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PROGRESS IN ION CONTAINING ORGANIC POLYMERS

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Abstract

Increased interest in highly conducting polymer electrolytes is clearly evident from the open literature, particularly on the specific area of energy-related applications. Poly(ethylene oxide), PEO, although well studied, continues to intrigue us and must still be regarded as playing a central role in polymer electrolyte research and development. Ion containing organic polymers involving essentially PEO as the solvent matrix are reviewed here. The greatest technological driving force for its continued study is still, by far, the desire for thin film rechargeable batteries that meet a multitude of ambitious energy, power density and safety requirements, while not being prohibitively expensive.

1. Introduction

During the last decade, appearance of ionically and electronically conductive polymers led immediately to their use as active components in new battery designs, as electrodes or electrolytes. They include the advantage of polymer materials as plasticity, good mechanical properties, easy processing and light weight in the area of solid state electrochemistry.

Our purpose here deals only with ion containing organic polymers: the organic polymer electrolytes. They alloy plasticity and mechanical properties of polymers to conductivity performances near that of liquids

without risk of leak formation and dendritic recrystallisation in batteries. Among them, we will address the poly(ethylene oxide) metal salt complexes, which are the first generation of polymeric solid electrolytes for self-contained power sources. These power sources are of a continuously growing interest in different fields such as biomedical devices, portable devices (pocket calculators, cameras, watches, toys and electrical tools), space applications, integrable power sources for microelectronics capable of providing permanently powered memory and logic, and high energy density power sources for electromagnetic propulsion. Significant progress in these directions requires further investigations on the polymeric electrolytes in order to improve some of their essential parameters. General considerations on these parameters and the basic principles where they reside are given in this paper.

2. Complex formation

The existence of complexes between polyethylene oxide (PEO) and alkali metal salts was first evidenced by Wright & al. [1,2] and the emphasis on the considerable potentialities of these materials as polymer electrolytes in solid state battery was later given by M. Armand & al. [3].

The basic principle of these compounds resides in the solvating power of a polymer matrix for salts and strong mineral acids in anhydrous media through direct interaction of cation and unshared electron pairs carried by a heteroatom: -O- (ether), -S- (sulphide), -N- (amine), -P- (phosphore) [4]. On Table I, formulas of common solvating polymers are given.

The salt adducts properties of polymer arise from several factors: the polarity of the heteroatoms, the distance between them for the solvation of alkali metal ions and strong mineral acids [4], the flexibility of the polymer

chain, the cohesive energy of the macromolecular network and the lattice energy of the salt.

Table I

Formula of common solvating polymers

	Linear polyether oxides
$[-CH_2-CH_2O]_n$	Poly(ethylene oxide)
$(-CH-CH_2-O-)_n$ $\mid$ CH_3	Poly(propylene oxide)
$(-CH_2-CH_2-NH-)_n$	polyethylene imine
$[(CH_2)_n-S-]_{2<n<6}$	poly(alkylene sulphide)
$[-CH_2-CH-]$ $\mid$ NO	poly vinyl pyrrolidone
$[(CH_3O-C_2H_4-OC_2H_4O)_2PN]$	poly(bis methoxy ethoxy) ethoxy phosphazene

Table II, from [5], summarises the interaction of PEO and PPO with the most common alkali salts.

This basic principle explains also the formation of complexes with strong inorganic acids by charge transfer yielding solvation of acids by hydrogen bonding.

Table II

Complex formation between various alkali metal salts and poly(ethylene oxide), PEO or poly(propylene oxide), PPO [5].

	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
F^-	-/-	-/-	-/-	-/-	-/-	-/-
Cl^-	+/-	-/-	-/-	-/-	-/-	-/-
Br^-	+/-	+/-	-/-	-/-	-/-	-/-
I^-	+/+	+/-	+/-	+/-	+/-	+/-
SCN^-	+/+	+/+	+/-	+/-	+/-	+/-
ClO_4^-	+/+	+/+	+/-	+/-	+/-	+/-
$CF_3SO_3^-$	+/+	+/+	+/-	+/-	+/-	+/-
AsF_6^-	+/+	+/+	+/-	+/-	+/-	+/-
$B(C_6H_5)_4^-$	+/+	+/+	+/-	+/-	+/-	+/-

+ complex formed

- no solubility

PEO/PPO

3. Structural considerations

Linear polymer chains like PEO (polyethylene oxide), PPO (polypropylene oxide), PEI (polyethylene imine) have a great ability to crystallise at room temperature. Obviously it is necessary to get polymer electrolytes with low glass transition temperature, T_g, for having good conductivity at room temperature.

Berthier & al. [6] have shown by NMR measurements that conductivity preferentially occurs in the amorphous phase. The establishment of phase diagrams for these systems, where the stability

regions of the several crystalline and amorphous phases present are defined, is then very useful for a prevision of their conductivity behaviour. Figure 1 [7] shows the phase diagram of PEO-($LiCF_3SO_3$) system built from differential scanning calorimetry and optical microscopy measurements. This system was prepared by mechanical mixing and hot and cold pressing. In the zone of better conductivity (salt/PEO mass relation less than 0.44 or n, molar ratio polymer to salt, higher than 8), it is not evident any eutectic. However, Robitaille and Fauteux [8] have found an eutectic, for 50<n<100, for the same polymer electrolyte prepared by solvent casting.
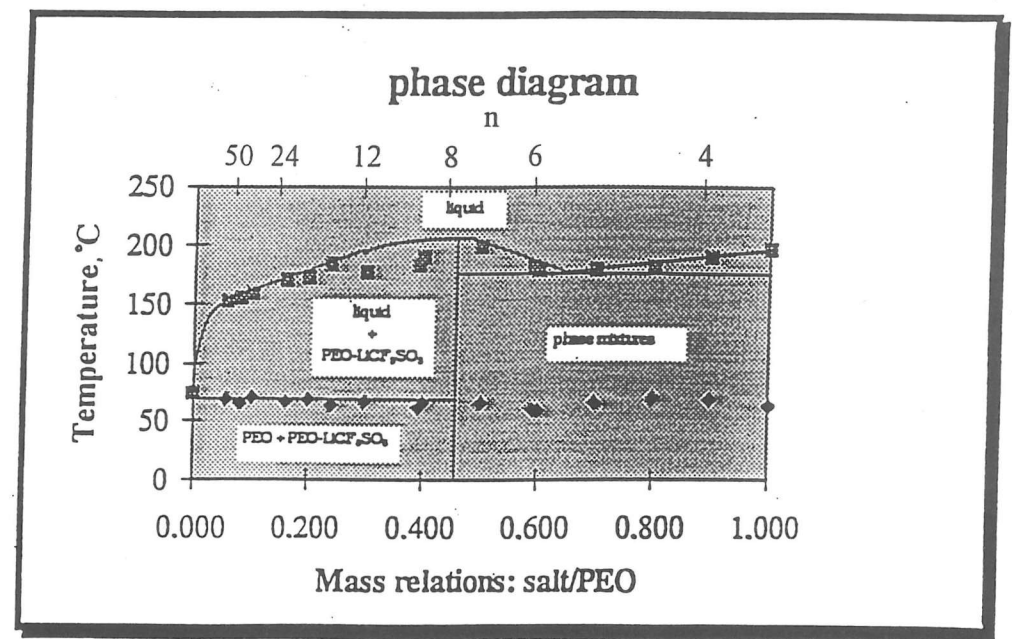

Fig. 1: Phase diagram of the PEO-LiCF3SO3 system built up from DSC and optical microscopy measurements [7].

The conductivity (σ) results obtained by these authors are in good agreement with the phase diagram drawn in their work, for this system. They have observed two regions of linear dependence of the log σ with the inverse of the temperature, separated by a knee. These discontinuities, where the conductivity had a sharp variation, are correlated with the phase diagram, as they appeared at the melting temperature of the eutectic, where the amount of amorphous phase increased. Ferloni & al. [9] have also examined the phase diagram of the PEO-LiClO$_4$ system and correlated it with the observed conductivity behaviour. They have found inflexions on the conductivity curves at transition temperatures predicted by the phase diagram, associated with the melting of the eutectic or with the melting of the complex formed in this system. When only the amorphous phase was present, a different trend was observed, showing the conductivity-temperature dependence, the expected curvature in all of the studied temperature regions.

The activation energies for the conductivity, are also correlated with the present phases. Below the melting of the eutectic, where two crystalline phases are present, the activation energies found are high. As the amount of the amorphous phase increases at transition temperatures, the activation energies diminish, as the ionic conduction becomes easier.

The phase diagrams for the lithium-based PEO electrolytes described here reveal that they are not single-phase homogeneous materials. However, if the conditions of concentration and temperature used are appropriate, a totally amorphous electrolyte can be obtained. The importance of the lithium-based PEO electrolytes for the electrochemical power source's field is due mainly to the high energy densities that can be achieved with this light weigh metal. The lithium's tendency to form thin passivating films that are ionically conducting and the great amount of Li$^+$-

insertion cathodes operating reversibly at high voltage (versus Li/Li$^+$ electrode) are other reasons for the continues use of these electrolytes.

4. Electrolyte preparation

The usual method for preparing polymer electrolytes is based in the physical mixing of the polymer and the salt, aided by a solvent. Essentially, the desired amounts of the polyether PEO, PPO or the polyimine PEI, and of the salt, sometimes hydrated, are weighed and dissolved in a suitable common solvent, or in some cases, in separate solvents. After complete dissolution by stirring the mixture for an adequate period, typically 48 hours, and in a dry environment, like a dry box containing argon or nitrogen, the solution is cast within a glass ring placed on a Teflon or silicone paper base. The solvent is then allowed to evaporate for several days, typically in a desiccator, over 5Å molecular sieve. To ensure that all traces of moisture and solvent are removed, heating and/or vacuum are applied to the obtained films, usually 100μm thick. Prior to use, the storage of the films is made under moisture-free conditions, in sealed containers within a dry box.

5. Factors governing ion mobility

To get polymer electrolytes exhibiting good ionic conductivity the phase polymer must have a low Tg, must be amorphous or in a very disordered state. The polymer chains segmental motions must be of high amplitude and high frequency, since they control the ionic motion related to conductivity.

In order to improve conductivity performances at room temperature, the occurrence of crystalline phases can be avoided by using crosslinked or

branched polymers [4,7,10]. The use of these polymers increases the conductivity by 1 or 2 orders of magnitude.

In the case of PEO, for example, improvements of conductivity are achieved by the formation of crosslinked network [11] with branched poly(methoxy-ethylene) glycol methacrylate, PMEGMA; its structure is as follows:

$$
\begin{array}{c}
CH_3 \\
| \\
(-CH_2-C-)_x \\
| \\
COO(CH_2CH_2O)_nCH_3 \qquad n=1,2,3
\end{array}
$$
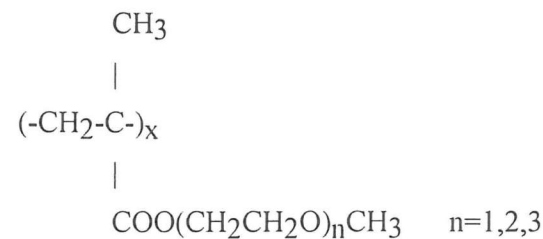
6. Conductivity measurements

Conductivity measurements are performed by A.C. impedance spectroscopy [12]. The temperature dependence of conductivity (Figure 2), from [5] does not follow a classical Arrhenius law, but exhibits a free volume behaviour, as in melting salts. It can be shown that temperature dependence of σ is described in the Vogel - Tamman - Fulcher (VTF) law [13] given by

$$\sigma = A \, T^{-1/2} \exp \left[-E_a / K(T-T_0) \right]$$

where A is proportional to the number of effective charge carriers, K is the Boltzmann constant, and T_0 is the ideal glass transition temperature.

This behaviour gives account of the chain motion's contribution to the ion's displacements.
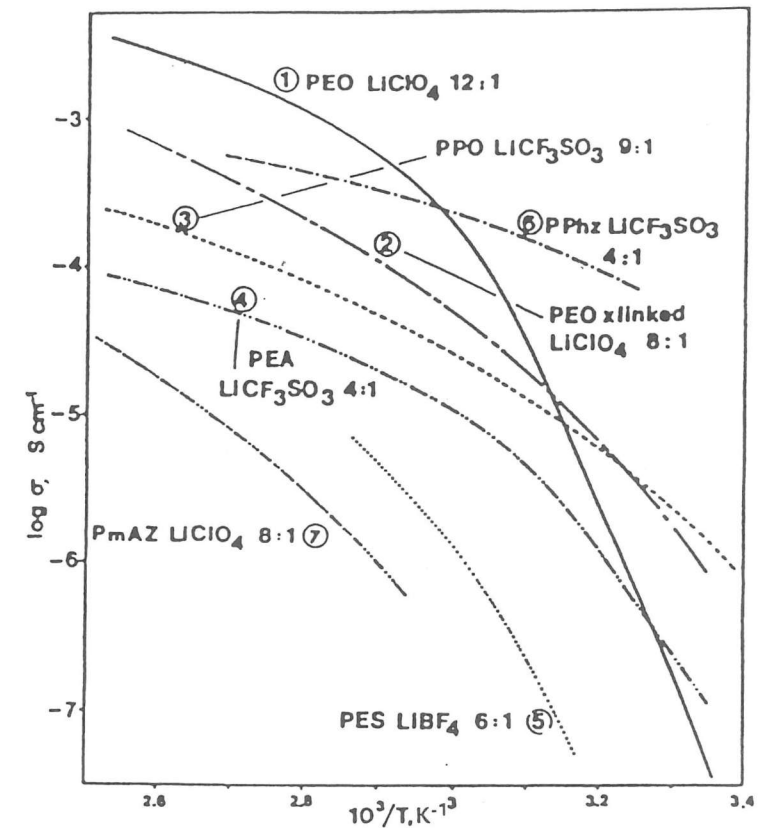
(1) PEO; (2) crosslinked PEO; (3) poly(propylene oxide); (4) poly(ethylene adipate); (5) poly(ethylene succinate); (6) polyphosphazene; (7) poly(N-methylaziridine).

Fig. 2: Plots of the conductivity of various polymer-cell adducts [5].

Usually, an optimum concentration exists between the number of solvating monomer units and ionic salt adducts [14-16], as it has been already underlined on Section 3. Since ion mobility is greatest in the

amorphous phase, maximum conductivity may be expected for eutectic compositions.

Figure 3 [17] shows the temperature dependence of the conductivity for interpenetrating polymer networks (IPN's) of $LiClO_4$-$(PEO)_n$. The conductivity did not increase directly with increasing amounts of added salt, because at very high salt concentrations neutral ion pairs were probably formed. Instead, it was shown that there seemed to be an optimum value for the conductivity which appeared at quite a low salt concentration where lithium perchlorate probably existed as mobile, free ions. The maximum conductivity at 25°C, 6.1×10^{-5} Scm^{-1}, was obtained with $LiClO_4$-$(PEO)_{88}$.
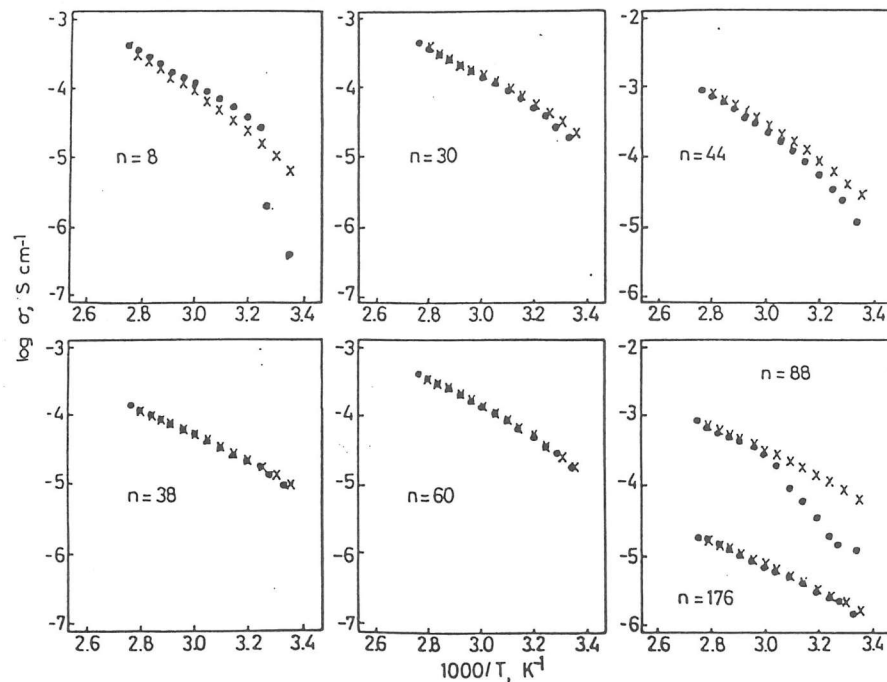

Fig. 3: Temperature dependence of the conductivity for IPN films of $(LiClO_4):(PEO)_n$ (●●●) heating; (xxx) cooling [17].

7. Redox stability domain

Before using these materials as solid electrolytes in batteries, it is necessary to have any information about their redox stability. The electrolyte has to be inert towards both electrode materials corresponding to widely different chemical activities, for example, in the system Li/PEO, $LiClO_4$/TiS_2, Li as negative electrode and TiS_2 as positive. This redox stability domain can be determined with the classical three electrodes cyclic voltammetry proposed by Sequeira & al. [18-20].

Figures 4 and 5 [18, 20] show typical results for the redox stability range of $(PEO)_{4.5}LiI$ and $(PEO)_9LiCF_3SO_3$, respectively.

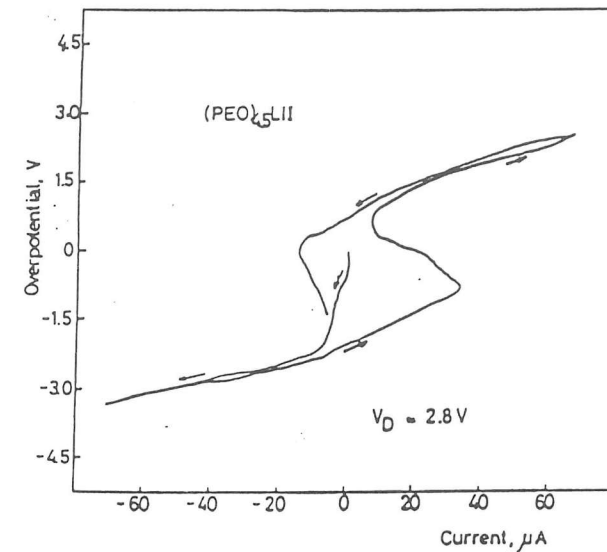**Fig. 4:** Cyclic voltammogram for $(PEO)_{4.5}$ LiI at 80°C with a scanning rate of 100 mV s^{-1} [20]. The arrows drawn indicate the direction of the potential sweep.

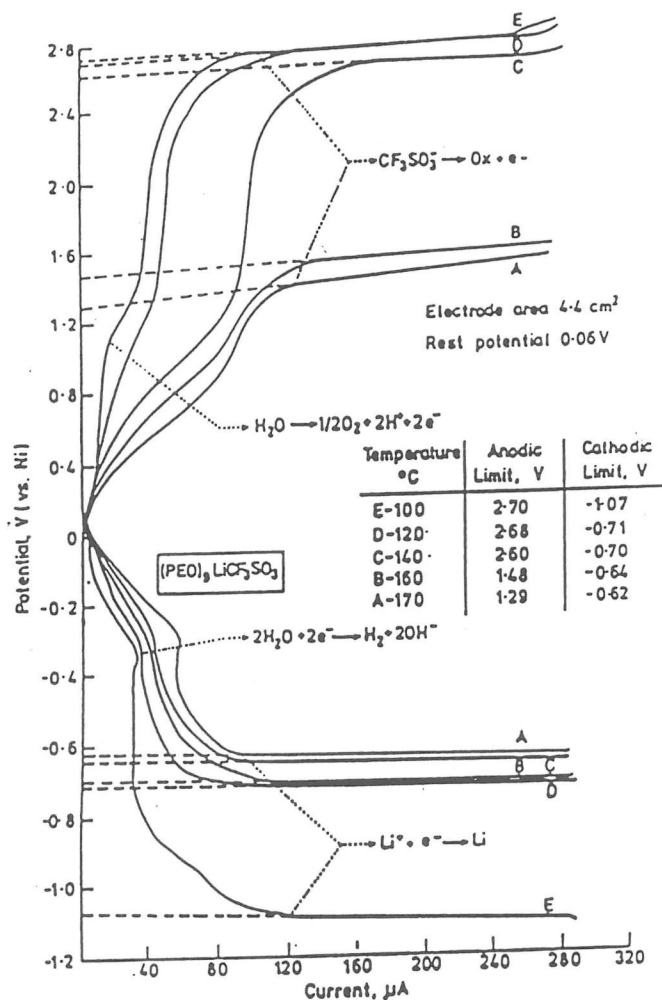**Fig. 5:** Anodic and cathodic polarization curves for (PEO)$_9$LiCF$_3$SO$_3$ at platinum electrodes [18]. The arrows drawn, roughly show the potential ranges where the electrochemical reactions indicated occur.

Using thermodynamically stable anions (I$^-$, Br$^-$), the stability of the polymer to reduction was investigated. For (PEO)$_{4.5}$LiI (Fig. 4), no peak

is visible before the Li$^+$→Li reduction at -2.2V. The absence of any parasitic reaction is corroborated by the excellent (>80%) recovery of the plated metal. Similar results have been obtained with NaI and LiBr. The polyether stability, expected from the strong C-O bonds (86kcal/mol) is thus at least similar to that of micromolecular ether solvents (dimethoxyethane, tetrahydrofuran...).

Some other anions, however, undergo a reductive cleavage visible before the metal deposition. Thiocyanate is reduced, according to:

$$SCN^- + 2e \rightarrow S^{2-} + CN^- \quad at -1.8V$$
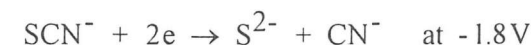
The cyclic voltammogram of Figure 4 shows clearly the anodic limit due to I$^-$ oxidation at +0.6V. The voltage stability window of LiI in PEO is thus 2.8V, in close agreement with the thermodynamic value (2.81V). The activity of the dissolved salt in the polymer is thus close to unity.

In Figure 5, the discharge electrode processes for the (PEO)$_9$LiCF$_3$SO$_3$ complex are shown. In the cathodic domain, before the reduction of the Li$^+$ ion, there is the formation of hydrogen due to the presence of water traces in the electrolyte. Since the trifluoromethane sulfonate anion is much more effective in resisting oxidation, an anodic wall is only visible at +2.7V, for temperatures close to 100°C. At this potential an irreversible reaction occurs, probably from the reaction of CF$_3$SO$_3^-$ on the polymer. With such stable (metastable) anion, a redox stability domain of 3.8V at 100°C versus Li/Li$^+$, is obtained.

Present results are similar to those reported by Armand for the same systems [21]. Stability windows close to 4.0V are sufficient for the projected use of these electrolytes in solid state batteries using intercalation compounds (Li$_x$TiS$_2$<2.6V versus Li/Li$^+$, with x being the molar ratio of Li to TiS$_2$; V$_2$O$_5$<3.2V versus Li/Li$^+$).

7. Transference number

Usually, solid electrolytes (glasses, crystallised ionic conductors) have unipolar conduction. In polymer electrolytes both ions move. Anion transference numbers, determined by different techniques are in the range of 0.2 to 0.8 [12, 22, 23]. The most frequently used techniques are the Tubandt's method, d.c. electrolysis steady state current, potentiometry methods, a.c. impedance spectroscopy, and NMR [4, 12, 23, 24].

Table III, from [12], summarises ac impedance related parameters for $(PEO)_n NiCl_2$ at different temperatures. R_b, the resistance of the electrolyte estimated from ac impedance data, and $Z_d(0)$, the diffusion impedance at reasonable low frequencies, are quantities used to estimate t_c, the transference number of the cation Ni^{2+}. Values of t_c, ranged from 0.02 to 0.44 indicating that the polymer is an anionic conductor.

In the case of batteries using liquid electrolytes, the mixed ion's transport (anion and cation) is a major cause of electrode degradation. The situation is different with polymer electrolytes, since the high viscosity of the backbone avoids ionic convection motions.

Table III

Measured and calculated quantities for different temperatures and compositions of the cell $Ni/(PEO)_n NiCl_2/Ni$ [12].

n	$T(^oC)$	$R_b(\Omega\ cm^2)$	$Z_d(0)(\Omega\ cm^2)$	t_c
6	72.0	668	20573	0.06
12	71.0	695	19050	0.07
19	58.5	1260	37862	0.06
24	60.0	12184	123939	0.16

Furthermore in polymer electrolytes, the flow current density is limited by anionic transference due to the anions backscattering induced by the gradient of chemical potential. Consequently, flow current density is limited to low values of the order of $0.1\ mA\ cm^{-2}$ [25].

8. Conclusions

Organic polymer electrolytes have generally good conductivity in the amorphous state in a wide redox stability area. The good performances of polymer electrolytes like $PEO-LiClO_4$ are already demonstrated in the realisation of lithium polymer electrolytes batteries [26-28], and in electrochromic displays [29]. Unfortunately, most of the linear polymers with high molecular weight are crystalline at room temperature. This major inconvenient can be avoided by using comb branched polymers with short chain length or by turning, for example, towards the organic-inorganic polymers: ORMOSILS (organically modified silicates), introduced and developed by H. Schmidt [30].

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