

Lithium and proton conducting gel-type membranes

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Abstract

We review the characteristics and the properties of various types of gel-type, ionically conducting membranes. We have mainly investigated two classes of membranes, one characterized by lithium ion transport and the other characterized by proton conductivity. We show that the former membranes are suitable to be used as separators in advanced lithium ion plastic batteries and that the latter show good promises to be considered as alternative, new separators in polymer electrolyte fuel cells.

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1. Introduction

In the last years there has been a progressively increasing interest in ionically conducting membranes having properties such as to be able to replace the conventional liquid solution used as electrolyte separators in electrochemical devices. Indeed, the use of ionically conducting membranes may favour substantial improvements for popular devices, e.g. lithium batteries and fuel cells, by allowing the development of light and diversified cell geometry and at the same time, improving safety and reliability, as well as decreasing cost. Large R&D activities are addressed to this new class of polymer electrolytes and in our laboratory we have concentrated our studies in gel-type membranes formed by the immobilization of selected liquid solutions in polymer matrices and/or by the swelling of large quantity of liquids. These membranes may be effectively used as polymer electrolytes since, despite the liquid component, they retain a good mechanical integrity. In this paper we review the properties and characteristics of some selected examples of these membranes.

2. Experimental

The basic procedure for the preparation of gel-type ionically conducting membranes involves the immobilization and/or swelling of selected liquid solutions in a polymer ma-

trix. The process is based on a phase inversion process involving a two-step procedure. A precursor membrane is first prepared by dissolving a poly(vinylidene fluoride) PVdF matrix in an ethylene carbonate–propylene carbonate, EC–PC 1:1 (w/w) mixture and then promoting gelification by slowly cooling to room temperature. This first step, that leads to a free standing membrane, is common for both types of membranes, with the only differences that in the case of the membrane for proton conductivity also a certain amount of fumed silica was dispersed in the starting solution. The second steps involved the activation of the precursor membrane by soaking it in proper swelling liquid solution. The latter may be a solution of 1 M LiPF₆ in EC–PC (1:1) in the case of the lithium membranes and a 2 M H₃PO₄ aqueous solution in the case of the proton membranes. During this step, the lithium salt diffuses in the membrane (lithium systems) and part of the EC–PC organic solvent mixture is exchanged by the acid aqueous solution (proton systems). In the latter, the phase inversion is favored by the presence of the ceramic filler which favours the swelling of the solution, as well its retention within the polymer matrix. Details of the synthesis of the lithium [1] and proton [2] membrane are reported in previous works. For sake of simplicity, the lithium and the proton membrane will be simply coded as LiPF₆–EC–PC–PVdF and H₃PO₄–EC–PC–SiO₂–PVdF, respectively.

3. Results and discussion

As already pointed out, the gel-type membranes can be profitably used as polymer electrolytes in electrochemical

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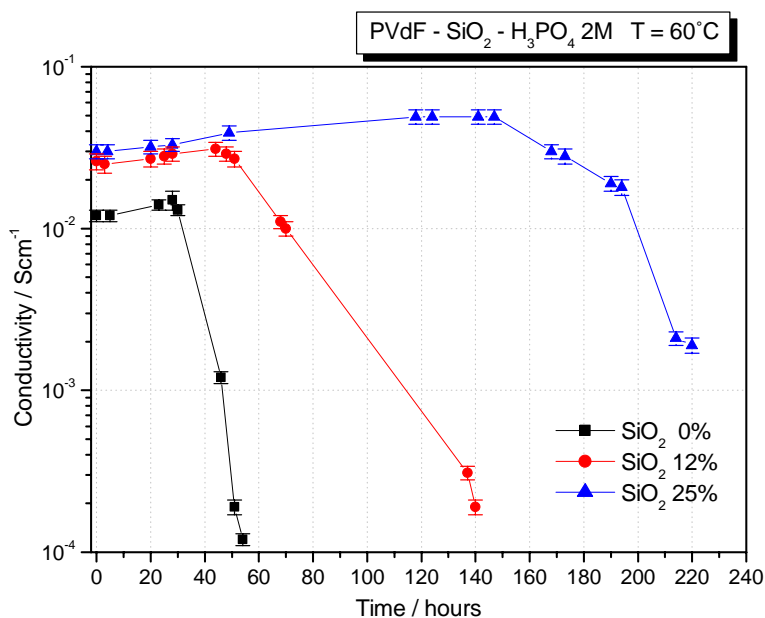


Fig. 1. Time evolution of the conductivity of $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ at 60°C of membranes with different SiO_2 loading.

devices since, despite the liquid component, they retain a good mechanical integrity. Furthermore, the conductivity of these membrane is quite high and stable. For instance, the conductivity of the lithium $\text{LiPF}_6\text{-EC-PC-PVdF}$ gel membrane varies from $2 \times 10^{-3} \text{ S cm}^{-1}$ to $5 \times 10^{-4} \text{ S cm}^{-1}$ passing from 20 to -20°C [1]. The conductivity of the $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ depends upon the content of the ceramic filler, reaching a value of a $3.5 \times 10^{-2} \text{ S cm}^{-1}$ for a SiO_2 content of 25 wt.% w/o. This is clearly demonstrated by Fig. 1 which compares the time evolution at 60°C of the conductivity of membranes at different SiO_2 loading.

3.1. Lithium conducting membranes

The profitable applications of the membranes in practical devices has been demonstrated in our laboratory. For instance, the use of the $\text{LiPF}_6\text{-EC-PC-PVdF}$ in lithium batteries has been shown [3,4]. We have shown that this electrolyte can be efficiently used as separator in lithium batteries using a modified LiFePO_4 cathode. Iron phospho-olivines are cathode materials which have attracted considerable interest due to the flatness of the two-phase, charge–discharge process which evolves in the 3.5 V range [5]. However, common iron phosphate electrodes suffer from loss of capacity with increasing current density, associated to the diffusion-limited transfer of lithium across the two-phase interface. We have shown that an effective way to by-pass the aforementioned kinetic is to enhance the iron phosphate inter-particle electronic contact by suitable metal doping [6].

Indeed, optimized metal-doped LiFePO_4 cathodes behave quite well in lithium batteries based on the $\text{LiPF}_6\text{-EC-PC-PVdF}$ gel-polymer electrolyte, demonstrated by the typical

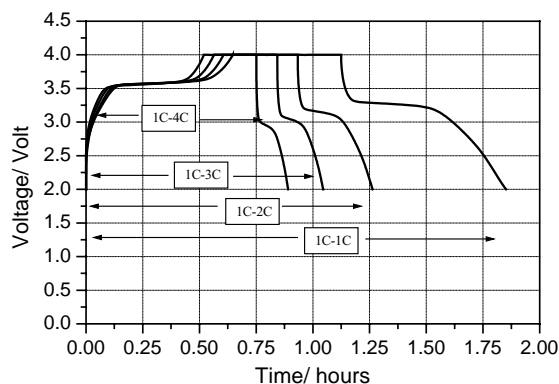


Fig. 2. Cycling response of $\text{Li/LiPF}_6\text{-EC-PC-PVdF/Ag-added LiFePO}_4$ battery at various discharge rates and at room temperature. The cycling rate is referred to the LiFePO_4 cathode.

example reported in Fig. 2. The battery, which operates on the basis of the following charge–discharge process:



can be cycled several times with very limited capacity fading and at very high rates.

4. Proton conducting membranes

The conductivity level of the $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ is sufficiently high to make it of interest for application in a fuel cell. The operation of the membrane in this type of device has been exemplified by running a sweep voltammetry on three platinum electrode cell using the $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ membrane as the electrolyte.

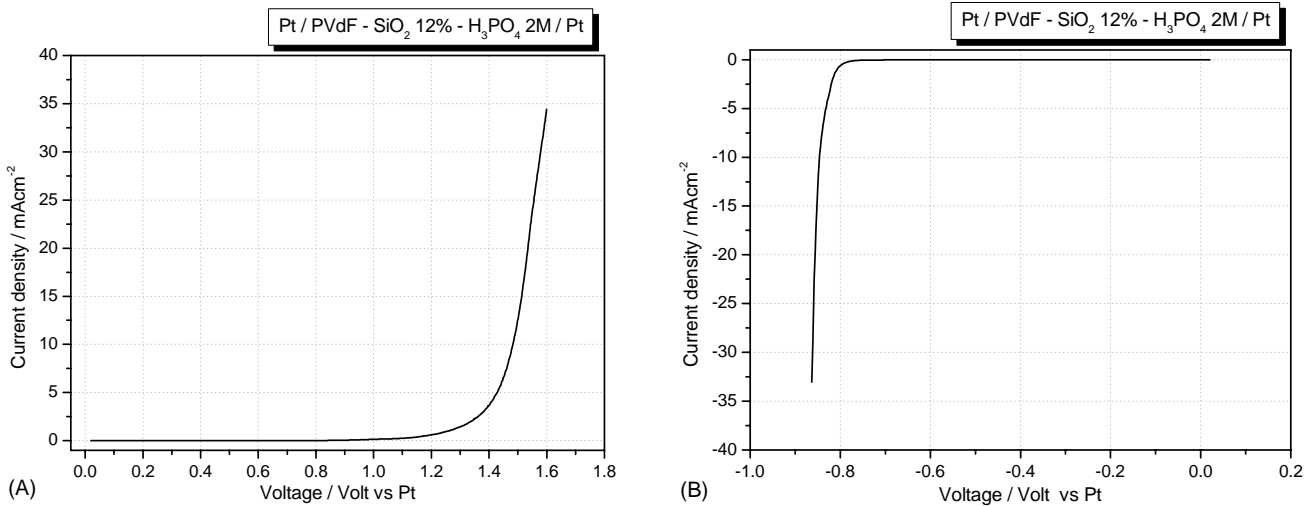


Fig. 3. Current–voltage curves of a Pt electrode in a cell using the H₃PO₄–EC–PC–SiO₂–PVdF membrane as the electrolyte. The anodic scan (A) reflects to oxygen evolution and the cathodic scan (B) reflects hydrogen evolution. Room temperature. Pt reference and Pt counter.

Fig. 3 shows the results in terms of anodic and cathodic current–voltage curves. The onset of the current are indeed representative of the oxygen and hydrogen evolution processes in the anodic and cathodic ranges, respectively.

In view of applications in fuel cells other properties in addition to proton conductivity may be of importance. One of these is the degree of methanol crossover. Fig. 4 combines the trend of the conductivity and of the methanol crossover for the H₃PO₄–EC–PC–SiO₂–PVdF membrane in function of the content of the loading of the ceramic filler. To be noticed that the crossover is quite low up to a critical value of SiO₂ content, i.e. about 25 w/o. Fig. 5 shows the SEM photograph of a membrane having the high SiO₂ loading. The image clearly reveals the presence of large ceramic

clusters arranged in coarse networks. Therefore, one can assume that at high loading, i.e. higher than 25 w/o, methanol can easily diffuse through the porous channels, while at low loading the crossover is hindered by the silica particles which are still finely subdivided in the polymer matrix [2].

These results suggest that for practical applications, membranes having a modest loading in SiO₂, e.g. around 15 w/o are to be preferred. Fig. 6 reports the characteristic curve of a laboratory type fuel cell based the H₃PO₄–EC–PC–SiO₂–PVdF membrane having a 25 w/o SiO₂ loading. The cell, although still far to be optimized in terms of catalysts loading and of MEA, shows a promising response.

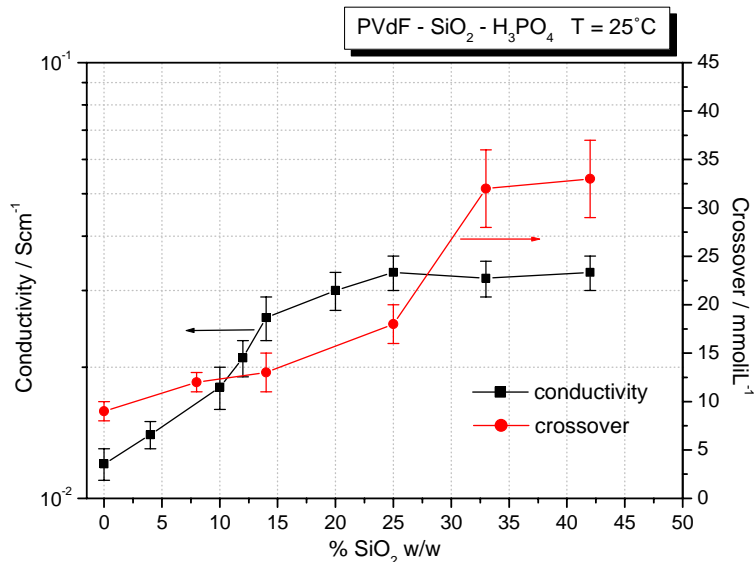


Fig. 4. Conductivity and methanol crossover for a H₃PO₄–EC–PC–SiO₂–PVdF membrane as a function of silica content.

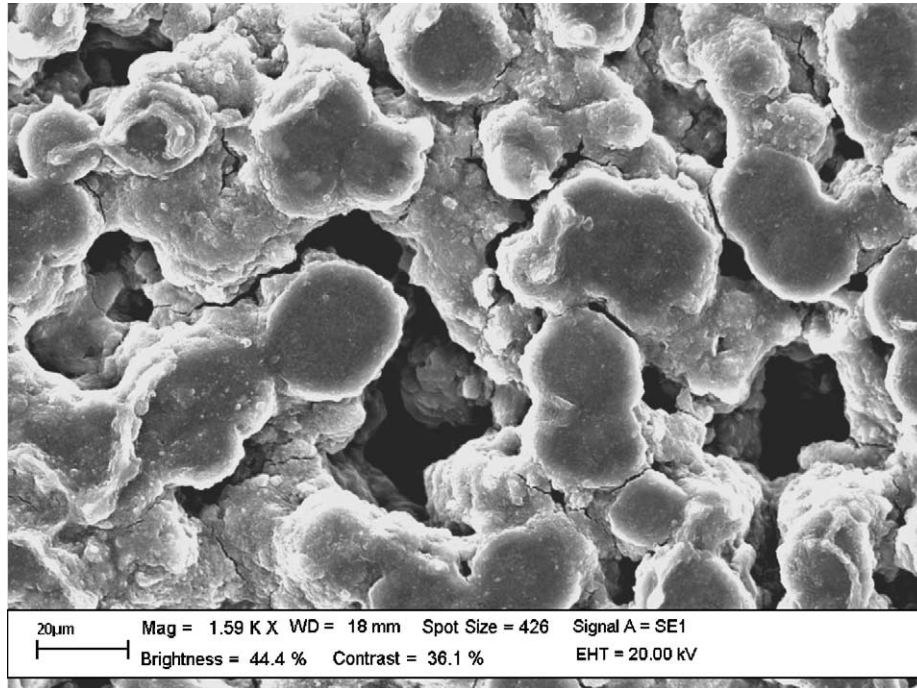


Fig. 5. Scanning electron micrograph of a $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ membrane having a 25 w/o SiO_2 loading (1.59 KX).

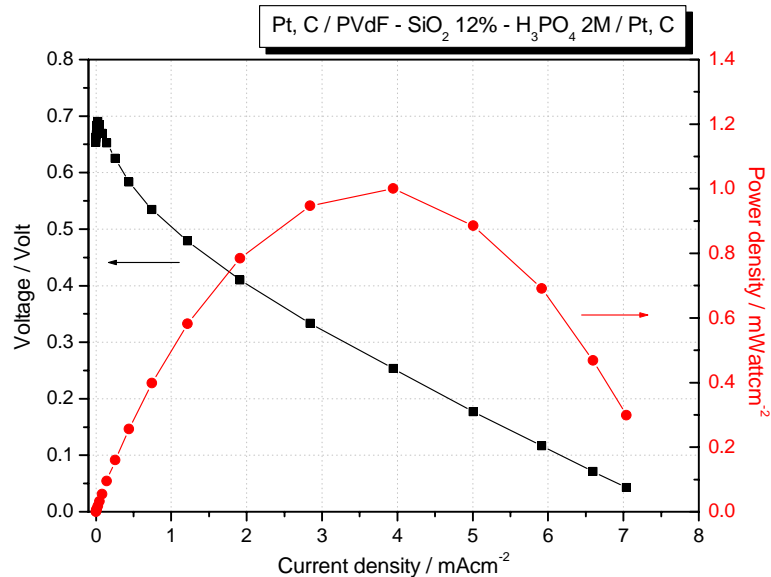


Fig. 6. Electrochemical response of a laboratory prototype fuel cell based on the $\text{H}_3\text{PO}_4\text{-EC-PC-14 w/o SiO}_2\text{-PVdF}$ membrane as the electrolyte. Pt dispersed in carbon E-TEK commercial electrodes. Room temperature.

5. Conclusion

The results here reported show that two classes of electrolytes here discussed can be profitably used for the development of practical devices. Results obtained with laboratory prototypes have demonstrated the feasibility of the $\text{LiPF}_6\text{-EC-PC-PVdF}$ membrane as electrolyte in advance-design, polymer lithium-ion batteries and that of

the $\text{H}_3\text{PO}_4\text{-EC-PC-SiO}_2\text{-PVdF}$ membrane as separator in non-conventional polymer electrolyte fuel cells.

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