LITHIUM DEPOSITION IN SOLID POLYMER ELECTROLYTE BATTERIES

A thesis presented to the University of London in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by

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ABSTRACT

This thesis is concerned with lithium deposition in solid polymer electrolyte batteries. Passivating layers are developed on the electrode even in polymer electrolytes as the cycling proceeds and perturbation of the morphology of the lithium deposited may be expected.

In this project, cyclic voltammetry was used as a probe for the presence of electroactive impurities in polymer electrolytes. The main electroactive impurity present was water. It was demonstrated that oxygen as well as water could affect the voltammetric behavior of polymer electrolyte test cells.

A galvanostatic experiment and theoretical analysis identified the presence of a critical current where the concentration of Li\(^+\) at the cathode surface approached zero. The expected dependence of the critical current on the polymer electrolyte thickness, the Li\(^+\) concentration and the Li\(^+\) diffusion coefficient was found. It was shown that the observed critical current density gradually decreased with the number of cycles because side reactions might produce the passivating layers during cycling.

In-situ microscopic observation of the electrochemical deposition of lithium on a Ni substrate was carried out in poly(ethylene oxide) based electrolytes containing LiClO\(_4\) and LiCF\(_3\)SO\(_3\). Globular lithium deposits were typically
observed at a current density lower than the corresponding critical current density. A transition to dendritic growth was seen at a current density far higher than the corresponding critical current density.

It was shown by the in-situ observation that dendrites grew via fine particles in the polymer electrolytes. These fine particles could accelerate the rate of side reaction between lithium and impurities by generating a high surface area and reactivity. They also changed the morphology of the lithium deposited in subsequent cycles towards dendrites. The presence of a passivating layer of \textbf{LiOH} was identified by FT-IR, \textit{in-situ}. 

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감사의 글

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오늘의 제가 있기에사람으로 감싸주신 부모님과 가족들에게는 평생을 깊이도 못다할 희한을 입었습니다. 이제 두고두고 그들의 사랑을 보답하려고 합니다. 어려운 영국생활에도 불구하고 늘 건강하고 행복한 가정을 만드느라 애써준 사랑하는 애리와 민지에게 이 논문으로 그들에 대한 영원한 사랑을 대신합니다.
CHAPTER 1. Introduction

1.1. Lithium Polymer electrolyte Batteries (LPB)

1.1.1. Background on Lithium Batteries

Lithium ambient temperature batteries represent one of the very active relatively new fields in battery technology. Primary (disposable) batteries based on lithium anodes have been developed during the past 20 years and large numbers of systems are presently in commercial production. These include batteries for pacemakers such as the lithium/iodine couple (Li/I₂) [1], thionyl chloride batteries (Li/SOCl₂) for military uses and uninterruptible power supplies [2], and lithium manganese dioxide batteries (Li/MnO₂) for cameras and memory back-up [3]. There are beneficial advantages to a lithium anode battery such as high energy density, high voltage and low self-discharge. The specific energy and volumetric energy density of lithium-thionyl chloride cells are 500 Wh. kg⁻¹ and 1000 Wh. dm⁻³ at low-rate small cell, which is among the highest of all practical battery system [2]. The electrode reactions are shown in table 1-1.

<table>
<thead>
<tr>
<th>System</th>
<th>Overall reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/I₂</td>
<td>2 Li + I₂ → 2 LiI</td>
</tr>
</tbody>
</table>
Li/SOCl$_2$ | $4\ Li + 2\ SOCl_2 \rightarrow 4\ LiCl + S + SO_2$
---|---
Li/MnO$_2$ | $\text{Mn}^{IV}_2O_2 + \text{Li} \rightarrow \text{Mn}^{III}_2O_2 (\text{Li}^+)$
Li/CF$_x$ | $x\ Li + CF_x \rightarrow x\ LiF + C$
Li/SO$_2$ | $2\ Li + 2\ SO_2 \rightarrow Li_2S_2O_4$

Table 1-1. The overall reaction in lithium primary batteries

Secondary (rechargeable) lithium batteries have made no significant impact on the market because rechargeable organic electrolyte cells with metallic lithium anodes have many critical problems, most notably poor safety which limits their size to smaller cells. The most commonly used lithium source is lithium metal foil. It is a lightweight material, which has many of the desired characteristics needed for a high energy and high power battery. However, the relatively poor cycling efficiency of the lithium anode arises because it is not thermodynamically stable in typical non-aqueous electrolytes. Cells contain typically a three to five fold excess of lithium in order to ensure a reasonable cycle life. Lithium plating and stripping during the charge and discharge cycles creates a porous deposit of high surface area and increased reactivity of the lithium metal with respect to the electrolyte. The reaction is highly exothermic and can lead to venting with flame if the cell is heated by internal mechanisms during abuse or is heated externally.
The reaction can be alleviated or reduced by the use of alternative anodes that undergo displacement or insertion reactions at activities less than unity. Concerns about safety, due to the low melting temperature and high reactivity of lithium with most liquid electrolytes, led to the investigation of lithium alloys as possible negative electrode [4]. The high melting point of the alloy offers a safety advantage over pure lithium since cells could withstand larger temperature excursions. However, the use of lithium alloys in ambient temperature batteries resulted in a dramatic decrease in cell capacity due to poor anode utilization at high current densities.

More recently, graphite carbons have been evaluated as negative electrodes because they could provide chemical stability, improved cycle life and safety [5]. The disadvantage is a decrease in the energy density compared to that of a pure lithium anode cell. Also, another main drawback, at this time, with Li\textsubscript{x}C composite negative electrodes is the complex processes needed to produce graphite carbons with desirable properties. Lithium n-doped conjugated conducting polymeric materials have been used as anode [6]. The use of these polymeric materials as compared to pure lithium provided various disadvantages such as lowering of the cell voltage and gravimetric energy density.

Conventional organic electrolytes have the high ionic conductivities required for designing high power batteries for electric vehicle applications. Unfortunately, lithium reacts with the liquid electrolyte solvents and electrolyte salts, and these
unwanted reactions cause premature cell failure. During charging/discharging cycling, electrolyte decomposition takes place and the decomposition products appear to react with the polymer separator. Deterioration of the separator can cause cell failure due to internal shorts. Ion-conductive solid polymer electrolytes have been proposed to alleviate these problems. Significant research activities to produce highly ionically conductive solid polymer electrolytes are being carried out. These solid polymer electrolytes are electrical insulators and therefore, the use of a separator film is not needed.

1.1.2. Lithium polymer electrolyte batteries

It is generally believed that solid polymer electrolyte cells will be considerably safer than liquid electrolyte cells. This may be due to the relatively slower reaction rate between lithium metal and the polymer electrolyte with reduced mass transport in the polymer electrolyte. Since the concept of such a battery, based on the use of poly (ethylene oxide)-lithium salt complexes was first discussed [7], their development has focused largely on rechargeable systems utilizing insertion/intercalation cathodes in conjunction with metallic lithium anode.

The concept of the rechargeable, solid electrolyte battery is based on two lithium-reversible electrodes, one acting as a source of lithium ions during
discharging, the other as a corresponding sink. The two electrodes are separated by a thin-film polymer electrolyte acting as a lithium-ion carrier. This technology combines the use of a thin-film electrolyte with lithium reversible electrodes. The most thoroughly studied general configuration of polymer electrolyte cell is shown schematically in figure 1-1.

![Figure 1-1. Configuration of polymer electrolyte cell](image)

In polymer electrolyte systems, the most commonly used lithium source is lithium metal foil. The cathode compartment of the practical lithium-polymer electrolyte battery (LPB) is a composite of a lithium sink, a suitable electronic conductor, and the polymer material used in the electrolyte. The lithium sink in the composite cathode comprises Li⁺ ion insertion compounds including TiS₂, V₆O₁₃, MoO₂, [8,9,10]. MnO₂, FeS₂ and FeS have been studied in primary systems [11]. P-doped conducting polymers have been used as cathode since these materials were inexpensive and had the flexibility of plastics with good
electrical conductivities similar to metals. Unfortunately these polymers are heat and air sensitive and, as a result, the desirable electrical properties deteriorated with time [12].

The most widely studied polymeric electrolytes are those based on poly (ethylene oxide) and other modified-polyethers which are readily soluble in common solvents (e.g., alcohol and acetonitrile). Consequently, simple continuous solution casting techniques have been developed for the fabrication of large area membranes. Doping of the film with an appropriate lithium salt is carried out prior to casting in a suitable co-solvent. Polymer films with initially poor mechanical properties may be improved by cross-linking using irradiation technique.

Despite the fact that the organic and the solid state technology are capable of using the same electrode materials, there are major advantages in favor of the solid state system [13,14].

(1) lower material cost and manufacturing cost due to ease of assembly and high automation potential
(2) Cell component compatibility and battery safety
(3) Low electrode surface loading and low current densities
(4) Thin homogeneous separator to avoid Li dendrites
(5) Higher energy density at high discharge rate
1.1.3. Application in electric vehicles

During the past two decades, rechargeable lithium batteries using metallic lithium and polymeric electrolytes have been touted as a possible solution to the electric vehicle (EV) battery problem. The effort to bring advanced batteries for electric vehicles has been undertaken by the United States Advanced Battery Consortium (USABC) whose members include Ford, Chrysler, GM, the Department of Energy and battery companies. The USABC has established a time line that includes goals for battery development.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>EV requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>150</td>
</tr>
<tr>
<td>Size (kWh)</td>
<td>25</td>
</tr>
<tr>
<td>Power (W/kg : W/l)</td>
<td>400 / 600</td>
</tr>
<tr>
<td>Peak Power (kW)</td>
<td>50</td>
</tr>
<tr>
<td>Average Power (kW)</td>
<td>12</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>&gt; 1,000</td>
</tr>
<tr>
<td>Year</td>
<td>10</td>
</tr>
<tr>
<td>Miles</td>
<td>100,000</td>
</tr>
<tr>
<td>Energy at C/3 rate</td>
<td>200 / 300</td>
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<tr>
<td>(Wh/kg : Wh/l)</td>
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</tr>
<tr>
<td>Battery Weight (kg)</td>
<td>550</td>
</tr>
<tr>
<td>Battery Volume (l)</td>
<td>280</td>
</tr>
<tr>
<td>Battery cost ($/kWh)</td>
<td>&lt; 100</td>
</tr>
</tbody>
</table>

Table 1-2. Battery goals for electric vehicle (USABC)
Lithium batteries are currently being studied to meet the USABC goals. These include lithium-ion and lithium-polymer batteries. Although the lithium-ion battery consisting of intercalation/insertion compounds as electrodes and organic electrolytes is being studied for electric vehicle, the disadvantages of this system are its very high cost and the ventilation system required to keep the batteries cool. The manufacturing costs are high because of a highly purified organic material for electrolyte and a complex cell control system. The lithium-polymer electrolyte battery is expected to cost 20% more than lead-acid battery but deliver twice the energy because much higher voltage would be achieved with lithium and lithium is much lighter in weight than lead.

1.2. Polymer electrolyte

In 1978 it was proposed that the complexes of poly (ethylene oxide) with alkali metal salts may be prove to be good solid-state electrolytes [7]. They are, in principle, compatible with the insertion compounds used as cathode. The potential difficulty for an all-solid-state battery is that the process of intercalation of lithium into a cathode material is accompanied by a volume change, which cycles during battery cycling. In the case of $V_6O_{13}$, lithium is inserted into intercalate host material, $V_6O_{13}$ to form insertion or intercalation compounds on discharge.
\[ x \text{Li} + V_6O_{13} \rightarrow \text{Li}_xV_6O_{13}, \quad 0 < x < 7.9 \quad (1.1) \]

At this stage, there is an increase in volume of the intercalation compounds and a resulting decrease in volume of the electrolyte. This process is reversed on charging. Whilst volume change is not a significant problem with batteries incorporating liquid electrolytes, it may cause a serious problem with solid-state batteries, leading to poor contact between the electrode and the electrolyte. However, since the elasticity of the polymer could accommodate volume changes on intercalation and maintain contact with the electrode on repeated cycling, a polymer electrolyte seems a good candidate for solid-state battery electrolyte.

1.2.1. Polymers

The most commonly used polymer matrix for electrolytes is poly (ethylene oxide) (PEO). The polymeric derivatives of ethylene oxide are divided into two classes, which are defined by molecular weight. Low molecular weight polymers with an average molecular weight of 200 ~ 20,000 are called poly (ethylene glycol)(PEG) and high molecular weight of \(1 \times 10^5 \sim 5 \times 10^6\) are called poly (ethylene oxide)(PEO). This polymer has the repeating unit of \((-\text{CH}_2=\text{CH}_2\text{O})_n\)
and the trademark Polyox™. The presence of the ether linkages is responsible for the unique properties of this polymer. The carbon-oxygen bond of ether is stronger than the carbon-carbon bond of a hydrocarbon with bond energy of 84.0 kcal·mol⁻¹ and 83.1 kcal·mol⁻¹, respectively [15]. The barrier to rotation around a carbon-carbon bond in a hydrocarbon is about 3 kcal·mol⁻¹, whereas the barrier to rotation around the carbon-oxygen bond of an aliphatic ether is only about 1.2 kcal·mol⁻¹ [15]. The presence of the electron-rich oxygen atoms in the backbone structure of the polymers offers a site to form complexes with alkali metals.

Poly (propylene oxide) (repeating unit \(-\text{CH}_2\text{-CHCH}_3\text{-O-}\) (PPO) has been studied as the polymeric matrix for electrolytes [16]. It was expected that electron density of oxygen atom in poly (propylene oxide) would be increased due to the secondary carbon atom. However it showed much less solvating property than poly (ethylene oxide). This can be attributed to the steric hindrance by the methyl group.

It was recognized that the most important requirement of suitable polymer hosts was segmental motion of the polymer backbone, and that the ionic motion depended to a large extent on flexibility of polymer backbone [17]. Network electrolytes were studied under the assumption that these polymers could keep as much of the amorphous regions as possible, since the crystalline phase has been shown to be non-conductive. Poly (ethylene oxide) cross-linked by irradiation or chemical method have been studied [18, 19]. An alternative method of increasing
the amorphous content of polymer electrolytes consists of attaching short chain polyethers to inert polymer backbones. Poly (bis-(methoxy ethoxy ethoxy) phosphazene) (MEEP) has been one of the most successful polymer electrolytes [20].

\[
\text{MEEP (n=2)} \quad \begin{array}{c}
\text{(OCH}_2\text{CH}_2\text{−)}_n\text{−OCH}_3 \\
\text{−[−N=P−]}_n \\
\text{(OCH}_2\text{CH}_2\text{−)}_n\text{−OCH}_3
\end{array}
\]

Electrolytes based on several other polymers have been the subject of some studies and these polymers are listed in table 1-3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyepichlorohydrin</td>
<td>((-\text{OCH}_2\text{CH}−)) \text{−CHCl}</td>
</tr>
<tr>
<td>Poly(ethylene succinate)</td>
<td>([-\text{O(CH}_2\text{)}_2\text{−O}−(\text{CH}_2\text{)}_2\text{−C}−]) \text{−O} \text{−O}</td>
</tr>
<tr>
<td>Poly(ethylene imine)</td>
<td>(- (\text{CH}_2\text{CH}_2\text{NH}−)−)</td>
</tr>
<tr>
<td>Poly(alkylene sulfide)s (n=2~6)</td>
<td>([- (\text{CH}_2\text{)}_n\text{−S}−])</td>
</tr>
</tbody>
</table>

Table 1-3. Structures of potential host polymers for electrolytes
1.2.2. Conduction in polymer electrolytes

The conductivity of most inorganic solid electrolytes and crystalline polymer electrolyte follows an Arrhenius equation:

\[ \sigma = A \cdot T^{1/2} \exp \left( -\frac{E_a}{kT} \right) \]  (1-2)

where \( E_a \) is the thermal activation energy and \( A \) denotes a pre-exponential factor, which includes the carrier concentration. In the early studies of PEO-salt complexes, it was suggested that cation hopping through the helices of the polyethers chain could be the mechanism for ion transport [21]. This interpretation showed a good agreement with Arrhenius behavior. However, this interpretation is no longer accepted.

A very important insight into the conduction mechanism in polymer electrolytes has been that the ions in the amorphous phases, not those in the crystalline phases, are responsible for the ionic conductivity of polymer electrolytes [22]. The well-known Vogel-Tammam-Fulcher (VTF) equation has been used to describe ion transport in polymer electrolytes. This equation showed a good agreement with the observed non-linear relationship between \( \log (\sigma) \) vs. \( (1/T) \) [23].
\[
\sigma = \sigma_0 \exp \left[ -\frac{B}{(T - T_a)} \right] \quad (1-3)
\]

where \( B \) is an apparent activation energy and \( T_a \) is a fitting parameter which can be referred to as the zero mobility temperature or ideal glass transition temperature.

When \( T - T_a \approx T \), the VFT equation becomes identical to Arrhenius equation. Also the VFT equation indicates that the higher conductivity can be achieved by reducing in the glass transition temperature, \( T_a \).

For high molecular weight poly (ethylene oxide), two or more phases may coexist. Poly (ethylene oxide) is a semi-crystalline solid composed of two phases at ambient temperature, one of the phase of being amorphous and the other crystalline. The same is true of polymer electrolytes based on poly (ethylene oxide). Below the melting point of pure crystalline poly (ethylene oxide), the conductivity is dominated by the ions in the dispersed amorphous regions and follows Arrhenius behavior showing linear \( \log \sigma \) vs. \( 1/T \). As the temperature is raised, it causes an increase in mobility of polymer chains. This results in an increase of the ionic conductivity. When the temperature is high enough that the salt-rich crystalline complex dissolves in the amorphous phase, the number of charge carriers is increased. Therefore, the ionic conductivity is increased further.

Since \( T_a \) of the polymer electrolytes is also affected to a large extent by the nature and concentration of the salt, the effect of the salt on the conductivity
should be considered. The effect on conductivity on increasing salt concentration in the amorphous region is clearly observed as an increase in the ionic conductivity. However, as salt is added further, the polymer-salt complex becomes more rigid due to a decrease in polymer flexibility. This is reflected by an increase in $T_g$. This indicates that the conductivity has a maximum value according to the concentration of salt in polymer electrolytes.

1.2.3. Salt effect on the conductivity; LiClO$_4$ versus LiCF$_3$SO$_3$

The technology for solid state lithium batteries is a very recent development and improvements and modifications are being made continuously. The initial cell configuration was based on the sulfonate-based complex (PEO-LiCF$_3$SO$_3$). An example of cell optimization is the introduction of another electrolyte – the perchlorate-based complex (PEO-LiClO$_4$) to improve the ionic conductivity and hence cell performance. It has been generally known that the sulphonate-based complex has some disadvantages compared to the perchlorate-based complex. The perchlorate-based complex has a higher conductivity ($2 \times 10^4$ S/cm vs. $2 \times 10^5$ S/cm at 100°C) than the sulphonate-based complex. But the perchlorate-based complex has lower cation transport number and is more difficult to handle because of hygroscopicity [24].

The use of the sulfonate-based complex results in the formation of a
crystalline complex, which does not become amorphous until above 120°C [25]. From observations under polarized light, it has been found that the sulfonate-based complex films are spherulitic in nature below 120°C. In polymer morphology, crystallites are often arranged in larger aggregates known as spherulites. Figure 1-2 shows how the polymer chains are thought to be arranged in the spherulites. Large spherulites contribute to stiffness in polymers resulting in a decrease in mobility of ions through polymer electrolytes. This is reflected in a decrease in conductivity. The structures obtained in recent diffraction studies on the sulfonate-based complex indicated that the triflate anions orient around helical polymer chains and direct the chain packing [26].

Figure 1-2.
(a) Crystalline, (b) spherulitic, and (c) amorphous regions in polymers from ref.[27]
Based on the literature, the mobility of the anion correlates linearly with the reciprocal of square root of formula weight, the mobility of $\text{ClO}_4^-$ anion be higher than that of $\text{CF}_3\text{SO}_3^-$ anion. This was assumed due to a higher tendency of $\text{CF}_3\text{SO}_3^-$ anion over $\text{ClO}_4^-$ anion to associate in complexes [28]. In turn, the cation-polymer interaction becomes weakened as a result of strong ion association. The migration of anions makes a contribution to the electrical conductivity.

PEO–LiCF$_3$SO$_3$ based polymer electrolytes may contain more semi crystalline pure PEO regions than PEO–LiClO$_4$ so that its arrangement becomes more spherulitic below 120°C compared to PEO–LiClO$_4$ based polymer electrolytes. Thus the use of (PEO)–LiCF$_3$SO$_3$ complex results in reducing ionic conductivity below 120°C. The PEO–LiClO$_4$ complex is known as being a superior ionic conductor since it contains larger amorphous regions at all temperatures above 60°C. Thus it has a far better rate-performance.

The thermal history of the PEO complex is an important factor in determining the degree of crystallinity and, hence, the conductivity. The PEO–LiCF$_3$SO$_3$ electrolytes have fast recrystallization kinetics, i.e., the formation of the various crystalline phases occurs within minutes of the film reaching room temperature. This may have a negative effect on the cell assembly process since a thermal lamination process is the essential cell assembly process for lithium polymer electrolyte batteries.
1.3. Lithium Passivation

Lithium is the most promising material for use as the anode of high potential and high energy density rechargeable batteries. However, the problem with the lithium negative electrode in conjunction with liquid electrolytes is the irreversible capacity loss that occurs during cycling. This irreversible capacity loss has been related both to the reaction of lithium with all the species in the electrolyte solutions, because of its high chemical reactivity. Organic solvents such as propylene carbonate (PC) and butyl lactone are non-volatile, polar and highly conductive and these are usually used as electrolyte solvent. However, they are too reactive toward metallic lithium. The formation of a passivating film causes loss of active lithium during the cycling. Therefore, the search for solvent-electrolyte combinations for high performance lithium rechargeable batteries continues still.

1.3.1. Lithium passivation in liquid electrolytes

The surface film formed on lithium anodes in carbonate-based electrolyte solution has been extensively studied by FT-IR and impedance spectroscopy. The composition of surface films and interfacial properties in relation to the cycling efficiency has been investigated [29,30,31,32]. The surface films formed in pure
Propylene carbonate (PC) were identified to contain mostly Li-alkyl carbonate (ROCO₂Li). However, when the electrolyte contained impurities such as water and CO₂, the surface films contained more types of surface species (e.g., Li₂CO₃ and ROCO₂Li). In tetrahydrofuran (C₄H₈O, THF)-based solution, Li-alkoxide (ROLi) was found. When the passivating films forms during the cycling, lithium ions must be transferred through these films. The electrochemical behavior of lithium in an electrolyte is surface controlled. If the passivating films formed is not uniform in composition, porosity or thickness, this may lead to less uniform Li transfer through the passivation layer. Hence, lithium deposition and dissolution is likely to be irregular and non-uniform, leading to dendritic growth. Dendrites are easily inactivated due to high surface area for the reaction with an electrolyte. These are easily disconnected from the electrode, which leads to lower cycling efficiency. For a similar reason, a uniform deposit is less likely to be inactivated than an irregular deposit. This is illustrated in figure 1-3.
Figure 1-3. The irreversible capacity loss mechanism showing the effect of deposit morphology on the formation of the passivating film by generating high surface area (1: less uniform, 2: uniform deposit)

The electrical properties of the Li-solution interface formed in the different salt solution are remarkably dependent upon the nature of the solution. Consequently, the morphology and Li utilisation in repeated charge-discharge cycling is also influenced.

For example, the morphology of the lithium deposited had the typical dendritic form in LiClO$_4$-PC, while suppression of lithium dendrites had been observed in LiAsF$_6$/2-MeTHF. Table 1.4 gives a summary of the present understanding of the composition of the passive films.
<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Component of surface films</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlCl₄-SOCl₂</td>
<td>LiCl</td>
<td>[33]</td>
</tr>
<tr>
<td>LiBr-SO₂</td>
<td>Li₂S₂O₄</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Li₂SO₃, Li₂S₂O₃, LiS₂O₃</td>
<td>[34]</td>
</tr>
<tr>
<td>LiClO₄-PC</td>
<td>Li₂CO₃</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Polymer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂CHCH₂OCO₂Li, CH₃CHCHOOCO₂Li</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>CH₂CH₂CH₂OCO₂Li,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₂CHCH₂OCO₂Li)₂</td>
<td>[36]</td>
</tr>
<tr>
<td>LiClO₄-DOL</td>
<td>Li₂O</td>
<td>[37]</td>
</tr>
<tr>
<td>LiClO₄-THF</td>
<td>Polymer</td>
<td>[33]</td>
</tr>
<tr>
<td>LiAsF₆-2MeTHF</td>
<td>-(O-As-O-)R</td>
<td>[38]</td>
</tr>
<tr>
<td>2MeTHF</td>
<td>As(OR)ₙFₚₚ (n=3,6)</td>
<td>[39]</td>
</tr>
</tbody>
</table>

PC : propylene carbonate, DOL : dioxolane, THF : tetrahydrofuran, 2MeTHF : 2-methyl tetrahydrofuran

Table 1.4. The surface films developed on lithium in several different battery liquid electrolytes
1.3.2. Dendrite growth in liquid electrolytes

There has been quite a lot of work done on electrochemical deposition of the lithium in organic electrolytes. One of the most serious problems in lithium secondary cells is dendritic growth of lithium deposits. As mentioned above, the morphology of the lithium deposited is dependent on the nature and composition of electrolytes that are used in electrochemical systems and the nature of the passive layer developed on lithium is dependent on the electrolyte.

If one considers the ideal electrochemical deposition process macroscopically, the first step would be the formation of stable nuclei on a smooth and defect free surface. Once stable nuclei have been formed, their subsequent growth might change the local conduction and therefore the local rate of growth. The evolving shape of the nuclei might thereby be changed as they grow. The rate of deposition of metal ions, therefore the rate of reduction, depends on the electron transfer process at the interface and on the rate of mass transport of ions through the electrolyte. Hence, a local increase in the rate of growth following the initial deposition process could be caused by the concentration of the applied electric field on the nuclei and by a change in diffusion geometry.

The applied electric field is concentrated more at the surface of a protruding crystal than at the flat electrode surface. The diffusion distance for metal ions to move to the electrode becomes shorter to a growing center than to a flat electrode surface. This would produce a faster growth rate. The rate of deposition will
increase further because the nuclei formed on the electrode increase the area available for further reduction.

As the individual nuclei with different sizes grow further, the distance between neighboring nuclei gets closer. Overlap between neighboring nuclei will occur. The rate of deposition will increase less rapidly than previously. When overlap of neighboring nuclei has occurred over the whole surface and been completed, the deposit layer will thicken as deposition continues over the total area of the substrate. This is the ideal case for an electrochemical deposition process.

However, when the deposition conditions around the nuclei have been changed enough as a consequence of their growth, the deposition process shows irregular behavior. The state of the electrode surface must be considered carefully since the interfacial reduction mechanism can be modified by the state of the electrode surface. Based on the results from literature sources [40,41], when low overpotential is caused by low interfacial resistance, homogeneous and compact deposits have been observed. When high overpotential is caused by high interfacial resistance at the electrode, dendritic and non-homogeneous deposits are observed. Hence these results indicate that the instability in growth producing dendrites has a close relation with the growth of the passive films on the electrode surface, which increase the electrical resistance.

Figure 1.4 presents the effect of a passive layer on the applied constant current
density. The deposition current density \( i \) is applied on the clean and defect-free electrode surface (fig. 1.4a).

(a) A clean electrode surface

![Diagram of a clean electrode surface](image)

(b) An electrode surface with the passive layer

![Diagram of an electrode surface with passive layers](image)

Figure 1.4. A schematic presentation of the concentrated current density on the electrode
However, if due to unidentified reasons resistive layers have been formed on the electrode surface, the applied current density will concentrate on the clean part of the surface (fig.1.4(b)). The clean part of the electrode surface will experience a higher current density than previously. At this part of the electrode, the deposition would become much faster and in the extreme case, dendrites could occur. Hence, the growth of deposits would be controlled by the nature of the passive layer, particularly by the electrical resistance of the passive layer.

1.3.3. Effect of the deposit morphology on battery performance

An electric current flowing in a galvanic cell is usually distributed uniformly over the whole surface of the electrodes. Ideally, the current density should be the same at any point of the surface. However, non-uniform distribution is possible if different segments of the surface are not equally accessible to the current. There are a few factors that determine the actual distribution of current density. The passive and native film layers on the electrode can control the actual distribution of current density.

The composition and morphology of the surface film layer are therefore important in determining the distribution of current density. If the surface layer formed is poorly electrically conductive, the non-uniformity of the current
density distribution becomes profound. In terms of ionic movement through the surface layer, a porous surface film is more favorable than a dense film. The composition and morphology of the surface film layer depend on the nature of the electrolyte used in the system and the effect of the surface film layer on the electrochemical behavior also depends upon the cell operation conditions (e.g., discharge-charge current densities). Recently, much work has been performed to investigate the nature and composition of the passive film at the lithium negative electrode-organic electrolyte interface [39,42,43] (see Table 1.4.) and native film at the commercially available lithium [44]. XPS analysis identified the native film found on the as-supplied Li metal and suggested that it probably comprised Li$_2$O, LiOH and Li$_2$CO$_3$.

Native surface films on a lithium electrode could produce an uneven resistance distribution at the surface since those films consist of many compounds. If the current were not sufficient enough for Li to dissolve from all parts of the lithium electrode, the applied current for deposition of lithium would be focused in the relatively low resistance part of the lithium electrode even at the very initial stage of Li deposition. This idea supports an advantage of high rate discharge in the practical cell because high rate of discharge can reduce the localization of current during discharging.

Much work on the deposition process in lithium/organic electrolyte systems suggests that it is not a uniform process. Instead of the three-dimensional regular
growth of the Li nuclei, irregular growth even fractal growth has been observed on the lithium negative electrode in organic electrolyte systems.

It is known that the cycleability of lithium secondary batteries employing a lithium metal negative electrode and organic electrolytes depends on both charge and discharge current densities. Much work has been done concerning the cycle life and lithium deposition morphology dependence on charge and discharge current densities. It has been demonstrated that cycle life decreases with increase in discharge current [42]. A cycle life dependence on charging current density has also been reported in Li/MoS$_2$ and Li/Li$_{0.3}$MnO$_y$ cells [43,45,46,47].

The cycle life dependence on charge/discharge current densities can be explained by the morphology of Li deposited. It has been reported that two types of Li deposit are observed from organic electrolytes [48]. These were needle-like Li and particle-like Li. The needle-like Li was thought to be 'dead lithium' since it remained on the electrodes after anodic dissolution. This lead to a decrease in the amount of needle-like lithium during charge-discharge cycles, thus eventually resulting in cycle life decrease.

According to the literature [48], Li deposition starts with needle-like Li, with particle-like Li subsequently growing at the top. In the dissolution process, the particle-like Li dissolves first followed by dissolution of needle-like Li, as illustrated in figure 1.5.
During the following charging process, the current will be focused at the point from which the Li was deposited during discharging. Since the fresh Li deposited on an inert cathode is more reactive than original lithium anode with native surface films, side reactions between the Li deposited and impurities and/or electrolyte could occur. Any newly formed passive film on the freshly deposited Li would play the same role as the native film. Any such passive layer would reduce the effective contact area between electrode and electrolyte, thus
resulting in the localization of current density. The actual current density would be higher than the applied charging current density. This actual charging current density would be much higher on the needle-like Li deposits than on the particle-like Li deposits. The formation of the passive layer on the deposited Li surface may be accelerated at the needle-like Li surface. During discharge-charge cycles, needle-like Li produces electrochemically inactive lithium referred to as 'dead lithium'. This 'dead lithium' is one of the commonly observed failure modes from the cell at the end of service. Much work has been directed at explaining the formation of an electrochemically inactive 'dead lithium' through the needle-like (dendritic deposit). One proposal is that electrochemically active lithium reacts with electrolytes (and/or impurities) to form needle-like lithium. Needle-like lithium can be easily passivated and finally disconnected from the electrode [49].

Also it has been proposed that metallic lithium can become isolated within passivating layers and that this leads to electrical isolation of the deposited lithium [48]. Accordingly, it has been suggested that needle-like Li leads to a cycle life decrease. This proposed mechanism suggests that the cycle life dependence on both charge and discharge current densities can be explained by morphological changes in the lithium anode and hence suggests the morphology of the Li deposited is an important factor determining the useful cycle life of lithium secondary batteries.

The morphology of the Li deposited depends upon the composition of
electrolyte that is used in the battery system. Needle-like Li is typically observed from the lithium cell in propylene carbonate (PC) containing 1.0 mol/dm$^3$ LiClO$_4$, whilst in propylene carbonate (PC) containing 5x10$^{-3}$ mol/dm$^3$ HF, the lithium deposited has a hemispherical form with no irregular shapes [50]. It has been argued that the addition of a small amount of HF to the electrolyte is effective in suppressing to the lithium dendrite formation by forming a uniform layer on the electrode. This uniform layer on the electrode is expected to make the current distribution uniform.

As a general summary, factors causing the reduction in cycle life of a lithium electrode in organic electrolytes are:

(i) existence of native film passive layer formation leading to an increase in cell impedance

(ii) needle-like Li deposition resulting in the formation of electrochemically inactive 'dead lithium' during cycling.

And these two factors are closely related with each other.

1.3.4. Lithium passivation in hybrid polymer electrolytes

Polymer electrolytes can be typically divided into two types. The first having conductivities ranging 10$^{-3}$~10$^{-4}$ S/cm at 100°C, comprises polymer electrolytes based on the simple combination of high molecular weight polymer matrix (e.g.,
poly(ethylene oxide) (PEO)) and lithium salts. The other comprises hybrid polymer electrolytes formed by the addition of plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) to common polymer electrolytes in order to increase conductivities at room temperature [51].

While there is much information on the nature and composition of the passive film formed at the Li electrode in organic electrolytes, little information is available on the composition and morphology of the passive film and its effect on the electrochemical behavior of polymer electrolyte systems. It has been reported that a polyacrylonitrile (PAN) based hybrid polymer electrolyte with the addition of propylene carbonate (PC) and ethylene carbonate (EC) shows a similar electrochemical behavior at the interface to that found in organic electrolyte systems [52]. The hybrid polymer electrolyte reacts with the lithium negative electrode. The accumulation of reaction products at the interface results in a passive surface layer. This is reflected in the interfacial resistance increasing continuously as a function of time. Polar solvents added as plasticizers to the polymer complex react with the lithium metal to form the passive layer, not a polymer matrix (in this case polyacrylonitrile (PAN)) since polar solvents are more likely to react with lithium than polymer matrix.

In terms of the morphology of the lithium deposited, the growth of dendrites in secondary cells employing polymer electrolytes has been considered as less serious than in cells employing organic electrolytes. However, as long as organic
solvents are added to the polymer complex, the resulting morphology is dependent on the amount of the added organic plasticizer. This means there might be an optimized ratio of polymer matrix to liquid electrolyte and salt concentration to secure the ionic conductivity and the favorable morphology at the same time.

Based on the literature [40,41], dendritic growth might be expected when a high overpotential is developed at the interface. The high overpotential reflects the high resistance at the interface. In hybrid polymer electrolytes containing both liquid solvents and solid polymer, the polymer raises the resistance in electrolytes. It might be expected that the higher the proportion of polymer, the higher the resistance of electrolytes. In terms of the ionic conductivity of polymer electrolytes, polymer matrices having lower glass transition temperatures \( T_g \) should be favorable since the most important factor in determining glass transition temperature \( T_g \) is the flexibility of polymer chains in a medium. As the weight ratio of host polymer to liquid solvent increases, the flexibility of polymer electrolytes will be decreased. This also results in the decrease in ionic conductivity. So, following the simple argument above, the likelihood of formation of Li dendrites should be increased. However, the result from the morphology observation in hybrid polymer electrolytes has been against this expectation [52]. As the weight ratio of host polymer to liquid solvent increased, lithium dendrites were suppressed.
Based on the results, the effect of host polymer on suppression of lithium dendrites can be explained as follows: when deposits grow at the electrode surface, initially they will experience similar conditions to lithium deposits in organic electrolytes. As lithium deposits grow further, they will encounter the stiff phase of polymer. Accordingly, a fractal growth leading to dendrite formation will be suppressed.

1.3.5. Lithium passivation in high-temperature polymer electrolytes

It was thought that polymeric electrolytes would provide better chemical and electrochemical stability toward metallic lithium than the liquid electrolyte systems. However, it has been shown by impedance spectroscopy that a passivating film layer forms at the Li/PEO$_2$LiCF$_2$SO$_3$ interface after aging at the elevated temperature corresponding to the nominal operating condition [53]. An increase in interfacial resistance ($R_i$) to a steady value with storage time and temperature was observed. A linear dependence of the interfacial resistance as a function of temperature ($(1/R_i)$ vs. $1/T$) was observed and it was assumed that $1/R_i$ reflected the ionic conductivity of the passive film. The behavior was interpreted as being indicative of the formation and growth of passive films on the lithium electrode surface. According to this literature, the formation of the passivating films is not simply caused by the reaction of water or oxygen with lithium to form LiOH and/or Li$_2$O. It has been suggested that LiF forms at high
concentration of LiCF₃SO₃, in reactions which were likely to occur simultaneously and competitively with the reaction of water or oxygen and with the electrochemical reaction. This assumption was based on the interpretation of the cyclic voltammetric study of PEO₄₄LiCF₃SO₃. A reduction process occurring prior to the deposition of lithium was interpreted as the reduction of CF₃SO³⁻ anion [54].

\[
\text{Li}^+ + \text{CF}_3\text{SO}_3^- + e^- \rightarrow \text{LiF} + \text{CF}_2\text{SO}_3^- \quad \text{(1-4)}
\]

Passivating film formation at the interface between lithium electrode and PEO-based electrolytes has been reported though without any clear identification of the nature of the films [55,56]. However, recently clear evidence by FT-IR spectroscopy of the nature of the passivating film formed in PEO-LiClO₄ electrolyte has been presented [57]. Lithium alkoxide was detected as a side product, assumed generated through the reaction between the freshly deposited lithium and polymer matrix, PEO. The cleavage of ether-type C-O bond to form alkoxide functionalities was suggested. A similar reaction mechanism was proposed for the reaction between lithium and ether-based electrolytes (dimethyl ether (DME), tetrahydrofuran (THF)). [58]. Electron transfer from lithium to a solvent molecule could form a radical anion, which is stabilized by a Li⁺ cation. This radical would then decompose to form lithium-alkoxide (RO⁻Li⁺, R= alkyl).
Another example showing degradation of polymer matrix to form a thin passivating film at lithium/electrolyte interface was reported. When the polymer electrolyte plasma-polymerized tris (2-methoxyethoxy) vinylsilane with LiClO₄ was used, the formation of a resistive layer consisting of a mixture of lithium alkoxide and lithium alkylsilanolates was identified by FT-IR measurement [59]. The degradation scheme of polymer matrix was proposed as given below.
Generally, a polymer is characterized by a molecular-weight distribution, which is entirely controlled by polymerization method. Commercially available poly (ethylene oxide) is mixture of chains of different lengths. Also, poly (ethylene oxide) contains some additives. Anti-oxidants such as 2-propanol (CH$_3$CHOHCH$_3$), ethanol (CH$_3$CH$_2$OH) are added to prevent degradation of polymer. It has been suggested that these low-molecular-weight compounds could react with lithium to form the passivating films. However, an electrolyte employing a highly pure PEO did not provide any significant amelioration of the formation of the passivating film [60].

1.4. The objectives of the project

It is clear from the above considerations that the major drawback to commercialization of lithium rechargeable batteries based on polymer electrolytes is the performance limitation caused by the passivating films during cycling. However, there is a need for more detailed understanding of the nature of these passivating films and their effect on battery performance. The objectives of this project can be summarized as:

1. Identification of the possible reactions that form the passivating films;

2. The effect of the passivating films on the cycling behavior of polymer
3. The effect of the passivating films on the deposition morphology of lithium and change in morphology during cycling;

4. Investigation of the relation between the deposition morphology and cycling efficiency;

5. Chemical characterization of the passivating films formed on the deposited lithium.
References


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CHAPTER 2.
EXPERIMENTAL
TECHNIQUES
CHAPTER 2. EXPERIMENTAL TECHNIQUES

This chapter outlines the experimental methods used for the work carried out for the preparation of this thesis. First, the procedure for producing high temperature polymer electrolyte using ball-milling method is described. Then, the preparation of test cell is given with a description of the analytical techniques such as cyclic voltammetry, galvanostatic ramp experiment, optical microscopy and FT-IR.

2.1. Materials

Polyethylene oxide (CH₂CH₂O)n (m.w 400,000) was purchased from Aldrich and used without further purification. Acetonitrile (ACN) (Aldrich, anhydrous grade) was stored over activated molecular sieve type 13A (BDH) for several weeks in a dry box before use. The inorganic lithium salts were purchased from Aldrich and Fluka. Before being used, LiCF₃SO₃ salt (Fluka) was recrystallized in acetonitrile (ACN, Aldrich), then dried under dynamic partial vacuum (rotary pump, 10⁻²~10⁻³ torr) for 48 hours at 100°C. The LiClO₄ salt was anhydrous grade (purity > 99.9%) and dried under dynamic partial vacuum for 48 hours at 100°C. All further manipulation of these chemicals was carried out in an argon-filled dry box.
2.2. Electrolyte film preparation

Preparation of electrolyte film and test cell was carried out in an argon-filled dry box. Polymer electrolyte films were prepared by adding the predetermined quantity of poly (ethylene oxide) (PEO) powder to 1,1,1-trichloroethane solution (CH$_3$CCl$_3$, Aldrich, anhydrous grade). The resulting solution was then vigorously stirred for 25 minutes to disperse the PEO. The correct quantity of lithium salt was dissolved with a portion of the total amount of acetonitrile. The dissolved salt solution and part of the remaining amount of acetonitrile were mixed and then was shaken for 10 minutes. The remaining acetonitrile was added. The completed electrolyte mix was then stirred for 10 hours to ensure homogeneity. During stirring, air bubbles were formed in the solution. In the polymer electrolyte film prepared without removing bubbles, holes were observed. In order to remove bubbles, the solution was allowed to stand for at least three days.

This viscous solution was very slowly poured into the reservoir of a home-built doctor-blade casting machine. The cast thickness was adjusted using a micrometer-controlled blade. The solution flowed under the blade on to a teflon sheet, which rested on a glass plate. After casting the solution, the glass plate was transferred into a drying tube. The cast solution was dried under dynamic vacuum at 100°C for at least 48 hours. After drying, the polymer electrolyte film was stored as it was in a drying tube with vacuum inside a glove box. The polymer
film was easily peeled from the teflon sheet. All test cells were prepared by using
the fully dried electrolyte film.

2.3. Electrochemical experiments

2.3.1. Cyclic voltammetry

In cyclic voltammetry experiments, a three electrode (working, reference, and
counter electrode) cell is used. The reactions under examination occur at a
working electrode. The basic operating principle of cyclic voltammetry consists
of a linear-potential ramp application between working electrode and reference
electrode. The experimentally measured response is the current passed between
working electrode and counter electrode.

The resulting cyclic voltammogram ($i$ vs.$E$) indicates the potentials at which
electrochemical reactions occur at the working electrode. The movement of
electroactive material to the surface and the electron transfer determine the
current response in the overall electrochemical process. The reaction rate is
proportional to the concentrations of $A$ and $B$ at the electrode surface. Thus the
current in the cyclic voltammograms can be expressed as follows;
\[ i = nF \left\{ k_r C_A(0,t) - k_r C_B(0,t) \right\} \]  \hspace{1cm} (2-1)

where \( C_A(0,t) \) and \( C_B(0,t) \) are the concentration of A and B at the electrode surface respectively.

The exponential dependence of \( k_r \) on the applied potential (\( E \)) causes a very steep increase in the current. However, in an unstirred solution diffusion is the principal mode of the movement of the electroactive material. When diffusion controls the overall reaction rate, the current falls with time. Hence a peak is observed in the \( i-E \) trace. Cyclic voltammetry is very useful for mapping out the electrochemical reactions occurring.

A teflon-bodied three-electrode cell with a spring to secure a tight contact between electrodes and polymer electrolyte film was used in this project. The cell design is schematically illustrated in figure 2-1. It incorporated a Ni working electrode, a lithium counter electrode, and a lithium reference electrode. Lithium reference electrodes constructed by mechanically pressing lithium onto a thin Ni wire were used. The reference electrode was situated close to the working electrode to minimize ohmic drop by inserting it between polymer electrolyte films. A BUCHI TI-50 heater controlled the cell operating temperature. All of the cyclic voltammetric experiments were carried out in an argon (BOC, Research grade) filled dry box equipped with a re-circulation gas purifier mounted inside the box.
2.3.2. Galvanostatic ramp experiments

Critical current densities were obtained with the three-electrode cell (see Ch.2.3.1). The potential difference across the cell ($\Delta E/mV$) was plotted against the applied current density ($i/mA cm^{-2}$). The critical current density ($i$) was determined from the current density value showing a sudden increase in the potential difference. The applied current density was increased in a linear ramp with time at rate $0.2 \mu A cm^{-2}s^{-1}$. 

Figure 2-1. Three-electrode cell used in electrochemical experiments in this project, Ni sheet was used as the working electrode and lithium as reference and counter electrode.
Wave-function generator

Potentiostat

Three-electrode test cell

High Impedance DMM with data logging system

High Impedance DMM with data logging system

ΔE

R*
2.3.3. Cycling efficiency

Cycling efficiency measurements of lithium electrodes were performed by electrochemically depositing lithium onto a nickel substrate followed by stripping of lithium at the same deposition current density. The total deposition charge passed was 1.0 C/cm². The overall cycling efficiency of a cycle was calculated by the following equation:

\[
E(\%) = \frac{i_{\text{dis}} t_{\text{dis}}}{i_{\text{dep}} t_{\text{dep}}} = \frac{Q_{\text{dis}}}{Q_{\text{dep}}} \quad (2.4)
\]

where \(i_{\text{dis}}\) and \(i_{\text{dep}}\) denote the current for dissolution and deposition, \(t\) the time and \(Q\) the charge.
2.4. Microscopic observation

*In-situ* microscopic observation was carried out by depositing lithium galvanostatically on a Ni wire substrate to study the changing morphology of deposits in polymer electrolytes. The corresponding critical current density was also obtained with a Ni wire to study its relation with the deposition morphology. In-situ FT-IR measurements were performed to characterize the passivating films on the deposited lithium.

2.4.1. Optical microscopy *in-situ*

Photographs of lithium deposits were taken using a two-electrode cell, which could be mounted on a microscope stage (figure 2-3).
Figure 2-3. (a) Two-electrode cell and (b) construction for \textit{in-situ} observation system.
A smoother surface was achieved by using Ni wire as substrate. Since the cut-edge of the Ni sheet substrate was rough, the surface effect on the deposition morphology could not be avoided. The Ni wire electrode was dipped in an ultrasonic bath containing pure water. After washing, the Ni wire electrode was dried and stored in vacuum chamber in an argon-filled dry box before cell assembly. Prior to experiments, the test cell was held at 100°C for two hours in an argon-filled dry box to secure better contact between electrodes and electrolyte. Deposition was carried out at a given constant current. Photographs were taken at various stages of the deposition. The test cell was cycled as the same procedure as described earlier. A Perspex box surrounded the microscope stage and optics so that an argon shroud could be maintained around cell.

2.4.2. FT-IR microprobe measurement in-situ

The characterization of the lithium deposited was performed by FT-IR microscopy. A good FT-IR spectrometer can typically obtain a spectrum from a sample at least as small as 0.5 mm using normal transmission optics. FT-IR microscopy is designed to use an external spectrometer beam and a dedicated small-area, high sensitivity MCT detector to provide viewing capabilities for selecting sampling areas with ultimate sensitivity.

The FT-IR microprobe used was Nicolet IRμS/Scanning Infrared Microprobe
(IRµS/SIRM) system. It comprised a FT-IR spectrometer mounted on an optical microprobe fitted with Cassegrain (reflection) optics. The spot size was 50 µm. FT-IR spectra obtained using a CaF₂ window on the test cell. In this case, care was required in the cell assembly because the window was easily cracked. FT-IR spectra of the cathode deposits were obtained after the test cell had been cooled to ambient temperature.
CHAPTER 3.
RESULTS
CHAPTER 3. RESULTS

The results being presented in this chapter are concerned with the passivating layer and its effect on lithium deposition in high-temperature solid polymer electrolyte cells (HT-SPE cell). Firstly, the results obtained by cyclic voltammetry, which was used for the identification of impurities in poly (ethylene oxide), are displayed. Secondly, the results concerning the critical current density of both polymer electrolytes are presented. Thirdly, the results obtained by in-situ microscopic observation are given with the resulting characterization of the cathode deposits by FT-IR.

3.1. Cyclic voltammetry

3.1.1. Cyclic voltammetry of a Li/PEO₈LiClO₄/Ni cell

Cyclic voltammetric experiments were carried out to characterize the electrochemical reactions that occurred at the electrolyte/electrode interface prior to lithium bulk deposition. Figure 3-1 displays the typical electrochemical processes occurring in the polyethylene oxide-lithium salt complex (PEO₈LiClO₄) at a Ni working electrode, recorded at scan rate 10 mV/sec. At the cell operating temperature of 100°C, the open circuit voltage (OCV) fell to 2.5 V vs. Li/Li⁺. All
Figure 3-1. Cyclic Voltammogram of a Ni/PEO\textsubscript{8}LiClO\textsubscript{4}/Li cell at the scan rate of 10mV/sec: (a) 1\textsuperscript{st} cycle, (b) 2\textsuperscript{nd} cycle and (c) steady-state.

Cell operating temperature: 100°C.
Polymer electrolyte film used here was dried at 100°C for 48 hours in vacuum.
polymer electrolyte films under CV examination were dried at 100°C for 48 hours in vacuum before cell assembly. Three pronounced cathodic peaks at 1.5, 0.8, and 0.5 V vs. Li/Li⁺ were observed in the first cycle of cyclic voltammograms as the potential was scanned in the negative direction from the open circuit voltage to lower potential. A broad superimposed anodic peak region appeared at 1.0 V vs. Li/Li⁺.

The first cycle of cyclic voltammograms obtained at the scan rate of 20 mV/s was characterized by three cathodic peaks at 1.3, 0.75, and 0.4 V vs. Li/Li⁺ and an anodic peak at 1.0 V vs. Li/Li⁺ as shown in figure 3-2. The correlation of the associated anodic peaks corresponding to various reduction process is possible by choosing different inversion potential limits as in figure 3-3. Cathodic peaks appearing in the region of 1~1.5 vs. Li/Li⁺ were associated with an anodic peak shoulder at 2.0 V vs. Li/Li⁺. Two cathodic peaks in the region of 0~1.0 V vs. Li/Li⁺ were associated with anodic peaks at 0.75, 1.25 V vs. Li/Li⁺, respectively. As shown in figure 3-1 and 3-2, the charge associated with the anodic process was low compared with the forward reduction process.

A prominent feature commonly observed in cyclic voltammograms recorded at relatively low scan rate (below 20 mV/sec) was three reductive reactions which occurred in advance of the bulk lithium deposition process. These reduction processes were irreversible. This suggests that the polymer electrolyte under CV examination could contain more than one reductive product. Water is likely to be
Figure 3-2. Cyclic Voltammogram of the consecutive lithium deposition-dissolution on a Ni working electrode in PEO₆LiClO₄ at 100°C: (a) 1st cycle, (b) steady-state, Sweep rate: 20mV/sec
Polymer electrolyte film used here was dried at 100°C for 48 hours in vacuum.
Figure 3-3 (a)

Figure 3-3 (b)
Figure 3-3. Cyclic Voltammograms obtained at different inversion potentials (a) 1.0, (b) 0.5, (c) 0.2 and (d) 0 V vs. Li/Li\(^+\). Sweep rate: 20mV/sec, Operating temperature: 100°C.

The experiments can identify cathodic peaks corresponding anodic peaks. Polymer electrolyte film used here was dried at 100°C for 48 hours.
the most ubiquitous of impurities in polymer electrolytes. Polyethylene oxide can be contaminated by water. Also during the preparation of polymer electrolyte films by a solvent casting method, the casting solvent acetonitrile (ACN) can contain water. Another impurity present in the system under investigation is oxygen. Oxygen can be transferred into the test cell from outside if the test cell is not tightly sealed.

In order to identify the origin of the reduction processes that occurred in the potential region of 1~1.5 V vs. Li/Li⁺ as shown in figures 3-1 and 3-2, CV was performed with a change of experimental surroundings. After the 1st scan of CV, the test cell was slightly open on purpose and CV was carried out under air atmosphere so that an air transfer from outside might be expected. This expectation is satisfied with cyclic voltammograms obtained from a Li/PEO₄LiClO₄/Ni cell at scan rate of 20 mV/sec as shown in figure 3-4. Two cathodic peaks at 1.25 and 1.45 V vs. Li/Li⁺ were found through successive cathodic scanning. In the first cycle of cyclic voltammograms, only a pronounced cathodic peak at 1.25 V vs.Li/Li⁺ was observed and this peak totally disappeared from the second cycle. No cathodic peak at 1.45 V vs. Li/Li⁺ was shown in the first cycle of cyclic voltammograms, but appeared as a tiny peak shoulder from the second cycle. Its peak magnitude increased clearly as the scan number increased.
Figure 3-4. Wet air effect on the cyclic voltammetric behavior in PEO$_4$LiClO$_4$ at 100°C: (a) 1$^{st}$, (b) 2$^{nd}$, (c) 5$^{th}$, and (d) 9$^{th}$ cycle. In order to study the effect of air (oxygen), this experiment was performed under atmospheric conditions. Polymer electrolyte used here was dried at 100°C for 48 hours in vacuum.
An increase in the peak intensity according to the successive scanning suggests that there is a continuous supply of electroactive species. If the peak at 1.45 V was directly related with H₂O reduction, no shift in peak potential was expected. A shift in potential from 1.45 to 1.25 V observed might be because water reduction to form LiOH is not responsible for the peak at 1.45 V, oxygen reduction being an alternative process. However, it is possible to explain the results by proposing that the peak at 1.25 V occurring on the 1st cycle could be attributed to the removal of oxide on the Ni. The appearance of two cathodic peaks at 0.75 and 0.5 V suggests that the air entering the cell was wet. The other peak at 1.25 V, might also related to H₂O reduction.

Based on literature, a cathodic peak appearing around 1.45 V vs. Li/Li⁺ can be attributed to O₂ reduction process. A typical oxygen reduction process that could occur in a Li/PEO₄LiClO₄/Ni cell can be represented by the following mechanism:

\[
\begin{align*}
\text{O}_2 + e^- & \leftrightarrow \text{O}_2^- \quad (3.1) \\
\text{O}_2^- + \text{Li}^+ & \leftrightarrow \text{LiO}_2^- \quad (3.2)
\end{align*}
\]

In the presence of Li⁺, the superoxide ion formed by the reduction of oxygen may react with Li⁺ to form lithium superoxide at a Ni electrode surface. Since lithium superoxide should be insoluble in polyethylene oxide-lithium salt
electrolyte, lithium superoxide precipitated on a Ni electrode should form eventually a layer thick enough to block the electrode surface even to further oxygen reduction. Since oxygen diffusion into the cell can in practice be largely eliminated, its effect on the formation of blocking layers becomes much smaller in the real system.

Based on cyclic voltammetry observations, another cathodic peak at 1.25 V vs. Li/Li⁺ is not likely to be related to oxygen reduction. Figure 3-5 shows cyclic voltammograms obtained from a Li / polymer electrolyte / Ni cell employing a polymer electrolyte dried further by extending the drying time from 48 hours to 72 hours. In the cyclic voltammograms, the cathodic peak at 1.25 V vs.Li/Li⁺ in the first cycle, which was commonly observed in other cyclic voltammograms, was greatly reduced to a small shoulder peak. Compared to other cyclic voltammograms, the cathodic peak at 1.25 V vs.Li/Li⁺ in figure 3-5 is negligible in terms of peak intensity.

The effect of the extension of drying condition on cyclic voltammograms indicates that the cathodic peak appearing in the first cycle at 1.25 V vs.Li/Li⁺ can be attributed to a water reduction process. An OH stretching band at 3500 cm⁻¹ was not detected from a surface FT-IR spectrum obtained from the polymer electrolyte dried at 100°C for 72 hours in vacuum, but was found for the material dried for 48 hours only, as shown in figure 3-6. Further extension of the drying condition did not make the small peak shoulder at 1.25 V vs. Li/Li⁺ disappear.
Figure 3-5. Effect of the drying condition of polymer electrolytes on the cyclic voltammetry of Ni electrode in PEO$_2$LiClO$_4$ at 100°C. First cycle with both polymer electrolytes dried at 100°C for (a) 48 and (b)72 hours in vacuum. Sweep rate: 20 mV/sec
Figure 3-6. IR spectra of PEO₈LiClO₄ dried at (a) 100°C / 48 hours and (b) 100°C / 72 hours in vacuum.
In electrochemical studies the potential at which water reduction is observed could be controlled by the hydrogen evolution reaction which could occur via the sequential reaction [1].

\[ \begin{align*}
    \text{H}_2\text{O} + e^- &\rightarrow \text{M-H} + \text{OH}^- \quad \cdots (3.3) \\
    \text{M-H} + \text{M-H} &\rightarrow \text{H}_2 \quad \cdots (3.4)
\end{align*} \]

A typical water reduction process to form LiOH can be represented by the following reaction mechanism:

\[ \begin{align*}
    \text{H}_2\text{O} + e^- &\rightarrow \text{OH}^- + \frac{1}{2}\text{H}_2 \uparrow \quad \cdots (3.5) \\
    \text{Li}^+ + \text{OH}^- &\rightarrow \text{LiOH} \quad \cdots (3.6)
\end{align*} \]

The mechanism explains the formation of the LiOH layer as being due to the electrochemical reduction of water followed by a consecutive reaction of Li\(^+\) with the OH\(^-\) product. There are many possible mechanisms for the formation of the LiOH but irrespective of the mechanism, the LiOH layer should act as a barrier delaying mass transport to and from the electrode surface.
Oxygen and water reduction processes occurring at the electrode during the linear scanning of the potential in the negative direction cause consecutive reactions with Li\(^+\) to form layers on the electrode as proposed previously. The properties of these layers could be deduced from the resultant cyclic voltammograms. As observed commonly in cyclic voltammograms, two cathodic peaks were seen at potential below 1.0 V vs. Li/Li\(^+\). This suggests that the formed layer(s) due to oxygen and water reduction do not cover the electrode totally, or that LiOH layer appears porous, letting other cathodic reactions occur.

It is apparent that considerable further electrochemistry occurred between the water (and/or oxygen) reduction peak and the onset of bulk lithium deposition. As shown figure 3-1 and 3-2, two cathodic peaks were observed in the region 0~1.0 V vs. Li/Li\(^+\). Based on the literature [2,3], cathodic peaks in the potential region of 0.5~1.0 V and 0~0.5 V vs. Li/Li\(^+\) can be attributed to the formation of Li-H and to an Li-Ni alloy formation process, respectively.

It is well known that M-H (Metal-hydride) and alloy formation processes are clearly seen in electrolytes contaminated with water and oxygen, thus forming well-developed oxide films on the electrode [3]. As seen in figure 3-4, two broad cathodic peaks in the potential region of 0~1.0 V vs. Li/Li\(^+\) were more pronounced in the subsequent cycle than in the first cycle in the case when oxygen is supplied continuously into the test cell. Thus, when considering the results collated from non-aqueous solvent systems and the test environment, Li-H
and Li-Ni alloy formation can be attributed to further reduction of water. Some water left in the hydrated LiOH layer may also be reduced resulting in a thicker LiOH layer. In parallel a further reduction of water in the LiOH layer could produce LiH by the following mechanism.

\[ \text{Li}^+ + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{LiH} + \text{OH}^- \quad (3.7) \]

Nickel has been regarded as the most stable substrate for lithium deposition [4]. One of the simplest methods for testing the suitability of an electrolyte system for a lithium battery is to measure the Coulomb efficiency of lithium deposition-dissolution by cyclic voltammetry. Since this measurement requires the use of a truly inert substrate for lithium deposition, several metals such as silver (Ag), gold (Au) and nickel (Ni) have been used as working electrodes. Even though Ag and Au are very inert to polar solvent and residual contamination, it has been observed that lithium diffuses into, and alloys with, these metals. In contrast, the degree of alloying of lithium and nickel has been observed to be much lower than Ag and Au in an electrochemical environment since nickel has very a low solubility in alkali metals. Thus Ni has been regarded as one of the best substrate materials for lithium deposition.
However, when the further reduction of water leads to the formation of a lithium hydride layer as explained earlier, and this Li-H layer contains an excess of lithium, Li-Ni alloy formation could be possible. However, no more detailed information can be supplied from these cyclic voltammetric experiments.

Figure 3-7 shows cyclic voltammograms obtained at the scan rate 50 mV/sec. In this case, no profound water reduction peak was found. Cyclic voltammograms obtained at the scan rate of 100 mV/sec, as shown in figure 3-8, demonstrated further the important effect of the scan rate on the water reduction peak. When scan rates of 50 mV/sec and greater were used in the present study cathodic current was observed at potentials below 1.0 V vs.Li/Li⁺ but no actual water reduction peak was recorded. This indicates that a scan rate above 50 mV/sec in the present study seems to be too fast to allow water to diffuse to the electrode surface.

As expected in cyclic voltammograms, when the sweep rate was increased, an increase in the reduction maximum peak current \( i_p \) was observed. The dependence of the maximum peak current \( i_p \) on scan rate \( v \) may be described by the following equation.

\[
i_p = 0.446 \left[ n^{1/2} \cdot R^{1/2} \cdot R_e^{1/2} \cdot T^{1/2} \right] A \cdot D \cdot C \cdot v^{1/2} \tag{3.8}
\]
Fig. 3-7. Cyclic voltammogram of lithium deposition-dissolution on Ni electrode in PEO₃LiClO₄ at sweep rate of 50 mV/sec, Cell operating temperature: 100°C

Polymer electrolyte used here was dried at 100°C for 48 hours.
Fig. 3-8. Cyclic voltammogram of lithium deposition-dissolution on Ni electrode in PEO₃LiClO₄ at sweep rate of 100mV/sec, Cell operating temperature: 100°C
Polymer electrolyte used here was dried at 100°C for 48 hours in vacuum.
where the peak current is expressed in amperes, \( A \) in cm\(^2\), \( c \) in mol/dm\(^3\), the reactant diffusion coefficient \( D \) in cm\(^2\)/s, and the scan rate \( v \) in V/s.

Equation (3-9) is often called the Randle-Sevcik equation and points to the analytically important conclusion that the peak current is linearly dependent on the reactant concentration, and on the square root of the scan rate.

### 3.1.2. Cyclic voltammetry of a Li/PEO\(_4\)LiCF\(_3\)SO\(_3\)/Ni cell

Figure 3-9 shows cyclic voltammograms obtained from a Li/PEO\(_4\)LiCF\(_3\)SO\(_3\)/Ni at scan rate of 20 mV/sec. The cell operating temperature was 100°C. Three cathodic peaks at 1.25, 0.75, and 0.3 V vs. Li/Li\(^+\) were seen in the first cycle of cyclic voltammograms. Their associated anodic peaks at 0.7, 1.5 and 2.0 V vs. Li/Li\(^+\) were also observed in the first scan of the potential in the positive direction. There was no profound difference in the observed peak potentials between PEO\(_4\)LiClO\(_4\) and PEO\(_4\)LiCF\(_3\)SO\(_3\) electrolyte. However, with the CF\(_3\)SO\(_3^-\) anion, cyclic voltammograms were characterized by an additional cathodic peak which appeared as a broad peak shoulder in the potential region of 1.0 ~ 1.5 V vs. Li/Li\(^+\) (compare figures 3-5 and 3-9).

In the cyclic voltammograms obtained at the scan rate of 50 mV/sec, a slight cathodic peak attributed to the water reduction process was seen (figure 3-10). The difference in behavior between PEO\(_4\)LiClO\(_4\) and PEO\(_4\)LiCF\(_3\)SO\(_3\) was found
Fig. 3-9. Cyclic voltammogram of lithium deposition-dissolution on Ni in PEO$_3$LiCF$_3$SO$_3$, Sweep rate: 20 mV/sec, Cell operating temperature: 100°C
Fig. 3-10. Cyclic voltammogram of lithium deposition-dissolution on Ni in PEO$_2$LiCF$_3$SO$_3$, Sweep rate: 50 mV/sec, Cell operating temperature: 100°C
in the case of 100 mV/sec scan rate, as shown in figure 3-11. A diffusion controlled peak was observed at the potential region of 1.0–1.5 V vs. Li/Li⁺.

As the cycle number increased, the cathodic processes decreased more markedly compared to the case of PEO₄LiClO₄ (figure 3-8). It can be proposed that the LiCF₃SO₃-based electrolyte contained a little bit more water than the LiClO₄ electrolyte although the same drying condition (100°C / 48 hours in vacuum) was employed. No further information can be supplied at this stage because of the difficulty of the quantitative comparison between two polymer electrolyte systems by cyclic voltammetry.
Fig. 3-11. Cyclic voltammogram of lithium deposition-dissolution on Ni in PEO₈LiCF₃SO₃ at sweep rate of 100 mV/sec, Cell operating temperature: 100°C
3.2. Critical current in a polymer electrolyte cell

3.2.1. Theory

3.2.1.1. The critical current density, $i^*$

On considering the reduction process of lithium in a polymer electrolyte, it is clear that when a constant current is passed through the cell, initially the current will be used in charging the double layer. At the cathode, there might be an excess electron density build-up and on the electrolyte side, positive ions are gathered on the electrode interface, resulting in excess positive charge density. As the current is continued further, the charge transfer reaction goes further by way of consuming Li$^+$ ions at the interface. The concentration of Li$^+$ at the interface departs from its initial value, which is the bulk concentration. The system is at non-steady state.

However, after the current is passed for a time, a steady state condition can be achieved. A schematic illustration of the transport of the ionic species through the electrolyte and the resulting concentration gradient at equilibrium, non-steady state, and steady state is given in figure 3-12.

The supply of Li$^+$ ions must be enough to sustain the applied current. The formation of a passivating layer consumes the reactant; Li$^+$ ions and the resulting
(a) \( t=0 \) at equilibrium

\[
\text{Conc. of } \text{Li}^+ \\
\text{distance, } x
\]

(b) \( t > 0 \) at non-steady state

\( t_1 : \quad \quad, \quad t_2 : \quad ----, \quad t_3 : \quad ------ \)

\( t_3 > t_2 > t_1 \)
(c) $t \to \infty$ at steady state

![Diagram showing concentration gradient at equilibrium, non-steady state, and steady state.](image_url)

**Fig.3-12.** The concentration gradient at equilibrium (a), non-steady state (b), and steady state (c)
passivating layers may hinder ionic movement as well. Hence, the supply of Li⁺ ions for the charge transfer reaction at the interface becomes insufficient to sustain the applied current.

There are two limiting cases; *(i)* when $t_{\text{charge}} \rightarrow \infty$, concentration gradient become linear (fig. 3-12(c)) and *(ii)* concentration of Li⁺ at the electrode surface becomes zero ($c_{\text{surface}} \rightarrow 0$). As $t_{\text{charge}} \rightarrow \infty$, the concentration gradient becomes linear as shown in figure 3-12(c). At this condition, the slope of concentration gradient can be expressed as follows:

$$\text{slope} = \frac{dc}{dx} = \frac{(c_0 - c_s)}{(h/2)} = \frac{2(c_0 - c_s)}{h} \quad \text{...(3.9)}$$

This concentration gradient can be inserted in Fick's first law to obtain the flux. However, the effect of coupled diffusion and migration (see Appendix) gives:

$$\text{Flux} = -2D \frac{dc}{dx} = +4D \frac{(c_0 - c_s)}{h} \text{ as } t_{\text{charge}} \rightarrow \infty \quad \text{...(3.10)}$$

$$I = 4zFD (c_0 - c_s) \quad \text{...(3.11)}$$
Under a more exact analysis by Williams [see appendix], the critical current, $I^*$, is expressed as follows:

$$I^* = 2 \times 0.636617 \pi z A c_0 F D / h$$

$$= 4 z A c_0 F D / h \quad \ldots(3.14)$$

where $I^*$ denotes a critical current (A), $z$ the ionic charge number, $A$ the cathode electrode area (cm$^2$), $c_0$ the Li$^+$ concentration (mole/cm$^3$) added to the polymer electrolyte, $F$ the Faraday constant (C/mole), $D$ the Li$^+$ diffusion coefficient (cm$^2$/sec), and $h$ the electrolyte thickness (cm).

The equation shows the dependence of the critical current on the polymer electrolyte thickness, $h$, the Li$^+$ concentration, $c_0$, and the Li$^+$ diffusion coefficient, $D$.

The critical current density was measured by the ramping current method. This technique is relatively easy to apply. In order to secure the steady state condition for the current ramp experiment the ramp current application time was controlled on the following assumption. Under steady-state condition, the charge-transfer reaction current density, $i_{CTR}$, must be equal to the current density due to the transport of lithium, $i_{TRANSPORT}$. The equality of the charge transfer flux ($\equiv$ current/$zF$) and the transport flux must be satisfied.
\[ \tau >> \frac{h^2}{D} \ldots \] (3.15)

where \( \tau \) denotes the time for transition to reach the critical current in the system (sec), \( h \) the thickness of electrolyte (polymer electrolyte film thickness, cm), and \( D \) the diffusion coefficient of Li\(^+\) (cm\(^2\)/sec).

Many techniques have been utilized in a determination of the diffusion coefficient, \( D \), such as NMR, Radiotracer, and the Extended X-ray Absorption Fine Structure (EXAFS) technique. Also the use of ionic conductivity measurements can be used for the measurements of the diffusion coefficient in polymer electrolytes. The Li\(^+\) mean diffusion coefficient, \( D \), can be calculated by putting the observed critical current into equation (3-14). This method can be one of the most simple electrochemical methods for the measurement of the mean diffusion coefficient.

3.2.1.2. Effect of the passivating layers on the critical current

As noted before, it is well known that Li surfaces in polar solvents are covered with films formed by precipitation of species which are the products of reactions between metallic lithium and solution components (e.g., solvents, salts and contaminants). These surface films control the electrochemical behavior of
Li⁺ in solution. The electronic properties and stability of surface films are important factors determining the battery performance. If the surface films are dense and electronically insulating, the reaction rate of further electrolyte reduction will be reduced. Conversely if surface films have a good lithium ionic conductivity, cycling efficiency may be improved.

Clearly the formation of passivating layers may cause detrimental as well as beneficial effects on battery performance. The passivating process proceeds through an electrochemical reaction that consumes irreversibly electrolyte and electrons. As observed from cyclic voltammetry of various Li/polymer electrolyte/Ni cells in the previous section, the formation of an LiOH layer occurs during deposition of lithium. Therefore, the charging current efficiency could be reduced as a consequence of the consumption of lithium ions through the reaction with water molecules. In addition, the passivating layer formed on the electrode may act as an obstacle to hinder the ionic movement during the charging process, thus leading to increasing charging overpotential.

It is sometimes observed when passivating layers are developed on the electrode in a current-delivering electrochemical cell that the reaction rate (electric current) diminishes gradually or suddenly although the active reactants are yet far from being exhausted. If the current is maintained constant by external devices, the electrode polarization is increased. In some cases the potential is pushed so high that a competing electrochemical reaction is initiated. In
rechargeable batteries with non-aqueous electrolytes, similar processes of electrolytic decomposition of the solvent or electrolyte can occur.

3.2.2. A measurement of a critical current in the PEO₄LiClO₄ electrolyte

Figure 3-13 shows a typical resulting curve when the potential difference across the cell is plotted against the applied current density during the reduction process of lithium, exhibiting the critical current density in PEO₄LiClO₄. A three-electrode test cell was used as depicted in figure 2-1. A working electrode was a Ni- sheet. The applied current density was increased in a linear ramp with time at the rate of 0.2 μAcm²s⁻¹. The cut-off potential difference across the cell (|ΔE|) was 1,000 mV. The thickness of a polymer electrolyte film (PEO₄LiClO₄) was 100μm and the cell-operating temperature was 100°C. In the resulting curve of potential difference across the cell plotted versus applied current density, the potential difference across the cell always has the positive value that is a measure of the departure from the equilibrium potential. The actual behavior of potential difference across the cell, ΔE, should be diminishing from the equilibrium potential in the negative direction. The observed critical current was 0.756 mA/cm².

For low current excursions below this critical current density, the curve of potential difference across the cell against current density is observed to be linear.
Figure 3-13. Variation of potential difference across the cell ($\Delta E$) with current density ($i$) in a Li/PEO$_x$LiClO$_4$/Nicell at 100°C, polymer electrolyte thickness: 100$\mu$m

The applied current density was increased in a linear ramp with time at rate 0.2 $\mu$Acm$^{-2}$s$^{-1}$
However, beyond the critical value of current density, an abrupt increase of potential difference on increasing the applied current density was observed. As explained briefly in the last section, the reduction process in a polymer electrolyte cell, Li/PEO₄LiClO₄/Ni, can not sustain the applied current density thus leading to an abrupt increase in the potential difference.

The critical current density, \( i^* \), obtained from a current ramp experiment allowed the determination of the mean diffusion coefficient of Li\(^+\) in polymer electrolyte system according to the equation (3.14) This equation yielded a value of \( D_{Li^+} = 1.95 \times 10^{-4} \text{ cm}^2/\text{sec.} \) The calculated diffusion coefficient at 100°C is comparable to the value reported for lithium self-diffusion coefficient in LiClO₄ doped polyethylene oxide and measured by NMR spectroscopy [5]. The calculated mean diffusion coefficient will be described separately.

From the region of lower current excursions showing a linear relationship between potential difference and the applied current as shown in figure 3-14, the conductivity, \( \sigma \), of the Li/PEO₄LiClO₄/Ni cell was calculated from the potential and current curve slope (\( V/T \)) and the geometry of the cell.

\[
\sigma = \frac{L}{A} \cdot \frac{I}{V} \quad \text{(3.16)}
\]

where \( L \) (cm) denotes the thickness of polymer electrolyte film, and \( A \) (cm²) the electrode area.
Figure 3-14. Calculation of conductivity from the curve of $\Delta E$ vs. $I$ as in figure 3-13.

Conductivity calculated from the curve slope and cell geometry
A value of \( \sigma = 2.8 \times 10^4 \text{ S/cm} \) was obtained. This conductivity value is about one order of magnitude lower than the value obtained by impedance spectroscopy reported by others [6]. This implies that there is another element of electrical resistance in the cell, which would be associated with the interface and the electrode reaction.

### 3.2.2.1. Temperature effect on the critical current

Ramp current experiments were performed on cells containing PEO\(_4\)LiClO\(_4\) electrolyte (all polymer electrolytes have the same thickness of 100\(\mu\)m) at different cell-operating temperatures ranging from 80~120°C as shown in figure 3-15. The critical current measurement also showed a similar phenomenon: *an abrupt increase in the potential difference on increasing the applied current beyond the certain values*. This is a typical case for showing the effect of cell-operating temperature on the critical current.

The potential difference across the cell, \( \Delta E \), against current density, \( i \), was plotted as in figure 3-15 (a). A higher value of the critical current was obtained from the cell with a higher operating temperature as shown in figure 3-15 (b). Values of the observed critical current were 1.89 mA/cm\(^2\) at 120°C and 0.216 mA/cm\(^2\) at 80°C. The value of the critical current obtained at 120°C is about 2\(\frac{1}{2}\) times higher than that of the value obtained at 100°C. The value of the observed
Figure 3-15(a). Temperature effect on the critical current density for lithium deposition on Ni electrode in PEO$_2$LiClO$_4$. Polymer electrolyte thickness: 100μm

Potential difference across the cell, ΔE, against current density, i. The applied current density was increased in a linear ramp with time, at rate of 0.2 μAcm$^{-2}$s$^{-1}$
Figure 3-15 (b). Critical current density vs. temperature.
SPE : PEO$_4$LiClO$_4$, thickness: 100µm
times higher than that of the value obtained at 100°C. The value of the observed critical current obtained at 80°C was \(3\frac{1}{2}\) times lower than the value at 100°C.

In addition, the potential difference/current curve allowed the calculation of the mean conductivity at each temperature. The calculated mean conductivity was \(4.8 \times 10^{-4}\), \(2.8 \times 10^{-4}\), and \(3.0 \times 10^{-5}\) S/cm respectively. These values are one or two orders of magnitude lower than values obtained from impedance spectroscopy (figure 3-16).

### 3.2.2.2. SPE thickness effect on the critical current

In figure 3-17(a), a plot of the potential difference versus current for the Li/PEO\(_4\)LiClO\(_4\)/Ni cells, shows the critical current density as a function of the polymer electrolyte film thickness at 100°C. The observed critical current decreases with increasing the electrolyte film thickness. An increase in thickness from 100 to 130 \(\mu\)m lead to a decrease in a critical current density from 0.756 to 0.555 mA/cm\(^2\). The critical current density obtained from the cell employing a 150-\(\mu\)m thick electrolyte film was further decreased, to 0.516 mA/cm\(^2\).

Since the diffusion coefficient of Li\(^+\) in polymer electrolytes is typically around \(10^{-8}\) cm\(^2\)/sec at 100°C [6], changes in electrolyte thickness of 30-50 \(\mu\)m can not be negligible in terms of the transport of ionic materials in the polymer
Figure 3-16. Conductivity against temperature, $T$ for PEO$_x$LiClO$_4$ film 100$\mu$m thick, as calculated from the curve slope ($d\Delta E/d\delta$) and cell geometry.
Figure 3-17-(a). Effect of SPE thickness on the critical current density. Potential difference across the cell, $\Delta E$, against current density, $i$ (a) 0.010, (b) 0.013 and (c) 0.015 cm

The applied current density was increased in a linear ramp with time, at rate $0.2 \, \mu\text{Acm}^{-2}\text{s}^{-1}$. 
electrolyte. The mean conductivity calculated from the slope of the resulting curve and cell geometry shows values decreasing slightly with increasing electrolyte film thickness, of $2.76 \times 10^{-4}$ (100 µm), $2.18 \times 10^{-4}$ (130 µm), and $2.04 \times 10^{-4}$ S/cm (150 µm). This observation is at least consistent with the presumption that there is an additional resistance in the cell associated with the interface. As shown in figure 3-17(b) plotting resistance ($R = I/\sigma$) against thickness ($h$), resistance of the passivating film formed was determined by the extrapolation of the curve. The calculated resistance was $1.1 \times 10^3 \Omega$.

3.2.2.3. Calculation of the diffusion coefficient

The diffusion coefficient, $D$, was calculated from critical current data using equation (3.14) derived in section 3.1.2. In table 3.1 a summary of the derived diffusion coefficients is given. Although no data are available from other works for precise comparison with these values, since experimental conditions are not the same, the values obtained here are consistent with previous work [5].

3.2.2.4. Effect of the substrate shape on the critical current

A Ni wire was used rather than a Ni sheet to study the effect of the substrate shape on the critical current at 100°C. As shown in figure 3-18, the observed
Figure 3-17 (b) . R vs. $h$ in PEO$_4$LiClO$_4$
<table>
<thead>
<tr>
<th>SPE Thickness (h/μm)</th>
<th>Temperature (T/°C)</th>
<th>Critical Current Density (i/mAcm²)</th>
<th>Diffusion Coefficient (D/cm²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>80</td>
<td>0.216</td>
<td>5.58 x 10⁹</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.756</td>
<td>1.95 x 10⁸</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1.890</td>
<td>4.88 x 10⁸</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.756</td>
<td>1.95 x 10⁸</td>
</tr>
<tr>
<td>130</td>
<td></td>
<td>0.560</td>
<td>1.88 x 10⁻⁸</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>0.520</td>
<td>2.01 x 10⁻⁸</td>
</tr>
</tbody>
</table>

\* \(c_a = 1 \times 10^{-3} \text{ mol cm}^{-3}\)

Table 3-1. The observed critical current density and the diffusion coefficient of PEO₈LiClO₄.
values of the critical current were 0.40 mA/cm² (80°C) and 1.69 mA/cm² (100°C). The higher value with a Ni wire substrate than with a Ni plate reflects spherical diffusion against linear diffusion. From geometrical considerations, the reaction rate is much higher at the wire electrode than at the flat electrode.

3.2.2.5. Cell cycling effect on the critical current

Figure 3-19 presents a variation of the critical current during cycling. Values of the observed critical current were obtained from a Li/PEO₅LiClO₄/Ni employing a 100-µm thick polymer electrolyte at 100°C. The observed critical current decreases with the number of cycles as shown in figure 3-20 plotting the critical current as a function of the cycle number. A gradual decay of the critical current may be explained as follows: the electrode surface seems to be covered gradually with increasing cycle number. If a LiOH layer is fully developed at the electrode surface, a further reduction of water can be hindered entirely.

More detailed information about the resistive layer build-up at the interface can be obtained from a plot of the conductivity, σ (S/cm), versus cycle number as shown in figure 3-21. At the initial stage of cycling, a steep decay of the conductivity was observed. For the following few cycles, the conductivity was reasonably constant. However, after the 5th cycle, the conductivity fell steeply again (Table 3-2).
Figure 3-18. Effect of the operating temperature on the critical current:
(a) 80 and (b) 100°C, SPE: PEO$_2$LiClO$_4$, thickness: 100µm

A Ni wire was used as working electrode. The applied current density was increased in a linear ramp with time at the rate of 0.2 µAcm$^2$ s$^{-1}$. 
Figure 3-19. Curves of potential difference across the cell ($\Delta E$) vs. applied ramping current density ($i$) with cycle number in PEO$_4$LiClO$_4$ at 100°C: (a) 1$^{st}$, (b) 2$^{nd}$, (c) 5$^{th}$ and (d) 10$^{th}$ cycle.

SPE thickness: 100\,\mu m

The applied current density was increased in a linear ramp with time at rate of 0.2 \, \mu A cm$^{-2}$ s$^{-1}$
Figure 3-20. Critical current ($i$) vs. cycle number in PEO$_x$LiClO$_4$ at 100°C, SPE thickness: 100 μm
The critical current density was measured in a galvanostatic ramp experiment with $di/dt = 0.2 \, \mu A \, cm^{-2} \, s^{-1}$
Figure 3-21. Calculated conductivity vs. cycle number at 100°C, polymer electrolyte: PEO₆LiClO₄, SPE thickness: 100μm

The conductivity was calculated from the slope of the curve (ΔE vs.İ) and cell geometry. A galavnostatic ramp experiment was performed at rate of 0.2 μA cm⁻² s⁻¹.
<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Critical current ((i/mAcm^2))</th>
<th>Conductivity ((\sigma/Scm^{-1}))</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.756</td>
<td>2.8 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.724</td>
<td>2.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.718</td>
<td>2.4 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.704</td>
<td>2.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.683</td>
<td>2.1 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.651</td>
<td>2.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.639</td>
<td>2.0 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.607</td>
<td>1.9 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.595</td>
<td>1.7 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.598</td>
<td>1.6 \times 10^{-4}</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.2.** Variation of the critical current and apparent conductivity with cycle number obtained with PEO\(_8\)LiClO\(_4\).
3.2.3. A measurement of a critical current in PEO₃LiCF₃SO₃ electrolyte

Figure 3-22 displays a typical potential difference versus applied current density trace used to determine critical current density in PEO₃LiCF₃SO₃ at 100°C. The cell employed a 100-μm thick film. At 1.95 mA/cm², the potential difference across the cell suddenly jumped to a high value as shown before for PEO₃LiClO₄ electrolyte. Compared to PEO₃LiClO₄ the critical current density value obtained from PEO₃LiCF₃SO₃ was much higher (0.756 mA/cm² versus 1.950 mA/cm²). A value of the mean diffusion coefficient, $D_{Li^+}$, of $5.14 \times 10^{-8}$ cm²/sec was obtained using equation 3.14.

Figure 3-23(a) shows the effect of temperature on the critical current of a Li/PEO₃LiCF₃SO₃/Ni cell employing a 100-μm thick film. Values of the critical current were 2.70 mA/cm² at 120°C and 1.26 mA/cm² at 80°C. As seen in the case of PEO₃LiClO₄ (figure 3-14), the critical current displays a temperature dependence (figure 3-23(b)). The critical current is directly proportional to mobility expressed by a diffusion coefficient, so the temperature dependence reflects this.

Figure 3-24 (a) displays the effect of polymer electrolyte thickness on the critical current density. As the electrolyte thickness is increased, the critical current decreases as expected. This follows as the same trend as experienced in PEO₃LiClO₄. The expected relation, $i^* \propto 1/h$, is supported by the experimental
Figure 3-22. Variation of potential difference across the cell (ΔE) against applied current density (i) for PEO$_3$LiCF$_3$SO$_3$ at 100°C, SPE thickness: 100μm

The applied current density was increased in a linear ramp with time, at a rate of 0.2μA cm$^{-2}$s$^{-1}$
Figure 3-23-(a). Temperature effect on the critical current density for PEO-LiCF$_3$SO$_3$, SPE thickness: 100 µm, temperature: (a) 80, (b) 100°C and (c) 120°C

Potential difference across the cell, ΔE, against current density, $i$. The applied current density was increased in a linear ramp with time at rate of 0.2 µA cm$^{-2}$ s$^{-1}$. 
Figure 3-23(b). Critical current density vs. temperature, SPE:PEO₆LiCF₂SO₃, thickness:100μm
Figure 3-24-(a). Effect of SPE thickness on the critical current density of PEO<sub>x</sub>LiCF<sub>3</sub>SO<sub>3</sub> at 100°C: (a) 0.008, (b) 0.010 and (c) 0.013 cm

Potential difference, $\Delta E$, against current density, $i$. The applied current density was increased in a linear ramp with time at rate of 0.2 $\mu$A cm<sup>-2</sup>s<sup>-1</sup>.
Figure 3-24 (b). R vs h in PEO₆LiCF₃SO₃
results. The measured critical current density and derived diffusion coefficient are summarized in table 3.3.

The results for the calculated conductivity are summarized in table 3.4. As temperature is increased, conductivity increases as shown in figure 3-25. This follows the same trend as experienced in PEO$_4$LiClO$_4$.

<table>
<thead>
<tr>
<th>Operating temperature (°C)</th>
<th>Conductivity (σ/Scm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>$2.95 \times 10^3$</td>
</tr>
<tr>
<td>100</td>
<td>$1.91 \times 10^4$</td>
</tr>
<tr>
<td>120</td>
<td>$2.95 \times 10^4$</td>
</tr>
</tbody>
</table>

Table 3.4. The effect of temperature on the conductivity of PEO$_4$LiCF$_3$SO$_3$,

SPE thickness: 100μm

The resistance of the passivating film was determined by the extrapolating the curve in figure 3-24 (b). A value of $1.9 \times 10^3$Ω was obtained.

3.2.3.1. Effect of the substrate shape on the critical current

The curve plotting the potential difference across the cell against current density employing a Ni wire rather than a Ni sheet as the substrate is shown in
<table>
<thead>
<tr>
<th>SPE thickness (h/μm)</th>
<th>Temperature (T/°C)</th>
<th>Critical Current density (i/mAcm²)</th>
<th>Diffusion coefficient (D/cm²sec⁻¹)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>80</td>
<td>1.26</td>
<td>3.32 ×10⁻⁸</td>
<td>Ni sheet</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.95</td>
<td>5.14 ×10⁻⁸</td>
<td>Ni sheet</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>2.70</td>
<td>7.11 ×10⁻⁸</td>
<td>Ni sheet</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>2.34</td>
<td>4.93 ×10⁻⁸</td>
<td>Ni sheet</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>1.95</td>
<td>5.14 ×10⁻⁸</td>
<td>Ni sheet</td>
</tr>
<tr>
<td>130</td>
<td></td>
<td>1.26</td>
<td>4.31 ×10⁻⁸</td>
<td></td>
</tr>
</tbody>
</table>

* *c₀ = 9.8 × 10⁻⁴ mol cm⁻³

Table 3.3. Measured and derived quantities for the cell: Li/PEO₉LiCF₃SO₃/Ni
Figure 3-25. Temperature vs. conductivity of lithium in PEO₄LiCF₃SO₃ at various temperatures, SPE thickness:100 μm

The conductivity was calculated from the cell geometry and the curve (ΔE vs. Δ) slope obtained from a galvanostatic ramp experiment with $\frac{d\Delta}{dt} = 0.2 \ \mu \text{A cm}^{-2} \text{s}^{-1}$. 
Observed values of the critical current were 1.45 mA/cm² at 80°C and 3.30 mA/cm² at 100°C, respectively. As before, a higher value in the critical current density was achieved for the wire.

3.2.3.2. Cell cycling effect on the critical current

Figure 3-27 presents the cell cycling effect on the critical current obtained from a Li/PEO₂LiCF₃SO₃/Ni cell at 100°C. As a cycle number increased, the critical current density decreased from 1.95 mA/cm² to 1.59 mA/cm². All calculated conductivities are plotted against the cycle number in figure 3-28. (see Table 3.5)

3.2.4. Cycling efficiency vs. critical current

Plating and stripping of lithium on a Ni electrode at constant current density was carried out to define the charge and discharge characteristics of the negative electrode in polymer electrolytes. In a given cycle, lithium was deposited on Ni electrode and stripped at constant current. The overall cycling efficiency of a cycle is defined as

$$E(\%) = \frac{i_{\text{dis}}t_{\text{dis}}}{i_{\text{dep}}t_{\text{dep}}} = \frac{Q_{\text{dis}}}{Q_{\text{dep}}} \quad \text{(3.16)}$$
Figure 3-26. Effect of the operating temperature on the critical current: (a) 80 and (b) 100°C, SPE: PEO₃LiCF₃SO₃, thickness: 100μm,

A Ni wire was sued as working electrode. The applied current density was increased in a linear ramp with time at the rate of 0.2 μAcm⁻² s⁻¹.
Figure 3-27. Curves of potential difference across the cell (ΔE) vs. applied ramping current density (i) with cycle number (1st, 3rd, 5th, 8th, and 10th cycle) in PEO₃LiCF₃SO₃ at 100°C, SPE thickness: 100μm.

The applied current density was increased in a linear ramp with time at rate 0.2 μAcm⁻²s⁻¹.
<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Critical Current Density (i/mAcm$^2$)</th>
<th>Conductivity ($\sigma$/Scm$^{-1}$)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.95</td>
<td>1.91 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.91</td>
<td>1.87 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.90</td>
<td>1.73 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.86</td>
<td>1.75 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.83</td>
<td>1.59 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.78</td>
<td>1.59 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.76</td>
<td>1.55 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.70</td>
<td>1.39 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.66</td>
<td>1.30 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.59</td>
<td>1.27 x 10^{-4}</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5. Variation of the critical current and conductivity with cycle number obtained with PEO$_4$LiCF$_3$SO$_3$.
Figure 3-28. Changes in the calculated conductivity with cycle number at 100°C, PEO$_4$LiCF$_3$SO$_3$ thickness: 100μm

The conductivity was calculated from the cell geometry and the slope of the curve of $\Delta E$ vs. $i$ from a galvanostatic ramp experiment at rate of 0.2μAcm$^{-2}$s$^{-1}$. 
where $i_{dis}$ and $i_{dep}$ denote the current for dissolution and deposition, $t$ the time and $Q$ the charge.

In experiments, each deposition process consisted of a given constant current, yielding 1.0 C/cm$^2$ of lithium deposited on Ni working electrode. After deposition, the polarity of the Ni electrode was immediately reversed and lithium stripped at the same current density. The cycle was terminated at +1.0 V. Prior to the beginning of the next cycle, a 45-minute rest time was given for relaxation.

Figure 3-29 displays variation of the Coulomb efficiency during cycling in PEO$_n$LiClO$_4$ at 100°C with cycle number at different current densities. The current densities applied to cells were 0.5, 1.0, 1.5, 2 and 3 mA/cm$^2$, respectively, yielding 1.0 C/cm$^2$. In this experiment, with fixed charge, the charging time increase as current density decreases. There is a different critical current density to that presented earlier. This current density is that below which the transition time (see Appendix I) is not exceeded during the experiment. An exact calculation is given in Appendix I. An approximate one, based on the Sand equation, is given here. For current density, $i$, and charge density $q$, the transition current density, $i^*$ is such that

$$i^* (q/i^*)^{1/2} = c_o F\pi^{1/2}D_e / D_e^{1/2}$$

That is,

$$i^* = c_o^{-2} F^2 \pi D_e^{2/3} D_e q$$

98
Figure 3-29. Variation of Coulomb efficiency of lithium deposition–stripping in PEO$_6$LiClO$_4$ at 100°C with cycle number, $i_p = i_o, Q_p = 1.0$ C/cm$^2$. 
With the assumption that $D_v = D_c = D$ (equivalent to assuming transport number, $t_s = 0.5$):

\[ i^* = c_o^2 F^2 \pi D / q \quad \text{(3.19)} \]

For this experiment, $i^* = 2.12 \text{ mA/cm}^2$.

At 0.5 mA/cm$^2$, no profound decrease in efficiency with cycle number was observed while at 1.0 mA/cm$^2$, a decrease in efficiency was found. The decrease in coulomb efficiency with cycle number became more significant at higher current densities over 1.0 mA/cm$^2$, which was higher than the critical current density.

The stripping efficiency for the first cycle increased from 80 to 85 % with increasing current density. Perhaps this was an effect due to the passive layer formed on the electrodes. However, the passivating layers formed by decomposition of the electrolyte when the current density exceeded the critical current density clearly degraded the cycling performance of the cell.

In figure 3-30 efficiency results with cycle number obtained with PEO$_x$LiCF$_3$SO$_3$ at 100°C are shown. The corresponding critical current density was 1.95 mA/cm$^2$. The efficiency curves with cycle number obtained with PEO$_x$LiCF$_3$SO$_3$ for up to 2 mA/cm$^2$, which was about equal to the corresponding
Figure 3-30. Variation of efficiency with cycle number in PEO₈LiCF₃SO₃ at various current densities, \( Q_\text{p} = 1.0 \text{ C/cm}^2 \), \( i_p = i_r \).
critical current density, showed no decay in cycling efficiency. When the applied current density for cycling was 3 mA/cm², the efficiency decreased gradually as the cycling proceeded. At the applied current density of 4.0 mA/cm², the efficiency dropped suddenly from the 15th cycle.

It was observed commonly in both electrolytes that good efficiency was achieved when the applied current density was lower than the corresponding critical current density. Conversely, when the applied current density for the cycling was higher than the critical current, it afforded poor cycling efficiency. This trend is expected, since decomposition of the electrolyte requires that transition occurs as well as application of a current density greater than the critical current.
3.3. Microscopic observation of Li deposit morphology

3.3.1. Experimental investigation of the morphology of the Li deposited in polymer electrolytes at elevated temperature

In this chapter, electrochemical deposition of lithium was carried out on a Ni wire substrate to study the morphology of deposit in polymer electrolytes. To minimize effect of the surface roughness of the substrate on the resulting morphology, a Ni wire was used as working electrode. A smoother surface could be achieved with wire than sheet. The critical current, measured as described earlier, was used to derive an "effective" diffusion coefficient for the wire by application of equation 3.13. This effective diffusion coefficient approximately takes account of the effect of geometry. Then, a transition time was calculated, again assuming the equation for linear diffusion (Appendix I) but using the effective diffusion coefficient to account for the geometrical effect. It was also necessary to make some assumption about the relative mobility of anions and cations, \( D_+ = D_- \), so \( D_+ = D_e \) (notation in Appendix I). Table 3.6 lists the effective diffusion coefficient and calculated transition times for the condition used in the study.
Table 3.6: The effective diffusion coefficient and calculated transition times for the conditions used in the study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Calculated diffusion coefficient (cm²/s)</th>
<th>Apparent diffusion coefficient (cm²/s)</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEOT:ICF₅₀₀³</td>
<td>10.0 × 10⁻⁶</td>
<td>10.0</td>
<td>100</td>
</tr>
<tr>
<td>PEOT:ICF₅₀</td>
<td>4.37 × 10⁻⁶</td>
<td>10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PEOT:ICF₅₀₀</td>
<td>4.37 × 10⁻⁶</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PEOT:ICF₅₀₀₀</td>
<td>1.03 × 10⁻⁶</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>PEOT:ICF₅₀₀₀₀</td>
<td>Calculated diffusion coefficient (cm²/s)</td>
<td>Apparent diffusion coefficient (cm²/s)</td>
<td>Experimental conditions</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
<td>----------------------------------------</td>
<td>-------------------------</td>
</tr>
</tbody>
</table>
3.3.2. Deposition morphology in PEO₈LiClO₄

Figure 3-31 shows typical lithium deposits in a polymer electrolyte (PEO₈LiClO₄) at 100°C obtained after deposition at 3.0 mA/cm² for 20 minutes on a Ni wire. This current density was greater than the critical current density \(i^* = 1.69 \text{ mA cm}^{-2}: \text{Ni wire}\). The expected transition time, \(\tau\), was 151 seconds (see Table 3-6), where the concentration of Li⁺ becomes zero at constant current application at the given condition (see Appendix II). The deposits were well developed semicircular. The growth distance from the substrate to the end of the deposits approximately ranged from 6 to 8 μm. Compared to the resulting growth distance in hybrid polymer electrolytes reported in the literature [7], the growth distance in the pure polymer electrolytes is much shorter. Lithium deposits are far from the 'needle-like' forms that are generally initially observed in the liquid electrolyte system. These results may indicate that mass transport in electrolytes and formation of the passivation layer can affect the growth distance and the structure of deposits.

Figure 3-32a to 3-32b shows a morphological comparison of deposited lithium with different cell operating temperatures (80 and 100°C). These deposits were produced under the same current density and time: 0.5 mA/cm² for 60 minutes. Again, in PEO₈LiClO₄ at 100°C, the deposits are globe-like (fig. 3-34 (a)). The observed thickness of deposit layer was about 7 μm. At 80°C needle-like deposits were observed on the top of the globular lithium deposits as seen in
Fig. 3-31. Electrochemically deposited lithium on a Ni-wire working electrode in PEO₄LiClO₄ at 100°C. The thickness of polymer electrolyte was 100μm.

The electrodeposition current was 3.0 mA/cm² and total charge passed was 3.6 C/cm² (deposition time: 1 hour). The expected transition time, τ, was 158 seconds.
Fig. 3-32. Photographs showing the effect of the cell operating temperature on the structure of deposits in PEO$_2$LiClO$_4$ at (a) 100, and (b) 80°C.

The thickness of polymer electrolyte was 100μm. The electrodeposition current was 0.5 mA/cm$^2$ and total charge passed was 1.8 C/cm$^2$(deposition time: 1 hour). The expected transition time at 80°C, $\tau$, was 1375 seconds.
The observed thickness of the deposit layer was about 4 μm. The deposition current density was less than the critical current density at 100°C but greater than the critical current density at 80°C. The expected transition time, τ, at 80°C was 1375 seconds.

Figure 3-33 shows the morphology of the lithium deposits obtained from various parts of the substrate after 1 mA/cm² deposition for 60 minutes at 100°C. The main structure of the deposits was still globular and the growth distance ranged from 8 to 10 μm (fig.3-33 (a)). However, hook-like lithium deposits isolated from other deposits were also seen (fig. 3-33 (b)).

Figure 3-34 shows lithium morphologies after deposition at 3.0 mA/cm² for 1 hour at 100°C. Even though globular lithium covers the majority of the electrode surface area, well-developed lithium dendrites were clearly observed as well. Dendritic deposition has not continued over the total area of the substrate but concentrated on a small part of the total area.

Figure 3-35 shows the FT-IR spectrum obtained from the surface of the dendrites shown in figure 3-34. A broad peak at around 3400-3600 cm⁻¹, which can be attributed to O-H stretching band, was observed. This confirms that the passivating film consists of LiOH and this layer perturbs the morphology into the dendritic growth.
Fig. 3-33. Photographs showing the effect of the cell operating temperature on the structure of deposits in PEO₄LiClO₄ at 100°C: (a) globular, and (b) hook-like Li deposits.

The thickness of polymer electrolyte was 100μm. The electrodeposition current was 1.0 mA/cm² and total charge passed was 3.6 C/cm².
Fig. 3-34. Dendritic growth in PEO$_x$LiClO$_4$ at 100°C.
The thickness of polymer electrolyte was 100 μm. The
electrodeposition current was 3.0 mA/cm$^2$ and total charge
passed was 10.8 C/cm$^2$(deposition time: 1 hour). The expected
transition time, $\tau$, was 151 seconds.
Figure 3-35. Surface FT-IR spectra obtained from lithium dendrite. Dendrites were observed after 1-hour deposition at the current density of 3.0 mA/cm$^2$ in PEO$_8$LiClO$_4$ at 100°C.
A continuous microscopic observation of the change of deposit morphology into dendrite was carried out as shown in figure 3-36. These photographs show clearly the formation of dendrites via growth of pillars where the current was concentrated. At the initial stage of deposition at 3.0 mA/cm², typical globular lithium deposits were observed which grew into a dense lithium deposit layer (fig. 3-36 (a)). A macro-rough deposit layer was then developed on the substrate with a pillar which shot out from the electrode (fig. 3-36 (b)). This pillar grew further (fig. 3-36 (c)). As seen in figure from 3-36 (d) to 3-36 (e), the current tended to focus on the tip of the grown pillar. As the deposition went on, deposition was localized to form tree-like deposit. In this experiment, the tree-like deposit developed further into dendrites.

When the same current density was applied in the reverse direction to dissolve lithium deposits, the lithium stripped from all parts of the tree-like deposit as seen in figure 3-37. The tree-like deposit disappeared totally in the following dissolution process (fig. 3-37 (b)). The applied current density for dissolution was clearly enough to dissolve the lithium in tree-like dendrites and the less passivated lithium.

3.3.3. Deposition morphology in PEO₄LiCF₃SO₃

Figure 3-38 displays the morphology of lithium deposited at 0.5 mA/cm² for 60 minutes from the PEO₄LiCF₃SO₃ electrolyte operating at 80°C. The deposition
Fig. 3-36. Photographs showing the formation of tree-like Li deposits in PEO$_x$LiClO$_4$ at 100°C:
(a) after first 10 minutes of deposition at 3.0 mA/cm$^2$
(b) after 30 minutes of deposition at 3.0 mA/cm$^2$
The thickness of polymer electrolyte was 100μm
Fig. 3-36.
(c) after 35 minutes of deposition at 3.0 mA/cm²
(d) after 40 minutes of deposition at 3.0 mA/cm²
The thickness of polymer electrolyte was 100μm
Fig. 3-36.
(e) after 42 minutes of deposition at 3.0 mA/cm²; tree-like Li deposits formed
Fig. 3-37. Dissolution of tree-like Li deposits as shown in fog.
3-36(e) : (a) after first 20 minutes of dissolution, and (b) after 30 minutes of dissolution.
The polarity of current was reversed without any pause before the following dissolution and the dissolution current was 3.0 mA/cm².
current density is much less than the critical current density. Compared to the morphology of PEO₄LiClO₄ at 80°C as in figure 3-32 (b), no needle-like lithium was seen in PEO₃LiCF₃SO₃. A dense and compact globular layer was clearly observed. The thickness of the deposit layer was about 2.5 μm, which was thinner than that of the layer in PEO₄LiClO₄ under the same conditions.

No profound change in deposition morphology was found in PEO₃LiCF₃SO₃ electrolyte at 100°C up to a deposition current more than 3 mA/cm². Figure 3-39 shows deposit morphology at 3.0 mA/cm² in PEO₃LiCF₃SO₃ electrolyte cell. The growth distance was about 8 μm. The deposition current density was again less than the critical current density. A typical deposit layer consisting of globular lithium was observed, while at the same current density. As seen in figure 3-34, dendritic growth was found with PEO₄LiClO₄ electrolyte.

Dendritic deposits were found in the PEO₃LiCF₃SO₃ electrolyte cell at a current density of 4.0 mA/cm², which was higher than the corresponding critical current density. The expected transition time, τ, was 184 seconds. A tree-like dendrite can be clearly seen in figure 3-40 (b). Figure 3-41 shows the FT-IR spectrum obtained from the tree-like deposit. A broad peak around 3400-3600 cm⁻¹ can be attributed to the O–H stretching band.
Fig. 3-38. The structure of lithium deposits in PEO$_2$LiCF$_3$SO$_3$ at 80°C. The thickness of polymer electrolyte film was 100μm. The electrodeposition current was 0.5 mA/cm$^2$, and the total charge passed was 1.8 C/cm$^2$. 
Fig. 3-39. The structure of lithium deposits in PEO$_2$LiCF$_3$SO$_3$ at 100°C after 1-hour deposition. The thickness of polymer electrolyte film was 100μm. The electrodeposition current was 3.0 mA/cm$^2$, and the total charge passed was 10.8 C/cm$^2$. 
Fig. 3-40. The structure of Li deposits in PEO₄LiCF₃SO₃ at 100°C after 1-hour deposition at 4.0 mA/cm²: (a) the Li deposited on the most part of the substrate, and (b) tree-like Li deposits.

The thickness of polymer electrolyte was 100μm. (deposition time: 1 hour). The expected transition time, τ, was 184 seconds.
at the current density of 4.0 mA/cm² in PEODLcPEO, 50° at 100°C.

Figure 3-41. Surface FT-IR spectrum obtained from lithium dendrite. Dendrites were observed after 1-hour deposition.
3.3.4. Variation of deposition morphologies during cycling

Deposition and dissolution of lithium on the Ni wire was carried out at constant current and optical photomicrographs of the lithium deposited were taken *in-situ*. Each deposition process consisted of a given constant current, yielding 1.0 C/cm$^2$ of lithium deposited on Ni working electrode. After deposition, the polarity of the Ni electrode was immediately reversed and lithium stripped at the same current density. Prior to the beginning of the next cycle, a 45-minute rest time was taken in every cycle. This experiment has a transition current density which is that for which the transition time is exceeded. It has a value larger than the critical current density discussed in section 3.2. *Appendix II* shows the calculation.

Figure 3-42 displays the change in deposit morphologies on Ni wire substrate in PEO$_4$LiClO$_4$ during cycling at current density of 3.0 mA/cm$^2$. The deposition current density is higher than the corresponding transition current density. A calculated transition current density for the conditions used in this study was 2.12 mA/cm$^2$. At the onset of deposition, formation and growth of lithium nuclei on Ni substrate were clearly observed. At the end of the first deposition, globular lithium was deposited on the substrate as seen in figure 3-42 (a) to (c).

The resulting deposits obtained at the end of the 2$^{nd}$ deposition revealed a slight difference from that of deposits in the 1$^{st}$ deposition in terms of the growth
distance: it was shorter, as seen in figure 3-42 (e). Also deposition occurred on the top of lithium already deposited which had not re-dissolved.

A passivating layer encapsulating lithium was seen in the resulting photographs taken at the end of the 2nd dissolution (fig. 3-42 (f)). This layer showed a tendency to thicken as the cycling went on (figure 3-42 (g), 3-42(h) and 3-42 (i)). As the layer became thicker as the cycling proceeded, the amount of lithium encapsulated by the passivating layer increased. This lead to a decrease in cycling efficiency.

Apparently no profound difference was seen in the structure of deposits obtained during the 30th dissolution and the following 31st deposition (fig. 3-42 (i) and 3-42 (j)). However, fully developed dendrites, which were not seen until the end of the 30th deposition, were clearly observed at another region of the substrate (fig. 3-42(k)). This indicates that lithium was not deposited on the region being observed in figure 3-42 (j), but that the current was diverted toward another growth region, more accessible to further electrochemical reaction, and concentrated on a flaw in the passivating layer. Since the accumulation of isolated lithium on the substrate leads to a smaller effective area, the actual current density experienced would be much higher than the deposition current density. This would lead to the dendrite formation observed.
Fig. 3-42. Change in morphology of the Li deposit in PEO₄LiClO₄ at 100°C during cycling.
(a) Li nucleus at the early stage of the 1st deposition
(b) Formation of globular deposits after 3 minutes
i_(deposition) = i_(dissolution) = 3.0 mA/cm²
Q_(deposition) = Q_(dissolution) = 1.0 C/cm²
The thickness of polymer electrolyte was 100µm. The transition current density was 2.1mA/cm².
Fig. 3-42. Change in morphology of the Li deposit in PEO₄LiClO₄ at 100°C during cycling.
(c) At the end of the 1ˢᵗ deposition
(d) At the end of the 1ˢᵗ dissolution
\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \text{ mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]
The thickness of polymer electrolyte was 100μm.
Fig. 3-42. Change in morphology of the Li deposit in PEO₅LiClO₄ at 100°C during cycling.
(e) At the end of the 2nd deposition
(f) At the end of the 2nd dissolution
\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \, \text{mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \, \text{C/cm}^2 \]
The thickness of polymer electrolyte was 100µm.
Fig. 3-42. Change in morphology of the Li deposit in PEO₆LiClO₄ at 100°C during cycling.

(g) At the end of the 3rd dissolution
(h) At the end of the 15th dissolution

\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \text{ mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100μm.
Fig. 3-42. Change in morphology of the Li deposit in PEO$_3$LiClO$_4$ at 100°C during cycling.

(i) At the end of the 30$^{th}$ dissolution

(j) At the end of the 31$^{st}$ deposition

\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \text{ mA/cm}^2 \]

\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100$\mu$m.
Fig. 3-42. Change in morphology of the Li deposit in PEO₄LiClO₄ at 100°C during cycling.

(k) Li dendrites observed at the end of the 31ˢᵗ deposition

\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \text{ mA/cm}^2 \]

\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100μm.
Figure 3-43 shows the variation in FT-IR spectrum obtained from the isolated lithium layer with cycle number. As the cycling went on, the resulting FT-IR spectrum was characterized by a broad peak around 3300~3600 cm\(^{-1}\), corresponding to the O–H stretching band. This FT-IR result confirms that the passivating layer consisted of mainly LiOH.

Figure 3-44 shows deposits observed on other parts of the substrate during cycling. Needle-like lithium deposits were clearly seen in the resulting photographs. The longest length of the needle-like lithium was about 16 µm.

Figure 3-45 clearly displays how lithium dendrites are formed through discharge/charge cycling of a Li/PEO\(_2\)LiCF\(_3\)SO\(_3\)/Ni cell at 100°C. Optical photomicrographs were obtained as the cycling proceeded at 4.0 mA/cm\(^2\). The deposition current density is higher than the corresponding transition current density. A calculated transition current density for the conditions used in this study was 3.63 mA/cm\(^2\).

On the 1\(^{st}\) deposition, typically globular lithium deposits were formed (fig.3-45 (a)). The observed growth distance was about 16 µm. Most of the lithium deposit was easily stripped on the following dissolution. However, very tiny unreduced lithium particles were observed (fig. 3-45 (b)).
Figure 3-43. Variation of FT-IR spectra from the passivated lithium layer with cycle number in PE/LiTFSI at 100°C: after (a) 2nd (fig. 3-42a), (b) 15th (fig. 3-42h), and (c) 30th (fig. 3-42j) dissolution. Deposition = 1 C/cm², constant current density for cycling = 3 mA/cm². Wave number / cm⁻¹

Reflectance / %
Fig. 3-44. Needle-like lithium growth in PEO₄LiClO₄ at 100°C after the 31ˢᵗ deposition.

\[ i(\text{deposition}) = i(\text{dissolution}) = 3.0 \text{ mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100μm.
As the 20th deposition proceeds, gradually the morphology of the lithium deposited change into smaller globules as seen in fig. 3-45 (c). On the following 20th dissolution, these globules were not stripped entirely at the end of dissolution (fig. 3-45 (d)). As seen in figure 3-45 (e), the passivating layer became thicker on further cycling. The passivating layer was much thicker than that seen after the first cycle, and it seems clear from the micrograph that there was a significant amount of encapsulated lithium.

Figure 3-45 (f) shows lithium deposits forming during the next cycle on top of the passivating layer. Needle-like lithium deposits were clearly seen in these deposits (fig. 3-45 (g) and (h)). The observations suggests that because of the large surface area generated by fine particles, smaller lithium particles are likely to be more easily passivated than larger globules. The passivating layer was identified as LiOH layer by FT-IR spectroscopy (fig. 3-46).
Fig. 3-45. Change in morphology of the Li deposit in PEO₄LiCF₃SO₃ at 100°C during cycling.
(a) Globular Li deposits at the end of the 1st deposition
(b) After the 1st deposition
\[ i(\text{deposition}) = i(\text{dissolution}) = 4.0 \text{ mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]
The thickness of polymer electrolyte was 100μm. The transition current density was 3.6 mA/cm².
Fig. 3-45. Change in morphology of the Li deposit in PEO$_2$LiCF$_3$SO$_3$ at 100°C during cycling.

(c) After the 20$^{th}$ deposition
(d) After the 20$^{th}$ dissolution

\[ i(\text{deposition}) = i(\text{dissolution}) = 4.0 \text{ mA/cm}^2 \]

\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100μm.
Fig. 3-45. Change in morphology of the Li deposit in PEO$_6$LiCF$_3$SO$_3$ at 100°C during cycling.

(e) After the 25$^{th}$ dissolution
(f) After the 26$^{th}$ deposition

\[ i(\text{deposition}) = i(\text{dissolution}) = 4.0 \text{ mA/cm}^2 \]
\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100µm.
Fig. 3-45. Change in morphology of the Li deposit in PEO, LiCF3SO3 at 100°C during cycling.

(g), and (h) needle-like Li observed after the 26th deposition

\[ i(\text{deposition}) = i(\text{dissolution}) = 4.0 \text{ mA/cm}^2 \]

\[ Q(\text{deposition}) = Q(\text{dissolution}) = 1.0 \text{ C/cm}^2 \]

The thickness of polymer electrolyte was 100 μm.
Figure 3-46. FT-IR spectrum obtained from the passivated lithium layer after 30 cycles, PEOLiCF3SO3 at 100°C.

Q deposition = 1 C/cm², constant current density for deposition and dissolution = 4.0 mA/cm².
References


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CHAPTER 4.
DISCUSSION OF
RESULTS
CHAPTER 4. Discussion of results

4.1. A voltammetric study of the lithium/polymer electrolyte interface

In this project, cyclic voltammetry has been used as a probe for the presence of electroactive impurities in polymer electrolytes. The major electroactive impurity that was found to be present was water.

Cyclic voltammograms of Li/PEO-LiX/Ni cells were characterized by the large cathodic peak attributed to reduction of water (fig.3-1 and 3-9). It was originally claimed that almost anhydrous films might be obtained by preparing the film by casting onto a hot plate under reduced pressure. Furthermore, water reduction waves are not commonly reported in the polymer film electrolytes. However, even though formidable efforts were made in the present work to remove water in the electrolytes, water-free electrolyte films could not be prepared. It was demonstrated that if cyclic voltammetry is not conducted at sufficiently slow scan rate enough to allow water to diffuse to the electrode surface, water reduction waves cannot be observed (compare fig.3-1 and 3-8). Accordingly, some workers might have missed the effects.
The results from cyclic voltammetry show that small amounts of contaminant(s) such as water (or possibly oxygen) exert a profound influence on the electrochemistry of lithium ion in polymer electrolyte systems. A passivating film of LiOH can be formed on the electrode and this LiOH film influences the electrochemistry by limiting the diffusion rate of species to the electrode. Also further reduction leads to another layer formation attributed to the formation of Li-H. This LiH layer might be the origin of Li-Ni alloy formation.

Water can modify the electrical properties of polymer electrolytes by an increase or decrease in ionic conductivity according to the amount of water present in polymer electrolytes. One interpretation is that water hydrates the lithium ions, thus hindering their ionic motion and then leading to a decrease in conductivity [1]. Alternatively, in the extreme, water may cause an aqueous solution of the lithium salt to be formed on the electrolyte surface leading to an increase in conductivity [2]. It is impossible to prepare water-free electrolyte. However, in terms of the stability of electrolytes toward the highly reactive lithium negative electrode, water may cause serious problems.

4.2. The critical current

In the last chapter, a hypothesis was put forward concerning the presence of the critical current showing a sudden transition in the potential difference across
the cell. This was based in the part on the CV results obtained with polymer electrolytes showing perturbation of the electrochemistry of lithium in polymer electrolytes due to the passivating layer. The formation of the passivating layers consumes lithium ions as observed from cyclic voltammetry in the previous chapter. Additionally, the passivating layer formed on the electrode may act as obstacle to hinder the ionic movement. In any case, even in the absence of a passivating film, when the current is maintained constant by external devices, the supply of Li$^+$ ions to the electrodes would be gradually diminished and in the extreme case it would not sustain the applied current at all. The potential difference across the cell would be correspondingly increased suddenly to a higher value at which other cathode reactions (e.g., decomposition of the polymer electrolyte) could occur. This is a hypothesis concerning the critical current density. The presence of the critical current density was identified by galvanostatic ramp experiments. The key results illustrating this are in figures 3-13 and 3-22. Where the potential difference across the cell varies linearly with applied current, ionic conductivities were obtained from the slope of $d\Delta E/di$ and cell geometry. The diffusion coefficient, as reflected in the critical current density, was calculated (table 3-1 and table 3-3).

An increase in the critical current density with temperature can be explained in terms of the temperature dependence of ionic conductivity of polymer electrolytes. Ion transport in most of the polymer-salt complexes occurs by a liquid-like mechanism in which the segmental motions of the polymer are
responsible for ion transport. The migration of a lithium ion is assisted by polymer segmental motion. The polymer segmental motion is increased as temperature increases. This predicts that the supply of Li\(^+\) ion from the bulk to the interface where the ion depletion may occur should increase as temperature increases. Hence, the cell can sustain a higher applied current. As expected, a higher value of the critical current was obtained from the cell with a higher operating temperature (figure 3-15 and 3-23).

The theory given in the last chapter (equation 3-14) predicts that the critical current density should be in inverse proportion to the electrolyte film thickness \((h)\). This prediction is satisfied by the observation in figure 3-17 and 3-24. The longer distance for Li\(^+\) ion to pass through to join the charge transfer reaction reflects a lower critical current density.

It was shown that higher critical current densities were achieved with Ni-wire than with Ni-sheet as substrate (figure 3-18 and 3-26). Spherical diffusion has a reaction coordinate which is hemispherical, in contrast to linear diffusion where the reaction coordinate along which diffusion occurs is considered to reach vertically out from the electrode surface. Therefore, the growth rate is much faster at the round surface than at the flat surface. This is reflected in the higher critical current density. This is illustrated schematically in figure 4-1.
Figure 4-1. A schematic presentation of the concentrated current at hemispherical surface, producing a faster growth rate than at the flat surface.

4.2.1. PEO₈LiClO₄ versus PEO₈LiCF₃SO₃

Even though the calculated conductivity of the LiCF₃SO₃ is smaller than that of the corresponding LiClO₄-based electrolytes, the effective diffusion coefficient of the LiCF₃SO₃–based electrolytes is greater, as reflected in the critical current density (table 3-3 and 3-5). These resulting trends agree with the literature [3,4].

This can be explained in terms of the anion contribution to the conductance mechanism in polymer electrolytes. The ionic conductivity (σ) of polymer
electrolytes is expressed as follows:

$$\sigma = \Sigma n q \mu \ldots (4.1)$$

where \( n \) denotes the number of ionic carriers per unit volume, \( q \) the charge of the carriers, and \( \mu \) the mobility.

The temperature dependence of the ionic conductivity indicates that the ionic conductivity is mainly controlled by the mobility, \( \mu \), that is directly affected by the segmental motion of the polymer matrix. However, even the polymer matrices with similar \( T_g \)s, the ionic conductivity is affected by the nature of the salts.

There are two possible mobile ionic species, that is, cation and anion. Based on the literature [5], it has been evident that the mobilities of the anions decrease linearly with the reciprocal of square root of formula weight. In most polymer electrolyte systems having the simple combination of a high molecular weight polymer matrix (e.g., poly (ethylene oxide) PEO) and lithium salts, the salts are usually not completely dissociated. This is due to low permittivity of the polymer solvent and the relatively high salt concentration which is required in battery systems. When the salt is not fully dissociated, it is possible to form further aggregated ions, so called ionic multiplets, such as ion-pairs, triplets, and even larger clusters of ions. A salt with a poorly coordinating anion such as CF\(_3\)SO\(_3\)^-
has a higher association tendency than a salt with a ClO$_4^-$, thus producing ion-pairs [6]. Therefore, it is expected that the mobility of ClO$_4^-$ anion is higher than that of CF$_3$SO$_3^-$ in electrolytes. Even if there are equal numbers of the various ions, those which have higher mobility contribute more to the ionic conductivity. The higher ionic conductivity with the LiClO$_4$-based electrolyte is supported by the higher mobility of the anions. (figure 3-16 and 3-25).

In the elementary treatment of the diffusion on the current delivering cell, it must be considered that the burden of carrying the current through the electrolyte is not shared equally. This resulting unequal mobility of cations and anions can be expressed as the transport number [7]. This transport number is defined by the fraction of the total current carried by the particular ionic species.

$$\sum t_i = \sum i/i = 1$$ (4.2)

where $i_i$ denotes the total current carried by $i$ specie and $t_i$ the transport number of $i$.

But when ion association takes place, it is impossible to distinguish free ions from associated species carrying current through the electrolyte solution. Therefore, transference number based on the transport of the gram equivalent of one Faraday has been considered instead.
In the case of polymer electrolytes containing two mobile species, the cationic transference number \( (t^+) \) is defined by

\[
\tau^+ = \frac{\mu^+}{(\mu^+ + \mu^-)} = \frac{D^+}{(D^+ + D^-)} \quad (4.4)
\]

where \( \mu \) and \( D \) denote ionic mobility and diffusion coefficient of cation(+) or anion(-), respectively.

In the literature \[8\], the transference number of Li\(^+\) in PEO\(_4\)LiClO\(_4\) is reported as only half that of Li\(^+\) in PEO\(_4\)LiCF\(_3\)SO\(_3\), due to the high mobility of the anions. This means that Li\(^+\) ions in PEO\(_4\)LiCF\(_3\)SO\(_3\) carry twice as much current through the polymer electrolyte as in PEO\(_4\)LiClO\(_4\). This is reflected in a higher diffusion coefficient, \( D_{Li^+} \) in PEO\(_4\)LiCF\(_3\)SO\(_3\) over that of PEO\(_4\)LiClO\(_4\).

4.2.2. Variation of the critical current during cycling

The CV results obtained with polymer electrolytes tell the nature of impurities which may react with lithium to form the passivating layers. It also turns out that the passivating layers perturb the electrochemistry of lithium in polymer electrolytes. The characteristic cycle performance in polymer electrolytes is
clearly shown by the observed results that the critical current density gradually decreased as the cycling went on. (figure 3-21 and 3-28)

In addition, the resistive layer build-up at the interface can be identified by the result that the ionic conductivity decreased with cycle number. The apparent ionic conductivity of PEO₄LiClO₄ decayed slightly more steeply than that of PEO₄LiCF₃SO₃ with cycle number.

The critical current gradually decayed until the passivating layers were stabilized. The stabilization may perhaps be achieved through the full development of a LiOH layer such that no further reduction of water can occur. Other side reactions to form passivating layers other than LiOH might occur. Both reflect the gradual decrease in the critical current as the cycling proceeds. It has been proposed that PEO-based polymer electrolyte might degrade through cleavage of the ether functionality [9]. When a current much higher than the critical current is applied to the cell, degradation of the polymer chain could be possible. However, it must be considered that the LiOH layer formed at the early stage can impede further side reactions effectively. At this stage, this assumption can not be confirmed without more detailed information on the nature of the passivating layers.
4.2.3. Cycling efficiency vs. critical current density

It was shown that the Coulomb efficiency during cycling was dependent on whether the Li⁺ reduction current was greater or less than the critical current density of the cell. The key results are displayed in figure 3-29 and 3-30. In consonance with the assumption given earlier, if the applied current density during constant charging-discharging cycle was less than the corresponding critical current density, no profound decrease in efficiency with cycle number was observed. On the contrary, when the applied current density was greater than the corresponding critical current density, the decrease in coulomb efficiency with cycle number became significant.

The decrease in coulomb efficiency with cycle number may be caused by the accumulation of isolated lithium by passive layer formation on the electrode surface. Simultaneously, this leads to reducing the effective area for electrochemical reaction as cycling progress. This, in turn, results in the formation of lithium dendrites as explained earlier.

As a preliminary summary, factors causing a decrease in efficiency are:

(i) formation of the passivated lithium layer: this is reflected by the presence of the critical current density.
(ii) continuous growth in the passivated lithium layer or initiation of other side reactions: this is reflected by gradual decrease in the critical current density with cycle number.

(iii) growth in the passivated lithium layer leading to the highly localized current to form dendrites. This is reflected by the decay in efficiency when the current density is higher than the critical current density.

4.3. Effect of the critical current density on the deposit morphology

In electrochemical deposition, the surface growth is directly related to the local current density. Of particular interest is to investigate how the passivating layers perturb the deposition morphology and how the critical current density is related to the corresponding morphology.

Typical lithium deposits in polymer electrolytes are globular, far from the irregular deposits reported for organic electrolytes. The key result is in figure 3-31. The proposed model for globular deposit formation is schematically illustrated in figure 4-2. The Ni substrate might be largely passivated against lithium reduction, perhaps as a result of the presence of a native oxide layer. Lithium is passivated as it is formed on the substrate (figure 4-2 (a) and 4-2 (b)). Lithium ions select easy-to-deposit places at the substrate surface. Further
reduction of lithium occurs only at flaws in the passivating layer. When the applied current density tends to concentrate at flaws in the passivating layer, perturbation of the deposit morphology will happen. The local current density becomes critical to whether or not irregularities will grow and initiate dendrite growth.

(a) Flaws in the passivating layer on the Ni substrate

(b) Flaws in the initial layer of passivated lithium
Figure 4-2. The proposed model for globular deposit formation in polymer electrolytes

It has been assumed in the theory given in chapter 3-2 that the concentration of lithium ions at the surface tends to zero after some finite time, referred to as the transition time, when the current density is greater than the critical current in
the galvanostatic experiment. After this time, transition into dendritic growth can be initiated. This presumption is well satisfied in both electrolytes. When the deposition current density was less than the corresponding critical current density, globular lithium deposits were observed. Conversely, when the deposition current density was much higher than the corresponding critical current density, dendrite growth was observed clearly. The key results illustrating this trend are in figure 3-34 and 3-39.

Evidence showing how the passivating layer perturbs the deposition morphology was given in the results (figure 3-33 and 3-34). Isolated hook-like lithium deposits are possibly caused by the passivating layer formed as lithium is deposited. When lithium is entirely passivated, lithium becomes isolated and stops growing further (figure 3-33). Isolated lithium is electrochemically inactive. This leads to loss in battery capacity. This is schematically depicted in figure 4-3.

![Figure 4-3. Formation of hook-like deposit in polymer electrolytes](image)
It was clearly shown that dendrites grow in polymer electrolytes when the deposition current density was much higher than the corresponding critical current density (figure 3-34). Perturbation of the morphology caused by the passivation layer leads to a high local deposition current density that leads to dendrites. These dendrites grow at flaws on the lithium layer already deposited, leading to tree-like deposits. At the following dissolution, these dendrites dissolved well but the passivated lithium remained. This is schematically illustrated in figure 4-4.
When deposition and dissolution of lithium on the Ni wire in both polymer electrolytes was carried out at constant current density, higher than the corresponding critical density, lithium dendrites were observed. The key results are given in the figure 3-44 and 3-45. It was shown that lithium was encapsulated to form a passivated lithium layer. This layer gradually grew as the cycling proceeded. As a result of this, the critical current decreased gradually. (figure 3-19 and 3-27). Since encapsulated lithium can not be recycled effectively, there will be a decrease in the stripping efficiency with cycle number. Simultaneously, the accumulation of encapsulated (isolated) lithium on the substrate leads to a
smaller effective Ni substrate surface area and further localization of current density occurs. This, in turn, may cause formation of lithium dendrites on the subsequent cycles.

FT-IR spectrum obtained from the layer of isolated lithium and mossy deposit which grew with increasing with cycle number shows that the nature of the passivating layer contained LiOH. The key result is given in figure 3-42. No other characteristic peaks attributable to polymer degradation were detected. This can be explained if the amount of the side products is not enough to detect or if the LiOH layer protects the electrode from further reaction of the lithium deposit with the electrolyte. Since the passivated lithium layer tends to grow as cycling proceeds, the solid polymer electrolyte could not penetrate into the deposited lithium to react. The cyclic voltammetry implied that LiOH was the product of chemical and electrochemical reaction of water.

It was shown that dendrites were formed in polymer electrolytes from the fine particles of deposited lithium. This might be the most significant route leading to cycle life limitation in lithium/polymer electrolyte secondary batteries. The key result is shown in figure 3-44. As the cycling proceeded, fine lithium particles were formed. If such fine deposits were gradually accumulated on the electrode as cycling goes on, it would be difficult for a polymer electrolyte in a solid state to penetrate sufficiently into this fine structure. Also these fine particles would tend to be electrochemically isolated more easily by generating a high surface
area and reactivity toward impurities. This could accelerate the rate of side reaction between lithium and impurities, thus passivating the lithium. This would then lead to irreversible capacity loss as well as perturbation into dendrites of the morphology of the lithium deposited in following cycles. This is schematically illustrated in figure 4-5.

Figure 4-4. The proposed model for dendritic growth via fine particle deposits in polymer electrolytes.
References


CHAPTER 5. CONCLUSION

It was shown that oxygen and water reduction processes occurring at the electrode would cause consecutive reactions with Li\(^+\) to form layers on the electrode as described in voltammetric studies here. The appearance of a water peak was commonly recorded except when a higher sweep rate of 50 mV/sec was employed. When sweep rates of 50 mV/sec and greater were used in the present study cathodic current was observed at voltage of 0.5 V vs. Li/Li\(^+\) but no actual water reduction peak was recorded. Highly reversible lithium deposition and stripping was not observed except when a higher sweep rate of 50 mV/sec was employed. Sweep rates slower than 50 mV/sec might be sufficiently slow to allow water to diffuse to the electrode surface. At sweep rates slower than 50 mV/sec, a passivating layer of LiOH prevents effective stripping of the plated lithium.

When voltammetric studies were conducted at relatively low scan rate (below 20 mV/sec), commonly three reductive reactions were identified, which occurred in advance of the bulk lithium deposition process. These reactions were assigned to water (and/or oxygen) reduction, Li-H and Ni-Li alloy formation. Possibly a further reduction of water could produce LiH and Ni-Li alloys.

Water could not be removed entirely from polymer electrolytes studied here.
Further extension of the drying condition could not remove water, even though an OH stretching band at 3500 cm\(^{-1}\) was not detected from a surface FT-IR spectrum. Hence, water contamination became a significant aspect of organic electrolytes for lithium anode cell as well as of the polymer electrolyte studied here.

The hypothesis that there would be present the critical current showing sudden transition in the potential difference across the cell due to the passivating layer, was put forward.

The presence of the critical current density was identified by galvanostatic ramp experiments. Ionic conductivities were obtained from the slope of \(\frac{d\Delta E}{df}\) and cell geometry. The diffusion coefficient, as reflected in the critical current density, was calculated.

A higher value of the critical current was obtained from the polymer electrolyte cell with a higher operating temperature. This was the same in both polymer electrolytes studied here. The critical current density obtained with both electrolytes was in inverse proportion to the electrolyte film thickness.

It was shown that the Coulomb efficiency during cycling was dependent on whether the Li\(^+\) reduction current was greater or less than the critical current.
density of the cell. In consonance with the assumption given in chapter 3, when
the applied current density during constant charging-discharging cycle was less
than the corresponding critical current density, no profound decrease in efficiency
with cycle number was observed. When the applied current density was greater
than the corresponding critical current density, the decrease in coulomb
efficiency with cycle number became significant.

It was shown in microscopic studies that typical lithium deposits in polymer
electrolytes were globular and the model for globular deposit formation was
described in chapter 4.

When the deposition current density was less than the corresponding critical
current density, globular lithium deposits were observed. Conversely, when the
deposition current density was much higher than the corresponding critical
current density, dendritic growth was observed clearly. The key results
illustrating this trend are in figure 3-34 and 3-39.

It was shown that dendrites were formed in polymer electrolytes from the fine
particles of deposited lithium. As the cycling proceeded, fine lithium particles
were formed and these fine particles could tend to be passivated easily by
generating a high surface area and reactivity toward impurities. This would then
lead to irreversible capacity loss as well as perturbation into dendrites of the
morphology of the lithium deposited in following cycles.
FT-IR spectra obtained from the layer of isolated lithium and mossy deposit, which grew with increasing cycle number show that the passivating layer contained LiOH, as identified in the cyclic voltammetry. No other characteristic peaks attributable to polymer degradation were detected. This could be explained if the amount of the side products was not enough to detect or if the LiOH layer protected the electrode from further reaction of the lithium deposit with the electrolyte.
Appendix-I: Solution of the transport problem for a thin layer cell

The objective is to find the time and position-dependence of concentration of the electroactive ion, for the case of discharge at constant current. The case of a binary 1:1 electrolyte, without another supporting electrolyte, is considered. For each species, $i$,

$$\frac{\delta c_i}{\delta t} = -\nabla \cdot J_i \ldots (1)$$

and

$$J_i = -D_i \nabla c_i - u_i c_i \nabla \phi \ldots (2)$$

where $J_i$ denotes the flux of species $i$, $D_i$ the diffusion coefficient, $c_i$ the concentration, $z_i$ the charge, $u_i$ the mobility and $\phi$ the electric potential.

In equation (2), the first term is the contribution of diffusion and the second that of electromigration. For a binary electrolyte with $z = 1$, $c_+ = c_− = c$ where the subscripts denote the ionic charges.

Therefore:

$$\frac{\delta c}{\delta t} = u_+ \cdot \nabla (c \cdot \nabla \phi) + D_+ \nabla^2 c \quad \text{(cations)} \ldots (3)$$

$$\frac{\delta c}{\delta t} = -u_- \cdot \nabla (c \cdot \nabla \phi) + D_- \nabla^2 c \quad \text{(anions)} \ldots (4)$$

Eliminate $\nabla \phi$ between equation (3) and (4), obtain

$$\frac{\delta c}{\delta t} = D_e \cdot \nabla^2 c \ldots (5)$$
With effective diffusion coefficient

\[ D_e = \frac{(u_+ D_+ + u_- D_-)}{(u_+ + u_-)} \]

\[ = \frac{2 (D_+ D_-)}{(D_+ + D_-)} \quad \ldots (6) \]

The anion is not consumed at the electrodes. Therefore, at the electrodes; \( J_- = 0 \).

Hence, from equation 2, applied at the electrode:

\[-D_- \nabla c + u_- c \nabla \phi = 0\]

\[ D_- \nabla c = u_- c \nabla \phi \]

or \( \nabla \phi = \left( \frac{D_-}{u_- c} \right) \nabla c \)

Hence \( J_+ = -D_+ \nabla c - \frac{u_+}{u_-} D_- \nabla c \)

Since \( \frac{u_+}{u_-} = \frac{D_+}{D_-} \) we have

\[ J_+ \quad (x=0,d) = -2D_+ \cdot \nabla c \quad \ldots (7) \]

If edge effects are ignored, the thin layer cell (thickness \( h \)) can be treated as a one-dimensional problem. If \( x \) denotes position in the cell (electrodes at \( x = 0, h \)) then, from eq.(7), the boundary condition is

\[ \frac{i}{(2z \cdot F \cdot D_+)} = -\frac{dc}{dx} \quad (x=0, h) \quad \ldots (8) \]

where \( i \) is the constant current density applied to the system and \( z \) is the charge number for the electrochemical reaction. The differential equation to solve is

\[ \frac{\delta c}{\delta t} = D_e \cdot \left( \frac{\delta^2 c}{\delta x^2} \right) \quad \ldots (9) \]
With boundary conditions eq. (8) and initial condition \( c = c_a \) at \( x = 0 \).

The equation can be cast in dimensionless form by suitable scaling of current, time, position and concentration:

\[
X = \pi \cdot x / h, \quad T = t \cdot D_c / h^2, \quad \Gamma = c / c_o \quad \text{and} \quad I = h \cdot i / (2c_o \cdot z \cdot F \cdot D_c \cdot \pi)
\]

Equation 9 then becomes:

\[
\delta \Gamma / \delta T = \pi^2 \cdot (\delta^2 \Gamma / \delta X^2) \ldots (10)
\]

With \( \Gamma = 1 \) at \( T = 0 \)

and \( \delta \Gamma / \delta X = -I \) at \( X = 0 \) and \( \pi, T > 0 \) \ldots (11)

The equation can be solved by the method of finite Fourier cosine transformation with respect to \( X \) followed by Laplace transformation with respect to \( T \). The finite Fourier cosine transformation resolves the differential form \( F''(X) \) on the interval \((0, \pi)\) in terms of the transform of \( F \), the boundary values \( F'(0) \) and \( F'(\pi) \). Constant current defines the boundary conditions in terms of the derivative, hence the cosine transformation is the appropriate one for this problem.
The solution is:

\[
\Gamma = 1 - X \cdot I + \pi I / 2 - (2 \cdot I / \pi) \cdot \sum_{n=1}^{\infty} \left\{ 1 - (-1)^n \right\} / n^2 \cdot \exp(-n^2 \pi^2 T) \cos(n \lambda)
\]

...(12)

Approximately 100 terms of the series are needed to give a good numerical result.

The solution shows that, if \( I > I_{\text{critical}} \) then \( \Gamma(\pi) = 0 \) at \( T = T_{\text{critical}} \).

However, if \( I < I_{\text{critical}} \) then \( T_{\text{critical}} \rightarrow \infty \). \( I_{\text{critical}} \) is the critical current density above which the surface concentration will be driven to zero at some time. Numerical calculation showed \( I_{\text{critical}} = 0.63661 \). The critical current density is therefore:

\[
i_{\text{critical}} = \left( 2 \times 0.63661 \cdot \pi \cdot c_0 \cdot z \cdot F \cdot D_+ \right) / h
\]

\[
= 4 \ c_0 \cdot z \cdot F \cdot D_+ / h \quad \text{... (13)}
\]
For \( I > I^* \), the transition time, \( T^* \), at which \( \Gamma(\pi) = 0 \), can be obtained by graphical or numerical solution of equation 12 for \( T \), setting \( \Gamma = 0 \) and \( X = \pi \). The result is shown in the figure. If the cell is thick enough, then the result should approximate to the Sand equation, which is valid when the cell thickness approaches infinity.

Taking into account the effects of coupled diffusion and migration described above, by solving differential equation 9 with boundary condition 8 applied at \( x = 0 \), the Sand equation becomes: \( (c_3 \) is the concentration at the electrode surface):

\[
\frac{(c_o - c_s)}{c_3} = \left( \frac{2}{n^2 F A} \right) \frac{D_+}{D_e} \frac{(v/\pi)^{1/2}}{\tau^{1/2}} \ldots (14)
\]

The transition time, \( \tau \), is reached when \( c_s = 0 \):

\[
\tau^{1/2} = c_o z F \pi^{1/2} D_+ / D_e^{1/2} \ldots (15)
\]

In order to compare the results with the solution from equation 12, equation 15 can be scaled using the same dimensionless variables, \( I \) and \( T \), used above:

\[
I = \left( 1/2 \pi^{1/2} \right) \frac{(T_{Sand})^{-1/2}}{\tau^{1/2}} \ldots (16)
\]

Where \( T_{Sand} \) denotes the transition time according to the Sand equation, scaled as above:

\[
T_{Sand} = \frac{\tau D_+}{h^2} \ldots (17)
\]

The figure compares transition time calculated from equation 16 with that calculated from equation 15.
Appendix – II. **Critical current density for the case when a fixed charge is passed**

In sections 3.2.4 and 3.3.4, the decline in cycling efficiency as a function of current density and the resultant change in deposition morphology, was studied, for the case when a fixed deposition charge was passed. In this case, the charging time decreases as the charging current increases. Now, the critical current density is that for which the transition time is exceeded during the charging. This current density is larger than the critical current density for which the transition time becomes finite. This transition current density can be calculated from the equation and figure given in Appendix I:

(a) given the deposition charge and current density, the deposition time is calculated. This time is converted to the corresponding dimensionless time, $T_{crit}$, using the value for $D_e$ calculated from the critical current density and assuming a value for the transport number. In this thesis, the assumption $D_e = D_e^*$, corresponding to transport number = 0.5, has been used.

(b) given $T_{crit}$, the corresponding dimensionless transition current is obtained from the figure or from equation 16 (if $T_{crit}$ is sufficiently small).

(c) given $I_{trans}$ the corresponding transition current density is calculated, using $D_e$, obtained from the measure of critical current density.
Figure. Transition time, $T$, against current density, $I$ (scaled dimensionless variables) calculated for the finite and semi-infinite (Sand equation) cases.