POLYMER ELECTROLYTES

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Summary

Solid solutions consisting of a lithium salt and a polymeric solid "solvent" can be used as electrolytes for lithium batteries. Among the conditions to be met by the polymer, in addition to a high conductivity, are a high dielectric constant (salt dissociation), electrochemical compatibility with lithium metal and the cathode material, and mechanical strength in order to act as a separator. The best results up to now have been obtained with high molecular weight poly(ethylene oxide) (PEO) above 60 °C. Below 60 °C, PEO is too crystalline and must be modified in order to decrease its melting temperature, thus increasing the solubility of the salt and its conductivity. We review some of the methods used for this purpose.

Introduction

Lithium is a highly desirable electrode material because of its lightness and high electropositivity. Lithium-based batteries should therefore be capable of storing more energy, weight by weight, than the other present commercial batteries such as those based on lead and Ni–Cd. So far, most of the lithium batteries on the market, except for the now commercially available Moli cells, have been of the primary, non-re-usable type. They are characterized by a high energy density and long shelf-life.

One of the main problems encountered in the development of a rechargeable lithium battery has been the high reactivity of lithium with many of the inorganic materials normally used as electrolytes, especially during battery recharge when Li is most reactive. A practical effect of this difficulty appears in "dendrite" formation and a low efficiency of Li deposition on the electrode. A solution to this problem was suggested over ten years ago by Armand [1]. He suggested using a polymer electrolyte formed by dissolving a lithium salt in a polyether as part of a lithium rechargeable battery.

Wright [2] has shown that poly(ethylene oxide) (PEO) forms solid state complexes with alkaline salts, and these complexes exhibit ionic conduction. Furthermore, the ether function is relatively inert, especially if there is no strain on the ether bond, as there would be in THF, for example [3]. This

material can be used as an Li^+ carrier in an all-solid electrochemical cell:

(−) Li (source) polymer electrolyte/Li sink (+)

The positive electrode is a composite made from a reversible lithium inserting compound (e.g., TiS_2, V_6O_{13}), an electronic conductor, such as carbon black, and some polymer electrolyte that also acts as a bonding agent. The polymer molecule, due to its bulk, cannot co-insert with lithium and does not participate in the electrode reaction. Furthermore, polymers can be designed so as to enhance their elastomeric character so that they can accommodate the volume variations that occur as lithium moves from one electrode to the other.

PEO-based electrolytes have a stability window of about 4 V [4]. They are only metastable towards lithium: a passivation layer is formed on the Li electrode. Fortunately, this layer, although resistive, permits the passage of the Li^+ ions. Moreover, the high viscosity of the polymer electrolyte might prevent its penetration of the porous layer, as would undoubtedly happen with a liquid electrolyte. The high stability of PEO towards oxidation is therefore enhanced by its polymeric nature. One might hope that the same phenomenon will also happen in the case of other, seemingly less stable, polymers, but our experience has shown us that there are stringent limitations to the use of most organic functional groups.

Polymer structure

A polymer is a macromolecule formed by linking chemically a large number of small molecules. They can be classified into many categories according to their composition and structure. If they are made from a single monomer, they are called homopolymers. If they are made from more than one monomer, they are called copolymers. The way the different monomer units are distributed in a copolymer also defines the categories of random, alternate, block and graft copolymers:

random   ABAABABBBAABA

alternate   ABABABABABABAB

block   AAABBBBBAAABBBBB

graft   AAAAAAAAAAAAAAAAAAAAAA
                  B   B
                  B   B
                  B   B
                  B   B

Most polymers are first synthesized as linear polymers since this is the form under which they can most easily be shaped by casting from a solution

or a melt. Low molecular weight polymer can be modified afterwards to obtain different molecular shapes: branched, crosslinked, network. The physical properties will be dependent on the molecular structure as well as whether it is crystalline or amorphous. Figure 1 [5] shows these different possibilities.

    An amorphous polymer is actually a very viscous liquid. If its molecular weight is high enough, it will creep only very slowly under stress and behave like a rubber. Permanent deformations will be achieved by prolonged force application but it will withstand a small amount of stress. It can sometimes be rendered more resilient by crosslinking, a process analogous to the vulcanization of rubber and with roughly the same result in terms of physical strength.
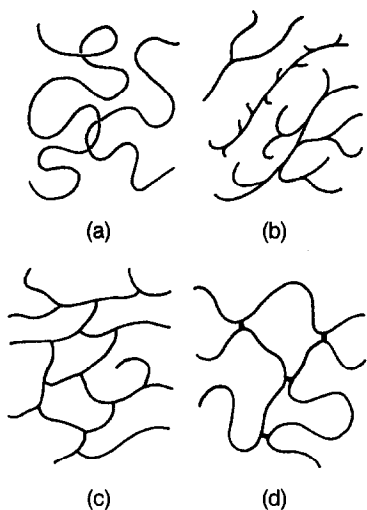

(a)   (b)

(c)   (d)

Fig. 1. Macromolecular architecture of polymers: (a) linear; (b) branched; (c) network; (d) crosslinked [5].

Electrolyte conductivity

    Compared with the liquid electrolytes used in conventional systems, polymer complexes have relatively low ionic conductivities. PEO exhibits a high enough conductivity around 100 °C, but there is a break in the curve at the temperature of crystallisation of the pure polymer [1] which prevents its use at room temperature. As a matter of fact, NMR studies [6] have shown that the conduction occurs mainly in the amorphous regions of the electrolyte.

    Fortunately, polymers can be processed into very thin films, which compensates, in part, for their reduced conductivity. If one wishes to obtain the same power density as in other types of batteries, the total thickness of a polymer electrolyte cell must be of the order of 0.1 mm. The electrolyte

itself should therefore be well under 0.05 mm; this is attainable by the techniques currently used in the plastics industry. One should therefore look for polymers with a low crystallinity, while a high mechanical strength is necessary in order to maintain a reliable separation of the electrodes.

Many people have looked for structures that should be less crystalline than PEO. One polymer which closely resembles PEO is poly(propylene oxide) [7]; the monomer contains an asymmetric carbon atom which, unless one wants specifically to make a crystalline polymer by reacting the two forms independently, should yield an amorphous one. It complexes lithium salts, but the conductivity is quite low, maybe because the propylene oxide unit is less mobile than its ethylene oxide counterpart.

Other polymers that have been investigated as possible substitutes to polyethers are poly(β-propiolactone) [8] and poly(ethylene succinate) [9]. The resulting solutions have even lower conductivities than PPO; their stability towards lithium has not been demonstrated.

Poly(N-substituted ethylene imine) (PEI) [10] and poly(ethylene sulfide) (PES) [11], the nitrogen and sulfur analogues of PEO, have also been considered as possible substitutes for PEO. These approaches do not seem to have yielded very good results up to now. PES does not have the same conformation as PEO. As for PEI, part of the problem comes from the difficulty of synthesizing samples that have both a high molecular weight and the linear structure necessary for solubility. Oxygen remains the complexing atom of choice for polymer electrolytes, in the particular sequence CH_2-CH_2-O. Other polyethers with the CH_2-O and the $CH_2-CH_2-CH_2-O$ sequences do not form conducting complexes.

High molecular weight PEO films have been radiation-crosslinked at high temperature in order to decrease their crystallinity [12]. The aim was to freeze the polymer molecules in a disordered state and prevent crystallisation. The attempt was only partly successful; the resulting conductivity curve does not show the break characteristic of crystallisation, but is still very low.

One possible way to decrease the crystallinity of a polymer is to decrease its molecular weight (MW): poly(ethylene glycols) with a MW under 600, for example, are liquid at room temperature. However, this will also decrease its mechanical strength. Unless one is ready to add fillers to the electrolyte to ensure the separation of the electrodes, one should therefore look for a way to recombine short polymer segments without making them crystalline. Many attempts have been made with this approach in mind. Most of them make use of poly(ethylene glycol) units linked together by a urethane group [13] or attached as pendant chains to a polymer backbone such as polysiloxane [14] or polyphosphazene [15]. A model structure of this type would consist of a poly(ethylene) backbone with branches made from a low MW poly(ethylene glycol).

Polymer networks have also been made by linking poly(ethylene glycols) or a block copolymer of ethylene oxide and propylene oxide with a trifunctional urethane [16]. Typically, their conductivities are less than PEO
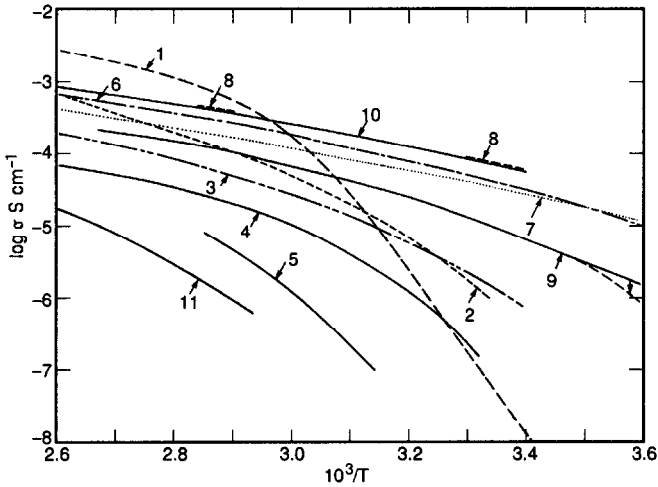
Fig. 2. Conductivity curves for selected polymer electrolytes. 1, PEO–LiClO$_4$ (12/1); 2, PEO, radiation-crosslinked, LiClO$_4$ (8/1); 3, PPO–LiCF$_3$SO$_3$ (9/1); 4, Poly(ethylene adipate)–LiCF$_3$SO$_3$ (4/1); 5, Poly(ethylene succinate)–LiBϕ_4 (6/1); 6, Polyphosphazene ME7P–LiCF$_3$SO$_3$ (16/1); 7, Polyphosphazene, crosslinked, 1XMP–LiCF$_3$SO$_3$ (21/1); 8, Polysiloxane–LiClO$_4$ (25/1); 9, Triol type PEO crosslinked with difunctional urethane–LiClO$_4$ (50/1); 10, PEO–PPO–PEO block copolymer crosslinked with trifunctional urethane–LiClO$_4$ (50/1); 11, Poly(N-methyl aziridine)–LiClO$_4$ (8/1).

above 60 °C, where they may be thought of as diluted PEO, and become better than PEO at some lower temperature, where they behave as a completely amorphous but still diluted PEO. The gain in conductivity can be as high as a factor of 1000 at room temperature.

Some conductivity curves selected from some of the above electrolytes are shown in Fig. 2 [17]. Other ways have been contemplated to improve the results. Chief among those is the use of plasticisers that dilute the polymer and decrease its crystallinity. For example, Kelly *et al.* [18] have mixed high and low MW PEO, thus hoping to combine the strength of PEO films and the high conductivity, at low temperatures, of poly(ethylene glycol) electrolytes.

Transport number

When polymer electrolyte batteries were first envisioned by Armand, the conduction mechanism suggested that most of the current was carried by the cation. However, the transport number of the Li$^+$ ion measured from NMR is generally between 0.2 and 0.5. An improvement in this area would decrease the electrode polarization and the associated overvoltage. The most promising way to increase the transport number seems to be by immobilising the anion by linking it chemically to a polymer chain: either a modified PEO or some other compatible polymer. The chemistry needed to do this is very

complex and costly. Besides, there is still the possibility that a mobile anion is necessary to the conduction mechanism.

The most popular salts for use in polymer electrolytes are $LiClO_4$ and $LiCF_3SO_3$. The perchlorate gives good results but safety considerations require that it is used in low concentrations which can, in some cases, impose power limitations. Lithium triflate is less dangerous and can be mixed with PEO in the molten state as well as in a common solvent. However, it is very crystalline and must be used at high temperatures, 120 °C or above. New lithium salts developed as a result of the ACEP project have resulted in good power performances at much lower temperatures [19, 20]. This illustrates how polymer electrolytes can be improved by appropriate choices of both the polymer and the lithium salt.

The formation of a complex means a strong interaction between the cation and the solvating polymer molecule. As the polymer cannot accompany the ion on its way to the cathode, it is likely that the positioning of the anion plays an important role in the displacement of the cation [21]. One might, for example, envision a steady-state type of equilibrium where an Li^+ ion jumps from its polymer cage, helped by a proper positioning of a neighbouring anion and another chain, to another polymer cage nearer to the cathode. It is also probable that since conductivity occurs in the amorphous areas, and taking into account that it is low, the complexes responsible for the conductivity involve more than one polymer molecule, and might include the anion as well as the formation of complex ions with one or more undissociated salt molecules.

Polymer purity

In all these attempts, one must beware of the presence of impurities that can significantly change the conductivity value and react with either of the electrodes. Very low amounts of impurities in the bulk of the polymer might concentrate on the polymer interface, thus increasing the interface resistance and reducing the cyclability of the cell. This was recognized very early in the ACEP project, and an important part of our research has been devoted to the synthesis and evaluation of very pure analogs of the industrial type polymers used in the ACEP project. This includes polymers already available commercially as well as the modified polyethers developed as part of the ACEP technology. We could, in this way, ascertain the intrinsic conductivity and redox domain of the polymer electrolytes. We could also point out any undesired reaction due to the nature of the polymer itself or to an impurity brought along by the polymerisation process.

For example, in order to evaluate the effects of the impurities contained in commercial PEO samples, we synthesized some high molecular weight PEO using an anionic initiator [22]. All the preparations were made on a vacuum line. The solvent and reagents were purified by such high vacuum techniques as cold-wall distillation and drying on sodium mirrors or sodium–potassium alloy. The only impurities are those left by the initiator, which is

very low, about one molecule for each polymer molecule, and even less if there is some chain transfer. For an MW of 10^6, this amounts to about 50 ppm of catalysis residues. Commercially available PEO contains 1 - 2% of inorganic impurities as catalysis residues, mostly silicates, as well as some antioxidant.

The addition of an antioxidant to a polyether is frequently used to prevent its degradation in the presence of air or U.V. radiations. In a PEO sample with an MW of 10^6, there are about 50 000 ether bonds. The breaking up of about 0.002% of these bonds is therefore sufficient to bring the MW down by half. The resulting decrease in mechanical strength will soon become unacceptable. The problem is compounded by the nature of the antioxidants: they are usually aromatic alcohols, and are quite likely to react with the lithium electrode.

Another advantage of anionic polymerisation is that it yields a polymer with a relatively narrow MW distribution without further fractionation. The usual industrial initiators exhibit a slow initiation speed followed by a very fast polymerisation. As a consequence, the first polymer molecules formed are very long and the last ones are rather short. Another consequence is the large amount of initiator needed, typically 1 - 2% of the total monomer weight. True anionic initiators exhibit a fast initiation and a slow propagation. The polymer molecules tend to have the same length, and the amount of initiator used is very low. Figure 3 shows the GPC curves of one of the samples we synthesized and of a commercial sample of PEO. The MW of both samples is about 5×10^6. Our sample has a slightly smaller polydispersity and there is no detectable low MW fraction.

POE E-11 (M=5x10^6)

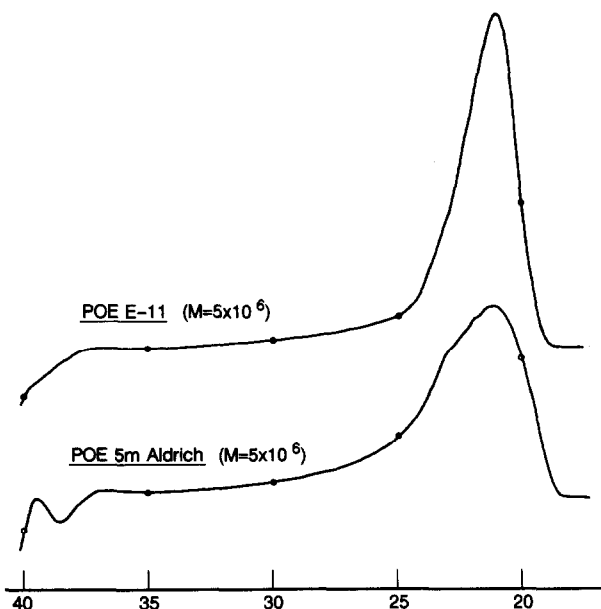POE 5m Aldrich (M=5x10^6)

| 40 | 35 | 30 | 25 | 20 |

Fig. 3. GPC traces of a commercial and an anionically synthesized PEO.

Comparative measurements [23] on anionic and commercial samples of equivalent MW (10^6) have shown a marked effect of the presence of impurities on the conductivities of the samples, resulting in a lower conductivity of the anionic polymer electrolytes. This effect is quite marked for the isotherms with $LiCF_3SO_3$, Fig. 4, and $LiClO_4$, Fig. 5, from ref. 24. This higher conductivity of the commercial sample is not advantageous in battery operation, since it is not due to an improved Li^+ conduction.

This issue of polymer stability and purity is very important for rechargeable batteries. Small size impurities will possibly be able to move through the passivating layer and react with the lithium electrode. They might also co-insert the positive electrode and decrease its efficiency. Most of the chemical processes used to create a polymer network will also leave some residue whose reactivity needs to be taken into account.

The ACEP project

From the beginning, the ACEP project has aimed at the practical goal of producing batteries. This has forced us to use "industrial solutions" to
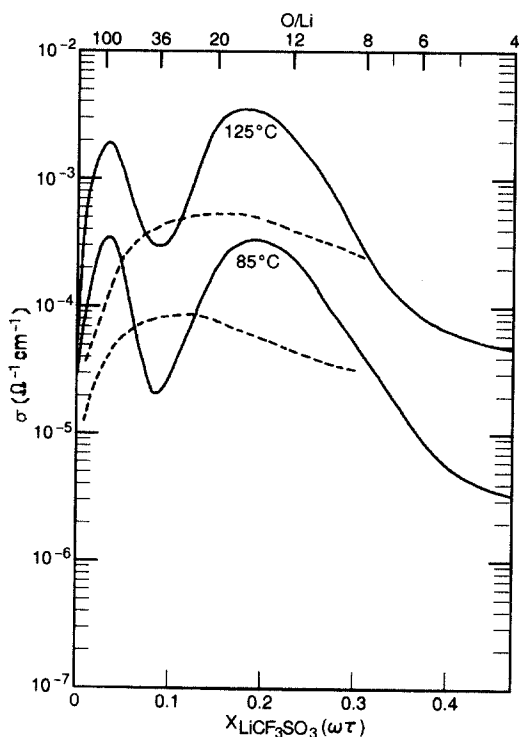

Fig. 4. Isothermal variation of the ionic conductivity as a function of the $LiCF_3SO_3$ fraction in a commercial PEO (———) and in an anionically synthesized PEO (— — —).
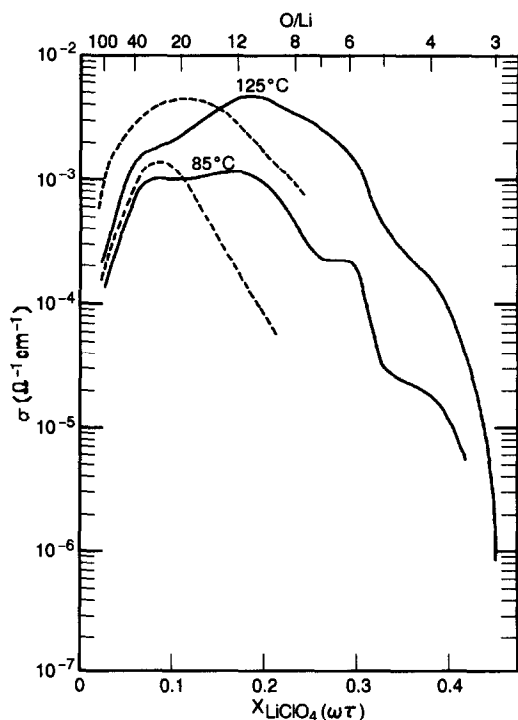
Fig. 5. Isothermal variation of the ionic conductivity as a function of the LiClO$_4$ fraction in a commercial PEO (———) and in an anionically synthesized PEO (— — —).

any problem encountered: either using commercially available products and technologies, or developing our own products and know-how while making sure they could be reproduced cheaply enough in an industrial process. The need to test new polymer electrolytes in complete cells, in addition to studying electrolyte characteristics, was recognized early in the project. This has enabled us to learn very quickly of any problem involving any combination of cell components. This approach can be painstakingly slow but has still enabled the ACEP team to obtain encouraging results. Recent results [19, 20] involving a new salt combined with a modified polyether show good prospects for use at room temperature.

Acknowledgements

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