CHARACTERISATION AND MODELLING OF LITHIUM-ION BATTERY ELECTROLYTES

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ABSTRACT

Rechargeable batteries play an important role as energy carriers in our modern society, being present in wireless devices for everyday use such as cellular phones, video cameras and laptops, and also in hybrid electric cars. The battery technology dominating the market today is the lithium-ion (Li-ion) battery. Battery developments, in terms of improved capacity, performance and safety, are major tasks for both industry and academic research. The performance and safety of these batteries are greatly influenced by transport and stability properties of the electrolyte; however, both have proven difficult to characterise properly.

The specific aim of this work was to characterise and model the electrolytes used in Li-ion batteries. In particular, the mass transport in these electrolytes was studied through characterisation and modelling of electrolyte transport in bulk and in porous electrodes. The characterisation methodology as such was evaluated and different models were tested to find the most suitable. In addition, other properties such as electrochemical stability and thermal properties were also studied.

In the study of electrochemical stability it was demonstrated that the electrode material influenced the voltammetric results significantly. The most versatile electrode for probing the electrolyte stability proved to be platinum. The method was concluded to be suitable for comparing electrolytes and the influences of electrolyte components, additives and impurities, which was also demonstrated for a set of liquid and polymer containing electrolytes.

A full set of transport properties for two binary polymer electrolytes, one binary liquid and the corresponding ternary gel were achieved. The transport was studied both in the bulk and in porous electrodes, using different electrochemical techniques as well as Raman spectroscopy. In general, the conductivity, the salt and solvent diffusivity decreased significantly when going from liquid to gel, and to polymer electrolyte. Additionally, low cationic transport numbers were achieved for the polymer and gel and significant salt activity factor variations were found. The results were interpreted in terms of molecular interactions. It was concluded that both the ionic interactions and the influences from segmental mobility were significant for the polymer containing electrolytes. The characterisation methods and the understanding were improved by the use of a numerical modelling using a model based on the concentrated electrolyte theory. It was concluded that electrochemical impedance spectroscopy and Raman spectroscopy were insufficient for determining a full set of transport properties. It was demonstrated that the transport is very influential on electrochemical impedance as well as battery performance.

Keywords: lithium battery, electrolyte, mass transport, stability, modelling, characterisation, electrochemical, Raman spectroscopy, impedance
SAMMANFATTNING


Målsättningen med avhandlingsarbetet var att karakterisera och modellera Li-jon batterielektrolyter. Masstransporten i dessa elektrolyter studerades i detalj, både i elektrolytens bulk och i porösa batterielektroder. Både karakteriseringsmetodik och transportmodeller studerades. Dessutom undersöktes andra elektrolytegenskaper såsom elektrokemisk stabilitet och termomekaniska egenskaper.


Nyckelord: litium batteri, elektrolyt, masstransport, stabilitet, modellering, karakterisering, elektrokemisk, Raman spektroskopi, impedans
LIST OF PAPERS


VI. Characterisation and modelling of the transport properties in lithium battery gele electrolytes: Part I –the binary electrolyte PC/LiClO4, Peter Georén and Göran Lindbergh, submitted to Electrochim.Acta.

VII. Characterisation and modelling of the transport properties in lithium battery gele electrolytes: Part II –the ternary electrolyte PMMA/PC/LiClO4, Peter Georén and Göran Lindbergh, submitted to Electrochim.Acta.

VIII. Characterisation and modelling of a high-power desnity lithium-ion positive electrode for HEV application, Shelley Brown, Peter Georén, Mårten Behm and Göran Lindbergh, manuscript.
CHRONOLOGY

In the first study, performed at Berkeley lab in California, I was educated in a method for characterising transport properties developed at that lab, and studied a PPO-electrolyte. The accuracy of the methodology was studied in detail. Furthermore, the thermal properties of the electrolyte system were studied. It was my co-supervisor at that time, Marca M. Doeff (Berkeley Lab), who finalised the paper.

On my return to the department of Applied Electrochemistry, KTH, the second study was conducted on another model polymer electrolyte (EOPO/LiTFSI). The characterisation method was improved by using mathematical modelling. The thermal and mechanical properties of that system were also studied, but were not included in the second publication. In order to verify the transport property results for the EOPO/LiTFSI system, and at the same time validate the mathematical model, a Raman spectroscopic method was employed in the third paper. The study was in collaboration with the materials physics group at Chalmers, and they contributed with the Raman expertise. The method facilitated direct in-situ measurement of the salt concentration profile as a function of time during a polarisation experiment. Thus, the predictions of the model with the transport parameters could be checked with direct measurements.

In the fourth paper, a novel impedance methodology was developed together with colleagues that were studying porous battery electrodes. It was not directly aimed at characterising electrolytes, but rather the behaviour of porous lithium-ion and metal hydride electrodes. However, the electrolyte transport properties play a significant role for the electrode behaviour. My colleagues contributed with electrode kinetics expertise, electrode material and electrochemical impedance knowledge.

A methodology for measuring the electrochemical stability of lithium battery electrolytes was studied, originally in collaboration with the Polymer technology department at Lund Technical University and the inorganic material science group at Uppsala University. The aims were to develop a suitable method and to characterise a novel electrolyte developed in the polymer group. This work resulted in my fifth paper, and is somewhat independent in that it is related to electrochemical breakdown.

A method to characterise gel electrolyte mass transport was also studied. The theory and the experimental methodology used in paper II were developed to suit a ternary electrolyte. This study was submitted as a paper in two parts, paper VI and VII, just before writing this thesis.

The final paper, which is a manuscript, deals with the impedance of a commercial HEV electrode. The study was a theoretical development of the impedance model, this time including a full description of the electrolyte transport. The resulting model was verified with impedance results using three of the characterised electrolyte systems. Furthermore, the influence from electrolyte transport on the impedance results and model was studied.
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Stockholm, 24/10-03, Peter Georén
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INTRODUCTION

1. INTRODUCTION

Rechargeable batteries play an important role as energy carriers in our modern society, being present in devices for everyday use such as cellular phones, video cameras and laptops. The demand for batteries rapidly increased at the end of the 20th century due to the large interest in wireless devices. Today, the battery industry is a large-scale industry producing several million batteries per month.

Although batteries have been around for quite some time there is still room for improvement. Most people have experienced the capacity limitations of batteries, for example when the cell phone or the laptop shuts down because of an empty battery. Improving the energy capacity is one major development issue, however, for consumer products, safety is probably considered equally important today. Another important drive for technological development in the battery field is the introduction of hybrid electric vehicles, reducing fuel consumption and gas emissions significantly. A rechargeable battery is used to buffer the electricity produced by a traditional combustion engine, and power the electrical engine. For this application, batteries optimised for high power, low cost and long service life are essential [1,2]. Battery development is a major task for both industry and academic research and the development of powerful, cheap and reliable rechargeable batteries continues.

The battery technology dominating the market today is the lithium-ion (Li-ion) battery. These batteries have rapidly replaced the less energetic and less environmentally friendly Ni-Cd batteries, as well as the bulkier Ni-MH cells, in portable devices. However, in large-scale batteries where cost is the key issue, the older battery types are still prominent. The idea to use lithium in batteries was first proposed in 1958 [3] and has been used for a long time in primary (non-rechargeable) batteries. Rechargeable ones were commercialised by Sony 1991[4] because they realised that the battery was a key technology, making their consumer products competitive. Sony is today a market leader in consumer products, partially due to their venturous development and introduction of a novel battery technology. Since this initial development, the market growth for Li-ion batteries has been tremendous. Furthermore, battery technology is today recognised as a strategic key technology for many devices. As a consequence, there has been an extraordinary amount of work done on all aspects of the Li-ion battery chemistry, design, manufacture and application, and the technology is still improving significantly [5].

1.1. Working principle of a Li-ion battery

A battery consists of two electrodes, one positive and one negative, and an electrolyte, as depicted in Figure 1. Current collector foils, supporting the active electrode material, are also necessary in Li-ion batteries. The depicted cell illustrates that, in general, Li-ion batteries are very thin; approximately 0.1-0.2 mm. Batteries are formed by winding or stacking the thin layers into cylindrical or prismatic shapes with the
The porous electrodes contain the chemical compounds that react and produce current. The electrolyte serves as the interconnecting media between the electrodes, transporting reacting species between the electrodes as an ionic current. The other task for the electrolyte is to keep the electrodes from electrically short-circuiting.

![Figure 1. Schematic figure of a Li-ion battery during discharge.](image)

During discharge, an electrochemical reduction reaction takes place at the positive electrode, consuming electrons. At the negative pole an oxidation reaction occurs, producing the electrons. The electrons travel in the external circuit, powering the actual application. In Li-ion batteries the reactions are lithium insertion in the positive electrode and extraction in the negative. The total discharge reaction of a lithium-ion battery, resulting due to the passage of one electron between the poles of the battery, is given by:

\[ \text{Li-HostA}(-) + \text{HostB}(+) \rightarrow \text{HostA}(-) + \text{Li-HostB}(+) \]

Host A represents the negative electrode and is generally based on a carbon material, e.g. graphite. Whereas host B, the positive pole, is today typically based on a lithiated metal oxide such as LiCoO₂ and LiNiO₂. The electrode materials determine the battery voltage and energy density. The high voltage of Li-ion batteries (4 V) is one major advantage, another is the low weight of the materials. The ultimate negative electrode material, in terms of energy density and voltage, is lithium metal (theoretical energy density 3862 mAh/g). It was tested commercially during the 80’s but the poor surface properties of the material caused dendrites to grow during charging, eventually short circuiting the cell internally, causing explosion and/or fire. The carbon based materials used today have poorer energy densities (graphite 372 mAh/g), approximately the same voltage, but are safer. A variety of metal oxides are presently used and all result in fairly high battery voltages (3-5 V). However, as a consequence of the poorer energy density of these materials (around 150mAh/g) they generally limit the
INTRODUCTION

overall energy density of the battery. When it comes to electrolytes there are presently two types in use: liquids and gels. Both are based on non-aqueous organic solvents, similar to acetone, and contain special lithium salts. The gels are solid-like because the liquid component is incorporated into a polymer matrix. There is also a great interest in electrolytes based on only polymer and salt, however, they are presently not used in commercial batteries due to their low conductivity [5].

1.2. Electrochemical stability

For the battery manufacturers, safety aspects are generally ascribed a very high priority since Li-ion batteries have rather reactive electrodes compared to other batteries. An important safety aspect is the use of stable electrolytes. If the stability limit of the electrolyte is violated it will start to decompose. A protective surface layer [5] may form, reducing further electrolyte decomposition significantly. Nevertheless, the process will cause ageing and may eventually cause cell failure. Due to the large surface area of the porous battery electrodes even a very slow decomposition may be disastrous. It may lead to gas evolution, eventually causing cell rupture and solvent leakage. At high temperatures electrolyte decomposition may in worst-case lead to fire or explosions.

Although there are great interests in increasing the electrochemical stability, i.e. the potential where electrolyte oxidation and reduction start to occur, it has proven somewhat complicated to characterise properly. Among the previously used methods [6-8] voltammetry has proven advantageous, being a rather rapid method as in comparison with cycling real batteries. Furthermore, voltammetry is based on a solid theoretical fundament [9,10], because it has been extensively used in a wide variety of other electrochemical investigations previously. Although the method has been utilised previously to study electrochemical stability the methodology still presents room for improvement.

1.3. Electrolyte mass transport

In a battery electrolyte the ions should be transported easily between the electrodes and within the pore electrolyte, i.e. with little resistance (high ionic conductivity). Furthermore, it is advantageous if only the lithium ions that carry the ionic current (cationic transport number=1), because then the concentration of salt in the electrolyte remains unaltered during the discharge. Such electrolytes have been developed, however they suffer from a very poor conductivity. If the transport number is less than unity, a portion of the lithium ions will have to diffuse across the electrolyte; a process described by the salt diffusion coefficient. These are examples of mass transport properties of an electrolyte.

The influence of the electrolyte transport on the performance of a typical Li-ion battery electrode will now be demonstrated. In Figure 2, potentiostatic discharge
curves are displayed for identical electrodes, using three of the different electrolytes studied in this thesis, having significantly different transport properties. The electrode potential was controlled using a reference electrode and was iR-corrected. This means that the results reflect the performance of the porous electrode alone and that influences from the bulk electrolyte voltage drop and counter electrode performance were excluded.

![Figure 2. Discharge curves (potentiostatic 3.1 V, iR-compensated, three electrode cell) for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ electrode in three different electrolytes: a liquid{PC/1M LiClO$_4$} (---); a gel {30%PMMA/PC/1M LiClO$_4$}(— - —); and a polymer {EOPO/0.8M LiTFSI} (- - -).](image)

It can be seen that using the liquid electrolyte 93% (13As) of the total capacity of the electrode could be discharged in approximately 10 000 seconds (~3 hours). When using a gel electrolyte only 30% was discharged during the same time. For the polymer electrolyte it is even worse. After 100 000 seconds (~30h) only half of the electrode capacity had been discharged. From the results it is clear that the electrolyte properties limit the discharge current of the two electrolytes containing polymer. However, without studying the mass transport properties in detail, it is difficult to deduce the underlying causes.

Great efforts have been aimed at quantifying and understanding the transport properties of electrolytes in general, and lately organic and polymer electrolytes have been in focus [11-13]. A major problem when studying electrolyte transport properties is that they are difficult to measure. Moreover, there are two major theories used to describe the transport, the dilute and the concentrated solution theory[14]. The dilute is valid when no ionic interactions take place and when the electrolyte is ideal. Although non-aqueous electrolytes generally experience non-ideal behaviour and strong ionic interactions, the theory for dilute electrolytes has been used in several methods proposed [15-25]. The characterisation methods can be classified into perturbing and
non-perturbing methods. Perturbing methods, such as chronopotentiometry (CPM) and electrochemical impedance spectroscopy (EIS), are based on measurement of the voltage response during passage of a current. They differ from non-perturbing methods, such as PFG-NMR etc.[26,27], in which a relaxed system is studied. Perturbing methods have the advantage of resembling the relevant processes occurring in a battery during use. Newman et al[28] developed an experimentally straightforward electrochemical perturbing method, which is based on the concentrated electrolyte theory and has been used to characterise different types of Li-ion battery electrolytes [29-33]. Electrochemical impedance spectroscopy (EIS) [9] has been utilised previously to study electrolyte transport [34-36]. A better understanding of the ionic mass transport has also been achieved by using simulation models based on the concentrated electrolyte theory, describing the underlying physical processes. The models have been used, together with accurate characterisation results, to predict the battery performance of electrolytes, yielding insights into limitations and failure modes caused by the electrolyte [37-41]. In the present thesis, the mass transport in different electrolytes was studied using the two latter methods in combination with simulations.

1.4. Aim of the thesis

The work presented in this thesis was a part of the Swedish national research program ”Batteries and Fuel cells for a better environment”, funded by the foundation for strategic environmental research (MISTRA), and the companies Volvo, Ericsson and Höganäs. One research topic was rechargeable lithium-ion batteries. Our research group at KTH participated in that program, on an applied research level, with characterisation and modelling of lithium cells. Two PhD-projects were defined, the first dealing with the electrodes (summarised in a different thesis [42]). The second is the present work, focused on electrolytes. The overall aim of the efforts in our group was to achieve mathematical simulation models, describing the behaviour of lithium-ion cells. The models were based on physical processes and parameters, so that they could be used for predicting battery performance for various materials and also for optimisation of the battery design. Additionally, the modelling yielded an increased understanding of the physical processes occurring in such batteries, and the influence of each process on the battery performance. Finally, characterisation results, in terms of property values, were achieved for several different materials during the development of the models.

The specific aim of this work was to characterise and model the electrolytes used in Li-ion batteries. In particular, the mass transport in these electrolytes, in bulk or in a porous electrode, was studied through characterisation and modelling. The characterisation methodology was evaluated and different models were tested to find the most suitable. In addition, other properties such as electrochemical stability and thermal properties were also studied.
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2.1. General laboratory equipment
The type of research performed in this thesis requires a large amount of specialised equipment that will be described briefly in the following section. Firstly, the materials used in this thesis work are very hygroscopic. All work dealing with lithium metal, which decompose in contact with water, was carried out in a Mecaplex GB80/82 glove box under a dry (H₂O<1ppm) argon atmosphere, where all chemicals and materials were handled and stored. Secondly, the methods employed were mainly electrochemical, making advanced electric power supplies and measuring devices a necessity. In this work, several types of such instruments, together with computer software, have been utilised.

2.2. Materials
Three types of electrolytes have been studied: non-aqueous binary liquid, binary polymer and ternary gel electrolytes. The latter two both contain polymer to a large extent and altogether four different polymers have been used in the work of this thesis. In the transport property papers (I-III, VI-VII) two binary polymer electrolytes, one liquid and one gel electrolyte, were studied. The first polymer electrolyte consisted of an amorphous poly(propylene oxide) (PPO, \( M_n \approx 5 \times 10^5 \) g/mol) with the salt LiCF₃SO₃, (LiTf). Electrolyte films (thickness 100µm) with compositions between 5.7-0.06 M (O:Li ratio 2 to 400) were prepared by solvent casting. The second polymer electrolyte, denoted EOPO/LiTFSI, was based on a statistical co-polymer(\( M_w = 1.2 \times 10^4 \) g/mol) of ethylene- and propylene oxide (EOPO), 75 and 25 wt-% of each monomer respectively, which was synthesised by others[43]. Electrolytes with compositions between 2.0 and 0.11 M (O:Li-ratio 8 to 200) were prepared by dissolving the salt, lithiumbis(trifluoromethanesulfone)imide (LiTFSI), directly in the polymer. The dissolution process could take up to several weeks for this electrolyte with the most concentrated samples. The PPO polymer electrolyte resulted in stiff rubber like opaque films, whereas the EOPO appeared as completely clear, highly viscous liquids, rubber-like at high salt concentrations. The liquid and gel were both based on propylenecarbonate (PC) with lithiumperchlorate(LiClO₄) salt. Liquid electrolytes with salt concentrations ranging from 0.1 to 2.0 M were studied. Gel electrolytes, based on the same solvent and salt, with up to 50 wt-% poly(methyl methacrylate) (PMMA) (\( M_n \approx 7.5 \times 10^4 \) g/mol) were prepared by first dissolving the salt in the liquid and then adding the polymer. For the samples with high salt and polymer content, the mixture had to be stored at 50°C for approximately a week after addition of polymer to yield homogenous gels. To be able to use the same electrochemical cells for the liquid electrolyte, and to make handling easier, the liquid were soaked into glass wool filter (Whatman, GFA).
In the stability study (paper V) 12 electrolytes were prepared; 4 liquid and 8 containing polymer. The liquid electrolytes were formed by mixing one of the two salts LiPF$_6$ or LiTFSI with either pure gamma-butyrolactone (gBL) or a mixture (2:1 by vol.) of ethylene carbonate (EC) and gBL, obtaining a 1 M solution. Then, 30 wt-% of either PMMA ($M_n$ 4×10$^4$ g/mol) or a novel amphiphilic graft copolymer ($M_n$ 4.8×10$^4$ g/mol) denoted FA77EO9[44,45] and depicted in Figure 3, was added to achieve the remaining 8 electrolytes. The samples containing polymer formed clear viscous liquids after some time.

Different electrodes have been used in the work of this thesis. For a large portion of the experiments lithium metal electrodes have been used. The high quality lithium metal was stored separately in the glove box to maintain pure surfaces. In the stability study, working electrodes of platinum (Pt), stainless steel (SS), nickel (Ni), glassy carbon (GC) and porous graphite plates (8% porosity) were evaluated. In the impedance studies (paper IV and VIII) porous battery electrodes were studied. Porous NiMH (MmNi$_{3.6}$Co$_{0.8}$Mn$_{0.4}$Al$_{0.3}$) electrode sheets were produced by cold pressing[46]. Electrodes with different thickness, 0.55 and 1.65 mm, were realised by assembling one or three layers of such sheets in a mechanically compressing frame[47], and spot welding the current collectors together. The resulting NiMH electrodes were rectangular with a geometric area of about 10 to 15 cm$^2$. LiMn$_2$O$_4$ electrodes were produced by tape casting a ball-milled slurry of 80wt% LiMn$_2$O$_4$, 15wt% Shewinignan Black and 5wt% EPDM-polymer in cyclohexane, using a common doctor blade technique [48], onto a carbonised aluminium foil. The resulting electrodes had a 20µm thick layer of active material, with LiMn$_2$O$_4$ particles in the size of 8 µm according to SEM-images. Commercial battery electrodes, based on LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (84 wt%), carbon black (8 wt%) and a binder (8wt%), coated on an aluminium current collector, were supplied by a producer. The active layer was 35 µm thick, had a porosity of 0.35 and an average particle diameter of approximately 1 µm according to SEM.

2.3. Experimental techniques

2.3.1. Chronopotentiometry

For the transport property characterisations chronopotentiometry (CPM) experiments were carried out, using a symmetrical two-electrode cell with lithium metal working
and counter electrodes (Li/electrolyte/Li). A constant current was passed for a certain time, causing a concentration polarisation to appear. Then the current was stopped and the open circuit potential (OCP) of the working (WE) versus counter electrode (CE) was recorded during the relaxation of the concentration gradient(s). For each electrolyte composition studied, a number of experiments were performed, using different currents. In paper II the CPM experiments differed in two ways. Firstly, a reference electrode (RE) was situated in the middle of the electrolyte compartment and the potential recorded was WE vs. RE. Secondly, a sensing electrode (SE), situated in the vicinity of the working electrode, according to Figure 4, was also used. The idea was that the SE would give additional information about the evolving concentration gradient in the electrolyte.

![Figure 4](image)

**Figure 4.** Sketch of the cell used for the CPM experiments in paper II.

### 2.3.2. Concentration cells

Concentration cells were also used to study the transport properties. The cell consisted of two slightly overlapping films of electrolyte (about 1 cm wide, 2 cm long and 1 mm thick) having different composition. They were placed on a glass plate and two ribbons of lithium metal were used as electrodes, one on each electrolyte edge. The cell voltage was recorded once it had settled from the initial disturbance, typically after about 30 minutes.

### 2.3.3. Diffusion experiments

To determine the diffusion rate of the solvent in the gels, a method based on mass increase was developed and employed. A sample of the gel of interest was placed in the cell, depicted in Figure 5. The soaked glass wool filter functioned as a solvent source, causing diffusion of solvent into the gel sample. At various times the Teflon ring with gel and membrane was removed from the soaked glass filter, excess liquid on the underside of the membrane was removed and the mass was measured, using a common high resolution (0.1 mg) laboratory balance.
2.3.4. Thermal and viscosity characterisation

For two of the electrolyte systems, PPO/LiTf and EOPO/LiTFSI, the glass transition temperature \( T_g \) was measured under helium atmosphere using a Perkin-Elmer Differential Scanning Calorimeter (DSC7). The samples were rapidly cooled to \(-100^\circ C\), and then heated to \(100^\circ C\) at a scan rate of \(5^\circ C/min\). Finally, they were subjected to a second cooling and heating between the same limits at a \(5^\circ C/min\) rate. This allowed observation of any salt precipitation phenomena and an accurate determination of \( T_g \), during the second heating cycle, because the thermal history of each sample was then controlled.

The viscosity at \(25^\circ C\) was measured for the system EOPO/LiTFSI with a Brookfield Rheometer DV-III, with a cp 52 measuring cell, using the software Rheocalc.

2.3.5. Raman measurements

In paper III, Raman spectroscopy was employed to study the concentration profiles in-situ during a galvanostatic polarisation using a documented method \([49,50]\). Raman spectra were recorded using a Dilor Labram spectrometer equipped with a confocal microscope. The CH2 modes of the polymer chain at \(\sim 1460cm^{-1}\) were utilised to normalise the spectra, and the intensity of the TFSI-ion mode at \(740 cm^{-1}\) was related to the salt concentration using an established a calibration curve.

The experimental cell is depicted in Figure 6. The electrolyte sample was placed in a closed Teflon cell, covered with a glass plate. The WE and CE were both made of lithium ribbons. A current density of \(0.5 A/m^2\) was applied to the sample during 60 minutes followed by an open circuit relaxation. During the experiment Raman-spectra were recorded at points with \(20\mu m\) interval starting from the WE vicinity. The optical beam of the confocal microscope was focused about \(300 \mu m\) below the glass plate to avoid boundary effects of the covering glass plate. Each recorded spectrum contained information from a scattering volume with a diameter of approximately \(5 \mu m\).

The recording time for each spectrum limited the number of positions and times feasible to record. In the first 10 minutes of each polarisation experiment, while the concentration profile started developing from the electrode, spectra were recorded only...
at point zero. Then, the points +20 and +40µm were also studied. After 30 minutes, spectra for distances up to 100 µm were recorded. This procedure allowed shorter intervals between the spectra at the beginning when the concentration changed rapidly.

**Figure 6.** The Raman cell set-up.

### 2.3.6. Voltammetry

Linear sweep voltammetry (LSV) was the main technique used in the stability study. A cylindrical (diameter:10 mm, length:2mm) three-electrode cell made of Teflon™, with lithium metal counter and reference electrodes, was used for the voltammetry measurements. Most experiments were carried out at a sweep rate of 5 mV/s, sampling data once each second, between OCP and 6 V vs. Li for the anodic sweeps, and OCP and −0.1 V for the cathodic sweeps. For some experiments the sweep rate was altered.

### 2.3.7. Electrochemical impedance spectroscopy

The ionic conductivity of the electrolytes were determined using EIS (10mV, 60kHz-1Hz) of a two electrode “swage-lok” cell, described in detail elsewhere [51], using SS electrodes. Spacer rings of Teflon were used to control the electrolyte thickness. However, in the later studies, the cell was equipped with a micrometer screw, measuring the electrolyte thickness in-situ. The electrolyte resistance was determined from the real axis intercept of the low frequency spur in the Nyquist plot. By employing cells with different thickness (0.50 and 2 mm) influences of the electrodes could be accounted for and the true electrolyte conductivity could be determined.

In the studies of the impedance of porous electrodes all electrodes were cycled galvanostatically, discharged to the desired state of charge (SOC) and relaxed for at least 12 hours prior to any EIS measurements. In paper VIII a three electrode cell was used, having a RE positioned between the WE and CE. In paper IV an improved EIS technique was developed, using a four-electrode cell. In that cell, an additional RE was positioned behind the WE, having electrolytic contact with the electrolyte in the porous WE (further described in Figure 9 in theoretical section). Thus, two impedances were measured.
EXPERIMENTAL

To achieve electrolytic contact between the pores and the backside electrolyte, the electrode material was coated on an Al current collector perforated with small holes (10 holes/cm², 100µm diameter) in the lithium case. Different references were used. For the lithium cells the RE consisted of a Teflon capillary (1 mm diameter) with a lithium metal ribbon inside, somewhat similar to a Luggin capillary RE. In the NiMH case Hg/HgO RE with Luggin capillary was used. For the porous electrodes EIS was measured potentiostatically at OCP, typically applying an AC perturbation of 5 to 10mV, and measuring the impedance between 60 kHz and 0.6 mHz.
3. NUMERICAL MODELLING AND MODEL FITTING

In most of the included studies, mathematical modelling has been employed as a tool to analyse results in terms of simulations or fitting models to experimental results. All modelling was performed numerically using the MATLAB® software. Numerical modelling is a key technique in this thesis and therefore the procedures employed are as important to consider as the experimental procedures.

In the transport property studies, the theories resulted in partial differential equations, describing the evolution of concentration gradients of the electrolyte components with time, i.e. an equation with derivatives with respect to both time and space. To solve this type of problem a numerical strategy was employed. By using finite difference approximations of the space derivatives, i.e. using a constant step space discretisation grid, initial value problems were obtained, described by a system of ordinary differential equations (ODEs) with only time-derivatives. MATLAB's built-in solver for ODE-systems, denoted “ode15s”, was employed to solve the problems. An advantage with this particular solver is that it is particularly suitable for diffusion-type problems, i.e. mathematically stiff problems. Furthermore, the solver employs variable time step length in the integration, increasing calculation speed and accuracy significantly.

In the first impedance paper (IV), a large emphasis was placed on finding analytical solutions to the equations. Having the analytical solutions greatly simplified the modelling. In principle, the impedance response could be calculated directly from the final equation by inserting the parameter values and the frequency. This model required very little computational power. In the second impedance study (VIII), a full description of the electrolyte transport was utilised in the impedance theory, making numerical methods necessary to solve the problem. The system of differential equations, describing the impedance, was solved using finite differences. The methodology results in an ordinary complex valued equation system, solved numerically by MATLAB. However, significantly more computational effort was required to calculate the impedance spectra in this case.

A great advantage of using a numerical methodology is that quite different problems can be solved using the same program code. For example, the parameters of the models were treated as, first being constant and later concentration dependent, within the same code. Different theoretical features of the models can easily be “turned on” and “off” in the programs. If analytical mathematical techniques had been utilised, a separate solution for every case would have been necessary to derive. In some cases, there simply was no analytical solution. However, an important consideration when employing numerical methods is the verification of the model. This was generally achieved by comparing the results of the model with an analytical solution (in a case for which an analytical solution exists).
For many of the studies based on modelling, characterisation results were achieved by fitting parameters of a model to make the model fit experimental data. Fitting is, mathematically, a minimisation problem. A merit function, $\chi$ (typically the deviation of the model from the measured data), is minimised by adjusting the specified parameters of the model. This is a very common mathematical problem for which MATLAB supplies several built-in functions. To perform the parameter fitting a numerical Levenberg-Marquardt\cite{52-54} optimisation algorithm, suitable for non-linear least square problems of several parameters, denoted “leastsq” in the MATLAB “Optimization Toolbox”, was employed. The minimiser experiences quadratic convergence, making it particularly suitable for problems having many parameters or problems that require significant computational effort for each iteration. In any minimisation case one can only be certain to find a local minimum, situated in the neighbourhood of the starting guess. There may exist multiple minima, but only one is the global. However, there is no established method to find a global minimum. Due to this limitation, several starting guesses were always evaluated. In the summarised studies, at least three starting guesses were always employed. If they resulted in the same solution, as they often did, it was considered to be the global minimum. Otherwise, more starting guesses were employed, the achieved minima compared and the best one was considered to be the final solution.

In the transport property studies several experimental measurements were often fitted. Typically, one or several measurements resulted in single value results, such as ionic conductivity, whereas others resulted in “curves”, e.g. CPM results. In the fitting procedure the single value results were treated as being equally important as each whole curve. This was achieved by including a weight, $W$, in front of the single value data in the merit function, being equal to the number of measured data points for the curve experiment. Furthermore, it is important to include the measurement error in the merit function. Otherwise, values below the actual accuracy may influence the minimisation results significantly. Thus, the merit function was typically defined according to:

$$
\chi = \left[ \frac{\Delta E_{exp}(t) - \Delta E_{sim}(t)}{\Delta E_{exp}(t) + \Delta E_{err}} \right] W \left( \frac{\kappa_{exp} - \kappa_{sim}}{\kappa_{exp}} \right)
$$

(1)

where the notations $exp$ and $sim$ represents experimental data and simulated, respectively. For the impedance studies the merit function was based on the real and imaginary part of the impedance, $Re(Z)$ and $Im(Z)$, according to the equation below:

$$
\chi = \left[ \frac{Re(Z_{exp}) - Re(Z_{sim})}{Re(Z_{exp}) + Re(Z_{err})} \right] \frac{Im(Z_{exp}) - Im(Z_{sim})}{Im(Z_{exp}) + Im(Z_{err})}
$$

(2)

The additional component, $Z_{err}$, is the measurement accuracy of the instrumentation.
4. THEORETICAL MODELS

4.1. Concentrated electrolyte mass transport theory

The model used to describe the ionic transport for all the studied electrolytes, and to evaluate experimental data, is based on the general, multi-component, mass transfer theory by Maxwell-Stefan[55]. It is conceptually depicted in Figure 7.

\[ c_j \nabla \mu_j = \sum_k K_{jk} (v_k - v_j) = R T \sum_k \frac{c_j c_k}{c_{\text{tot}} D_{jk}} (v_k - v_j) \quad j \neq k \quad D_{jk} = D_{kj} \]

\( c_j \) is the concentration of specie \( j \), \( c_{\text{tot}} \) the sum of all concentrations, \( T \) the temperature and \( R \) is the gas constant. The friction coefficients, \( K_{jk} \), are expressed as diffusion coefficients, \( D_{jk} \) [14,56], to yield expressions comparable to those of the dilute theory. A low value of \( D_{jk} \) means a high degree of interaction, i.e. a large friction. However, the concentrated theory introduces a conceptual difference in the introduction of, \( K_{+-,} \), the friction between anions and cations.

The gradient in electrochemical potential, \( \nabla \mu \), is used as the driving force, including gradients in both potential and concentration. For species \( j \) it follows from:

\[ \nabla \mu_j = R T \nabla \ln(c_j \cdot f_j) + z_j F \nabla \phi \]
THEORETICAL MODELS

where \( f_j \) is the activity factor, \( z_j \) is the charge of specie \( j \), \( F \) is the Faraday constant and \( \phi \) is the electric potential. The activity factor introduces a second conceptual difference compared to dilute solution theory, allowing non-ideal behaviour, i.e. \( f_j \) deviating from unity.

4.2. Binary electrolyte

For a binary electrolyte with monovalent cations (+), anions (-) and a solvent (0) as the independent species, eq.3 results in two independent equations [14].

\[
N^+ = c_s v^+ = -\frac{c_{tot}}{c_0} \left( 1 + \frac{\partial \ln f^+}{\partial \ln c_s} \right) \frac{2D_0+D_0-}{(D_0+ + D_0-)} \nabla c_s + \frac{i}{F(D_0+ + D_0-)} + c_s v_\theta
\]

\[
N^- = c_s v^- = -\frac{c_{tot}}{c_0} \left( 1 + \frac{\partial \ln f^-}{\partial \ln c_s} \right) \frac{2D_0+D_0-}{(D_0+ + D_0-)} \nabla c_s - \frac{i}{F(D_0+ + D_0-)} + c_s v_\theta
\]

\( D_{0+} \) and \( D_{0-} \) are similar to \( D_+ \) and \( D_- \) of the dilute solution theory. The cationic transport number, \( t_+ \), and Fick’s salt diffusion coefficient, \( D_s \), can be identified.

\[
D_s = \frac{c_{tot}}{c_0} \left( 1 + \frac{\partial \ln f^+}{\partial \ln c_s} \right) \frac{2D_0+D_0-}{(D_0+ + D_0-)}
\]

\[
t_+ = 1 - t_- = \frac{D_0+}{(D_0+ + D_0-)}
\]

So far the solvent has been chosen as reference. However, in order to relate the model results with experimental, using electrodes at fixed positions, the eqs. 5 and 6 were transformed from solvent-fixed to room-fixed co-ordinates. If the cationic transport number is less than unity a flux of salt will occur initially during the passage of a current. For a closed cell with a constant volume, the salt flux may cause a solvent flux, with opposite direction. Additionally, in the case of free flowing low viscosity electrolytes, convective fluxes may also occur. Taking a mass balance of an electrolyte volume, assuming constant molar volumes of the salt, \( V^m_s \), and polymer, \( V^m_0 \), yields eq.9, relating the solvent and salt fluxes.

\[
V^m_s N^+_s = -V^m_0 N^-_0 \Rightarrow v_\theta = -\frac{c_s V^m_s}{c_0 V^m_0} v_s
\]

The final expression used to calculate the change of salt concentration with time at a fixed position follows below. In this work it was solved for one dimension, being normal to the WE surface.
THEORETICAL MODELS

\[
\frac{\partial C_s}{\partial t} = \nabla \cdot \left( \left( 1 - \frac{c_s V_s^m}{c_0 V_0^m} \right) \left( D_s \nabla C_s \right) + \frac{i(1-t_s)}{F} \right)
\]

(10)

In the experiments, the voltage difference of two electrodes in the electrolyte was measured. In the model the potential difference was calculated from the concentration profiles according to eq.11 [28].

\[
\nabla \phi = \frac{2RT}{F} \nabla \left[ \left( 1 - t_s \right) \left( 1 + \frac{\partial \ln f_s}{\partial \ln c_s} \right) \ln c_s \right] - \frac{i}{\kappa}
\]

(11)

with

\[
\kappa = \frac{F^2 c_{\text{tot}}}{RT} \left[ \frac{1}{D_{+s}} + \frac{c_0}{c_s} \frac{1}{(D_{0s} + D_{0m})} \right]^{-1}
\]

(12)

In the expression for the ionic conductivity, \( \kappa \), it can be seen that if there are no interactions present between the anions and cations \( D_{+-} \) becomes large, \( c_{\text{tot}} \) approaches \( c_0 \), and \( \kappa \) becomes identical to that for dilute solutions [14].

4.3. Binary electrolyte in porous media

In paper VI, a model for a binary liquid electrolyte contained in a porous structure was employed. The porosity, \( \varepsilon \), was taken into account and eq.10 was replaced by eq.13.

\[
\varepsilon \frac{\partial C_s}{\partial t} = \nabla \cdot \left( \left( 1 - \frac{c_s V_s^m}{c_0 V_0^m} \right) \left( D_s^{\text{eff}} \nabla c_s \right) + \frac{i(1-t_s)}{F} \right)
\]

(13)

with

\[
D_s^{\text{eff}} = \varepsilon^{1.5} D_s
\]

(14)

Furthermore, in eq. 11 \( \kappa \) is replaced by \( \kappa^{\text{eff}} \), which similarly to \( D_s^{\text{eff}} \) was calculated using Bruggemans equation.

4.4. Ternary electrolyte

In a ternary electrolyte consisting of cations(1), anions(2) solvent(3) and polymer(4) eqs.2 and 3 results in three independent equations. The were expressed in vectors and matrices, and were solved for the velocity difference vector \( (v-v_4) \), i.e. using the polymer as reference, according to:

\[
(v - v_4) = M_1^{-1} \times \frac{c_{\text{tot}}}{RT} c \nabla \mu
\]

(15)
For the binary electrolyte models, the salt activity was expressed using the mean activity factor, \( f_{±} \), which was considered to vary with composition, and solvent activity variations were not taken into account. For a ternary electrolyte, with salt, solvent and polymer, there are three activity factors, \( f_{±}, f_{sol} \) and \( f_{poly} \). In this case, they may all vary with composition, especially if the ternary phase diagram is complex. Similar to the binary models the solvent and polymer activity variations were assumed to be insignificant. However, with two independent concentrations, \( c_s \) and \( c_{sol} \), the driving force vector becomes:

\[
c\nabla\mu = RT \left[ \begin{array}{c} c_s \frac{\partial \ln f_s}{\partial c_s} \nabla c_s + c_s \frac{\partial \ln f_s}{\partial c_{sol}} \nabla c_{sol} + \frac{c_s F}{RT} \nabla \phi \\ c_{sol} \frac{\partial \ln f_s}{\partial c_s} \nabla c_s + c_s \frac{\partial \ln f_s}{\partial c_{sol}} \nabla c_{sol} - \frac{c_s F}{RT} \nabla \phi \\ \end{array} \right]
\]

The concentration profiles in the electrolyte were calculated from eq.17, together with boundary conditions.

\[
\frac{\partial c_i}{\partial t} = -\nabla \mathbf{N}_i = -\nabla \mathbf{M}_2 \times \left[ \begin{array}{c} c_s \frac{\partial \ln f_s}{\partial c_s} \nabla c_s + c_s \frac{\partial \ln f_s}{\partial c_{sol}} \nabla c_{sol} + \frac{c_s F}{RT} \nabla \phi \\ c_{sol} \frac{\partial \ln f_s}{\partial c_s} \nabla c_s + c_s \frac{\partial \ln f_s}{\partial c_{sol}} \nabla c_{sol} - \frac{c_s F}{RT} \nabla \phi \\ \end{array} \right]
\]

with

\[
\mathbf{M}_2 = \left( \frac{K_{jk}}{c_{sol} c_j} \right)^{-1} = \left[ \begin{array}{ccc} -\left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{13}} + \frac{c_4}{D_{14}} \right) & \frac{c_1}{D_{12}} & \frac{c_1}{D_{13}} \\ \frac{c_2}{D_{12}} & -\left( \frac{c_1}{D_{12}} + \frac{c_3}{D_{13}} + \frac{c_4}{D_{14}} \right) & \frac{c_2}{D_{23}} \\ \frac{c_3}{D_{13}} & \frac{c_3}{D_{23}} & -\left( \frac{c_1}{D_{13}} + \frac{c_2}{D_{23}} + \frac{c_4}{D_{34}} \right) \\ \end{array} \right]^{-1}
\]

and

\[
c'_i = \frac{c_i}{c_{sol}}
\]
THEORETICAL MODELS

An explicit expression for the potential was derived knowing that the current is the sum of the ionic fluxes multiplied by the charge of each ion.

\[
\nabla \phi = \frac{RT}{c_s F} \left[ i - k_2 \left( 1 + \frac{\partial \ln f_s}{\partial \ln c_s} \right) \nabla c_s - k_2 k_s \frac{\partial \ln f_s}{\partial \ln c_s} \nabla c_{sol} - k_3 \nabla c_{sol} \right]
\]

(20)

with \( k_1 = M_{2,1}^s - M_{2,2}^s - M_{2,3}^s + M_{2,2}^s \) \( k_2 = \frac{1}{k_1} (M_{2,1}^s - M_{2,2}^s) \) \( k_3 = \frac{1}{k_1} (M_{2,3}^s - M_{2,3}^s) \) \( k_4 = \frac{1}{k_1} (M_{2,3}^s - M_{2,3}^s) \)

(21)

(22)

(23)

From the equations above the transport properties can be derived according to the following equations:

\[
t_+ = \frac{N_+ z_+}{i F} \bigg|_{c_s=0} = 1 - t_- = \frac{M_{2,1}^s - M_{2,2}^s}{k_1}
\]

(24)

A consequence of eq.24 is that \( k_2 = (t_+ - t_-) \), a relation that is used in the following properties.

\[
t_{sol} = \frac{N_{sol}}{i F} \bigg|_{c_s=0} = \frac{M_{2,1}^s - M_{2,2}^s}{k_1}
\]

(25)

\[
\kappa = -\frac{i}{\nabla \phi} \bigg|_{c_s=0} = -\frac{c_s F^2 k_1}{RT}
\]

(26)

\[
D_s = -\frac{N_+}{\nabla c_s} \bigg|_{c_s=0} = \left( \frac{[M_{2,1}^s]^2 - M_{2,1}^s \cdot M_{2,2}^s}{k_1} \right) \left( 1 + \frac{\partial \ln f_s}{\partial \ln c_s} \right)
\]

(27)

\[
D_{sol} = -\frac{N_{sol}}{\nabla c_{sol}} \bigg|_{c_s=0} = \left( \frac{M_{2,1}^s - M_{2,2}^s}{k_1} \right) \left( k_3 + (t_+ - t_-) \frac{c_s}{c_{sol}} \frac{\partial \ln f_s}{\partial \ln c_{sol}} \right) - M_{2,3}^s
\]

(28)

The sixth and final independent transport property can be defined from eq.17 in two different ways, either as the drag of solvent in case of salt diffusion, \( d_{sol} \), or as the drag of salt in case of solvent diffusion, \( d_s \), according to eqs.29a and 29b, respectively.
4.5. Impedance of insertion electrodes

In this thesis there are two papers dealing with EIS of porous battery electrodes having different electrolytes. In paper IV, the traditional equations describing the impedance response based on the potential probed both in front and behind the working electrode were solved analytically. Furthermore, solutions for the “differential” impedance, being the difference between front and back impedances, were derived and analysed in terms of limiting cases for insertion electrodes. The description of the electrolyte ion transport was rather simple in that study because the main focus of the study was to evaluate the possibilities with the new experimental approach. In paper VIII on the other hand, a more detailed model was developed, including the concentrated electrolyte theory among other features.

Both models were based on the same basic equations, describing the impedance behaviour of a porous insertion electrode, depicted in Figure 8. The impedance was defined according to eq. 30

\[
Z = \frac{\Delta \tilde{\phi}}{\tilde{t}_2(x = L)} = \frac{\tilde{\phi}_1(x = 0) - \tilde{\phi}_2(x = L + \delta)}{\tilde{t}_2(x = L)} + R_b
\]

\[ (30) \]

\( R_b \) represents the bulk electrolyte resistance occurring between the reference electrode and the beginning of the diffusion layer. The notation with (\( ~ \)) indicates that the variables are Laplace transformed in the equation. The subscripts (1) and (2) correspond to solid and electrolyte phase, respectively. In order to calculate \( Z \), an
expression for the current density in the pore electrolyte at the electrode/electrolyte interface was necessary to derive. For a porous electrode it is related to the local current density, i.e. the sum of the Faradaic current (described according to Butler-Volmer kinetics \([57]\)) and double layer currents occurring at the surface of the particles. In the impedance measurements a small perturbation around equilibrium was applied, making linearisation of the equations applicable and the final equation describing the electrolyte phase current, \(i_2\), becomes:

\[
\frac{d\tilde{i}_2}{dx} = S \left[ \frac{di_F}{dc_{1sv}} \tilde{c}_1 + \frac{di_F}{dc_{2sv}} \tilde{c}_2 + \frac{di_F}{d\phi_1} \tilde{\phi}_2 + \frac{di_F}{d\phi_1} \tilde{\phi}_1 + C_{DL} j \omega (\phi_1 - \phi_2) \right] 
\]  

(31)

4.5.1. Differential impedance

Figure 9. Schematic figure of the differential impedance measurements.

In paper IV, an additional impedance response was utilised, measured with a reference electrode positioned behind the working, depicted in Figure 9. The backside impedance was defined as defined according to eq. 32.

\[
Z_{x=0} = \frac{\Delta \tilde{\phi}}{\tilde{i}_2(x=L)} = \frac{\tilde{\phi}_1(x=0) - \tilde{\phi}_2(x=0)}{\tilde{i}_2(x=L)} 
\]

(32)

In the model, the electrolyte phase transport was greatly simplified by assuming Ohm’s law, i.e. only taking electrolyte potential and ionic conductivity into account. As a consequence, the diffusion layer was unnecessary to consider. The concentration dependence of the equilibrium potential, \(E_{eq}\), was expressed using Nernst equation and the Langmuir isotherm according to eq. 33.
\[ E_{eq} = E^0 + \frac{RT}{F} \ln \left( \frac{1 - \theta}{\theta} \right) \]  \hspace{1cm} (33)

For this model an analytical solution to eq.31 could be found [47,36], greatly simplifying the model and the analysis of the measured impedance. Finally, the differential impedance, \( Z_{\text{diff}} \), was defined according to eq.34, and solved analytically.

\[ Z_{\text{diff}} = Z - Z_{x=0} = \frac{\eta_{\text{tot}} - \eta(x = 0)}{t_{\text{tot}}} \]  \hspace{1cm} (34)

Analysing this final impedance expression with respect to limiting values at high and low frequencies it was found that the difference of the differential impedance at very high and low frequencies becomes independent of local kinetics, as described in the eq.35

\[ \Delta Z_{\text{diff}} = \lim_{o \to 0} \{Z_{\text{diff}}\} - \lim_{o \to \text{inf}} \{Z_{\text{diff}}\} = \frac{L}{2\kappa_{p2}^{\text{eff}}} - \frac{L}{\kappa_{p1}^{\text{eff}} + \kappa_{p2}^{\text{eff}}} \]  \hspace{1cm} (35)

This theoretical finding means that by measuring the differential impedance, either the effective conductivity of the solid, \( \kappa_1^{\text{eff}} \), or liquid phase, \( \kappa_2^{\text{eff}} \), can be accurately determined if the other one is known.

### 4.5.2. Impedance model 2

In paper VIII, the model was developed significantly to include electrolyte transport according to the concentrated electrolyte theory, a diffusion layer, an empirical equilibrium potential relation and particle size distribution. The electrolyte salt concentration, \( c_2 \), and potential, \( \phi_2 \), were defined according to the concentrated electrolyte theory for a binary electrolyte.

\[ \varepsilon c_2 j\omega = D_2 \varepsilon^{1.5} \frac{d^2 c_2}{dx^2} + \left( 1 - t_+ \right) \frac{d\tilde{r}_2}{dx} \]  \hspace{1cm} (36)

\[ \frac{d^2 \tilde{\phi}_2}{dx^2} = \frac{1}{K_2 \varepsilon^{1.5} \frac{d\tilde{r}_2}{dx}} \frac{RT}{c_2} \left( 1 - 2t_+ \right) \left( 1 + \frac{d\ln f_a}{dc_2} \right) \left( \frac{d^2 c_2}{dx^2} - \frac{1}{c_2} \left( \frac{dc_2}{dx} \right)^2 \right) \]  \hspace{1cm} (37)

In this model \( E_{eq} \) was based on empirical results of a different study [58], replacing the term related to the Langmuir isotherm in eq.31, resulting in the following equation:

\[ E_{eq} = A + \left( 1 - \frac{c_1}{c_1^{\max}} \right)^B + \frac{RT}{F} \ln(c_2 f_2 a^\theta) \]  \hspace{1cm} (38)

The parameters \( A \) and \( B \) were determined by fitting the \( E_{eq} \) vs. SOC-curve measured using galvanostatic intermittent titration (GITT), for an identical electrode in a constant concentration electrolyte [58].
\[ \tilde{\xi} = \left( \frac{1}{S} \frac{d\xi}{dx} - C_{DL} j \omega (\tilde{\phi}_1 - \tilde{\phi}_2) \right) \cdot \frac{1}{A_{tot}} \sum_k \left( \frac{A_k r_k}{F D_i} \left[ 1 - \sqrt{\frac{\omega j r^2_k}{D_i}} \coth \left( \sqrt{\frac{\omega j r^2_k}{D_i}} \right) \right]^{-1} \right) \]  

(39)

In the model, a diffusion layer outside of the porous electrode was also considered (see Figure 8). Mathematically it is a separate domain; however, the concentration and potential in the layer were also described by eqs.36 and 37.

To calculate the impedance for this second model eq.31 was solved numerically due to the inclusion of the electrolyte transport.
5. RESULTS

5.1. Electrochemical stability

In this part of the work, a voltammetric method was developed and used to study the electrochemical stability of a set of different electrolytes, including a novel gel electrolyte. Firstly, different electrode materials were first evaluated. For the most promising materials the nature of the occurring reactions was studied by varying the sweep rate. Finally, to demonstrate the abilities of the method, a set of electrolytes, with varying salt, solvent and polymer, were probed using the developed voltammetric method.

The ordinary battery electrode materials cannot be used when probing for electrolyte breakdown reactions because lithium insertion will dominate the response. Several other electrode materials have been evaluated, however difficulties have been observed with many of them [59-62]. Furthermore, it has previously been observed that the choice of electrode material influences the results [63]. One way of overcoming the latter problem is to choose electrodes that result in the most limited stability window, i.e. the thermodynamic stability window of the electrolyte. Then, it seems reasonable to assume that the voltammetric results, in terms of stability limits, should be applicable to real batteries. In order to find a suitable electrode material for probing electrolyte stability limits, Pt, SS, Ni, GC and graphite were tested as electrode materials, using the electrolyte gBL/LiPF\textsubscript{6}. Nickel was not evaluated in the anodic region due to it’s known corrosion problems [59].

Studying the anodic sweeps displayed in Figure 10, it can be observed that all samples experienced a “background” current, caused by non-Faradaic processes e.g. double layer charging. Such currents increase with sweep rate, hence a low sweep rate, e.g. 0.1mV/s, has been used in some previous studies. However, as long as these currents do not dominate the results, the use of such low sweep rates only makes the experiments unnecessarily tedious and time consuming. The influence of these background currents has been treated more extensively in other work [64].

More importantly, the results clearly demonstrate that the electrode material used influences the results. A suitable electrode material should experience rapid electrode kinetics, in this case resulting in a high current density at a certain potential. In Figure 10 it can be seen that the porous graphite electrode experienced the highest geometric current density in the whole potential region. However, this was an effect of the large surface area rather than rapid kinetics. A problem when using this electrode was to perform repeatable measurements. The wetted surface area was difficult to control and measure; hence the porous graphite electrode was considered improper. Of the remaining materials, Pt resulted in the largest current densities, indicating its
suitability for stability measurements. In contrast, the stainless steel electrode experienced the lowest currents.

**Figure 10.** Anodic voltammograms (OCP to 6 V vs. Li) for different electrode materials in gBL/LiPF₆, as indicated in the figure. The sweep rate was 5mV/s, and the temperature 25°C.

It was difficult to determine an absolute stability limit. In this work, the stability limit was defined to be the potential where a current density of 50 µA/cm² was reached. If a stability limit would be defined on required battery shelf life (e.g. self discharge in 1 month) or lifetime (e.g. decomposition of 20 µm electrolyte in 2 years), the limit in terms of current density would be significantly lower, in the range of a few µA/cm² or pA/cm², respectively. However, to monitor current densities at pA/cm², great effort would be necessary to reduce the background signals below such levels. The limit defined here is merely used as a tool to compare the results rather than a strict reaction rate limit. As can be seen in Figure 10, the current density increased very dramatically above that limit for all materials. Using this definition, the oxidation stability limit of the electrolyte studied could be determined for the different electrodes used. It was 4.7 V using Pt, 5.1 V for GC and 5.5 V for SS. Again, the differences probably reflect the varying kinetics of the electrodes. The thermodynamic stability limit of the electrolyte should be independent of electrode material. The results indicate that the limit should be somewhere just below 4.7 V vs. Li. A speculative explanation for the delay of oxidation currents on SS until above 5.2 V is the breakdown of the passivation layer of the SS, which may appear at these potentials [65]. If so, SS is inappropriate because of the dominant effect of the passivation processes of the material. However, further investigations are necessary to clarify this matter.
RESULTS

To further investigate the suitability of the electrodes, the nature of the occurring reactions was studied by varying the sweep rate. Rigorous theories of the influence of sweep rate on CV for different reaction types are available [9,66]. Two categories of reactions could be separated; diffusion controlled and surface related reactions. Sweep rate analysis was employed for Pt, SS and graphite electrodes with gBL/LiPF$_6$ electrolyte; using 1, 5 and 25 mV/s. The analysis indicated that platinum is the most suitable material for electrolyte stability measurements, and that SS should be used with care due to the presence of surface related currents, employing lower sweep rates (<1mV/s) to reduce the signals from electrode surface reactions.

Voltammetry has been utilised previously to study the influences of salt, solvent and polymer on the electrochemical stability window [59-61,67-70]. Also in this study, voltammograms were recorded for a variety of electrolytes to study the influences of the electrolyte components. Comparison of the voltammograms for samples based on gBL and EC-gBL showed that no clear difference could be detected. The salt, on the other hand, displayed an influence in terms of stability. It was observed that the electrolytes based on LiTFSI presented a different behaviour than those based on LiPF$_6$. The LiTFSI salt experienced an increased sensitivity towards oxidation compared to LiPF$_6$. A limited stability of the TFSI-anion has also been observed previously [70,71].

![Figure 11](image)

**Figure 11.** Anodic sweeps for different electrolytes showing the influence of polymer. Electrolytes based on EC-gBL/LiPF$_6$ with: no polymer(—), PMMA(— –) and FA77EO9( - - -) are displayed.

When polymer was added to the electrolytes, other significant trends could also be observed in the voltammograms. As can be seen in Figure 11, the electrolytes with FA77EO9 resulted in the highest oxidation currents above 5V. However, following the previous stability definition of 50µA/cm$^2$, most electrolytes showed a roughly similar stability limit of around 4.5V. This could mean that the polymer FA77EO9 promotes
the oxidation rate in some way, without significantly changing the potential where oxidation starts, i.e. the thermodynamics. The result is supported by conclusions from another study [72] based on cycling results for LiMn$_2$O$_4$ in the same electrolytes. In contrast to FA77EO9, the addition of PMMA seemed to reduce the oxidation rate to some extent, as concluded from the observed current plateau between 4.6 and 5V. This may have been caused by a reduced mass transport in these electrolytes, also reflected by the higher viscosities they experienced. Another plausible explanation for the behaviour is the formation of a polymer rich layer on the surface of the electrode, reducing the oxidation rate by shielding parts of the surface or by causing slower transport to/from the surface of the reactants. However, in a recent study [73] addition of polymer presented no influence on the Li-insertion kinetics. Thus, the latter proposed mechanism may be faulty. Clearly, the two different polymers tested differ in the effect on the oxidation rate.

The different electrolytes were also compared in the cathodic region. It was interesting to observe that the influence of polymer on the reaction rate is similar to that in the anodic region. Again, PMMA seemed to reduce the reduction rates, whereas FA77EO9 caused an increase. It is difficult to conclude the reason for the behaviour based on this study. However, it is clear that the addition of polymer influences the reaction rate rather than the stability of the electrolytes studied.

Application of the stability limit, previously defined, to the cathodic sweeps resulted in an unreasonably wide variation in the stability limit, from 2 to 0.5V. If one instead studies the potential where the main reduction starts, i.e. where the current starts to increase rapidly, it can be seen that most electrolytes have onsets around 1V. This stability limit would correspond well with that reported recently by Zhang et al.[74] for several electrolyte solvents, and is probably close to the true thermodynamic limit. This demonstrates that the definition of the stability limit is important to consider, especially when comparing results.

![Figure 12](image.png)

**Figure 12.** DSC heating traces (2$^{nd}$ heating 5$^\circ$/min) for the electrolyte system EOPO/LiTFSI (left) and PPO/LiTf(right) at various salt concentrations.
5.2. Physical properties of polymer electrolytes

The presence of more than one phase in a polymer electrolyte system complicates analysis of the transport property data. For this reason, the thermal and mechanical properties were studied. The three polymer systems studied (PPO/LiTf, EOPO/LiTFSI, PMMA/PC/LiClO₄) were optically clear and appeared to be amorphous, one-phase systems.

For the PPO and EOPO systems the thermal properties were studied. The results have only been briefly published and will therefore be described quite detailed herein. Firstly, DSC was applied to investigate how the glass transition temperature varied with composition, and to study phase transformations, e.g. crystallisation and melting. In Figure 12, heating traces are displayed for both systems at several salt concentrations. Both electrolyte systems experience glass transitions that appear at higher temperatures as the salt content increases. This is an expected behaviour caused by the formation of physical cross-links between polymer chain dipoles and the ions of the salt. For the EOPO/LiTFSI system clear crystallisation (-50 to -30°C) and melting peaks (–10 and 0°C) were observed for the most dilute samples, being caused by slow crystallisation kinetics resulting in a “frozen in” free volume during the preceding cooling. However, above 0°C, the EOPO/LiTFSI system was a fully amorphous, one-phase electrolyte, according to the DSC results.

![Figure 13](image)

**Figure 13.** Thermo-mechanical properties. Glass transition temperatures ($T_g$) for the polymer electrolytes PPO/LiTf (x) and EOPO/LiTFSI (□) at various salt concentrations are displayed together with viscosities for EOPO/LiTFSI (-○-) at 298K.

An interesting phase-related anomaly was present for the PPO/LiTf electrolyte. For the samples with 1.2 and 1.6 M salt, two glass transitions seemed to be present. This can also be viewed in Figure 13, where $T_g$ is plotted versus $c_s$. The presence of two $T_g$'s
indicates the existence of micro phase-separation at these temperatures. To find out if the separation was present at ambient temperatures, the ionic conductivity was measured at several temperatures in the range of 30 to 90°C, and the VTF-equation [75], eq.40, was fitted to the results, yielding values according to Table 1.

\[ \kappa = \kappa^0 T^{-0.5} \exp \left( -\frac{B}{T - T_0} \right) \]  

\begin{table}[h]
\centering
\begin{tabular}{llllll}
\hline
\( c_s \) & O:Li & T\(_g\) [K] & T\(_0\) [K] & T\(_g\)-T\(_0\) [K] \\
\hline
3.37 & 5 & 259 & 222 & 37 \\
2.49 & 8 & 254 & 208 & 46 \\
2.13 & 10 & 243 & 199 & 44 \\
1.87 & 12 & 243 & 184 & 59 \\
1.57 & 15 & 233 (215) & 183 & 50 (32) \\
1.25 & 20 (226) & 216 & 176 (49) & 40 \\
0.87 & 30 & 214 & 175 & 39 \\
0.23 & 100 & 213 & 169 & 44 \\
0.10 & 200 & 213 & 172 & 41 \\
\hline
\end{tabular}
\caption{VTF fitting results for PPO/LiTf.}
\end{table}

The conductivity followed the VTF-behaviour from 30-90°C with no anomalies, indicating that the phase-separation had vanished and that the system behaved like a “normal” amorphous polymer electrolyte.

The three polymer electrolyte systems presented quite different mechanical behaviour. PPO/LiTf resulted in rubbery rigid films. For the EOPO/LiTFSI system the viscosity was measured at 25°C. The results, presented in Figure 13, show that the viscosity increases greatly at concentrations above 1.5 M. The samples with low salt concentrations were viscous liquids whereas the samples having 1.5 M salt or more were rubbery and solid-like. They did not experience gravitational flow at 25°C, due to the high viscosity. The final system, PMMA/PC/LiClO\(_4\), changed from being liquid at low polymer contents and low salt contents, becoming a rubber-like gel, at 40 wt% PMMA, and solid-like at 50 wt%.

5.3. Transport properties

The mass transport properties were studied for different types of electrolytes at various compositions. In the first study, the system PPO/LiTf was characterised using a previously developed method. However, for the other electrolytes, the method was gradually developed. These method developments comprise an essential part of this thesis work and are therefore described first. Secondly, the characterisation results in terms of transport properties are presented. Finally, measured and simulated concentration profiles are presented and discussed.
5.3.1. Characterisation methodology

In the first paper, an established characterisation method [28] was utilised. In brief, two experiments are performed to determine the salt diffusion coefficient and the cationic transport number: chronopotentiometry and concentration cell experiments. Separately, EIS is employed to determine the ionic conductivity. The CPM-results are analysed in two ways. The relaxation of the potential at long relaxation times is used to determine the salt diffusivity. It follows the analytical expression below if the diffusion is semi-infinite and the transport properties are constant.

\[
\ln \Delta E_{cell}(t) = \frac{\pi D_s}{L^2} t + k_i
\]  

(41)

The cationic transport number is then calculated using two additional experimental observations, \(m\) and \(dE/d\ln c_s\), according to the following formula:

\[
t_s^0 = 1 - \frac{c_s^0 F \pi^{0.5}}{4} m D_s^{0.5} \left( \frac{dE}{d\ln c_s} \right)^{-1}
\]  

(42)

The parameter \(m\) is the slope of the plot of initial relaxation potential vs. the property \(i\sqrt{t}\) for the CPM experiments, i.e. \(d\Delta E_{init}/d(i\sqrt{t})\). The final parameter, \(dE/d\ln c_s\), is determined from the concentration cell experiments.

In paper I it was demonstrated that the method suffers from low accuracy, especially for \(t_+\), being calculated from three separate experimental observations. Furthermore, it was shown that a large portion of the error is related to the determination of \(D_s\), which was rather inaccurate. The limited accuracy observed could have been related to that particular system, because recently Newman et al demonstrated that the method is accurate by determining the properties for a well-known system [76]. They also pointed out that the method is affected significantly by side reactions, especially at low salt concentrations.

As can be seen in the equations above, the transport properties are assumed to be constant within each experiment. Thus, erroneous results may be achieved unless small perturbations are applied both in the CPM and the concentration cell experiments. In the PPO-study, the former requirement was met, but not the latter. For all concentration cell experiments a reference electrolyte having 2.1 M salt (O:Li 10) was used. Thus, for concentrations deviating significantly from 2.1 M the results may include significant errors. However, the methodology is straightforward and simple to use. If care is taken to overcome the mentioned issues, the method will yield accurate results.

In the other studies, a different analysis approach was employed based on a similar set of experiments. To overcome the issues with property variations within the experiments, the evaluation process was modified. A transport model (described in the
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theoretical section), based on the same theory but fitting the fundamental parameters, \( D_{jk} \), to describe the three experimental observations \( \kappa, \Delta E_{cell}(t) \) and \( \frac{dE}{dc} \). In this case, \( \frac{dE}{dc} \), depicted in Figure 14, represents the concentration cell results and \( \Delta E_{cell}(t) \) is the whole relaxation transient of the CPM experiments.

![Figure 14](image)

*Figure 14.* Concentration cell results for EOPO/LiTFSI(o) together with fits for case 1 (---); case2 (-o-); and the final concentration dependent case3 (---). Additionally, theoretical limits are displayed for an ideal electrolyte having \( t_+ = 0 \) (upper- - -); and \( t_+ = 0.5 \) (lower- - -).

During the analysis process the \( D_{jk} \)'s were firstly fitted as being constant for each experiment, and secondly as being concentration dependent. In the first fitting procedure, one CPM curve was fitted together with the value \( \frac{dE}{dc} \) with one set of \( D_{jk} \)-parameters. From the first results, concentration dependence functions for each parameter could be established. In a second parameter fit, the experimental data for all concentrations was fitted simultaneously with one set of parameters, using the established dependences. For the binary electrolytes the following equation was used to describe the concentration dependence of each \( D_{jk} \).

\[
\log D_{jk} = k_1 + k_2 c_i + k_3 c_i^2
\]  

Thus, to describe three \( D_{jk} \)’s, nine fitting parameters were used and the transport behaviour for all concentrations was then described. Hence, the total number of fitted parameters was greatly reduced in the second fitting procedure. Furthermore, it was observed that the fits for the binary electrolytes were improved by using concentration dependent parameters. In Figure 15 the fit of CPM-curves for several concentrations, achieved using concentration dependent \( D_{jk} \)’s are displayed. As can be seen, the
measured results were very accurately described using the second fitting approach, although the concentration, and consequently also the transport properties, changed from 0.2 to 2 M

![Figure 15. Fitting results(--) together with CPM-curves (-) for the EOPO-LiTFSI electrolyte, using the final concentration dependent model (case 3).](image)

For the ternary PMMA/PC/LiClO₄ system a similar evaluation approach was employed. The model included three additional $D_{jk}$'s. However, only two more experiments were used for the fitting, the solvent diffusion experiments and a second concentration cell. To ensure a high accuracy even though more parameters were fitted, four different CPM experiments were carried out for each sample composition, and fitted simultaneously in the constant parameter case. In the second fit, all data was fitted simultaneously again. The ternary models fitted the data accurately, however, in this case the fits were not improved by using varying $D_{jk}$'s. This may have been caused by the choice of concentration dependence functions. Although a great effort was put into finding proper functions there is probably room for improvement. Nevertheless, the final models were advantageous in that they described the electrolyte transport in the whole studied composition region with one set of parameters.

The evaluation methodology also enabled testing of models and/or model assumptions. The concentration cell results could be used to draw conclusions about the activity factor variation prior to fitting the results with a model. For example, for the EOPO/LiTFSI system, it could be concluded that the parameter $\frac{d\ln f_\ell}{d\ln c}$ had to be larger than zero, i.e. a non-ideal electrolyte, to describe the results, depicted in Figure 14. Thus, by studying the equation describing the electrolyte potential, in the example
eq.11, the maximum value of the potential difference becomes $2RT/F (1-t_\ast)$ if $\frac{d\ln f}{d\ln c}$ is zero. Thus, because the measured values were higher at high salt contents it was realised that $\frac{d\ln f}{d\ln c}$ must be above zero, i.e. the electrolyte behaves non-ideal. This possibility was especially explored in the study of gels, for which several concentration cell experiments were performed. Different model assumptions could be tested prior to performing the fitting. Then the most promising models could be evaluated by fitting. The model resulting in the best fits was assumed to represent the most appropriate model. As indicated by the concentration cell results, better fits were indeed achieved for EOPO/LiTFSI if $\frac{d\ln f}{d\ln c}$ was non-zero in the model. In the study of gel electrolytes, the concentration cell results were used to find three different feasible models that were evaluated and compared by fitting: two ternary models (ternary 1 and ternary 2) and one engineering model. However, the fitting results were inconclusive in that both ternary models yielded similarly accurate fits, although the corresponding transport properties differed. It was realised that complementary experiments, focusing on the solvent gradients, were necessary to with certainty distinguish between the models.

### 5.3.2. Results for different electrolytes

![Figure 16](image)

**Figure 16.** Ionic conductivity at various salt concentrations for the electrolytes: PPO/LiTf 30°C (O), EOPO/LiTFSI 25°C (□), PC/LiClO₄ 25°C (*) and PMMA/PC/LiClO₄ 25°C with 20%(△), 40%(▽) and 50 mol-% PMMA(▼).

The ionic conductivity, $\kappa$, is perhaps the most widely studied electrolyte property, being easy to measure and understand. The first electrolyte studied, PPO/LiTf, resulted in the lowest conductivities, as can be seen in Figure 16. The EOPO/LiTFSI electrolyte resulted in significantly higher conductivities, being similar to those of
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P(EO) based electrolytes[77]. Also the variation with salt content was less pronounced. For the gel studied the conductivity varied significantly with both salt and polymer content. As can be seen the polymer caused a strong effect on \( \kappa \). An increase of the polymer content resulted in a very pronounced decrease of the conductivity. For the solid-like gels with 40 wt-% PMMA, the conductivity was reduced by more than one order of magnitude as compared to the liquid pre-cursor electrolyte. The liquid electrolyte resulted in the highest conductivities, as expected.

All electrolytes experienced a conductivity maximum at intermediate salt concentration. This is a feature of electrolytes in general, and polymer electrolytes in particular [30]. The behaviour can be explained as a trade-off between increasing number of charge carriers, increasing ionic interactions and increased microscopic viscosity (reduced chain mobility) due to ionic cross-linking. The first should cause an increase, being proportional to concentration, whereas the two latter may result in non-linear decrease of the conductivity, as salt concentration increase. The position and significance of the maximum varied between the electrolytes. For the PPO/LiTf the maximum was situated at approximately 1.5M, and was very pronounced. For EOPO/LiTFSI, it occurred at 0.8 M, and for the PMMA/PC/LiClO\(_4\) system it shifted from 0.5 M for the pure liquid, to 0.2 M for the electrolyte having 50% PMMA.

![Figure 17](image)

**Figure 17.** Ionic conductivities for the system EOPO/LiTFSI (- - - ) at 298K; for PPO/LiTf (-x-) at the indicated temperatures, and at iso-viscosity(T-T\(_g\)=100K) (-o-).

For the PPO/LiTf electrolyte the conductivity was measured at various temperatures, as displayed in Figure 17. With \( T_g \) at hand, the effect of segmental mobility of the polymer could be decoupled by studying the conductivity at iso-viscosity, \( \kappa^\theta \), i.e. at
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constant $T-T_g$. The initial increase of $\kappa^0$, up to 1.9 M (O: Li 12), is explained by the increased number of charge carriers. However, the decrease above the maximum must then be related to ionic interactions, described by $D_+\kappa$ in the models, causing gradually increasing ionic aggregation. For the EOPO/LiTFSI and PC/LiClO$_4$ the model parameter $D_+$ was studied in detail. It was realised that increasing ionic interactions caused the decreasing conductivity, observed above the maximum. For the EOPO system there was also an influence from increasing cation-polymer interactions, caused by the reduced segmental mobility. Thus, for the polymer electrolytes there were two significant conductivity-decreasing effects present: influence from ionic interactions and influences from ionic-cross linking reducing the segmental mobility. Furthermore, they seemed to be equally important.

![Figure 18](image.png)

**Figure 18.** Salt diffusion coefficient at various salt concentrations for the electrolytes: PPO/LiTf 85°C(○); EOPO/LiTFSI 25°C c-dep. model (□); PC/LiClO$_4$ 25°C c-dep. model(—); and PMMA/PC/LiClO$_4$ 25°C ternary 2 model for 20%(-△-), 40%(-▽-) and 50 mol-% PMMA(-▽-).

Similar to the conductivity, the salt diffusion coefficient, $D_s$, differed significantly between the studied systems. In contrast to the conductivity, it experienced a decrease with salt concentration for all electrolytes. In this case it is the interactions between solvent (polymer) and both ions that control the diffusivity. As a consequence, the reduction in segmental mobility was reflected in stronger interactions and lower values of the corresponding $D_{jk}$’s. As can be seen in Figure 18, a dramatic decrease was observed as polymer content increased for the gel. This can be explained by ion-polymer interactions, but also by the present solvent-polymer interactions.

Figure 19 shows the cationic transport numbers, $t_+$, of the various electrolytes as a function of salt content. The liquid electrolyte resulted in the highest values, with $t_+$...
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around 0.3, varying little with salt concentration. All polymer electrolytes experienced quite low $t_+$, decreasing with $c_s$, with values around 0.1 or lower for concentrations above 0.5 M. This is a common behaviour for polymer electrolytes based on ether polymers and is explained by the interaction between the cation and the ether oxygen of the polymer chain. The anion on the other hand is believed to experience little interaction with the polymer. Due to the reduction in segmental mobility with increasing concentration, $t_+$ is reduced. The gel electrolyte experienced quite low $t_+$-values and a very small influence from salt content. It was observed that the addition of even a small amount of PMMA to the liquid PC/LiClO$_4$ caused a dramatic reduction of the cationic transport number. This suggests that the interaction between cations and the polymer is strong and that the cations preferentially are associated to the PMMA.

![Figure 19](image-url)

**Figure 19.** Cationic transport number at various salt concentrations for the electrolytes: PPO/LiTf 85°C(O); EOPO/LiTFSI 25°C c-dep. model (□); PC/LiClO$_4$ 25°C c-dep. model(—); and PMMA/PC/LiClO$_4$ 25°C ternary 2 model for 20%(△), 40%(▽) and 50 mol-% PMMA(▼).

For the PPO-system negative values were obtained at some concentrations. These are not included in the figure. According to the definitions used in this thesis $t_+$ represents the fraction of the current carried by the cation, and can only have values between zero and one. However, in the PPO-study a different definition was used following from the different methodology, allowing negative values. There, $t_+$ was interpreted according to Spiro’s definition [78] to represent the net number of moles of cations crossing a reference plane during the passage of one mole of charge, in a situation where no concentration gradients are present. Thus, a negative $t_+$ would indicate that the charge carriers are ionic clusters rather than separately solvated ions. However, the method used in that study was susceptible to propagation of measurement errors. Furthermore, it has recently been discovered that side-reactions may cause erroneous results using
this method [76], especially for dilute samples. For the samples above 2 M values around –0.7 were achieved, indicating ionic aggregation. For these reasons it is believed that the negative numbers achieved were a product of method errors rather than being the true values.

The variation of the salt activity factor, expressed as \( \frac{d \ln f}{d \ln c_s} \), was calculated from the concentration cell results and is depicted in Figure 20 for the various electrolytes. For the PC/LiClO\(_4\) electrolyte \( \frac{d \ln f}{d \ln c_s} \) is almost zero up to 0.5 M, indicating that the liquid behaves almost ideally. However, for concentrations above 0.5 M the parameter increases and the electrolyte clearly is non-ideal above 1 M. The polymer electrolytes also experienced significant non-ideal behaviour. The gels and the EOPO/LiTFSI system both resulted in positive values of \( \frac{d \ln f}{d \ln c_s} \). Interestingly, the EOPO-system experiences a change from negative to positive values, indicating a minimum for \( f_s \).

This has been observed previously for binary polymer electrolytes. From literature data [32,33] \( \frac{d \ln f}{d \ln c_s} \) could be calculated for similar PEO-based systems. The resulting values agree well with those observed here for the EOPO-system. The PPO-system deviated from the others in that it experienced negative values in the whole concentration range, indicating a constantly decreasing \( f_s \).

For the gel electrolyte system, the concentration cell results indicated that it was necessary to take activity factor variations with both salt and solvent concentrations into account. The variation with solvent, expressed as \( \frac{d \ln f}{d \ln c_{sol}} \), was thus included in the models. According to the fits it was negative, around (-4) at low salt
concentrations, increasing to around (–2) for samples with 1M salt, indicating that the activity factor decreased with solvent concentration.

For the gel electrolytes, three additional transport properties were determined: solvent diffusion coefficient, $D_{sol}$, solvent transport number, $t_{sol}$, and salt drag number, $d_s$.

![Figure 21. Measured solvent(PC) diffusivity for various gel compositions: 30 (■), 40 (◆) and 50 mole-% (▲) depicted together with fits for model ternary 2 (---). Literature data[79,80] for the liquid PC/LiClO4 system are included (*) as well as the polynomial fits (---) used for model fitting.]

As can be seen in Figure 21, the PC-diffusivity decreases significantly with both salt and polymer concentration. The decrease seems to become worse as the polymer content increases. Comparing the results with the literature values for PC/LiClO4, indicated in the figure, it can be seen that the PC-diffusivity only decreases slightly as PMMA is added to the liquid. This indicates that the interactions between solvent and polymer are initially weak, but increase as more polymer is added.

The solvent transport number, $t_{sol}$, is best interpreted using Spiro’s definition of a transport number. It can be thought of as the drag of solvent appearing during the passage of current. A positive value means that the net flux of solvent is in the direction of the ionic current, i.e. with the cations. The salt drag coefficient, $d_s$, is defined for a situation where only solvent concentration gradients are present in the absence of ionic current. It represents the net flux of solvent as one mole of salt diffusing across a unit area.

The values determined for $t_{sol}$ and $d_s$ experienced significant discrepancies between the two evaluation models, indicating that they were ill determined from the experiments.
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However, some trends could be seen. $t_{sol}$ was negative for all concentrations using both models. This suggests that the solvent travels mainly with the anions, i.e. towards the anode of a cell, in the absence of concentration gradients. Thus, during discharge a solvent concentration profile will evolve due to the drag.

For $d_s$, the results of the two ternary models showed better agreement. Negative values in the range of -0.2 were found, indicating that the salt travels against the solvent diffusion. This behaviour can be explained by the negative values of $\frac{\text{dln}f}{\text{dln}c_{sol}}$ that were observed. A positive gradient of solvent will then result in a negative salt activity gradient, causing salt diffusion in the direction against the solvent diffusion. $d_s$ increased in magnitude as salt and polymer content increased. However, the two final parameters should be confirmed before drawing too many conclusions about the mass transport in the gel. This can be achieved by performing additional experiments, measuring the solvent concentration profiles.

5.3.3. Measured and simulated concentration profiles

A great advantage of using modelling as a tool to determine the transport properties, is the fact that the model is validated and accurate model parameters ($D_{jk}$’s) are also achieved. The models can be used to simulate the concentration or potential profiles in the electrolyte, and the development of these with time under different operating conditions.

![Figure 22. Concentration profiles in EOPO/LiTFSI measured with Raman(o and x) and modelled at the positions: a) “point zero”, b) +20 µm, c) +40 µm. Three different model cases are plotted: constant parameter (—); constant parameters with activity factor variations (...); final model (—). The vertical dotted line indicates the cathodic current cut-off time.](image)

In paper III, the characterisation method and the binary transport model were verified for the EOPO/LiTFSI electrolyte. Utilising in situ Raman spectroscopy, the concentration profile was measured during polarisation-relaxation experiments similar to the CPM experiments used in the characterisation. The model predictions were compared with the Raman results for several model cases. The three cases were: case 1, constant $D_{jk}$’s assuming ideal solution, i.e. not including the activity factor; case 2,
constant parameters including the activity factor; and case 3, concentration dependant properties including the activity factor. As can be seen in Figure 22, the results from the final case agreed very well with the measured concentrations. The differences between the model cases were significant only in the vicinity of the electrode.

Although case 1 and 2 differed significantly for the electrochemical results in the transport property characterisation, they did not differ much in predictions of the concentration changes. This indicates that the inclusion of the activity factor in case 2 mainly affected the electrochemical potential. From these results it could be concluded that direct concentration measurement, such as Raman, is insufficient for a full characterisation of the properties necessary to describe the electrochemical behaviour of an electrolyte. Furthermore, concentration results alone cannot be used to deduce which transport model should be used. However, the combination of Raman, electrochemical characterisation techniques and modelling prove to be a very versatile combination of techniques for studying mass transport in electrolytes. Furthermore, the good agreements seen between simulations and Raman measurements certainly corroborate the validity of the transport property characterisation method, in terms of model and transport properties.

Once a transport model with parameters has been established for an electrolyte it is possible to study the concentration changes, i.e. the concentration polarisation, in detail through simulations. To better visualise the concentration polarisation and understand the transport in the electrolyte, concentration profiles for the EOPO/LiTFSI electrolyte were simulated for a polarisation experiment and the results are depicted in Figure 23.
Figure 23. Simulated concentration profiles for EOPO/LiTFSI with a cathodic current density of 0.5 A/m² during 60 minutes and a following relaxation. The profiles displayed represent a) 10, b) 30, c) 60, d) 65, e) 90 and f) 240 minutes.

Close to the electrode the salt concentration starts to drop as soon as a cathodic current is applied due to non-unity $t_+$. The concentration gradient at the electrode surface is related to $D_s$ and $t_+$ according to:

$$
\frac{dc_s}{dx} \bigg|_{x=0} = -\frac{i(1-t_+)}{FD_s}
$$

(54)

During the relaxation the concentration profile slowly flattens out due to salt diffusion from the bulk towards the surface. In Figure 22c) it can be seen that the measured concentration continued to decrease after the current was stopped. This phenomenon is opposed to the expected immediate increase, typical for ordinary diffusion. However, using the model it could be explained. Studying the simulated concentration at positions grater than 40 µm the phenomenon can also be seen. According to the model, the unexpected behaviour was caused by a bulk flux compensating for the decreasing volume, occurring due to decreasing salt content and density changes. Thus, the observation was explained by having an accurate model.

In the gel study transport simulations were also performed. In this case, the transport property characterisation resulted in two different models, being equally accurate in describing the experiments but resulting in different transport properties. In order to understand the differences of the models, concentration profiles were simulated. The
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Simulation resembles the situation for a typical Lithium-ion battery under discharge, using the characterisation results for a 40% PMMA gel with 0.95 M salt. In Figure 24, simulated concentration profiles for the salt and for the solvent are displayed. The models yielded similar results for the salt concentration profile although the transport properties differed.

Figure 24. Concentration profiles for a gel with 40 mol-% PMMA and 0.95 M salt after a 1A/m² (~C/10) polarisation after various relaxation times. The profile of the salt (a) and solvent (b) are displayed using the models ternary 1 (grey) and ternary 2 (black) at the polarisation times: 60 s (-), 600 s (- -) and 3600 s (- - -). The direction of the ionic current is also indicated.

The profiles of PC were on the other hand quite different for the models. The first ternary model yielded a small solvent gradient, gradually increasing with time. The model ternary 2 resulted in a significant solvent concentration profile during the initial part of the polarisation. As the transport approached steady state, the solvent profile diminished almost completely for that model. From these results, it is clear that the models with parameters differed mainly in the predicted solvent transport. It was previously seen that the most significant difference in the characterisation results was present in $t_{sol}$ and $d_s$. These results indicate that the characterisation method should be complemented with experiments yielding solvent profiles, e.g. in-situ Raman spectroscopy. Such results would distinguish between the two models and improve the determination of the two final transport properties.

The appearance of a PC-profile is however interesting and an explanation is in place. The observed initial increase of the solvent profile can be explained by $t_{PC}$, which was significantly larger for ternary 2 then for ternary 1. Initially, it is the solvent transport number that causes the solvent flux, i.e. the solvent is dragged by the migrating ions. The observed decrease is related to $d_s$, according to the following explanation. If $t_+$ is small the migration is dominated by the anions. Consequently, a significant back diffusion of salt will occur at steady state. The salt diffusion also drags solvent. For the model ternary 2 the property $d_{sol}$ was equal to $t_{sol}$, which means that the total solvent
drag at steady state is close to zero. Thus, the initial solvent profile will relax by diffusion after some time. This example also serves to demonstrate the advantage of using modelling as a tool in the studies of electrolyte mass transport.

Finally, the introductory example showing the influence of mass transport, presented in Figure 2, can now, with the transport properties at hand, be explained. For the tested electrolytes the salt diffusion coefficient decreased significantly, about one order of magnitude, when going from the liquid to the gel, and from the gel to the polymer electrolyte. Furthermore, the cationic transport number decreased somewhat when going to the gel and polymer. With the low salt diffusion coefficient for the gel and polymer electrolyte and the low transport number large concentration differences will occur during the discharge, both in the pores and in the bulk of the electrolyte. After a short time of discharge, salt depletion will occur at the positive electrode limiting the reaction rate. After that, the maximum current of the cell is controlled by the rate of salt diffusion, as dictated by eq.54. Thus, the poor discharge performance of the gel and the polymer electrolyte is explained by a low salt diffusion coefficient in combination with low cationic transport number.

### 5.4. Electrolyte in a porous battery electrode

In two of the papers (IV and VIII) electrochemical impedance spectroscopy was employed to characterise porous battery electrodes. Two different approaches have been used to study and model the impedance of the electrodes. First, in paper IV, a novel impedance measurement method was evaluated using the conventional porous electrode theory. The equations were solved to suit the new method and used to fit the results, however, concentration changes in the electrolyte were neglected. Second, in paper VIII, traditional impedance was measured and the model was developed by implementing the concentrated electrolyte theory.

The electrochemical behaviour of a porous battery electrode is determined by several factors and processes: the macroscopic structure of the electrode; the electrode kinetics of the material; the double layer charging; the mass transport and potential drop in the electrode material and in the electrolyte. In both studies, the impedance response was evaluated using model fitting. The models were based on the basic equations describing the physical and chemical processes. In this thesis it is the influences from electrolyte mass transport on the impedance that is of interest. However, the other processes must be modelled properly. Therefore, the two impedance studies were performed together with co-workers having detailed knowledge about the other processes, and a detailed analysis of the other processes can be found in their Ph.D.-theses [42, 81].

In paper IV the experimental methodology was developed. Two impedances were measured, using references in front of and behind the studied electrode, and the difference, denoted ”differential impedance”, $Z_{\text{diff}}$, could be studied. In addition, the
governing equations were derived for the “differential impedance”. The equations were based on previously used theory for electrode kinetics and solid phase diffusion. The electrolyte was in this study greatly simplified. It was treated as being a simple resistor, in order to achieve an analytical solution for the impedance expression. One of the results was the theoretical insight that the effective electrolyte conductivity could be determined from the differential impedance without knowing the other processes. The difference between the real axis intercepts of $Z_{\text{diff}}$ at infinitely high and low frequency is directly related to the effective conductivity according to eq.44. This is demonstrated in Figure 25. The result is valid for any electrode experiencing a limited capacity behaviour, e.g. any insertion electrode.

![Figure 25](image_url)

**Figure 25.** Simulated differential impedance using parameters typical for a porous LiMn$_2$O$_4$ electrode with a high solid phase conductivity using different kinetic parameters, $R_{\text{ct}}=3.67$ (—) and 36.7 m$\Omega$ m$^2$(— - — —), but the same effective electrolyte conductivity.

Furthermore, it was realised that electrodes limited by the solid phase conductivity resulted in a different differential impedance spectrum than electrodes limited by the electrolyte conductivity. Thus, by studying $Z_{\text{diff}}$, it is possible to distinguish between voltage drop in the electrolytes and voltage drop in the solid phase. This cannot be accomplished using traditional impedance, using a reference located between the working and counter electrode.

In order to test the first theoretical finding experimental results were conducted for two metal hydride electrodes, having different thicknesses and the results are displayed in Figure 26. The low frequency intercept of the differential impedance could not be evaluated from the Nyquist plot. This means that the effective conductivity could not be measured directly from the real axis intercepts. Instead, the effective conductivity was determined by fitting the impedance model. As can be seen in the figure, accurate fits could be achieved and the effective conductivity was determined for both electrodes at several states of charge. The resulting effective conductivity values were
RESULTS

compared with those predicted using Bruggemans equation. It was concluded that the fitted conductivity agreed well for the both electrodes, although the fitted value for the thicker was slightly higher than the predicted. Thus, the effective conductivity could be determined from the measurements. However, the simple approach, taking the difference of the real axis intercepts, could not be utilised due to the difficulties in measuring impedance at sufficiently low frequencies.

The differential impedance was also measured for a LiMn$_2$O$_4$-based Li-ion battery electrode using a common Li-ion liquid battery electrolyte. In this case, the measured effective conductivity was significantly lower than that predicted by Bruggemans equation, the bulk conductivity and the porosity. This could have been related to poor backside measurements, due to bad electrolyte contact through the holes in the current collector. However, according to a recent publication it could also be explained by failure of Bruggemans equation, observed for electrodes with odd-shaped particles, e.g. flakes [82].

![Figure 26. Impedances measured at the front(□) and at the back(○) of the electrode, together with the differential impedances(◇) of two metal hydride electrodes with different thickness, (a) 0.55 mm thick (b) 1.65 mm thick. The impedance was collected with 10 samples per decade. Included in the figure are also curves for the model fit(—).](image)

An advantage of measuring both front and backside impedances worth mentioning is that the investigation of electrode kinetics is greatly improved. The methodology improves the resolution of the effects of current distribution from those related to the local electrode kinetics. However, this is not the focus of the present thesis and those
RESULTS

interested should consult paper IV, or the theses by Anton Lundqvist [81] or Anna-Karin Hjelm [42], where the issue is further discussed.

In paper VIII traditional impedance experiments were utilised and the model was developed to include: concentrated electrolyte mass transport, particle size distribution and an empirical relation between electrode equilibrium potential and state of charge. Because the concentration in the electrolyte phase was included in the model a numerical solution approach was necessary to employ. Impedance was measured for identical electrodes in three of the previously characterised electrolytes, a liquid (PC/LiClO₄), a gel (30% PMMA/PC/LiClO₄) and a polymer (EOPO/LiTFSI), having significantly different transport properties. The ionic conductivity and salt diffusion coefficient were known to decrease about one order of magnitude when going from liquid to gel, and from gel to polymer.

Significant differences were observed in the measured impedance as a consequence of the different transport properties, as depicted in Figure 27. The magnitude increased when going from the liquid to the poorer conducting gel and polymer electrolytes. The frequency behaviour, i.e. the phase angle, also differed. The high frequency semicircle, being related to charge transfer and double layer charging, shifted to lower frequencies when going from liquid to gel and from gel to polymer. A distinctive feature of the polymer electrolyte was observed at low frequencies. The capacitive behaviour, related to solid phase concentration, was suppressed in comparison with the other electrolytes, even though the impedance was measured at lower frequencies. The choice of electrolyte clearly affected the impedance result of the electrode, indicating the importance of modelling it properly.
RESULTS

Figure 27. Experimental impedance results(*) and model fits for: combined mass transport control (-o-); solid phase control (-∇-); and electrolyte control(-□-), using a LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ electrode at 48% SOC in three different electrolytes: a)PC/1M LiClO$_4$; b) 30% PMMA/PC/1M LiClO$_4$; and c)EOPO/0.8M LiTFSI.

To further investigate the influence of the electrolyte transport, the model was fitted to the results for three cases. The cases differed in the solid and electrolyte phase diffusivities. In the first case, the salt diffusion coefficient, $D_2$, was fixed to a large value, and the solid phase $D_1$ was fitted. Thus, the electrolyte diffusion was rapid and the diffusion limitations appeared only in the solid phase i.e. solid phase diffusion control. Secondly, the $D_1$ was fixed to a large value and $D_2$ was fitted, i.e. electrolyte transport control. Thirdly, a case of combined control was evaluated by fitting $D_1$ and using the previously determined $D_2$-values.

For the liquid electrolyte, case one and three both resulted in about equally accurate fits as can be seen in Figure 27a), whereas case two resulted in a poor fit and is not depicted. The main difference in the fits of case one and three was located in the low
frequency region, where solid phase and electrolyte phase transport are present. A slight increase in the real part occurred when salt diffusion was also considered. This additional low frequency impedance is caused by the concentration gradients present in the electrolyte at low frequencies. These gradients are present due to the non-unity cationic transport number, making electrolyte diffusion appear. Studying the results for the gel similar trends were observed, however, being more pronounced. Again, the second model case could not describe the impedance results. The fits resulting from case one and three deviated even more at low frequencies for the gel, indicating a pronounced influence from electrolyte transport. The differences demonstrate that the electrolyte phase transport is important to consider.

As a consequence of the additional impedance present when taking $D_2$ into account higher values of $D_1$ were achieved from the fits, especially for the gel. However, it is believed that solid phase diffusion should be independent of electrolyte; hence $D_1$ should be equal for the three electrolytes. It was seen that the $D_1$ results agreed significantly better for the fits where salt diffusion was taken into account. This result, together with the fact that the combined control case yielded the best fits, highlights the importance of taking electrolyte phase transport into account if electrode properties such as $D_1$ are of interest, as in ageing studies.

For the polymer, the accuracy of the fit, using combined control and the pre-determined electrolyte properties indicated in Figure 27c) as circles, was good. However, a very accurate fit could be achieved if $\kappa_2$ was fixed to a value being 1/10 of the previously determined. There are two possible reasons for this discrepancy: (1) it could be related to a poor wetting of the electrode, resulting in significantly lower effective porosity and consequently lower $\kappa_2^{\text{eff}}$; (2) it could also be related to a different value than 1.5 of the exponent in Bruggeman’s equation, a matter that has been discussed recently [82]. Using the lower value of $\kappa_2$ it was seen that the salt diffusion control case resulted in significantly better fits than the other cases. Also, the fitted value of $D_1$ was unreasonably low for the solid phase diffusion control case, being almost two orders of magnitude lower than the results using the other electrolytes. This result suggests that the polymer electrolyte impedance is controlled by electrolyte diffusion in the frequency range studied. The result was not unexpected because the salt diffusion coefficient is very low for the polymer electrolyte, whereas the solid phase diffusion coefficient should remain unaltered. In order to determine both $D_2$ and $D_1$ accurately for electrolytes with very low salt diffusivity, the impedance should be measured at even lower frequencies, allowing for the expected capacitive behaviour to appear. However, accurate and repeatable measurement of impedance at frequencies below one mHz is both tedious and difficult.
6. DISCUSSION

The discussion will start with a short remark on electrolyte stability measurements, which, in my opinion, remains difficult to measure and interpret properly. In the complex research field of organic electrochemistry it is generally accepted that all experimental parameters affect the reaction paths and rates, i.e. electrode, additives, temperature etc. From this point of view it is almost ridiculous to state that the stability results, achieved using other systems than the real battery, yield the true stability limits of an electrolyte in a battery. However, as demonstrated in this thesis, voltammetry can be used to compare the influence of electrolyte components if a suitable electrode material is used. For example, the influences of varying the salt and polymer could be studied. Another example is the influence of moisture. Although the study was small, compared to the vast efforts made by other groups in the field, I believe that I contributed by achieving results using some general electrochemical tools. For example, the use of sweep rate variation to investigate the reaction type might be helpful. The work performed in this thesis on stability is merely a first step in evaluating the use of electrochemical methods to study electrochemical breakdown. It is difficult to say whether the trends observed are valid in a real battery. Additional investigations, studying the chemistry of the breakdown reactions on both platinum and battery electrodes, may help to unravel these issues.

The electrolyte mass transport is in this thesis described using the concentrated electrolyte theory, based on the Stefan-Maxwell transport theory originally developed to describe gases. The Stefan-Maxwell theory is founded on a simple physical model, utilising friction parameters to describe the intermolecular interactions. In the theory these frictions, or interactions, are described by the inverses of diffusivity parameters, $D_{jk}$’s (as described in the theoretical section). Thus, large $D_{jk}$’s mean weak frictions/interactions. The concentrations of the two species considered are also included in the expression for the friction, resulting in a higher friction as concentration increases. According to the results, this theory could describe the transport in all electrolytes accurately. However, it was observed that the $D_{jk}$-parameters varied significantly with electrolyte composition, especially for the electrolytes based on polymer. Ideally, the theory and model should describe the change of each friction, making the $D_{jk}$’s nearly constant. The results thus indicate that the Stefan-Maxwell theory is not ideally suited for these electrolytes. This is not surprising, considering the fact that the theory was originally developed to describe the friction between gas molecules. The situation in a liquid or polymer-based electrolyte is quite different from a gas. Instead of separate gas molecules at high velocity, the liquid electrolytes comprise rather slow moving ions, situated in solvation shells of solvent molecules. For polymer electrolytes the situation is even further removed from gases, with ions solvated through co-ordination to certain regions of a polymer. From
this point of view it is rather surprising that a gas transport theory actually describes the electrolyte transport quite well.

In the results section it was concluded that two conductivity-reducing mechanisms were present for polymer electrolytes: (1) ionic interactions and (2) decreasing segmental mobility. To improve the concentrated electrolyte theory for polymer (or polymer containing) electrolytes a description of the variation of segmental mobility could be included. It should then only affect the $D_{jk}$’s related to the polymer. The other friction parameters, for example inter-ionic, should be unaltered. One possible description is the William-Landell-Ferry theory (WLF), describing the local mobility of a polymer chain [84]. It is already utilised to describe the great variation in conductivity with temperature (or salt concentration), observed for many amorphous polymer electrolytes. The conductivity is then described using the VTF-equation, eq.50, which is a special case of the WLF-theory. In the results section, it was employed for the PPO/LiTf system in order to evaluate if the electrolyte behaved properly. Using the VTF-equation, the inherent conductivity, $\kappa^0$, which is decoupled from segmental mobility, is calculated from the measured conductivity. In the equation, $T^0$ should be equal to $T_g$, which is measurable, plus a constant. The proposed improvement is that the polymer related $D_{jk}$’s could be described similar to $\kappa$. Doing so, the VTF- or WLF-equation would be employed to calculate the $D_{jk}$’s from $T_g$, the VTF- or WLF-constants and the $D^0_{jk}$’s. The $D^0_{jk}$’s would then only relate to intermolecular interactions and might be constants. However, this approach requires knowledge of the VTF- or WLF-constants. For the WLF-equation, a universal set of constants exists if $T^0$ is assumed to be equal to $T_g$ [84], making it particularly interesting. To test this approach a polymer electrolyte would first have to be characterised with respect to glass transition temperature at several compositions. Then, transport property characterisation results could be modelled to retrieve the $D^0_{jk}$-parameters. However, this is a task for future studies.

An advantage of the physical basis of the transport theory is that it allows for microscopic interpretations, studying the intermolecular interaction described by the $D_{jk}$’s. However, as pointed out in the previous paragraph, the polymer related $D_{jk}$’s should be interpreted carefully. In the presently used theory, they are influenced by segmental mobility variations, related to salt concentration. Thus, a decrease in $D_{jk}$ with concentration can be caused by two effects: (1) a real increase in the interaction and/or (2) a decrease in segmental mobility caused by physical cross-linking. Nevertheless, knowing this limitation an interpretation of the $D_{jk}$’s in terms of molecular interactions increases the understanding. This is exemplified for the EOPO/LiTFSI polymer electrolyte, having three interactions: (1) inter-ionic, (2) cation-polymer and (3) anion-polymer. Firstly, the results for this electrolyte indicated that the friction between anion and cation is significant and increase with salt concentration. This friction should remain unaffected by variations of segmental mobility. The increasing cation-anion friction could thus be interpreted as the ions
experiencing less separation, approaching ion pair formation and interacting stronger, as salt concentration increases. With the theoretical approach employed, full ion pair formation would correspond to a very low $D_{+-}$, i.e. a very strong interaction or friction. The concentrated electrolyte theory handles the change from a fully dissociated salt to electrolytes with ion pairs as the main specie with the parameter $D_{+-}$, and can thus describe intermediate stages of solvent separated ions. Analysing the conductivity results, in terms of contributions from the different friction parameters, it was realised that the anion-cation friction became increasingly important with increasing concentration. At 0.5M the friction between the ions is responsible for 20% of the total friction. Above 1M the ionic interaction becomes dominant and controls the resistivity. A similar increase in the importance of the anion-cation friction was also observed for the liquid electrolyte PC/LiClO$_4$, indicating that it is a general electrolyte phenomenon and not specific for polymer electrolytes. Secondly, it was seen that the interaction between anion and polymer was weak and unaffected by salt concentration. This indicates that the anions experience little or no coordination to the polymer and that they are transported via a mechanism without influences from the polymer. Finally, the cation-polymer was also significant, and also increased with salt concentration. This increase was expected since the cation transport is often strongly coupled with the mobility of the ether-oxygen of the polymer in this type of system [85]. The mobility generally decreases with increasing salt content due to physical cross-links. Hence, increasing the salt content reduces the mobility, which appears in the model as decreasing cation-polymer diffusivity, $D_{0+}$.

A similar reasoning could be employed for the liquid electrolyte. For the gel on the other hand, the situation is somewhat more complex, having six interaction parameters. Nevertheless, some conclusions could be drawn. The dramatic decrease of $t_+$, when adding polymer, could be explained. It was related to the friction between cation and polymer. Furthermore, the decrease in $D_+$, as the polymer content increased, was explained by a combination of increasing frictions between cation-polymer and anion-solvent. The molecular explanations possible to draw from the $D_{jk}$’s should be viewed as suggestions and not as facts. Being model parameters, they can vary significantly if model assumptions are changed. This was seen in the gel study, where a similar model, based on different assumptions, yielded equally accurate fits but significantly different $D_{jk}$’s. Nevertheless, as demonstrated, the use of a model that allows for molecular interpretation certainly helps in the understanding of the transport.

In this work, different transport property characterisation methods have been utilised, including both different electrochemical methods and also a spectroscopic method. It was seen that the spectroscopic method, yielding the concentration profile as a function of time, was an effective tool in understanding the transport processes. The method may be used to study the magnitudes of concentration differences and relaxation processes. However, in case a full characterisation of the transport
properties is of interest, the limited positioning accuracy may present problems. More importantly, methods based on measuring concentration profiles or gradients yield no information about the thermodynamic activity factor or the electrochemical potential. It is in this respect that the electrochemical methods are advantageous. In the electrochemical methods the measured potential is related to the activity and the electrolyte potential. Thus, apparent diffusion coefficients, and possibly also transport numbers, can be determined from spectroscopic methods, such as in-situ Raman. However, electrochemical methods are necessary to determine conductivity and activity factor variations.

The different electrochemical methods utilised resulted in different descriptions of the transport. In the transport property characterisation studies a combination of CPM and concentration cell experiments were employed. The analysis procedure was improved significantly in the second study. However, there were also minor modifications applied to the experiments in the later studies. In the second study, and the following, the analysis was based on numerical model fitting instead of analysing the results more directly using analytical solutions. A great advantage of using numerical model fitting was that the variations in the transport properties within each CPM experiment, due to the produced concentration gradients, could be handled in the analysis. Additionally, model modifications could be easily evaluated using this method. Also, simulations could be performed to visualise the consequences of having a particular set of transport properties, using the evaluation model. The modelling method was also used to characterise ternary gels. For this system, this was the only feasible approach, because the governing equations are difficult to solve analytically.

Impedance was employed to characterise the behaviour of porous electrodes. The electrolyte transport is then one part of the full model, also including electrode kinetics and solid phase transport. In paper IV, the effective conductivity of the electrolyte in the pores was determined from the impedance results. In paper VIII, a full implementation of the mass transport was evaluated. It was demonstrated that the electrolyte transport influenced the impedance significantly. Moreover, in both cases transport properties were determined through impedance model fitting. It was seen that conductivity and salt diffusion coefficient could be fitted, but not all properties. However, that was not the purpose of the studies.

There is a major difference between impedance and the CPM-based method. In the latter, the system is studied under conditions where no electrode reactions occur. Impedance, on the other hand, deals with a system with both reactions and mass transport. Thus, impedance is a somewhat more interesting method in that it resembles a battery in use. Influences of concentration changes on the electrode kinetics are also present. However, the method requires an accurate description of the electrode kinetics and solid phase transport to enable studies of the electrolyte transport. In the final paper it was shown that the electrolyte influenced the impedance for liquid, gel and
polymer electrolytes. For the polymer electrolyte the electrolyte transport dominated the low frequency behaviour, for the gel it was important and for the liquid the influence was small but present. It was also seen that the fitted solid phase diffusion coefficient was affected by the electrolyte transport, varying less between the studied electrolytes if the electrolyte transport was considered.

One of the observations from the first impedance study was that the effective ionic conductivity in the lithium ion electrode was significantly lower than the value predicted by Bruggemans equation. In the final study, a similar observation was made for the polymer electrolyte case. Similar results have also been observed in previous impedance studies [48]. One explanation could be the influence from odd shaped particles. According to a recent study, the exponent in Bruggemans equation may be more than twice as high as the commonly used value of 1.5, for electrodes with disc-shaped particles. With a porosity of say 50% the difference is large: the compensation factor becomes 0.35 if the porosity is raised to 1.5; and 0.12 if raised to 3.0. Another hypothesis is that the porosity decreases when the electrode is wetted with electrolyte. Having a binder in the electrode that swells in the electrolyte can cause this. To study this discrepancy between measured and predicted effective conductivity in detail, and improve the understanding of the transport in the pore electrolyte, it would be interesting to combine the model of the final paper and the experimental method in the first, however that remains for future work.

Finally, there is an important difference between aqueous and non-aqueous electrolytes in the behaviour of the activity factor, related to the thermodynamics. In all of the investigated electrolytes the activity factor of the salt varied significantly from unity, as determined from concentration cells. The variation of the activity factor, $\frac{\text{d}\ln f}{\text{d}\ln c}$, affects the driving force for transport and is thus important to consider. For the electrolytes studied in this thesis $\frac{\text{d}\ln f}{\text{d}\ln c}$ was both positive and negative. Also, the activity variation was very pronounced at high polymer contents. A positive value of $\frac{\text{d}\ln f}{\text{d}\ln c}$ indicates that the mean salt activity factor, $f_s$, increases with concentration. This is a somewhat unexpected behaviour. For water-based electrolytes the activity factor generally decreases from unity at low concentrations to lower values at high salt contents, i.e. negative $\frac{\text{d}\ln f}{\text{d}\ln c}$. Thus, zero or negative $\frac{\text{d}\ln f}{\text{d}\ln c}$ were expected, and not positive. However, theoretically $f_s$ may experience values above unity, meaning that the activity is higher than the concentration. With positive $\frac{\text{d}\ln f}{\text{d}\ln c}$ the activity gradient is larger than the concentration gradient, causing an increased diffusion flux. This is also reflected in the theory.

For the gel the situation was even more interesting, with two $\frac{\text{d}\ln f}{\text{d}\ln c}$, one related to salt and one to solvent concentrations. According to the results, the first was positive and the second negative. This means that the salt activity increases with salt concentration but decreases with increasing solvent content. For the gel the activity factors impacted additional transport processes. As can be seen in the theoretical
section, the solvent diffusion coefficient, $D_{sol}$, and the salt drag factor, $d_s$, are related to $\frac{d \ln f_s}{d \ln c_{sol}}$. In the results section simulations were used to demonstrate the concentration profiles in a gel (Figure 24). Significant solvent profiles developed initially, using the model *ternary 2* with it’s corresponding transport properties. This was explained by the negative values of $d_s$ determined for the gel. Looking at the equation for $d_s$, eq.29b, it can be seen that the negative values probably were caused by the negative $\frac{d \ln f_s}{d \ln c_{sol}}$. A negative $\frac{d \ln f_s}{d \ln c_{sol}}$ means that the presence of a solvent profile causes a salt activity profile, sloped in the opposite direction of the solvent profile. This will cause “salt diffusion” in the direction against the solvent diffusion, i.e. salt and solvent counter-diffusion. Thus, a consequence of having negative $\frac{d \ln f_s}{d \ln c_{sol}}$ is that a salt concentration profile will develop if a solvent profile is present, being reversed as compared with the solvent profile. This is an interesting and very unexpected example that can be described by the concentrated electrolyte theory.

To increase the understanding of the activity factor it would be desirable to directly measure the activity of the ions, and solvents, in these types of electrolytes. However, this is problematic. In water-based electrolytes the activity has been measured by studying, for example, vapour pressure or freezing point. These methods are not applicable to systems with a large content of polymer. For an amorphous polymer electrolyte there simply is no distinctive freezing point and no measurable vapour pressure. For gels on the other hand, vapour pressure measurements may be possible to perform. However, the theory becomes quite complex for such ternary systems, with influences from both solvent, salt and polymer activity. Nevertheless, results from concentration cells should be complemented by direct measurement of activity in some way to increase the understanding of the activity in these types of electrolytes. This issue also remains as a challenging task for the future.
7. CONCLUSIONS

After having studied the properties of different non-aqueous electrolytes it is clear that they behave significantly differently from traditional water-based electrolytes. Because they are based on organic compounds they experience complex reaction chemistry. This issue was studied briefly. They also experience pronounced non-ideal mass transport. The mass transport was the subject for a majority of the studies. It was studied in detail for several types of electrolytes. The characterisation methodology was studied, and mathematical modelling used, to evaluate and visualise the results. Finally, porous battery electrodes containing these electrolytes in the pores were studied to investigate the impact of the electrolyte transport on the application using electrochemical impedance spectroscopy together with suitable models.

7.1. Electrochemical stability

In the study of electrochemical stability it was demonstrated that the electrode material influenced the voltammetric results significantly. The most versatile electrode for probing the electrolyte stability proved to be platinum. It was shown that a general definition of stability limits in terms of onset current density is problematic to achieve due to influences from the electrode material and the used sweep rate. The method was concluded to be suitable for comparing electrolytes and the influences of electrolyte components, additives and impurities, but not for determining the real stability window of an electrolyte in a battery.

Different electrolytes, both with and without polymer, were also studied in terms of stability limits. No significant effect could be related to the choice of solvent. However, the salt and polymer caused variations in the electrochemical reaction rates and the apparent stability window.

7.2. Mass transport

The mass transport properties of two binary polymer electrolytes, one binary liquid and the corresponding ternary gel were characterised and some general trends could be established. Generally, the ionic conductivity and salt diffusion coefficient both decreased significantly when going from liquid via gel to polymer electrolyte. Furthermore, the conductivity was observed to decrease above a certain salt concentration whereas the salt diffusivity experienced a constant decrease with increasing salt concentration. For the polymer electrolytes it was concluded that both decreasing trends were attributed to decreasing segmental mobility. Additionally, the conductivity was decreased by ionic interactions. Moreover, a dramatic decrease in cationic transport number was observed when going from liquid, via gel, to polymer electrolyte. In the polymer electrolytes, \( t_c \), was as low as 0.05. For the gels it was observed that addition of even a small amount of polymer to the liquid caused a dramatic reduction of the cationic transport number. Furthermore, three additional
transport properties, related to solvent transport, were defined and determined for the gel: solvent diffusion coefficient, solvent transport number, and salt drag number. Similar to the conductivity and salt diffusivity, the solvent diffusivity was also observed to decrease with increasing polymer content. The solvent transport and salt drag numbers were also determined. However, these two parameters require additional experiments to be accurately determined.

An electrochemical characterisation method was gradually developed during the work. To analyse the electrochemical results a numerical model was employed in the later studies. The advantages of using a numerical evaluation approach were considerable. The transport properties could be treated as being concentration dependent, and the whole range of concentrations studied could be described with one set of parameters. Moreover, the models with parameters could be employed to simulate concentration profiles, significantly improving the understanding of the transport. Finally, due to the physical basis of the models, interpretations on a molecular level (in terms of molecular interactions), could be performed, increasing the understanding of the transport mechanisms. In the characterisation method, concentration cell experiments were utilised to determine the activity factor variations. For all electrolytes the activity factor variations were significant. It was concluded that the electrolytes were all significantly non-ideal, and that this feature needs more attention in order to be completely understood.

In one of the studies, in-situ Raman spectroscopy was employed to directly study the concentration polarisation in a polymer electrolyte. The results were compared with model predictions, using a model with parameters determined using the electrochemical method. Good agreements were observed and it was concluded that the electrochemical method yielded accurate models and accurate transport properties.

In this thesis, there are two studies of porous battery electrodes, utilising electrochemical impedance spectroscopy in combination with modelling. The electrolyte transport was then one part of the full model, also including electrode kinetics and solid phase transport. In the first study, the features of a novel impedance method were explored. It was demonstrated that the effective conductivity of the electrolyte and the solid phase could be determined accurately from the “differential impedance”. In the last work, the concentrated electrolyte theory was implemented in the porous electrode impedance model. The influence of the mass transport was evaluated using traditional impedance measurements of identical electrodes in different, previously characterised, electrolytes, one liquid one gel and one polymer electrolyte. A significant influence of the mass transport was observed. Moreover, it was demonstrated that if an evaluation model, lacking a proper electrolyte transport description, is used the fitted values of electrode properties, such as solid diffusion coefficient, are affected. It was also concluded that a full set of transport properties could not be determined from the impedance.
CONCLUSIONS

From the different methods used to study the electrolyte transport some general conclusions can be drawn. Direct concentration measurement, such as Raman, is insufficient for a full characterisation of the properties. Electrochemical methods are advantageous in that they relate to the potential, which is of primary interest to batteries. They also enable determination of activity factor variations. Impedance methods are also insufficient to characterise the electrolyte fully. However, they yield information about electrolyte transport in the pores of an electrode that the other methods cannot.

Generally, this thesis has once again demonstrated the benefits of using different techniques. Firstly, the results can be cross-validated. Secondly, a better understanding of the studied processes was achieved. Modelling also proved to be a versatile tool. The results of the different techniques could be interpreted and compared using the same theory.

Finally, some suggestions on future work are in place. Firstly, as concluded in this thesis, the model shows room for improvements, especially for polymer and gel electrolytes. It may be possible to describe the electrolyte transport in a range of compositions, and possibly also for various temperatures, if a combination of the WLF- and the concentrated electrolyte theory is utilised. The WLF-theory would then describe the influences of segmental mobility on the transport. It may result in a concentrated electrolyte model that experiences constant parameters in a large composition and temperature range. Secondly, it would probably be very fruitful to analyse results from the proposed novel method using the model of the final study. It would certainly improve the understanding of the electrolyte transport in the pores. Thirdly, additional work with the activity factor variation seems to be necessary to fully understand the thermodynamics of these electrolytes.
8. LIST OF SYMBOLS

\begin{itemize}
\item \textit{c} concentration, \([\text{mole m}^{-3}]\)
\item \textit{c’} dim.less concentration
\item \textit{C} capacitance, \([\text{F m}^{-2}]\)
\item \textit{d} drag factor, dim.less
\item \textit{D} diffusion coefficient, \([\text{m}^2 \text{s}^{-1}]\)
\item \textit{D}_{jk} pair wise diffusion coefficient, \([\text{m}^2 \text{s}^{-1}]\)
\item \textit{E} potential, \([\text{V}]\)
\item \textit{\Delta E} potential difference, \([\text{V}]\)
\item \textit{f} activity factor, dim.less
\item \textit{f}_\text{\pm\text{*}} mean activity factor, dim.less
\item \textit{F} Faradays constant, \([\text{A s mole}^{-1}]\)
\item \textit{i} current density, \([\text{A m}^{-2}]\)
\item \textit{i}_0 exchange current density \([\text{A m}^{-2}]\)
\item \textit{j} imaginary unit, \(\sqrt{-1}\)
\item \textit{t} time, \([\text{s}]\); or transport number, dim.less
\item \textit{k} constant
\item \textit{K}_{jk} Friction parameter, \([\text{N s m}^{-4}]\)
\item \textit{L} thickness, \([\text{m}]\)
\item \textit{N} flux, \([\text{mole m}^{-2} \text{s}^{-1}]\)
\item \textit{r} particle radius
\item \textit{R} gas constant, \([\text{J mole}^{-1} \text{K}^{-1}]\)
\item \textit{R}^b bulk electrolyte resistance, \([\Omega \text{ m}^{-2}]\)
\item \textit{T} temperature, \([\text{K}]\)
\item \textit{T}^0 reduced temperature \([\text{K}]\)
\item \textit{v} velocity, \([\text{m s}^{-1}]\)
\item \textit{V}^m molar volume, \([\text{m}^3 \text{mole}^{-1}]\)
\item \textit{W} weight factor (in merit function), dim.less
\item \textit{z} charge, dim.less
\item \textit{Z} impedance, \([\Omega \text{ m}^{-2}]\)
\end{itemize}

\textbf{Greek}

\begin{itemize}
\item \textit{\varepsilon} porosity, dim.less
\item \textit{\eta} overpotential, \([\text{V}]\)
\item \textit{\theta} normalised surface concentration in solid phase, dim.less
\item \textit{\kappa} conductivity, \([\text{S m}^{-1}]\)
\item \textit{\mu} electrochemical potential, \([\text{J mole}^{-1}]\)
\item \textit{\phi} electric potential, \([\text{V}]\)
\item \textit{\chi} merit function, dim.less
\item \textit{\omega} angular velocity, \([\text{rad s}^{-1}]\)
\end{itemize}
List of Symbols

Subscripts
- 0, sol: solvent
- 1,+: cation, or solid phase
- 2, -: anion, or electrolyte phase
- 4, poly: polymer
- ctr: charge transfer
- diff: differential
- dl: double layer
- exp: experimental
- eq: equilibrium
- F: Faradaic
- loc: local (based on true surface area)
- part: particle
- s: salt
- sim: simulated
- tot: total

Superscripts
- ~: Laplace transformed variable
- 0: standard, reference
- b: bulk
- eff: effective
- max: maximum
9. REFERENCES

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