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Cycling behavior of poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP) membranes prepared by phase inversion method

A. Manuel Stephan [a,*], N.G. Renganathan [a], S. Gopukumar [a], Dale-Teeters [b]

[a] *Advanced Batteries Division, Central Electrochemical Research Institute, Karaikudi 630 006, India*
[b] *Department of Chemistry, The University of Tulsa, Tulsa, OK 74104, USA*

Abstract

A novel highly porous poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) membrane was prepared by phase inversion method with 1-butanol or methanol as non-solvent. These films where characterized by ionic conductivity, SEM and nitrogen adsorption/desorption analysis. The prepared membranes were employed as separator in $LiAl_{0.01}Co_{0.99}O_2/Li$ cells and their charge–discharge performances are presented. Although, these membranes vary slightly in the physical properties like, morphology and surface area no discernible changes could be seen in charge–discharge studies.
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1. Introduction

Lithium polymer battery has been found as a potential energy source for electric vehicles and portable electronic devices. The use of polymer electrolyte makes the battery highly safe and flexible [1]. Although, the polymer electrolyte was launched by Fenton in 1973 [2], their technological significance was not appreciated until the research undertaken by Armand et al. [3]. To date, several types of polymer hosts have been developed which include poly(ethylene oxide) (PEO) [4,5], poly(acrylonitrile) (PAN) [6], poly(methyl methacrylate) (PMMA) [7], poly(vinyl chloride) (PVC) [8], poly(vinylidene fluoride) (PVdF) [9], etc. Gel polymer electrolytes are usually obtained by incorporating a low molecular weight plasticizer to a polymer host along a lithium salt which is capable of forming a stable gel. However, these types of polymer electrolytes lose their mechanical strength when they are plasticized [10–12]. These films must be hardened by either chemical or physical curing which results in high processing costs. In order to rectify these problems, Gozdz et al. [13] developed a reliable rechargeable lithium ion-batteries in which unplasticized polymer membrane was used.

The membranes prepared using activation/extraction process have several advantages. The mechanical strength of the membranes is restored and it requires the critical moisture control only at the time of loading the samples. Instead of choosing commonly employed gel electrolytes, in the present investigation PVdF-HFP membrane has been chosen for its appealing property which, contains an amorphous domain capable of trapping large amounts of liquid electrolytes and crystalline region that acts as a mechanical support for processing a free-standing films [14].

Recently, micro porous PVdF-HFP membranes were developed by Bellcore in which dibutyl phthalate was used as an additive; the conductivity of the films however, were expectedly low [15]. Enhancement of conductivity was achieved by the addition of fumed silica. But these films unfortunately, suffer from poor rate capability when these membranes are employed as separator in lithium ion cells [16]. So for to the best of our knowledge not much attention has been devoted on the preparation of PVdF-HFP membranes by phase inversion method using different non-solvents.

In the present study, PVdF-HFP membranes were prepared by phase inversion method with 1-butanol or methanol as non-solvent. The cathode material $LiAl_{0.01}Co_{0.99}O_2$, has been prepared using the method as described elsewhere [17–19] and was used as cathode material in the present study.

* Corresponding author. Tel.: +91-4565-227801;
fax: +91-4565-227779.
E-mail address: amanstephan@yahoo.com (A. Manuel Stephan).

1.1. Experimental procedure

Microporous polymer films were obtained by phase inversion technique as described elsewhere [15,16,20]. PVdF-HFP co-polymer (Elf Atochem, Japan) was dissolved in a mixture of acetone (a volatile solvent) and a non-solvent (X) (X: 1-butanol, methanol) such that the amount of the non-solvent was low enough to allow solubilization (solvent:non-solvent ratio of 10:0.5–2.0 volume) and high enough to allow phase separation upon evaporation.

The resulting solution was spread as a film on a glass substrate and the solvent was allowed to evaporate at ambient temperature. Traces, if any, of non-solvents were removed by vacuum drying for 12 h at 110 °C. All experiments were performed in a dry room. Morphological examination of the films was made by a JSM-5410LV scanning microscope under a vacuum condition (10^{-1} Pa) after sputtering gold on one side of the films. The BET (Brunauer–Emmett–Teller) surface area and pore-size distribution were determined by a continuous-flow nitrogen gas adsorption/desorption apparatus (BELSORP 28, Japan). BET method is the most widely used procedure for the determination of surface area of solid materials using equation:

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + C - \frac{1}{W_m C}\left(\frac{P}{P_0}\right)$$

where W is the weight of gas adsorbed at a relative pressure P/P_0 and W_m the weight of absorbate constituting a monolayer of surface coverage. C is BET constant and is related to the energy of the absorption in the 1st adsorbed layer and consequently its value is an indication of the magnitude of the adsorbant/adsorbate interaction.

The ionic conductivity (σ) of the films were measured at nine different temperatures viz., −30, −15, 0, 15, 30, 40, 50, 60 and 70 °C by soaking the membranes in non-aqueous solution of 1 M $LiPF_6$ in ethylene carbonate (EC) and di-methylcarbonate (DMC) of EC:DMC (1:1, v/v) for 12 h. The Arrhenius conductivity plots of the various electrolyte samples were determined by measuring the temperature dependence of the impedance of cells formed by sandwiching the given sample between two stainless steel blocking electrodes. The measurements were performed by EG&G Princeton Instruments frequency analyzer for the range 100 KHz to 10 mHz.

The $LiAl_{0.01}Co_{0.99}O_2$ powders were synthesized by solid-state reaction method [17]. A stoichiometric amount of Li_2CO_3, Co_3O_4 and $Al(OH)_3$ were ground and heated at 400 °C for 12 h and then at 800 °C for 12 h with intermittent grinding. The cathode was prepared by brush-coating a slurry of 85% of $LiAl_{0.01}Co_{0.99}O_2$, 5% of poly(vinylidene fluoride) and 10% acetylene black in 1-methyl-2-pyrrolidinone on an aluminum substrate and they drying in a vacuum oven at 120 °C for 12 h. The prepared polymer membrane was soaked in non-aqueous solution of 1 M $LiPF_6$ in ethylene carbonate and di-methylcarbonate of (1:1, v/v) for 12 h. The lithium foil was used as anode. The $LiAl_{0.01}Co_{0.99}O_2$/polymer membrane/Li cells were assembled in an argon filled glove box. The charge–discharge studies of the $LiAl_{0.01}Co_{0.99}O_2$/Li cells were performed at 50 °C as reported in [17,18] and also by us [19]. Since the samples which were prepared with methanol as non-solvent exhibited low ionic conductivity at room temperature.

2. Results and discussion

SEM pictures (Figs. 1 and 2) reveal the morphology of the polymer membranes prepared with 1-butanol and methanol as non-solvent, respectively. It appears, that the morphological characteristics of the phase-separated membranes can be tailored by the nature of the non-solvent. A flack surface with evenly sized pores is developed when 1-butanol was used as an aliphatic non-solvent. An almost similar surface morphology is also seen for the membrane prepared with methanol as non-solvent. Generally, the ionic conductivity in conventional battery separator is achieved due to the continuous pathways developed by the absorbed liquid electrolyte within the interconnected pores of the membrane. The porous structure is one of the important factors in determining the ionic properties of an electrolyte in a separator. Also of importance, the ionic conductivity of a porous membrane undoubtedly, depends on the conductivity of the electrolyte embedded in the pores of the membrane [20]. Therefore, the conductivity is affected by the membranes porosity, tortuosity of the pores, the conductivity of the liquid electrolyte, the thickness of the membrane and the extent to which the electrolyte wets the pores of the membrane.

Accordingly, the porous structure is one of the important factors in determining the ion transport properties of an electrolyte in a separator. Although the SEM picture depicts the surface morphology of the typical PVdF-HFP membrane the pore diameter and distribution of pores cannot be determined even when the magnification is set as large as 35,000 times. Because, polymeric specimen like PVdF-HFP are prone to damage by electron beams when they are magnified [15]. But the pore-size distribution and surface area can be analyzed using nitrogen adsorption/desorption method. Fig. 3 represents the pore-size distribution of PVdF-HFP membrane prepared by phase inversion method with 1-butanol or methanol as non-solvent. The pore diameter was plotted as a function of differential ratio of pore volume to pore diameter. R_p denotes the pore diameter and V_p denotes the pore volume. It is seen from Fig. 3 that almost all pores of PVdF-HFP membranes are smaller than 50 nm. According to the IUPAC convention all the pores are "meso pores" i.e., ranging from 2 to 50 nm. As mentioned in [16] the average pore diameter and BET surface area of the commercially available Celgard 2400 are 26 nm and 41.79 $m^2 g^{-1}$, respectively. In the present study, the PVdF-HFP membranes prepared with methanol (sample C) and 1-butanol (sample F) as non-solvent exhibited the average pore diameter of
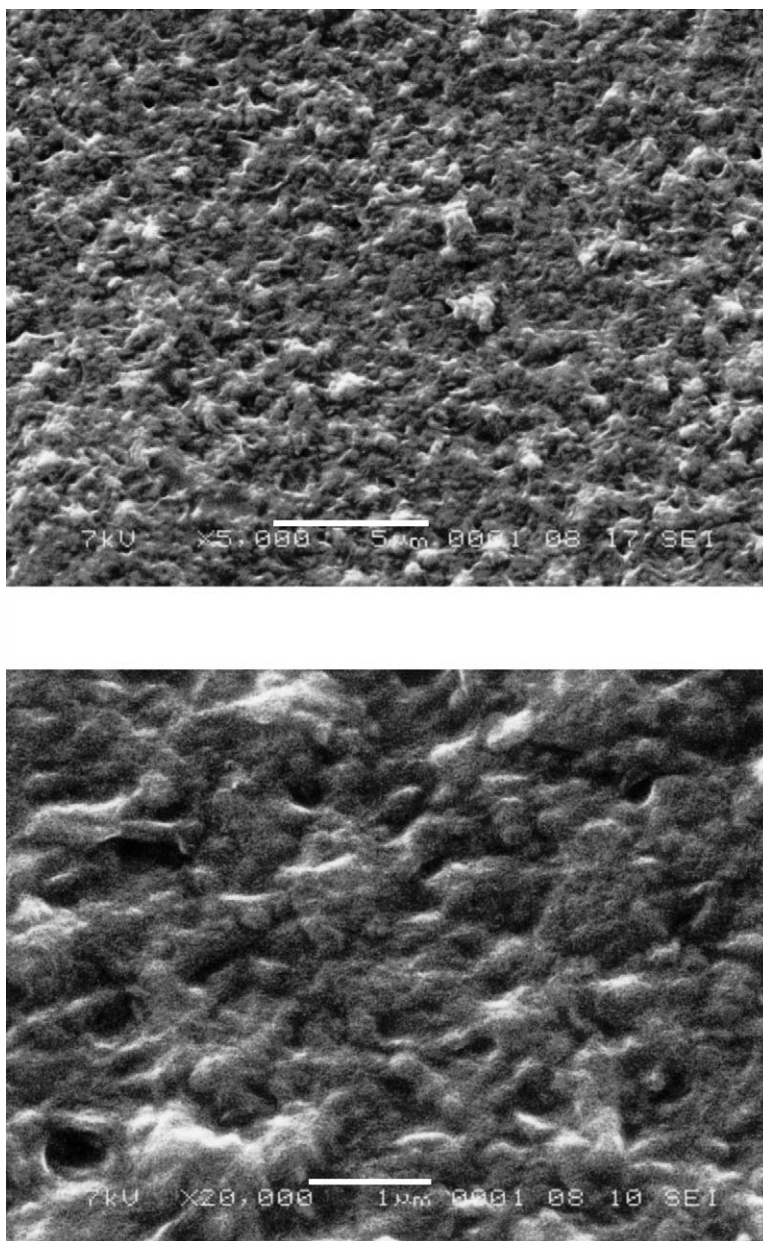
Fig. 1. Scanning electron micrograph of PVdF-HFP membrane prepared with 1-butanol as non-solvent.

32 and 29 nm and surface area of 41.72 and 42.98 m^2 g^{-1}, respectively, which is more or less the same surface area of commercially available Celgard 2400. Figs. 4 and 5 show the Arrhenius behavior of PVdF-HFP membranes soaked in the non-aqueous solution of 1 M of LiPF$_6$ in ethylene carbonate/di-methyl carbonate EC:DMC (1:1, v/v) for 12 h. These membranes were prepared for different volume of non-solvent (1-butanol or methanol) in the polymer solution before casting the membrane. The conductivity of the membranes ranging from 10^{-6} to 10^{-3} S cm^{-1} for the temperatures between -30 and 70 °C when 1-butanol was used as non-solvent. On the other hand, the ionic conductivity of the membrane vary from 10^{-7} to 10^{-4} S cm^{-1} for

the same temperatures studied when methanol was used as non-solvent. More interestingly, it is obvious from the figures, when the volume of the non-solvent increased the porosity of the membrane was also increased.

In phase inversion method, the membrane was formed by polymer precipitation, which occurs as a consequence of concentration variation following diffusive interchange between the solvent and the non-solvent. When the volume of the non-solvent increased, the porosity of the membrane was increased which in turn, increases the amount of uptake of electrolyte solution. Consequently, it increases the ionic conductivity as evidenced in Figs. 4 and 5. Table 1 shows the volume of the non-solvent and intake of electrolyte
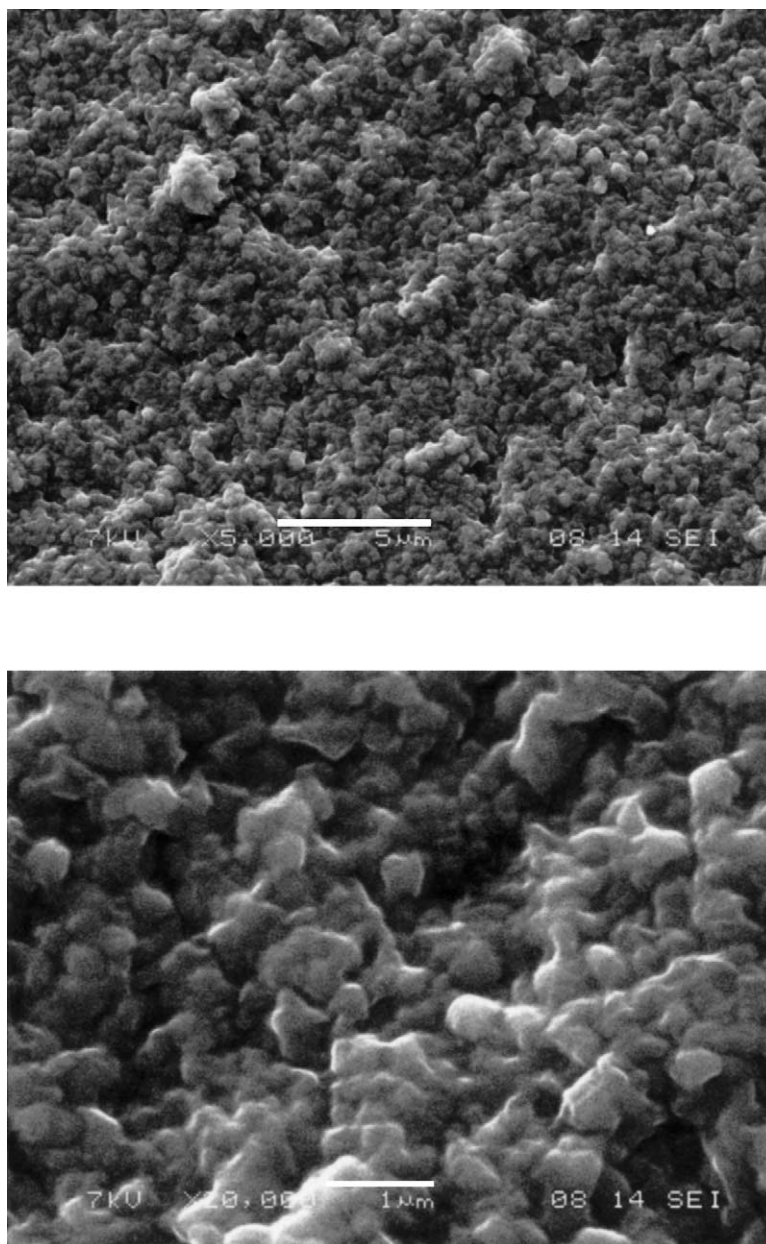
Fig. 2. Scanning electron micrograph of PVdF-HFP membrane prepared with methanol as non-solvent.
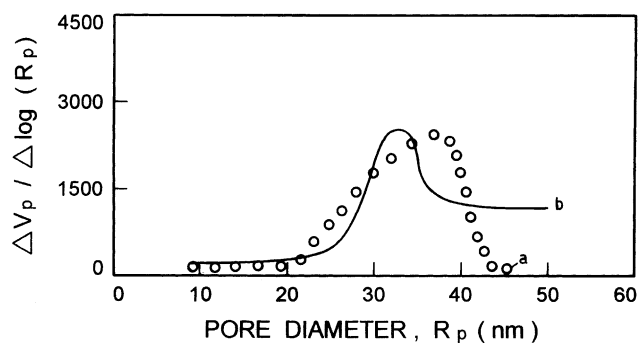

Fig. 3. Pore-size distribution of PVdF-HFP membrane determined by nitrogen adsorption/desorption method: (a) 1-butanol and (b) methanol.

solution by the membrane. High ionic conductivity, although a desirable property is not sufficient to make a membrane completely useful in practical terms.

Cyclability with the electrode materials is also an important parameter to guarantee acceptable performance in electrochemical devices when reliability and safety are concerned. Fig. 6 shows the discharge capacity curves with the number of cycles for the lithium/polymer membrane (PM)/LiAl$_{0.01}$Co$_{0.99}$O$_2$ cells at constant current rate (C/20). For charge–discharge studies samples C and F (Table 1) were employed as separators as they exhibited highest intake of electrolyte solution. Although, the physical properties (morphology and ionic conductivity) of the membranes were different, no discernible changes could be seen in the
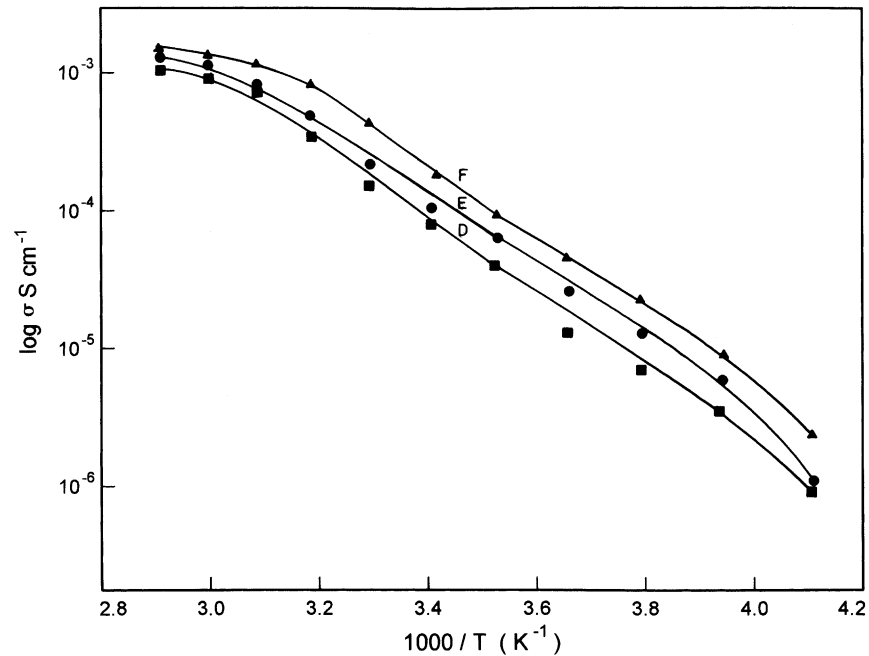
Fig. 4. Arrhenius plot of PVdF-HFP membrane prepared by phase inversion method for different concentration of non-solvent (1-butanol). Sample prepared with D = 0.5, E = 1.0 and F = 2v of 1-butanol.

charge–discharge behavior of the two membranes. However, generally the fade in capacity mainly depends on the nature of the cathode materials used. In the present study Al-doped LiCoO$_2$ was used because it is cheaper and lighter cathode material and it has electrochemically attractive properties such as high intercalation voltage and higher energy density

[21]. On cell safety as well, Al-doped LiCoO$_2$ exhibits better thermal stability than pure LiCoO$_2$ [18]. It is seen from Fig. 6, the initial capacity of the cells, 105 and 107 mAh g^{-1} fell rapidly to 85 and 75 mAh g^{-1} upon cycling for the membranes prepared with 1-butanol and methanol, respectively. In both cases, almost 25% of its initial capacity is lost.
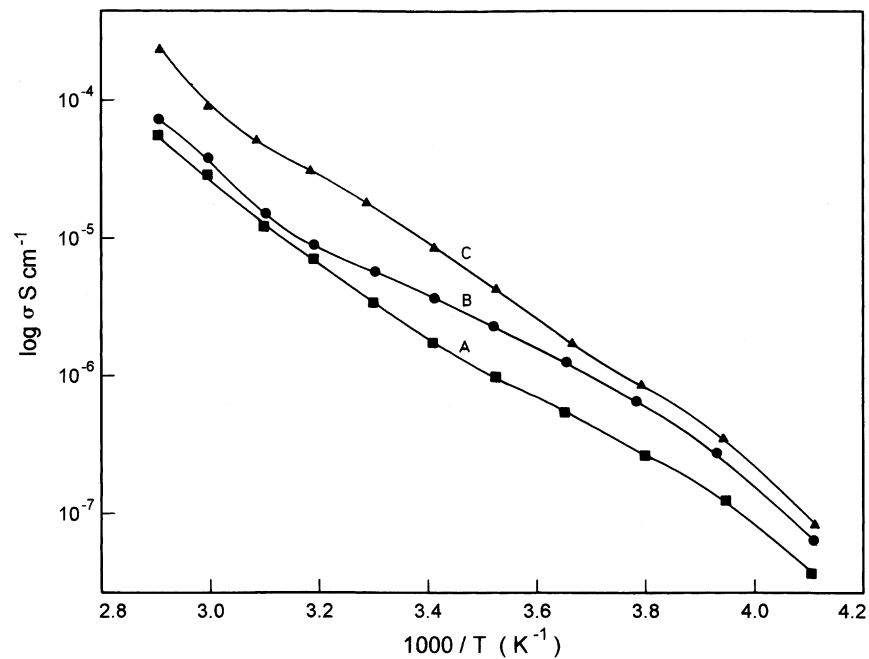

Fig. 5. Arrhenius plot of PVdF-HFP membrane prepared by phase inversion method for different concentration of non-solvent (methanol). Sample prepared with A = 0.5, B = 1.0 and C = 2v of methanol.

Table 1
Pore-size, BET surface area and percentage of electrolyte solution uptake in PVdF-HFP membranes

Sample	Non-solvent	Volume of non-solvent	Pore diameter (nm)	% of solution intake	BET surface area ($m^2\,g^{-1}$)
A	1-Butanol	0.5		52	
B		1.0		62	
C		2.0	32	65	41.72
D	Methanol	0.5		51	
E		1.0		58	
F		2.0	29	62	42.98

Fig. 6. Discharge capacity vs. cycle number of Li/PM/LiAl$_{0.01}$Co$_{0.99}$O$_2$: (a) 1-butanol and (b) methanol.

electrolyte solution which in turn increases the conductivity of the membrane when the amount of non-solvent was increased in the solution. Although, these membranes vary slightly in the physical properties like, morphology and surface area no discernible changes could be seen in charge–discharge studies.

According to Yoon et al. [18], Al-doped LiCoO$_2$ calcinated at 600 °C is more stable during electrochemical cycling because LiAlO$_2$ is stable in the α-NaFeO$_2$ structure at temperature below 600 °C. Further, increase of calcination temperature leads to phase changes leading to reduced capacity. In the present study, since the Al-doped LiCoO$_2$ cathode materials were heated at 800 °C. This fade in capacity may be due to higher calcination temperature of cathode material.

3. Conclusion

PVdF-HFP membranes were prepared by phase inversion method with 1-butanol as non-solvent. The intake of

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