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New concepts for the development of lithium and proton conducting membranes

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Abstract

A new approach for the development of lithium and proton conducting electrolyte membrane is here reported and discussed. Basically, the lithium polymer electrolyte is prepared by swelling a PVdF "precursor membrane" with a $LiPF_6$ solution in EC–PC. Similarly, the proton polymer electrolytes are obtained by swelling a ceramic-added composite PVdF-based membrane in a H_3PO_4 aqueous solution. The results, even if in a preliminary stage, confirm that the membrane technology used for lithium can be extended to the proton case. The PVdF-based, acid-swelled membranes show high values of ionic conductivity and good thermal properties and thus, they appear of interest for practical applications, e.g. fuel cells.

Keywords: Lithium conducting membrane; Proton conducting polymer electrolyte

1. Introduction

Consistent progress has been achieved in the development and characterization of ionically conducting membranes. In this respect, particularly relevant are the successes obtained in the area of lithium conducting membranes especially in view of their utilization as electrolyte separators in new-design, advanced polymer batteries [1–5]. Another class of ionic polymers having important practical outputs is that involving proton conducting membranes to be addressed to the development of polymer membrane fuel cells (PMFCs) [6]. Although obviously different by the nature of their mobile species, the two classes of membranes may in principle have some similarities, e.g. in their polymer architecture and/or in their transport characteristics. However, the approaches so far used in the development of the two types of membranes are quite different. Practical lithium systems have been mainly based either on solvent free membranes, e.g. blends of a lithium salt and poly(ethylene oxide) (PEO) [7], or on gel membranes, e.g. lithium salt solutions trapped in a polymer, e.g. poly(vinylidenedifluoride) (PVdF) matrix [8]. In both these membranes the lithium transport is an inherent feature of the system and thus, no external solvent supply is required to assure proper levels of conductivity. On the contrary, the most popular proton membranes are based on perfluorosulfonic acid polymers, e.g. Nafion®, where the transport mechanism requires continuous water assistance [9].

It has appeared to us of interest to explore whether these two separate approaches of membrane preparation could somewhat merge. Accordingly, in this work we report the synthesis and the characterization of PVdF-based gel membranes which, depending upon their plasticizing solution can be alternatively used as lithium and as proton polymer electrolytes.

2. Experimental

The lithium and proton conducting PVdF-based gels have been prepared by a phase inversion process involving a two-step procedure. A precursor membrane was first prepared by dissolving the PVdF polymer (Solef 6020 for lithium systems and Kynar 1000LD Atofina for proton systems) in an ethylene carbonate–

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propylene carbonate (EC–PC) 1:1 w/w mixture (Merck, Battery grade). The composition ratio was 80 w/o EC–PC and 20 w/o PVdF. The solution was heated at 120–130 °C for 1.5 h and then gelled 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 (Aldrich, 99.8%, 380 m^2 g^{-1} specific surface area) was dispersed in the starting solution. The second preparation step involved the activation of the precursor membrane by soaking it in proper swelling liquid solution. The latter was a solution of 1 M $LiPF_6$ in EC–PC (1:1 w/w) (Merck Battery Grade) in the case of the lithium membranes and a 2 M H_3PO_4 aqueous solution in the case of the proton membranes. During this step, the lithium salt diffuses in the membrane (lithium systems) or part of the EC–PC organic solvent mixture is exchanged by the acid aqueous solution (proton systems).

The thermal properties of the membranes were investigated by thermal gravimetric analyses (TGA) (Perkin–Elmer), carried out under air. The morphology was evaluated by Scanning Electron Microscope (SEM) (LEO 1450VP).

The ionic conductivity was determined by impedance spectroscopy (Solartron 1255B) run on cells formed by placing the given membrane sample between two metal electrodes. The latter were stainless steel for lithium membranes and platinum for proton membranes. A spacer was inserted in the cell in order to fix the sample thickness.

Methanol crossover was preliminary measured by detecting, with the gas-chromatography technique, the CH_3OH moles that in 1 h pass across a PVdF membrane separating a water solution from a methanol 1 M solution.

The lithium cell prototypes were assembled by contacting in sequence a lithium metal disk anode, the PVdF activated membrane and a composite cathode. The latter was a film formed by casting a 1-methyl-2-pyrrolidinone slurry of $LiFePO_4$ (83% active material, typically 3–4 mg cm^{-2}), carbon 12% (Super P, conducting additive) and PVdF (5% Solef 6020, binder). Lithium iron phosphate ($LiFePO_4$) doped with 1% Ag was prepared with a special synthesis procedure in order to obtain it in an optimized morphology. This procedure was described in details in a previous work [10].

The cells were tested using a Maccor battery cycler.

3. Results and discussion

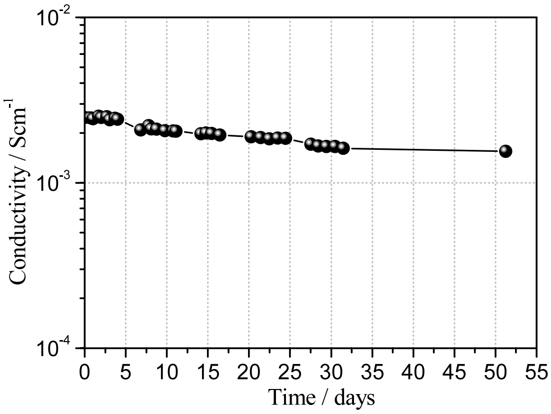

Fig. 1. Time evolution of the conductivity of the $LiPF_6$–EC–PC–PVdF membrane at room temperature.

Lithium conducting membranes were obtained by soaking a PVdF precursor membrane with a 1 M $LiPF_6$ solution in EC–PC. For simplicity sake, these membranes will be hereafter coded as $LiPF_6$–EC–PC–PVdF.

Conductivity values in the range of 10^{-2}–10^{-3} S cm^{-1} have been measured for this membrane (see Table 1). Furthermore, this high conductivity remains stable for several days, see Fig. 1, this demonstrating that the good retention of the liquid solution within the membrane bulk.

Table 1
Ionic conductivity of the $LiPF_6$–EC–PC–PVdF membrane at various temperatures

Temperature (°C)	Conductivity (S cm^{-1})
−22	3.6×10^{-4}
0	1.2×10^{-3}
21	2.0×10^{-3}
60	6.1×10^{-3}

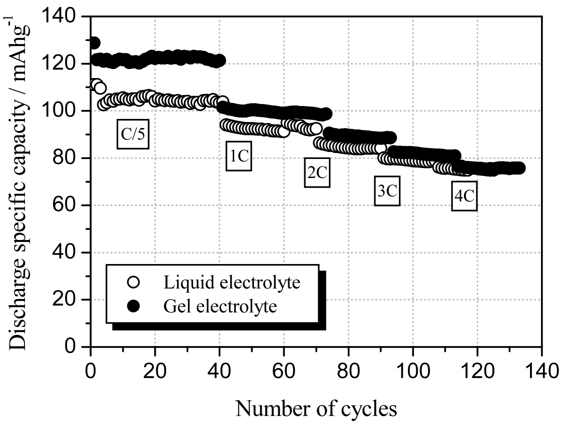

Fig. 2. Cycling response at various discharge rates and at room temperature of Li/$LiFePO_4$ 1% Ag cells using a $LiPF_6$–EC–PC–PVdF membrane electrolyte and a parent $LiPF_6$–EC–PC liquid electrolyte. The cycling capacity is referred to the $LiFePO_4$ 1% Ag cathode. Charge rate: first 40 cycles: 0.2 C, remaining cycles: 1 C.