current interruption the potential difference is dominated by the double-layer capacitance and other possible surface phenomena and is not an accurate measure of concentration difference. They also suggested that the discrepancy between their model predictions and experiments at slightly longer times could be attributed to variation in the properties due to the concentration variation in the cell. It was pointed out that the galvanostatic polarisation method is primarily suited for use with polymer rather than liquid electrolytes, since the required semi-infinite diffusion condition is more easily provided in polymer films where convection problems are absent.

The galvanostatic polarisation method was further developed by Georén and Lindbergh who determined a complete set of ionic transport properties and thermodynamic factor of a solid polymer electrolyte system [7] and a liquid electrolyte system [8], respectively. A galvanostatic polarisation experiment was combined with conductivity measurements and concentration cells, that is, one set of experiments less than earlier methods. Numerical solution of the model equations, and optimisation of the parameters to the experimental data made it possible not to require semi-infinite diffusion in the galvanostatic experiment. This allowed concentration-dependent parameters in the model, and use of a considerably shorter cell also for the liquid electrolyte. The main problems with liquid electrolytes brought up by Hafezi and Newman [6] were thus overcome. In a subsequent paper the model and parameters for the SPE were used to simulate concentration profiles that were experimentally confirmed with in-situ Raman spectroscopy [12].

Valøen and Reimers determined the complete set of transport and thermodynamic properties of $LiPF_6$–EC–PC–DMC [9]. The methodology was similar to that of Ma et al. [5] with the exception that a Hittorf experiment replaced the restricted diffusion experiment. The lithium-ion transport number was determined from the Hittorf experiments while the ratio between the lithium-ion transport number and the square root of the diffusion coefficient was measured with the semi-infinite galvanostatic polarisation method.

The methods for a full characterisation are still time-consuming and experimentally difficult, and the factors affecting the accuracy are not well understood. As a consequence such investigations are rarely undertaken and published despite their importance. In this study, we characterise $LiPF_6$ in EC:EMC (3:7) with an electrochemical method that builds on the one introduced by Georén and Lindbergh [8]. The aim is both to study the properties of a technically important electrolyte system and to contribute to the further development of the characterisation method, exploring its possibilities and limitations. Although the EC:EMC solvent is a mixture it was treated as one specie in the mass transport model.

2. Experimental

The electrolyte was prepared by dissolving lithium hexafluorophosphate ($LiPF_6$, Strem Chemicals, max 20 ppm water) in an ethylene carbonate and ethyl methyl carbonate mixture (EC–EMC, Quallion, 3:7 by weight). In total, eight samples were made where the salt concentrations varied from 0.2 to 2.2 mol/dm^3. The solvent was stored over molecular sieves in order to remove residual water traces. All experimental work was carried out in a dry glove box filled with argon. A Gamry PCI4/750 potentiostat/galvanostat was used in all experiments except for the conductivity measurements.

The partial molar volumes were calculated from the salt concentrations and the solvent concentrations of the samples. The solvent concentration was determined by measuring the mass of solvent that had to be added to dilute a certain amount of salt to the desired concentration.

The conductivity of the electrolytes was measured with a Consort K912 conductometer with a four-electrode glass/platinum probe. The conductometer was calibrated with potassium chloride solutions outside the glove box before use to calculate the cell constant of the probe. The temperature of the electrolyte during the conductivity measurement was also measured with the conductometer to assure an electrolyte temperature of 25 ± 1 °C. The conductivity was measured five times at two different occasions for each electrolyte concentration.

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