

# Poly(vinylidene fluoride-hexafluoropropylene)-based membranes for lithium batteries

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Received 16 July 2007; received in revised form 4 October 2007; accepted 5 November 2007

Available online 12 November 2007

## Abstract

Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) copolymer membranes were prepared by a phase inversion technique with poly(ethylene glycol) as an additive and tetrahydrofuran or acetone or dimethylformamide as solvent. The morphology, ionic conductivity and uptake of electrolyte solution by the polymer membranes were studied. The amount of intake of electrolyte solution by the polymer membranes increases with the increase of PEG content. The morphology and ionic conductivity of the polymer membranes (PM) are correlated with the physical properties of the solvents used in the phase inversion process. The cycling behavior of the membrane was examined with Li/LiCoO<sub>2</sub> cells. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Polymer electrolyte membranes; Phase inversion method; Lithium batteries; Ionic conductivity; Charge–discharge studies

## 1. Introduction

A booming microelectronics industry and in prospect the evolution of the electric/hybrid car market that depend on power packs with higher energy and power densities place an immediate demand for new and improved energy sources [1–4]. Rechargeable lithium batteries represent an excellent choice for electrochemical power sources characterized by high energy densities, good cyclability and reliability [5,6]. The realization of such power is beset with several problems, especially concerning electrolytes. Lithium polymer batteries are safe and lighter than their liquid counter parts. Dry solid polymer electrolytes comprising a polymer host and lithium salt offer appreciable ionic conductivity only above 80 °C [7,8]. The poor ionic conductivity of such electrolytes at ambient temperatures limits their use in common electrochemical devices. The popular gel polymer electrolytes have high ionic conductivity, but the plasticizers employed in the electrolyte adversely reduce the mechanical strength of the polymer membrane and diminish its compatibility with lithium metal anode,

leading to safety hazards [9]. On the other hand, the compatibility, mechanical strength and the safety characteristics of composite polymer electrolytes formed by enhanced incorporation of nanofillers like ZrO<sub>2</sub>, TiO<sub>2</sub>, AlO[OH]<sub>*n*</sub>, etc., make them attractive. However, their low ionic conductivity at ambient temperature excludes their immediate practical application [10–13].

Gozdz et al. [14] launched a reliable rechargeable lithium-ion battery in which, an un-plasticized polymer membrane was prepared by an activation/extraction process. The polymer membranes prepared using the activation/extraction process retains their mechanical strength. Moreover, the membrane requires critical moisture control only at the time cell assembly. Recently, Bellcore Technology developed microporous PVdF-HFP membranes in which dibutyl phthalate was used as an additive. However, complete removal of dibutyl phthalate was not successful, which resulted in minimum porosity and, therefore poor rate capability [15]. Among the polymer hosts examined so far, PEO is the most extensively studied system. However, the commercially available PEO contains about 1 wt.% of calcium compounds originating from the neutralization of the catalyst used for its synthesis. Furthermore, CaO particles used to modify the fluidity of the polymer remain in the PEO (>2%), may react with lithium metal anode [16].

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To date, the most impressive results have been obtained with a class of copolymers based on poly(vinylidene fluoride-hexafluoropropylene). The amorphous HFP phase aids ionic conduction while the crystalline PVdF phase acts as a mechanical support [17]. The liquid electrolyte component is present almost exclusively in the amorphous domains of the polymer matrix. One of the authors has made a series of studies on PVdF-HFP membranes prepared by the phase inversion technique with different non-solvents as porogenic agents [18,19]. However, the morphology and cycling performance of the membranes were found to be poor.

Commercial separators are uniaxially drawn poly ethylene (PE) or poly propylene (PP), biaxially drawn PE, or multi-axially drawn PE/PP/PE. The polymers are hydrophobic and do not wet in conventional lithium battery electrolytes. Over membranes, based on PVdF-HFP, taken in battery electrolytes in their matrix, form gels and contribute to  $\text{Li}^+$ -ion conductivity. This way their conductivities are an order higher than those of conventional membranes. It must, however, be pointed out that the thermal degradation temperature of PVdF-HFP membranes are about  $20^\circ\text{C}$  lower than those of conventional membranes [20]. In the present study, an attempt has been made to prepare PVdF-HFP membranes by the phase inversion method with three different solvents, acetone, tetrahydrofuran (THF), dimethyl formamide (DMF) and poly(ethylene glycol) (PEG) as an additive. Also, the morphology of the membrane is correlated with the physical properties of the solvents employed in its preparation.

## 2. Experimental

Polymer membranes were prepared by the phase inversion technique as reported earlier [13,14]. The PVdF-HFP (PVdF:HFP = 88:12) copolymer (Elf Atochem, Japan) was dissolved in a mixture of a volatile solvent acetone or THF or DMF and PEG ( $M_w = 6000$ ) for different weight ratios of PVdF-HFP and PEG. This was used for casting the polymer membranes. The resulting solutions were cast on glass substrates to evaporate the solvents to form films. The casting procedure involved an improvised doctor blade technique in which a glass rod with cellophane tapes rolled at this ends was used [21]. The approximate wedge height provided by this tape was  $150\ \mu\text{m}$ . A mixture of the ingredients in the appropriate consistency was poured over a glass plate and the glass rod was run over it and the solution was allowed to dry by natural evaporation in air. The films prepared were kept under vacuum for 12 h at  $100^\circ\text{C}$  to remove traces of the solvents. The films were then soaked in double-distilled water for 12 h to remove the PEG in the film, and subsequently dried at  $80^\circ\text{C}$  in vacuum for 6 h to remove the traces of water. The approximate thickness of the cast membranes was  $70 \pm 10\ \mu\text{m}$ . The morphological examination of the films was made by a JSM-5410LV scanning electron microscope under vacuum ( $10^{-1}\ \text{Pa}$ ) after sputtering gold on one side of the films. The prepared membranes were immersed in *n*-butanol for 1 h and the weight of the membranes before and after immersion was measured. The porosities of the membranes were

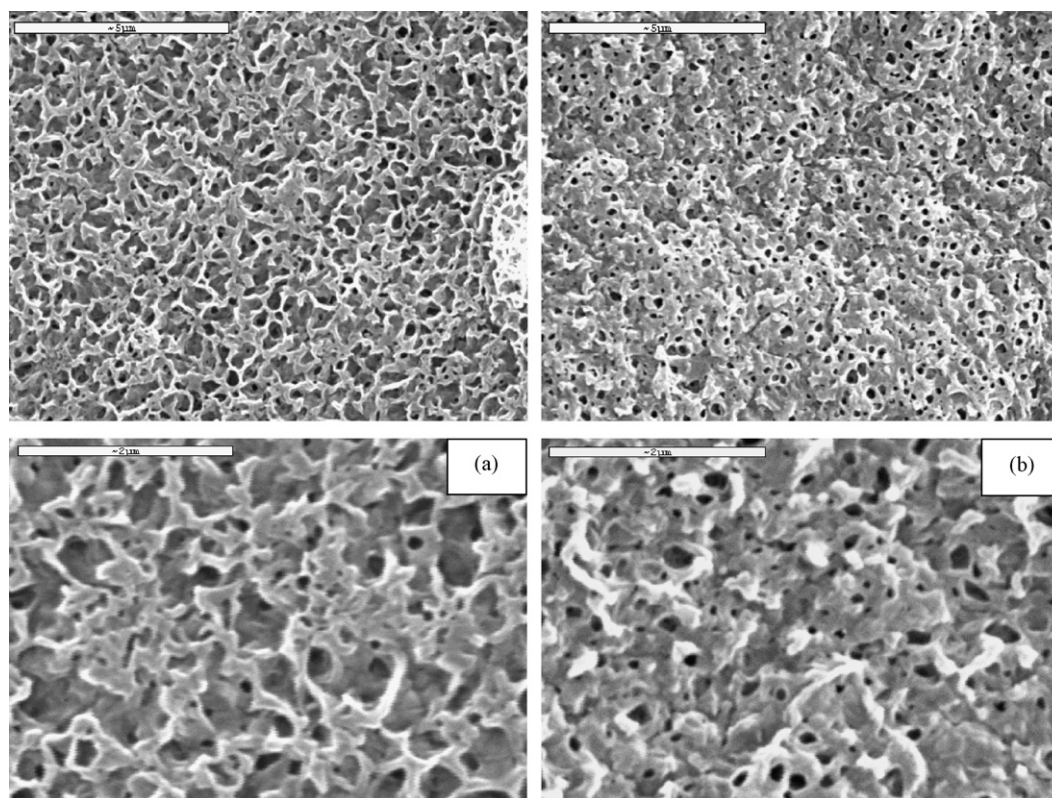


Fig. 1. SEM images of (a) sample S1 and (b) sample S2.

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