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POLYMER ELECTROLYTES, PROBLEMS, PROSPECTS, AND PROMISES

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ABSTRACT

Ionically conducting polymer electrolytes have generated, in recent years, wide-spread interest as candidate materials for a number of applications including high energy density and power lithium batteries. In the early 70s the first measurements of ionic conductivity in polyethylene oxide (PEO)-salt complexes were carried out by Wright (1). However, Armand (2) was the first to realize the potentialities of these complexes (polymer-salt complexes) as practical ionically conducting materials for use as electrolytes in lithium batteries. Subsequent research efforts identified the limitations and constraints of the polymer electrolytes. These limitations include (a) poor ionic conductivity at RT ($< 10^{-8}$ S/cm), (b) low cation transport number (<0.2) etc. Several different approaches have been made to improving the ionic conductivity of the polymer electrolytes while retaining the flexibility, processibility, ease of handling and relatively low impact on the environment that polymers inherently possess. In this paper we will review the evolution of polymer electrolytes from the conventional PEO-LiX salt complexes to the more conducting polyphosphazene and copolymers, gelled electrolytes etc. We will also review the various chemical approaches including modifying PEO to synthesizing complicated polymer architecture. In addition, we will discuss the effect of various lithium salts on the conductivity of PEO-based polymers. Charge/discharge and cycle life data of polymer cells containing oxide and chalcogenide cathodes and lithium (Li) anode will be reviewed. Finally, future research directions to improve the electrolyte properties will be discussed.

KEY WORDS: Polymer electrolyte, Ionic conductivity, Cycle life

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1. INTRODUCTION

There is a growing need for improved rechargeable batteries for a variety of applications including military, consumer and space. The new rechargeable batteries should be environmentally benign and safe in the hands of the users. However, currently available batteries contain heavy metals such as cadmium, mercury etc. The heavy metal components pose problems both at manufacture and disposal by the user. This prompted a quest aimed at identifying new battery systems that not only inherently possess more power and energy over current technology but have low toxicity and low hazard ratings. To meet the above requirements all-solid-state lithium polymer electrolyte (LPE) technology was proposed as a viable candidate. This consists of either a metallic lithium or a lithiated carbon (Li_xC_6) as anode a polymer-salt complex as electrolyte and either a transition metal chalcogenide or an oxide as cathode. In this paper we will mainly discuss the logical evolution of the polymer electrolyte as new research identified new constraints. There are many principal properties that a polymer has to concurrently satisfy to act as a successful polymer host (3). These include (a) high relative dielectric constant (>10) to dissociate the lithium salt, (b) facile polymer segmental motion, (c) easy processibility into thin films etc. The polymer electrolyte (polymer -salt complex) needs to satisfy again concurrently, a number of electrochemical and transport properties including (a) high ionic conductivity ($>10^{-3}$ S/cm) at operating temperature for high power, (b) cation transport number ~1 to reduce concentration polarization and electrolyte electrode interface degradation, (c) low electronic conductivity to mitigate self discharge, (d) low activation energy with temperature for ionic conduction, (e) chemical and electrochemical stability in the cell operating environment, (f) no phase change in the operating temperature regime that alters the conduction mechanism, i.e. no break in the conductivity vs. 1/T plot (g) low glass-transition temperature (T_g) for higher ionic conductivity and (h) free standing robust films to act as a separator (4). Initial research was centered around the traditional polyethylene oxide-based polymer containing well known lithium salts such as $LiClO_4$, CF_3SO_3Li etc. (5). The electrolytes showed a very poor room temperature ionic conductivity. For example PEO-($LiClO_4)_{0.125}$ exhibited a room temperature ionic conductivity of $\sim10^{-8}$ S/cm and a T_g of -15°C which is higher than the T_g (-60°C) of the virgin PEO polymer . Even at temperatures close to 100°C the ionic conductivity is only $\sim10^{-4}$ S/cm which is an order of magnitude lower than the required minimum of 10^{-3} S/cm. The room temperature conductivity is not only very low but the plot of log (σ) vs. 1/T shows a break at around 65°C which indicates a phase change in the polymer electrolyte. Further, the cation transport number is very low ~0.1. In addition, it has been shown earlier (6) that ionic conduction in PEO-based polymer electrolytes mainly occurs in liquid-like region and very little conduction occurs in crystalline regions and the amorphous regions increase with temperature. The phase diagrams of typical polymer complexes, e.g. complexes based on PEO and lithium salts reveal that the amorphous phases which permits fast ion mobility are reached at temperatures higher than ambient, typically >65°C. Consequently these electrolytes require a relatively high operating temperature and this may not be acceptable for devices directed to a commercial market. Although PEO possesses the required mechanical properties the conductivity and transport properties fall shy of the acceptable minimum. The data show that a simple complex of PEO and lithium salt may not be useful for any of the applications mentioned above. Below we describe the several approaches pursued by different research laboratories to address the problems mentioned above. The approaches include modifying PEO structure, adding different lithium salts (7), synthesizing copolymers, blends etc.

2. PREPARATION OF POLYMER ELECTROLYTE THIN FILMS

Two different solution casting procedures were reported in the literature for the preparation of polymer electrolyte thin films (<2 mil) preparation. One of the procedures involve dissolving the lithium salt in a solvent (compatible with PEO) beforehand followed by the addition of appropriate amount of PEO and the solution was stirred overnight for complete swelling of the polymer (8). The viscous solution was poured into a Teflon mold and the solvent was slowly evaporated to obtain a thin film. The second procedure involves dissolving the lithium salt in methanol (MeOH) and the solution was heated to ~50°C (9). The exact amount of PEO was added to the warm solution and the solution was kept at ~50°C with constant stirring. Again the viscous solution was poured into a Teflon mold for solvent evaporation. This procedure also gave free standing thin films comparable to the films obtained by the first procedure. For continuous electrolyte production more elaborate procedures based on "doctor-blade" technique have been developed. This is beyond the scope of the paper to describe the technique and the procedure is described in several references (10).

3. STRUCTURAL MODIFICATION OF PEO

Although PEO-based polymer electrolyte exhibits sufficient mechanical properties to act as a separator in a cell, the electrochemical and transport properties are inferior and need improvement. The poor conductivity is linked to the crystalline nature and to the restrictive segmental motion of the of PEO especially the high molecular weight PEO. The crystallinity is due to the stereoregularity (long-range order) and symmetry in linear chain PEO. So the first attempt was to break the crystallinity and this could be done in various ways including structurally, chemically and by a combination of these methods. To increase the segmental motion a more flexible polymer backbone was introduced.

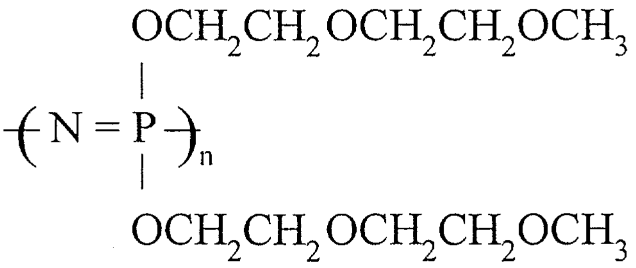
Structural Modification

Structure of PEO:

$$-\left(CH_2CH_2O \right)_n-$$

The first approach put forward to reduce the symmetry was to introduce substitutents in the ethylene oxide monomeric unit. Examples include nonstereoregular polypropylene oxide (PPO, CH_3CHCH_2O). PPO is amorphous and less crystalline than PEO at room temperature.

Yet another, structural modification includes introducing spacers such as urethane to reduce the symmetry. While these approaches increased the amorphous nature of the PEO, the conductivity of these materials didn't improve over that of PEO because the conduction mechanism in these materials is the same as in PEO: conduction occurs by the segmental motion of the molecular chains. Because of the inherent limitations the segmental motion can't offer higher conductivity. To overcome this shortcoming more flexible inorganic backbones to which short chain PEO units are attached were designed and synthesized. An example of this is the well known MEEP (methoxy ethoxy ethoxide phosphezene). The structure and some physical and transport properties are given below.

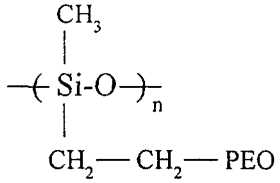


$$\left(\mathrm{N}=\underset{\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}}{\overset{\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}}{\mathrm{P}}}\right)_n$$

Table-1. Physicochemical Properties of MEEP and MEEP-based Polymer Electrolytes

Material	Glass Transition Temp. (^{o}C), T_g	Conductivity (S/cm) at RT
MEEP	-83	-
MEEP$(LiClO_4)_{0.04}$	-58	1.7×10^{-5}
MEEP$(LiCF_3SO_3)_{0.02}$	-69	1.5×10^{-5}
MEEP$(LiCF_3SO_3)_{0.04}$	-62	1.5×10^{-5}
MEEP$(LiBF_4)_{0.25}$	-	1.7×10^{-5}

MEEP polymer and MEEP-based electrolytes exhibit lower T_g than PEO (-60^{o}C) and the corresponding PEO-based electrolytes (-15^{o}C). There is a significant improvement in the room temperature conductivity of the MEEP-based electrolytes over the PEO electrolytes ($\sigma \sim 10^{-8}$ S/cm at RT). Another flexible inorganic backbone studied extensively is the silicone based poly(dialkyl siloxanes) $(Si-O)_n$. An example of the polymer containing this backbone structure is shown below.



$$\left(\underset{\mathrm{CH_2-CH_2-PEO}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{-O}\right)_n$$

The glass transition temperature of the polymer and the electrolyte containing $LiClO_4$ salt are lower than the corresponding PEOs and the room temperature conductivity is 5×10^{-5} S/cm. Although both the MEEP and the silicone based polymer electrolytes show improved conductivity, it is still lower by 2 orders of magnitude than what is needed for battery applications ($\sigma \sim 10^{-3}$ S/cm at RT). In addition, the electrolytes exhibit poor mechanical properties.

3.1 Plasticizing Effect of Lithium Salts:

The methods discussed above to increase the conductivity are based on modifying the polymer architecture. The electrolyte properties may also be modified by changing the lithium salt. For example, lithium salts with large anions such as $LiCF_3SO_3$, $LiClO_4$, $LiBF_4$ exhibit higher conductivity than salts with smaller anions such as LiCl, LiBr etc. It has been shown earlier that lithium salts such as $LiN(CF_3SO_2)_2$ and $LiC_4F_9SO_3$ in PEO exhibit higher conductivity than $LiCF_3SO_3$. In the following table, the conductivity of PEO-based electrolytes for a few of the salts are compared.

Table-2. Conductivity of PEO-based Electrolytes for Different Salts(11)

Polymer Electrolyte	Conductivity (S/cm) at RT
PEO $(LiCF_3SO_3)_{0.125}$	6×10^{-8}
PEO$(LiC_4F_9SO_3)_{0.125}$	$\sim10^{-6}$
PEO$(LiN(CF_3SO_2)_2)_{0.125}$	7×10^{-5}

The enhancement in conductivity has been mainly attributed to two factors: (a) low lattice energy of the lithium salts with large anions which increases salt dissociation. e.g. $LiBF_4$ with a lattice energy 700 kJ/mol has a higher conductivity than LiSCN which has a lattice energy of ~810 kJ/mol and (b) plasticizing effect of the larger anion. The plasticizing effect of the larger anions is evident in the conductivity vs. 1/T plot where the temperature at which the break in conductivity occurs is shifted to lower temperatures. One such plot is shown below.

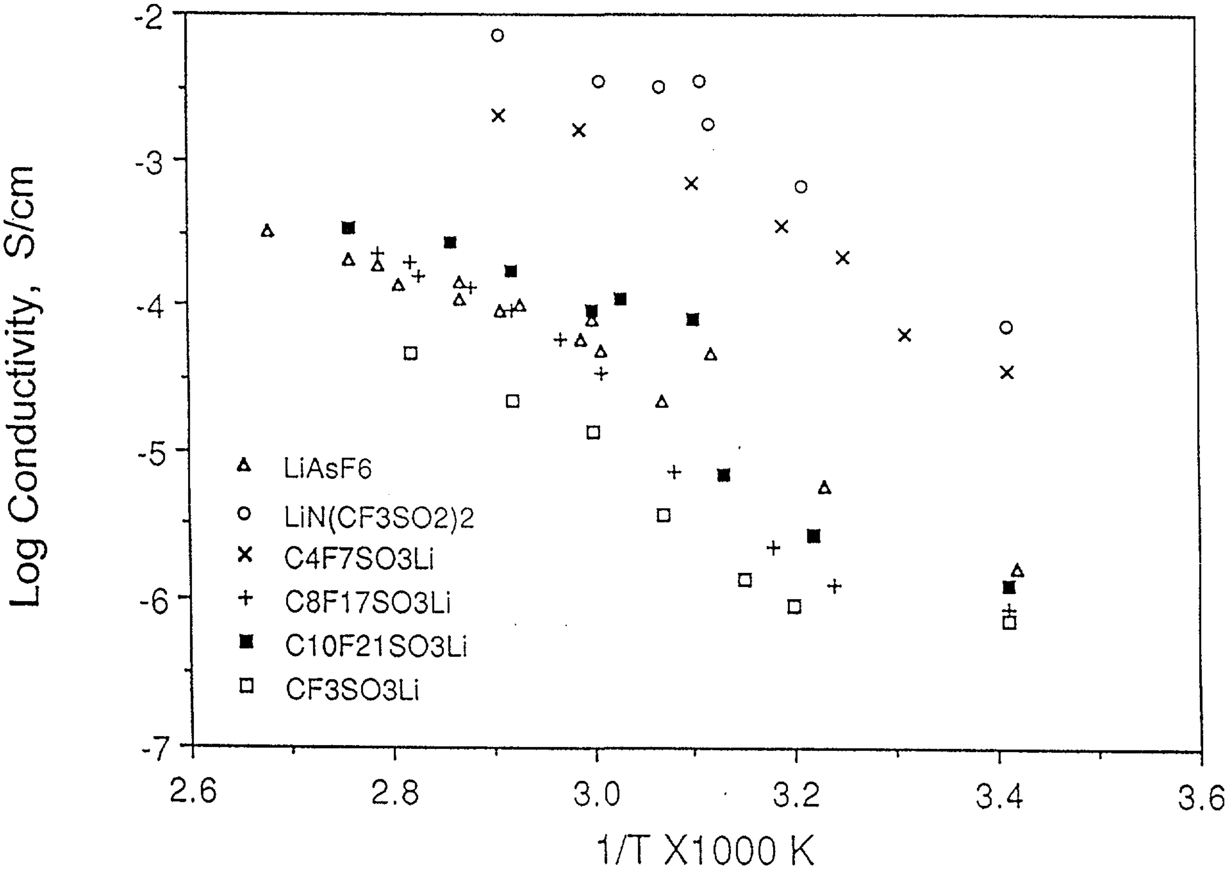


Figure 1. Conductivity vs. 1/T of PEO-based Electrolytes for Different Salts.

The plots show that the break occurs at a lower temperature for PEO/LiN(CF_3SO_2)$_2$ compared to PEO/$LiCF_3SO_3$ (with the same ratio of oxygen to lithium (8:1)). Although the plasticizing effect of the large anions is tangible, the improvement in conductivity is still not enough to use these electrolytes in polymer batteries directed toward industrial/commercial applications. This led to the development of gelled electrolytes.

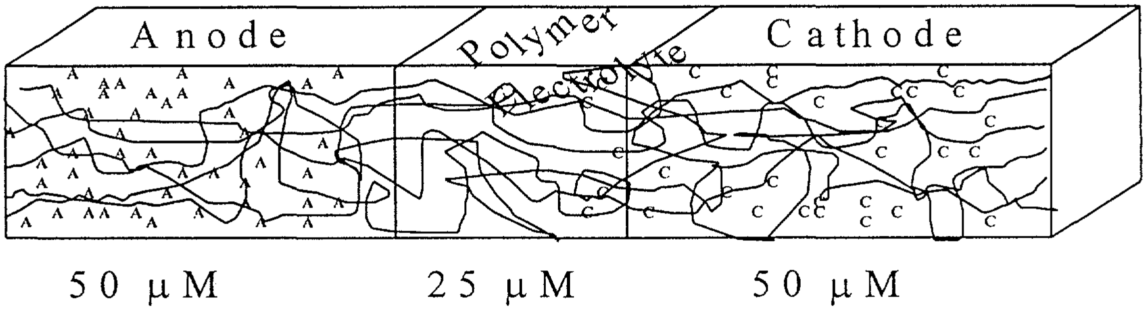
3.2 Gelled Electrolytes

To improve, still further, the room temperature conductivity of polymer electrolytes gelled electrolytes are being investigated. Gelled electrolyte consists of liquid organic electrolyte(s) soaked in electrochemically inactive polymer host matrix. These can be made either thermally or by photocuring. The formation of thin films by these two techniques are described in references 12 and 13. Polyacrylonitrile (PAN) based and polyvinylidene difluoride (PVDF) based gelled electrolytes containing different organic liquid electrolytes have been studied extensively (14 and 15). The bulk ionic conductivity of these systems is $>10^{-3}$ S/cm at RT, which is comparable to that of liquid electrolytes. The mechanical strength of these electrolytes is also very good. However, the electrochemical and chemical stability, in contact with metallic lithium, of these electrolytes is a major problem. The use of carbon as anode (rocking chair configuration) could potentially improve the stability of these electrolytes.

4. CELL STUDIES

Small experimental prismatic cells of capacity ~50 - 100 mAh were fabricated and tested for cycle life and capacity. The cells employed either a lithiated carbon anode and a variety of cathodes including $LiCoO_2$, TiS_2 etc. Usually the cell is case neutral in design. Fabrication of composite cathode/anode with optimum electronic and ionic conductivity properties is extremely important to maximize cell performance. Several techniques were used for the fabrication of composite electrodes. One of the commonly used techniques is the solution casting technique. This technique is described below for PEO-based TiS_2 composite electrodes. The exact amount of lithium salt was dissolved in acetonitrile followed by the addition of PEO weighed beforehand. The solution was allowed to stir till a homogeneous solution was obtained. To the homogeneous solution was added appropriate amount of TiS_2 and the solution was stirred to disperse TiS_2 particles uniformly in the solution. The solution was poured onto a stainless steel foil (precleaned) kept at the bottom of a Teflon mold. The solution was allowed to evaporate slowly. After complete evaporation of the solvent, the film was dried in vacuum at 40 - 50°C for two days. Several volume ratios of TiS_2/PEO ranging from 20/80 - 80/20 were investigated. Exact amount of lithium salt was added to yield O:Li ratio of 8:1. Among the several compositions investigated 50/50 of TiS_2/PEO seems to be the best in terms of cathode utilization, reversibility etc.

The presence of the same electrolyte in both composite cathode and composite anode could potentially mitigate if not completely eliminate the electrode/electrolyte interfacial problem. Further, the cell could be fabricated in a monolithic structure. A schematic of the cell is shown below.



Schematic of a Lithium Polymer Cell.

In this structure the polymer is present in all the three components mixed with anode on the left and cathode on the right. In this structure the interfaces are not abrupt and this could, as mentioned above mitigate interface resistance. Cell fabrication has been described elsewhere (11). In Table 3 some of the anodes, cathodes and polymer electrolytes investigated in full cells are collected and assembled.

Table 3. Anodes, Cathodes and Polymer Electrolytes Studied in Full Cells.

Polymer Electrolyte	Cathode	Anode	References
PEO/$LiCF_3SO_3$	TiS_2	Li	16
PEO/$LiC_nF_{2n+1}SO_3$	TiS_2	Li	11
PEO/$LiN(CF_3SO_2)_2$	MnO_2	Li	17
PEO/$LiCF_3SO_3$	LiV_3O_8/ LiV_6O_{13}	Li	18/19, 20
PAN/EC+PC-$LiClO_4$	$LiMn_2O_4$	Li	21
PAN/EC+PC-$LiClO_4$	$LiMn_2O_4$	Carbon	21

In figures 2, 3 and 4 cycle life vs. capacity are given for PEO-TiS_2 system containing lithium imide ($LiN(CF_3SO_2)_2$) and $C_4F_9SO_3Li$. These data and a number of published data pertaining to the charge/discharge characteristics (21) show that the polymer cells can be charged and discharged over 80 cycles and in some cases over 200 cycles at reasonable rates.

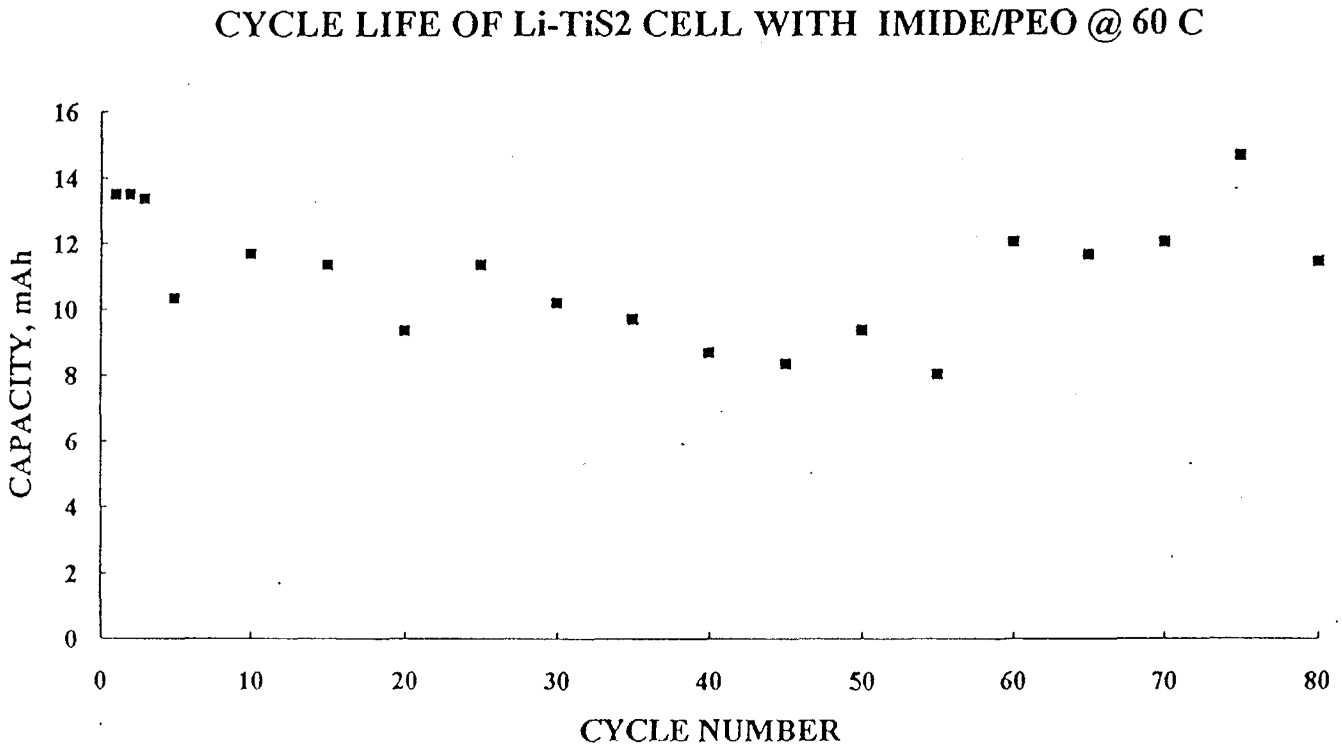


Figure 2. Capacity vs. Cycle # for Li/PEO-LiN$(CF_3SO_2)_2$/TiS_2*. Cell at 60°C. The discharge currents were 5 mA and 3 mA before and after 55 cycles, respectively. The charge current was 1 mA. *: composite cathode.

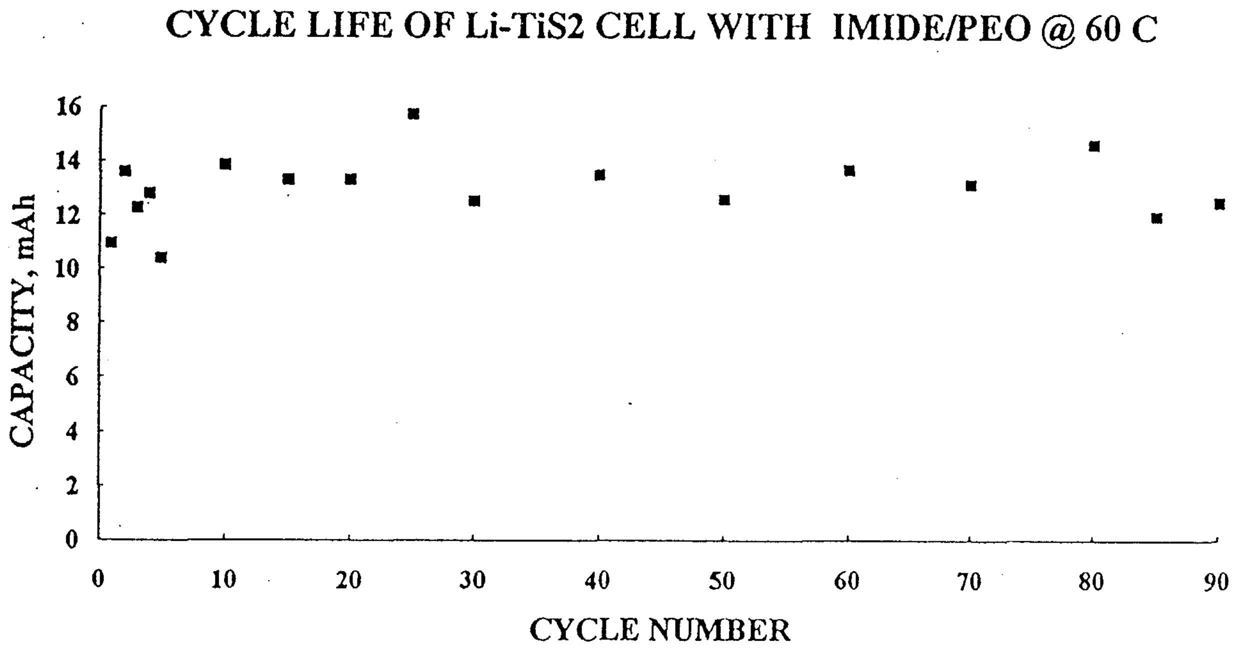


Figure 3. Capacity vs. Cycle # for Li/PEO-LiN$(CF_3SO_2)_2$/TiS_2^*. Cell at 60°C. The discharge and charge currents were 4 mA and 1 mA respectively. *: composite cathode.

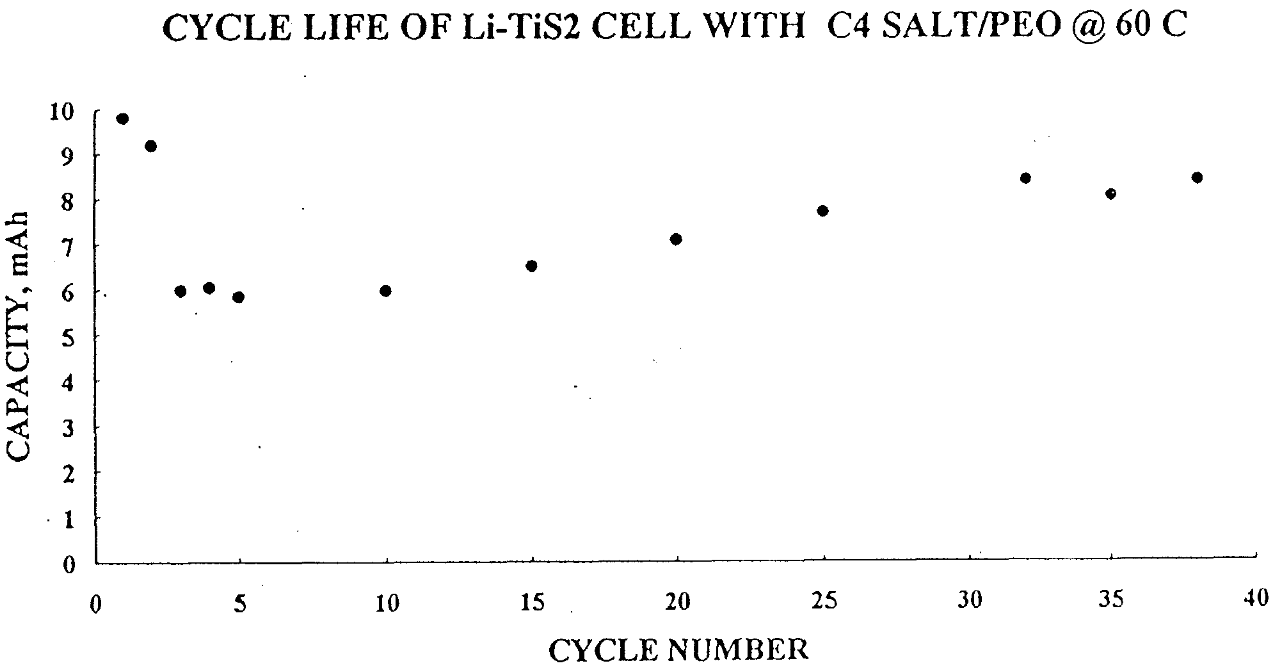


Figure 4. Capacity vs. Cycle # for Li/PEO-$C_4F_9SO_3Li/TiS_2^*$. Cell at 60°C. The discharge currents were 0.5 mA and 1 mA before and after 2 cycles, respectively. The charge current was 0.5 mA. *: composite cathode.

5. CONCLUSIONS

A significant improvement has been achieved in the research and development of lithium polymer batteries. Encouraging results have been obtained which led to a steady technological progress. Large area pin hole free thin films (~1 mil) can be prepared routinely. Recently, polymer cells have been fabricated and tested for cycle life, capacity decline etc. at or close to room temperature (as opposed to cell operating temperatures >100°C few years ago). Because of the tangible improvements in the polymer properties polymer cells have exhibited reasonable cycle life at moderate rates (>C/3). However, there remains a number of potential technological problems to overcome. Further optimization of the cells remains to be achieved before the full potential of the technology can be exploited for commercial applications. These problems include lack of fundamental understanding of ion transport in polymer electrolytes (PEs) for the development of PEs with higher room temperature ionic conductivity ($\sigma > 10^{-3}$ S/cm) and lithium ion transport (~1). Optimization of these two properties could avoid limiting current effects and parasitic side reactions such as accumulation and decomposition of anions of the salt at the polymer/electrode interface. Further, a clear understanding of the chemical and electrochemical instabilities of PEs in contact with electrodes is necessary to mitigate/avoid capacity decline with cycling (>500 cycles) and to improve cycle life. In addition, the polymer electrolytes should be able to form composite electrodes (cathode and anode) which could lead to the preparation of monolithic (refer to "Schematic of Polymer Cells") cells to avoid interfacial effects.

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