# New conducting polymer networks

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## Abstract

These new polymer networks are based on cross-linked polyethers. The cross-link reaction is carried out by reaction of a diglycidyl compound with a polyether having two terminal primary amine groups. Ionic conductivity depends on the level of cross-linking, the salt concentration and the nature of the polyether. At room temperature, the best obtained conductivity exceeds $4 \times 10^{-5}$ S/cm. Mechanical properties are good. These polymer electrolytes are completely amorphous and stable up to 250 °C. The measured glass-transition temperature is close to −56 °C. These networks are also used to synthesize hybrid electrolytes which include a liquid polymer or a high dielectric constant solvent. The conductivity of these electrolytes is close to organic liquid electrolytes.

## Introduction

Conventional polymer solid electrolytes based on poly(ethylene oxide) (PEO) have low ionic conductivity at ambient temperature because of their semicrystalline nature. Only the amorphous phase provides conduction [1], and conduction is only really good beyond the melting temperature of the polymer. Comb-shaped polymer electrolytes with oligo(ethylene oxide) units as side-chains show high conductivity, but the counterpart of this improvement is often a degradation of the mechanical properties. The elaboration of cross-linked conductive polymers can increase film strength and suppresses crystalline zones [2]. Meanwhile, conductivity is generally limited. We present in this paper new polymer networks [3] combining good electrochemical and mechanical properties.

## Experimental

### Electrochemical measurements

The conductivity of the polymers was measured by impedance spectroscopy (Solartron 1250 frequency response analyser and 1286 electrochemical interface) on symmetrical nickel/nickel cells. Lithium/lithium cells were used for the study of the interfaces. Cyclic voltammograms were recorded using a potentiostat EG&G PAR mod. 273 on lithium/nickel cells.

### Sample preparation

The networks were prepared from 400 to 20 000 mol. wt. PEO/PPO (poly(propylene oxide)) copolymers with terminal primary amine groups. Some of them are commercially

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available (Sigma and Jeffamine from Texaco). The curing agent was ethylene glycol diglycidyl ether (EGDGE) or butanediol diglycidyl ether (BDDGE). The lithium salt was dissolved in ethanol or in acetonitrile and mixed with the bis-amino polyether. After complete evaporation of the solvent, the curing agent was added to the polymer. All the reactions were carried out in a glove box and the cross-linked polymer samples were dried under primary vacuum at 100 °C for 15 h.

## Results and discussion

### Network elaboration

The network basis is a copolymer of polyethers having two terminal primary amine groups. The cross-link reaction is carried out by reaction of a diglycidyl compound (di-epoxy) with the amine groups (Fig. 1). The amine functions of the polyether react with the epoxy groups which open. The secondary amines that are formed react in turn with the epoxy groups. This set of reactions ensures that cross-linking takes place and that a three-dimensional lattice is formed. The maximum cross-link density is obtained for an epoxy/amine ratio of 2. This reaction is thermally initiated and occurs within a few min at moderate temperature ( > 80 °C) in presence of a suitable catalysis which is an electron acceptor. Figure 2 shows a possible reaction mechanism [4]. The epoxy oxygen approaches the alkaline metal-amine complex and the attraction point is the metal atom. Epoxy oxygen acquires a partial positive charge causing a partial shift of electrons from an adjacent carbon of the epoxy ring. The electron deficiency created is an attack point for the nearby nucleophilic nitrogen and the amine/epoxy reaction can take place. The overall reaction would be a Lewis acid accelerated reaction. In the case of an alkaline metal salt, the charge carrier is also the catalyst.

## Electrochemical and physical properties

Ionic conductivity depends on the level of cross-linking (Fig. 3). It is minimum for the stoichiometry, and deviation causes an increase of the relative size of the
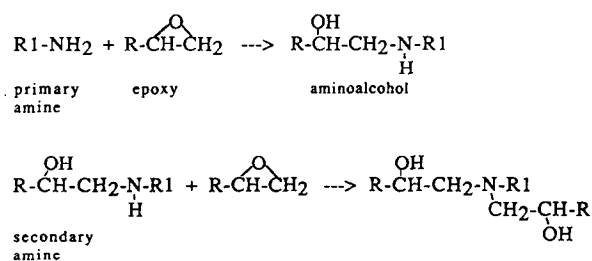
$$R1\text{-}NH_2 + R\text{-}\overset{O}{\overset{\diagup\diagdown}{CH\text{-}CH_2}} \longrightarrow R\text{-}\overset{OH}{\underset{}{CH}}\text{-}CH_2\text{-}\underset{\underset{H}{|}}{N}\text{-}R1$$

primary      epoxy           aminoalcohol
amine

$$R\text{-}\overset{OH}{\underset{}{CH}}\text{-}CH_2\text{-}\underset{\underset{H}{|}}{N}\text{-}R1 + R\text{-}\overset{O}{\overset{\diagup\diagdown}{CH\text{-}CH_2}} \longrightarrow R\text{-}\overset{OH}{\underset{}{CH}}\text{-}CH_2\text{-}\underset{\underset{\underset{OH}{|}}{CH_2\text{-}CH\text{-}R}}{N}\text{-}R1$$

secondary
amine

Fig. 1. Cross-link reaction of a diglycidyl (di-epoxy) with amine groups.

R1-NH$_2$- - - LiX                 R1-NH$_2$ - - - LiX

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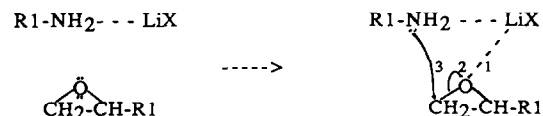CH$_2$-CH-R1                     CH$_2$-CH-R1

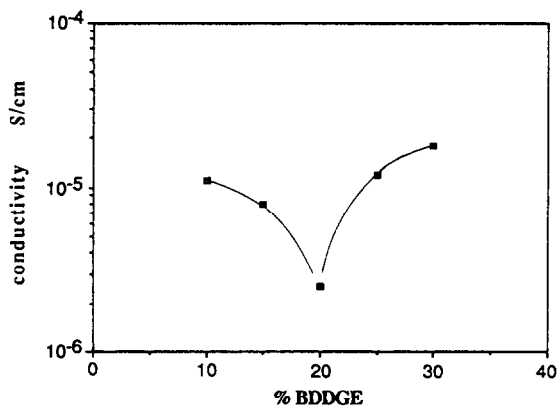Fig. 2. Epoxy/lithium salt-amine complex reaction: possible reaction scheme.

Fig. 3. Variation of conductivity with curing agent concentration (BDDGE, 10% LiClO$_4$, 2000 mol. wt. PEO/PPO, at 25 °C).
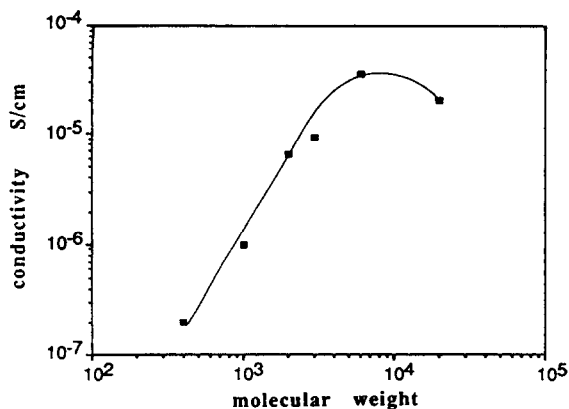


Fig. 4. Variation of conductivity with polymer molecular weight (20% EGDGE, 10% LiClO$_4$, epoxy/amine = 2, at 25 °C).

network. The molecular weight of the polyether also modifies the conductivity (Fig. 4). The highest conductivity is obtained between 5000 and 10 000 mol. wt. Below this range, the cross-linked network is rigid and has low segmental motion. Above this range, the polymer can be partially crystallized. At room temperature, in presence of a lithium salt and for an ether/cation ratio of 18, the conductivity is close to $4 \times 10^{-5}$ S/cm for a 6000 mol. wt. (PEO/PPO) and to $6 \times 10^{-6}$ S/cm for a 2000 mol. wt. (PEO/PPO) (Fig. 5). The variation with the temperature is low (Fig. 6) and the activation energy, according to Arrhenius theory, is less than 18 kJ/mol. The electrochemical window is about 4.6 V. The cyclic voltammogram of cross-linked PEO/PPO (Fig. 7) shows sharp peaks for the plating and stripping of lithium on a nickel electrode. Mechanical properties of these networks are excellent in comparison with those of classical polymer electrolytes. They are completly amorphous and stable up to 250 °C. The measured glass-transition temperature is nearly −56 °C (6000 mol. wt. PEO/PPO).
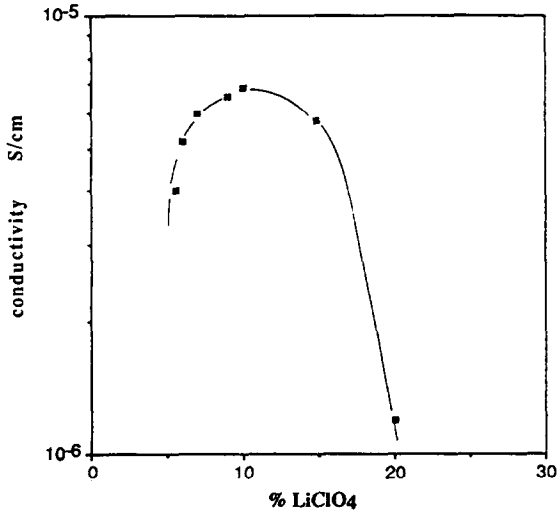
Fig. 5. Variation of conductivity with salt concentration (LiClO$_4$, 20% EGDGE, 2000 mol. wt. PEO/PPO, at 25 °C).
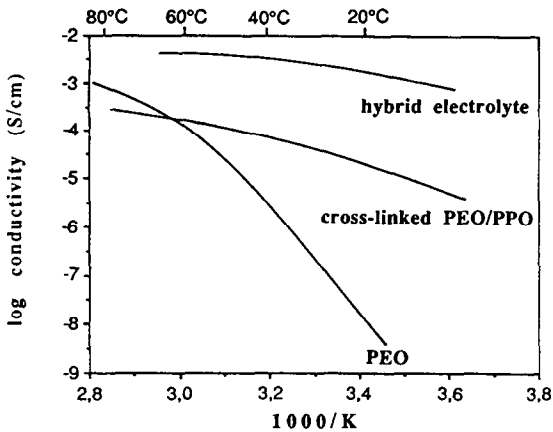


Fig. 6. Variation of conductivity with temperature for nonplasticized and hybrid electrolytes (20% EGDGE, 10% LiClO$_4$, 6000 mol. wt. PEO/PPO).

These networks are also used as a basis to synthesize hybrid electrolytes which include a liquid phase [5]. This last phase is a liquid polymer or a high dielectric constant solvent. The salt, which is soluble in the two phases, improves the compatibility between the liquid and the polymer. The cross-link reaction is accomplished in presence of the plasticizer to minimize the internal stresses. The conductivity of these electrolytes is comparable to that of organic liquid electrolytes ( > 10$^{-3}$ S/cm at 25 °C with propylene carbonate as plasticizer, Fig. 6). For the same conductivity, the hybrid electrolyte needs less liquid than a common gelled electrolyte (inert polymer swollen by a liquid solvent) (Fig. 8). Mechanical properties and time stability are equally better. Transport numbers were measured by a d.c. polarization technique [6]. Figure 9 shows the
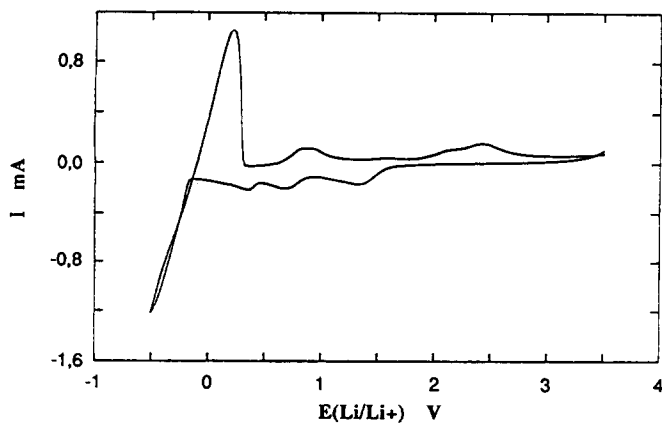
Fig. 7. Cyclic voltammogram of cross-linked PEO/PPO (Ni electrode, 10% LiClO$_4$, 20% EGDGE, 2000 mol. wt. PEO/PPO, 10 mV/sec, at 60 °C).
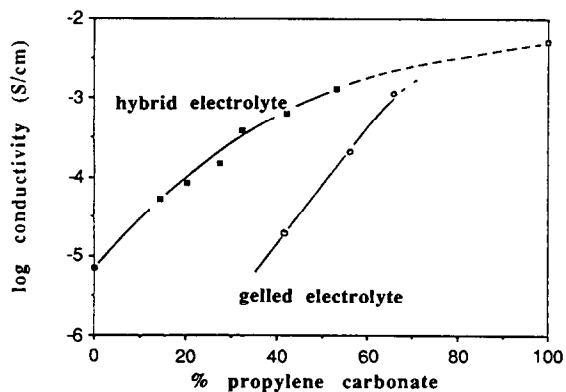


Fig. 8. Variation of conductivity with plasticizer concentration (Ni/Ni cell, 2000 mol. wt. PEO/ PPO, 10% LiClO$_4$, 20% BDDGE, at 25 °C).
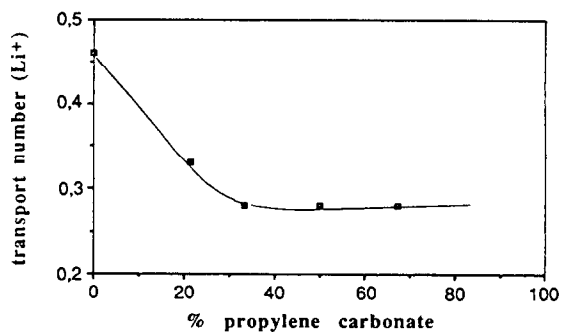


Fig. 9. Variation of transport number with plasticizer concentration (propylene carbonate, Li/ Li cell, 20% EGDGE, 10% LiClO$_4$, 6000 mol. wt. PEO/PPO, at 25 °C).
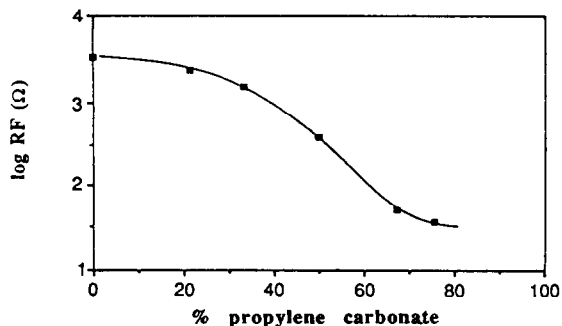
Fig. 10. Variation of interfacial polarization resistance with plasticizer concentration (propylene carbonate, Li/Li cell, 20% EGDGE, 10% LiClO$_4$, 6000 mol. wt. PEO/PPO, at 25 °C).

transport-number evolution versus the electrolyte composition. Below 30% of plasticizer, transport properties are influenced by the polymer network. Above this value, they are only controlled by the liquid phase. The analysis of the transfer resistance at the lithium/electrolyte interface (Fig. 10) shows a different behaviour. It is possible to distinguish three different zones. The first one (<30% plasticizer) corresponds to the polymer/lithium interface. The second one (between 30 and 65% of plasticizer) is a gradual change from the solid state to the liquid state. The last one (>65%) is only representative of the liquid plasticizer. At low concentration, the plasticizer seems to be surrounded by the polymer. At medium and high concentrations, open channels of electrolyte could exist between the two electrodes.

First experiments have been done on all solid-state lithium batteries and super-capacitors with these electrolytes. The nonplasticized electrolytes allow to obtain the best cycling life for the batteries. Due to their high conductivity and specific capacitance, hybrid electrolytes are preferentially used for supercapacitor-type applications.

## Conclusions

Promising results have been achieved with these polymer electrolytes. The ionic conductivity is high and the mechanical properties are good. The polymer networks are easy to make and it would be simple to modify their properties by grafting pendant chains onto the three-dimensional lattice. Due to their electrochemical characteristics, they can meet the requirements of applications such as lithium batteries and super-capacitors. In comparison with other types of cross-link networks for the realization of composite electrodes, these new electrolytes do not need complex processes such as electron beam or gamma-irradiation curing. The use of lithium salt as catalyst instead of another reactive catalyst or sensitizer for radiation cure is also an advantage for the electrochemical stability.

## Acknowledgement

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