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

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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$_2$ cells.
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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$_2$, TiO$_2$, AlO[OH]$_n$, 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 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 °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 (Mw = 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 μm. 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 °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 °C in vacuum for 6 h to remove the traces of water. The approximate thickness of the cast membranes was 70 ± 10 μm. The morphological examination of the films was made by a JSM-5410LV scanning electron microscope under vacuum (10^{-1} 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
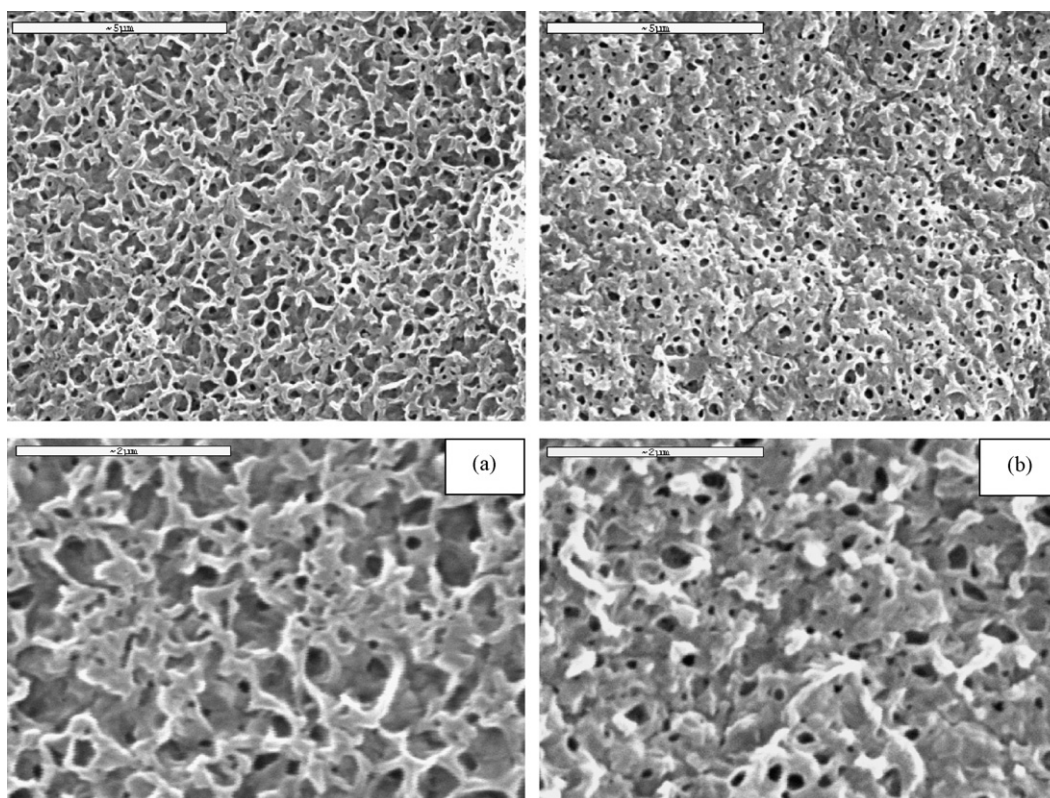

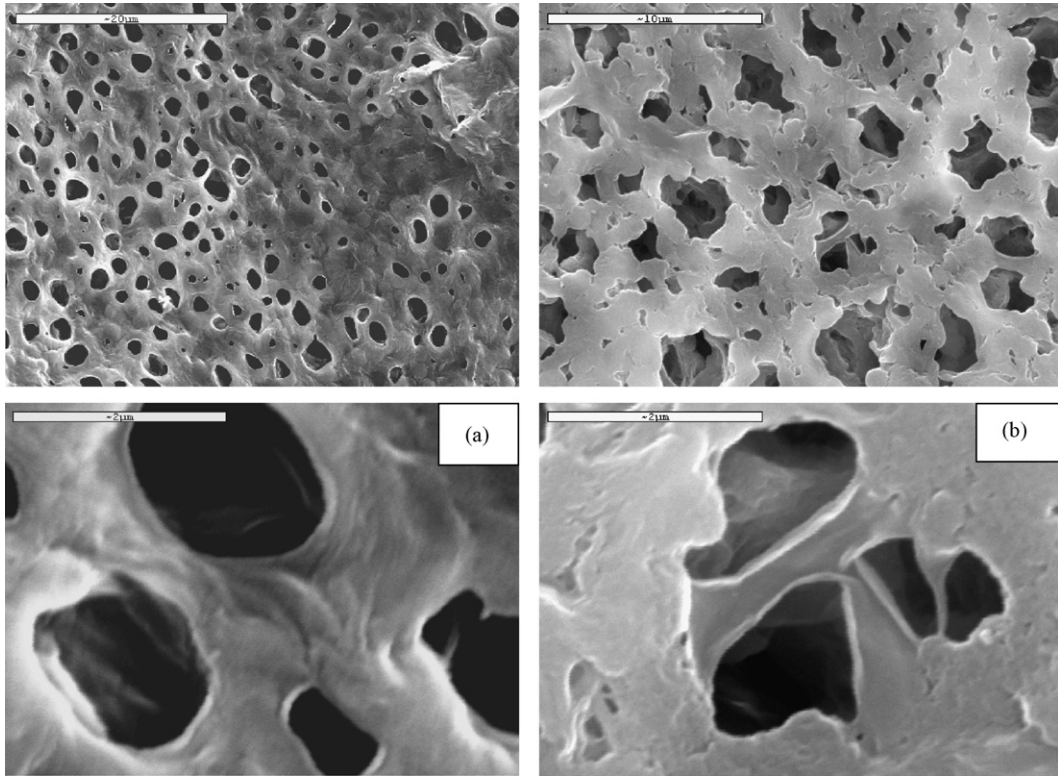Fig. 1. SEM images of (a) sample S1 and (b) sample S2.

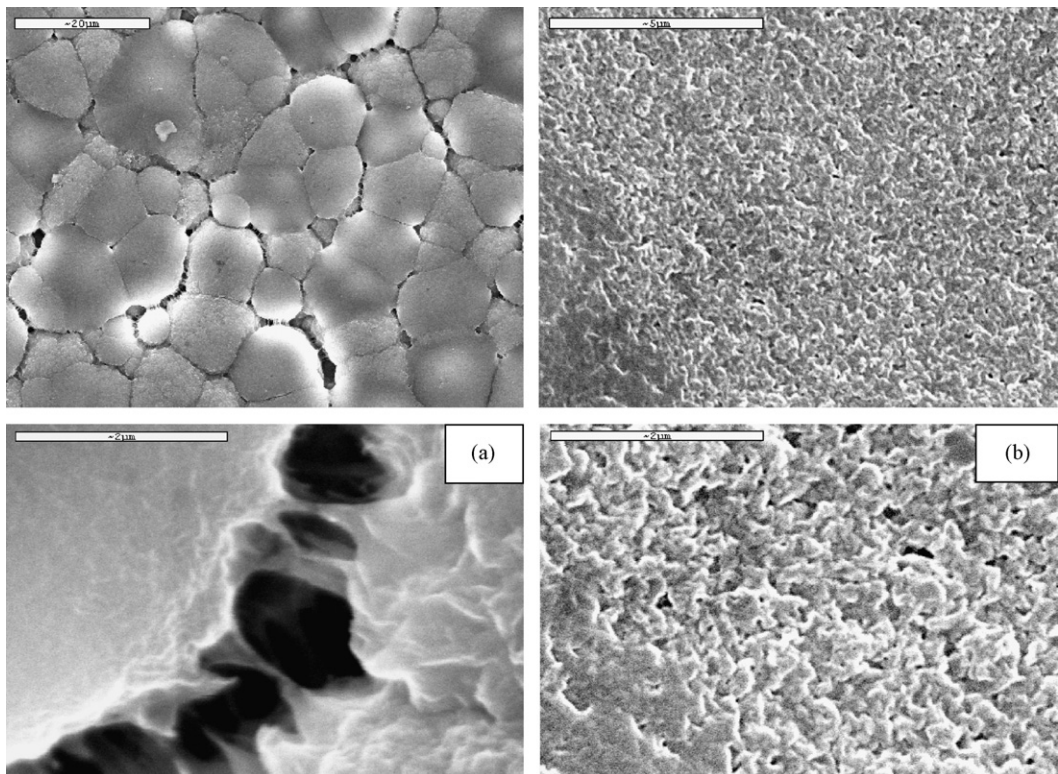Fig. 2. SEM images of (a) sample S3 and (b) sample S4.

Fig. 3. SEM images of (a) sample S5 and (b) sample S6.

Table 1
The composition of PVdF-HFP, PEG and porosity of the membrane

Sample	PVdF-HFP (wt.%)	PEG (wt.%)	Porosity (%)	Percentage of electrolyte intake after 10 min	Solution leakage, R_l	Thickness of the films (μm)
Solvent THF						
S1	0.75	0.25	54.1	50	0.21	68
S2	0.50	0.50	57.7	65	0.23	72
Solvent acetone						
S3	0.75	0.25	60.1	80	0.07	76
S4	0.50	0.50	63.8	115	0.09	79
Solvent DMF						
S5	0.75	0.25	48	65	0.06	69
S6	0.50	0.50	52	100	0.08	67

determined using the following equation:

$$P = \frac{M_a/\rho_a}{M_a/\rho_a + M_p/\rho_p} \tag{1}$$

where M_p, M_a are the mass of the dry membrane and *n*-butanol absorbed in the membrane, respectively and ρ is the density of the polymer. The solution leakage of the porous polymer electrolytes was measured by the technique as reported by Shi et al. [22].

The leakage ratio of the electrolyte solution "R_l" is defined as the ratio of electrolyte absorbed by the membrane and after the solution leakage test [22].

$$R_l = \frac{R_{af} - R_{ai}}{R_{ai}} \tag{2}$$

where R_{ai} and R_{af} respectively denote initial and final absorption of the electrolyte before and after the test. The PVDF-HFP porous membranes were cut into a specimen of 1-cm diameter and weighed. The weighed membrane was soaked in the electrolyte solution and was covered with three layers of filter paper. A weight of 75 g was applied and again the specimen was weighed. All these experiments were done in an argon-filled glove box.

The percentage of uptake of electrolyte solution was calculated according to Xi et al. [23]. The cathode was prepared
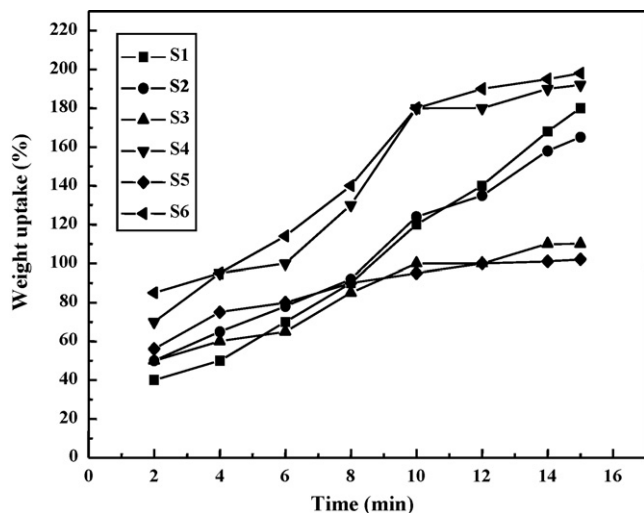
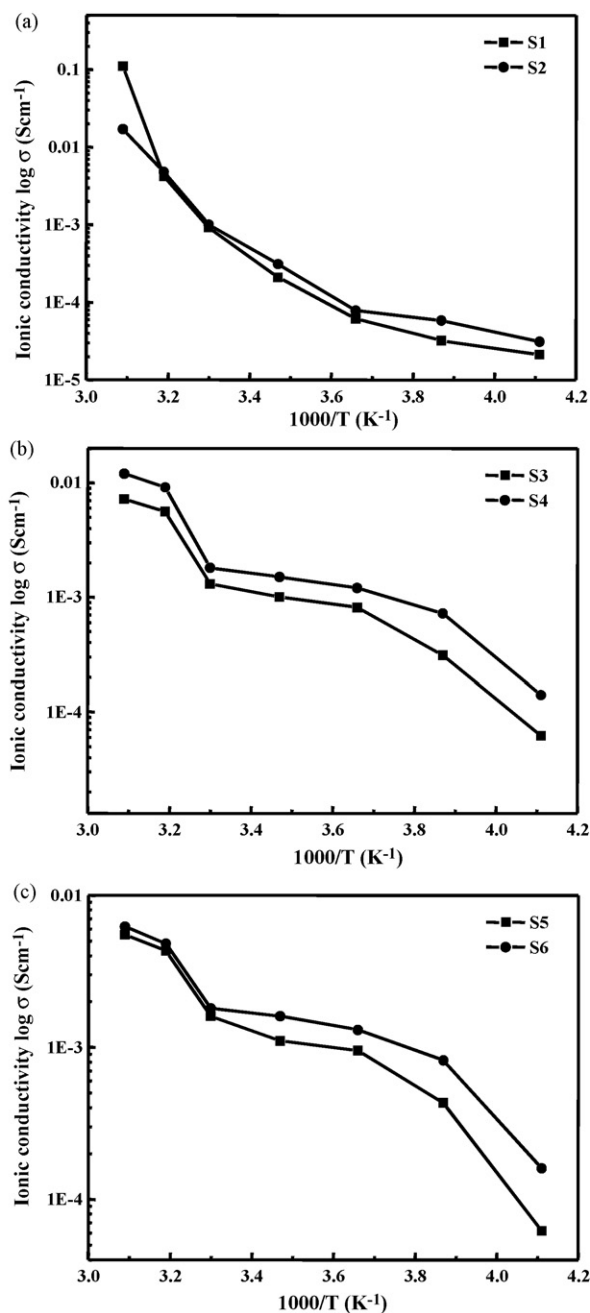Fig. 4. Variation of electrolyte intake as a function of time.

Fig. 5. Ionic conductivity as a function of temperature for the samples S1, S2, S3, S4, S5 and S6.

by brush-coating a slurry of 85% LiCoO$_2$ (Sigma–Aldrich), 5% poly(vinylidene fluoride) and 10% acetylene black in 1-methyl-2-pyrrolidone on an aluminum substrate, and drying in a vacuum oven at 120 °C for 12 h. The polymer membrane (PM) was soaked in a solution of 1 M LiPF$_6$ in ethylene carbonate and di-ethylcarbonate (1:1, v/v) for 12 h. The lithium foil was used as anode. Standard 2032-type coin cells of configuration Li/polymer membrane/LiCoO$_2$ were assembled in an argon-filled glove box and subjected to cycling between 2.8 and 4.2 V at 0.1 C rate. The ionic conductivity of the polymer membranes was analyzed using an impedance analyzer (Solartron, UK) over the frequency range of 1 mHz–100 kHz at 25 °C.

3. Results and discussions

3.1. SEM analysis

SEM images reveal that the morphology of the polymer membranes depends on the solvent used (Figs. 1–3). It can be seen that the morphology varies greatly with the solvent. A homogenous phase with uniform-sized pores was obtained for the membrane when THF was used as a solvent (Fig. 1a). A more or less similar morphology is seen for the membranes with acetone as solvent (Fig. 2b). On the other hand, the membranes prepared with DMF exhibit a rough morphology with lesser number of pores
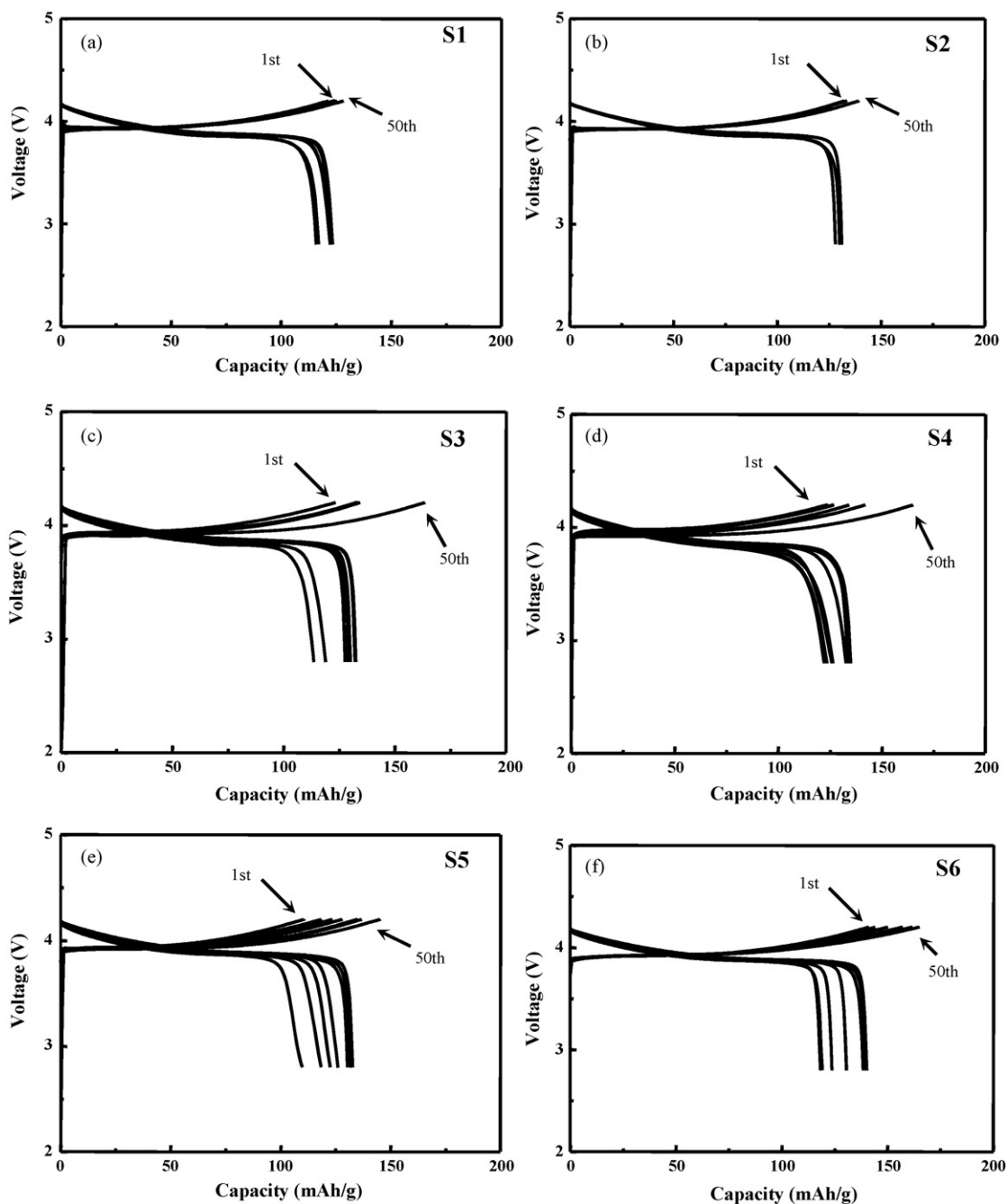

Fig. 6. Charge–discharge profile of Li/LiCoO$_2$ cells: (a) sample S1, (b) sample S2, (c) sample S3, (d) sample S4, (e) sample S5 and (f) sample S6.

(Fig. 3b). It can also be seen from the figure that the porosity of the membrane increased with PEG content. It must be noted that the SEM images represent this general morphology in each category of the membranes. The representative images presented here were chosen from at least three similar images in each category.

3.2. Porosity and electrolyte intake

Ionic conductivity in the conventional battery separator is achieved by continuous pathways formed by the absorbed liquid electrolyte within the interconnected pores of the separator. Thus pore structure is an important factor that determines the ionic transport of polymer membranes. The porosity of the membrane formed by phase inversion was determined by Eq. (1). It is seen from Table 1 that the porosity of the membrane increases with an increase in PEG content in the polymer solution. These results are in accordance with those of Xi et al. [23] who reported the effect of pore configuration of PEO in PEO-PVDF blend electrolyte membranes. In the phase inversion method, the membranes are formed by polymer precipitation, which occurs as a consequence of concentration variations following diffusive interchange between the solvent and the additive. In the present study, the polymer membranes were prepared using three solvents with the aim of making membranes with different morphologies.

Fig. 4 shows the variation of amount of the electrolyte intake of the solution as a function of time. It must be noted that the electrolyte used for this electrolyte uptake studies and coin cell studies was the same. It is clear from Fig. 4 that the intake of the electrolyte solution increases with increasing soak period. However, after 15 min of soak period, the amount of intake of the solution reaches an upper limit except in the cases of films S1 and S2, these shallow slopes of which beyond the 15 min mark suggest nearness to saturation. The ionic conductivity of the membrane is mainly determined by membrane porosity, tortuosity of pores, conductivity of the liquid electrolyte, thickness of the membrane and extent to which the electrolyte wets the pores of the membrane. Although the electrolyte intake by the membranes becomes stable after 15 min considering the above-mentioned aspects, these membranes were soaked in the electrolyte solutions for 12 h in the present study. The average pore diameters of membranes formed from acetone-based cast solutions are 1 and 2 μm for 0.75 PVdF-HFP:0.25 PEG and 0.50 PVdF-HFP:0.50 PEG, respectively. The values for those formed from THF-based cast solutions are submicrons (100–200 nm). It must be noted that small pores have the ability to retain the electrolyte solutions.

Also removal of PEG from the cast solution results in the formation of pores, which means more the PEG content, larger the porosity. Fig. 3 shows SEM images of membranes formed with DMF as a solvent. It is clear that as the PEG content is increased from 0.25 to 0.5, the pores get finer and larger in number per unit area. In fact, it is seen that the electrolyte intake increased from 65% for the film generated from a cast solution of 0.75 PVdF-HFP and 0.25 PEG to 100% for that generated from a

cast solution containing 0.50 PVdF-HFP and 0.50 PEG. A similar trend was obtained with the films formed from cast solutions containing THF and acetone (Figs. 1 and 2 and Table 1).

3.3. Solvent effect

THF and acetone are flat and nearly linear molecules, respectively. Therefore, their escape from the cast solutions would leave voids that are rather small. Moreover, the molecules do not have groups that can bond strongly with the host polymer or with PEG.

Their molecules, therefore, escape freely upon evaporation leaving uniform pores. This situation is different in the case of DMF, which can interact with the polymer matrix and PEG through its amide group. Consequently, during evaporation, its molecules tend to pull away molecules to which they are bonded. In this process, the film surface breaks non-uniformly, leaving large crack-like voids.

3.4. Ionic conductivity studies

Variation of the ionic conductivity as a function of temperature for different contents of PEG is depicted in Fig. 5(a)–(c). The conductivity in conventional battery separators is related to the interconnectivity of the pores in them. Thus, pore structure is a major factor that determines the ionic conductivity of an electrolyte in a separator, although other factors such as conductivity of the electrolyte embedded in the pores, tortuosity of pores, ionic conductivity of the liquid electrolyte, thickness of the membrane and the wetting properties of the electrolyte into the membrane do influence the ionic transport properties of this electrolyte-laden membrane.

The ionic conductivity of the membrane is also determined by the amount of solution entrapped by the membranes [22,23]. It is evident from Fig. 5 that the ionic conductivity increases with the increasing temperature and also with increasing PEG content in the polymer solution. Obviously, the porosity of the
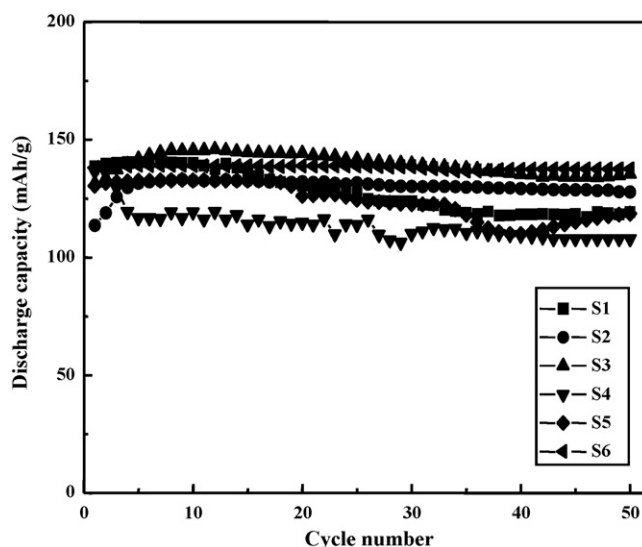

Fig. 7. Discharge capacity vs. cycle number of Li/LiCoO$_2$ cells.

membranes increased as more and more amount of PEG was used. The increased porosity leads to entrapment of large volumes of the liquid in the cavities accounting for the increased ionic conductivity. But at higher temperature, the conductivity values are almost the same irrespective of the amount of PEG. In a recent study [8,11–13], we suggested that the amount of liquid electrolyte trapped in such gel membranes was determined by the volume of the cavities (porosity) and that the ionic conductivity of such a porous membrane was largely dictated by the conductivity of the electrolyte embedded in the pores, the conductivity of the non-aqueous electrolyte solution used and the thickness of the membrane. It can be seen from Table 1 that the porosity of the membranes formed with acetone as a solvent was the highest. The resulting membrane would therefore, accommodate larger volumes of the electrolytes than those found with THF or DMF. Consequently, acetone-based electrolyte membranes gave the highest conductivity.

3.5. Cycling studies of Li/PM/LiCoO₂

The first charge–discharge behavior of Li/PM/LiCoO$_2$ cells is displayed in Fig. 6. These films were prepared with PEG contents of 0.25 and 0.50 employing THF as solvent. The membranes with highest porosity (PEG: 50 wt.%) gave cells with better performance (Fig. 6). The charge–discharge profiles shown in Fig. 6 are similar even though the polymer membranes used in the cells are different. This is only expected since the profiles reflect characteristics of the anode/cathode. It must, however, be mentioned that the profiles may show variations if, for example, the ionic conductivities of electrolyte-laden membranes differ by wide margins. The better productivity of this membrane is reflected in the higher capacities delivered by the cell. In fact, even the cyclability of the cell also depends on the ion transport properties of the membrane (Fig. 7) The discharge capacities of the cell with the polymer membrane S5 (PEG = 0.25) were 130 and 115 mAh g^{-1} of LiCoO$_2$ at its first and 50th cycles, respectively with a capacity fade of 0.3 mAh g^{-1}/cycle. On the other hand, the membrane, S6 (PEG = 0.50) exhibited an initial capacity of 138 mAh g^{-1} of LiCoO$_2$ with a fade in capacity of 0.42 mAh g^{-1}/cycle and the samples prepared with acetone and THF as solvent also exhibited a similar cycling behavior.

Other things being identical, the performance of the cells must necessarily reflect the ionic transport behavior across the separator membrane. However, a direct correlation of cell behavior with any one characteristic, say conductivity, would mean over looking other factors such as tortuosity of pores, leakage behavior under test conditions, etc. An analysis of such dimensions is beyond the scope of this paper.

It may be noted that membrane S4 showed the lowest capacity even though its electrolyte intake was the highest. The apparent anomaly may be explored by the fact that while a membrane with larger pores may absorb large volumes of electrolyte, under compaction as in our crimp-sealed coin cells they are prone to expel the extra liquid.

4. Conclusions

Porous PVdF-HFP/PEG membranes were prepared with different solvents. The morphology of the membranes can be tailored by varying the content of PEG and the solvent. The porosity of the membranes can be increased by increasing the content of PEG. Electrolyte intake was increased with an increase in the porosity which in turn enhances the ionic conductivity of the polymer membrane. However, when the content of PEG is increased beyond 50% it increases the leakage of electrolyte solution from the membrane. The cycling behavior of the cells reveals convincing results and the polymer electrolyte membranes developed in this study seem to be promising candidates for rechargeable lithium battery application.

Acknowledgement

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