

Research Article

A New Class of P(VdF-HFP)-CeO₂-LiClO₄-Based Composite Microporous Membrane Electrolytes for Li-Ion Batteries

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Composite microporous membranes based on Poly (vinylidene fluoride-co-hexafluoro propylene) P(VdF-co-HFP)-CeO₂ were prepared by phase inversion and preferential polymer dissolution process. It was then immersed in 1M LiClO₄-EC/DMC (v/v = 1 : 1) electrolyte solution to obtain their corresponding composite microporous membrane electrolytes. For comparison, composite membrane electrolytes were also prepared by conventional phase inversion method. The surface morphology of composite membranes obtained by both methods was examined by FE-SEM analysis, and their thermal behaviour was investigated by DSC analysis. It was observed that the preferential polymer dissolution composite membrane electrolytes (PDCMEs) had better properties, such as higher porosity, electrolyte uptake (216 wt%), ionic conductivity (3.84 mS·cm⁻¹) and good electrochemical stability (4.9V), than the phase inversion composite membrane electrolytes (PICMEs). As a result, a cell fabricated with PDCME in between mesocarbon microbead (MCMB) anode and LiCoO₂ cathode had better cycling performance than a cell fabricated with PICME.

1. Introduction

High energy density rechargeable lithium batteries are important to the development of several applications such as portable electronic devices; electric or hybrid cars still requires the optimization of some critical operational features with special concern directed toward those related to safety and design flexibility [1]. Conventional lithium batteries, liquid electrolyte make batteries unsafe due to electrolyte leakage and electrochemical instability due to the repeated oxidation/restoration reaction at the interface between the electrode and electrolyte [2]. To overcome this, polymer electrolytes were introduced that plays an essential role in rechargeable lithium ion batteries. Hence, the control of the miscibility and stability between the liquid electrolytes and the host polymer itself has become one of the prominent factors for polymer electrolytes [3]. Indeed, microporous structure of the host polymer matrix is one of the convenient tools for ionic transport and enhances ionic

conduction [4]. In this regards, P(VdF-co-HFP) host have attracting properties such as high dielectric constant ($\epsilon = 8.4$) and strong electron-withdrawing functional group (-C-F) which may be swollen in carbonate, but does not solvate, therefore facilitates higher concentration of charge carriers. It comprises both an amorphous and crystalline phase where an amorphous phase of the polymer support higher ionic conduction and crystalline phase assists to enhance the mechanical strength for the polymer electrolytes [5]. P(VdF-co-HFP) based polymer electrolyte is one of the most commonly commercialized plastic lithium ion batteries (PLiON) by Telcordia Technologies (formerly Bellcore) since Gozdz et al found the preparation process of porous membrane [6-9]. However, in the process di-butyl phthalate (DBP) extraction step is inconvenient since it increases the cost of the preparation. Some researchers and also our research groups have reported an alternative method to form the porous structure by the phase inversion technique as well as polymer dissolution techniques on the polymer matrix, such

as polyacrylonitrile (PAN) [10, 11], poly(vinylidene fluoride) (PVDF) [12, 13], poly(acrylonitrile-methyl methacrylate) (PAN-MMA) [14, 15] and poly(vinylidene fluoride-co-hexa fluoropropylene) P(VdF-co-HFP) [16–21], and so forth. Moreover, effect of inorganic oxides such as ZrO₂ nanofiller [22], SiO₂ [23, 24], MgO [25], Al₂O₃ [26] and TiO₂ [27–29] on the electrochemical properties of P(VdF-co-HFP) based porous structure polymer electrolytes have been studied. Recently, Rajendran et al. [30] reported a solid polymer electrolyte, with the addition of microscale CeO₂ filler in PMMA polymer matrix. Uvarov et al. has studied the effect of adding some rare earth oxide ceramics such as CeO₂, SiO₂, fly ash, and Eu₂O₃ as dispersoids, and verified the fact that other than γ -Al₂O₃, the above mentioned dispersoids also help in achieving the modest enhancement in electrochemical properties include the ionic conductivity and bulk properties of the composite solid electrolytes [31]. But it is an ever first time we have compared the addition of nanoscale CeO₂ for enhancing the properties of P(VdF-co-HFP) polymer electrolytes [32] by phase inversion and polymer dissolution (removal of PVP additive on the host polymer matrix) techniques which improved the membrane microporous structure world as well as electrochemical behaviour of the composite microporous polymer electrolyte.

In the current research work, we report a new class of P(VdF-co-HFP)-CeO₂ and P(VdF-co-HFP)-CeO₂/ PVP (additive extracted) based polymer electrolytes to seek an importance in the structural and electrochemical properties. This composite microporous membrane electrolyte (PICME/PDCME) has expected to retain excellent electrochemical properties such as ionic conductivity, interfacial stability, electrochemical stability window, and also good cell performance. The morphology and thermal properties of both polymer membranes are described herein. Moreover, the effect of CeO₂ fillers on composite polymer electrolyte and determination of its optimal content further gave a guide line for the preparation of PVP-removed PDCME with good morphological structure and electrochemical properties for rechargeable lithium ion polymer batteries.

2. Experimental Details

2.1. Materials and Its Pretreatment. Poly (vinylidene fluoride-co-hexafluoro propylene) (P(VdF-co-HFP), $M_w = 40,000$) as a host polymer matrix, and lithium perchlorate (LiClO₄) as the electrolyte salt were purchased from Aldrich (USA). The host polymer was dried at 80°C in a vacuum oven under pressure 133.322×10^{-3} Pa (10^{-3} Torr) for 8 h. Nanoscale cerium oxide (CeO₂, average size of ~10–20 nm and surface area ~80–100 m²/g) filler purchased from Aldrich (USA) and LiClO₄ salt were used after drying at 100°C under vacuum for 12 h. Polyvinyl pyrrolidone (PVP, $M_w = 58,000$) was used as an additive received from Across Organic Chemicals (Belgium) and treated under vacuum for 8 h at 60°C. N-methyl pyrrolidone (NMP) obtained from E-Merck. Ethylene carbonate (EC) and dimethyl carbonate (DMC) obtained from Aldrich (USA) were used as plasticizer without further purification.

TABLE 1: Residual weight (%) of PVP after the removal of additive PVP in the composite microporous membranes by preferential polymer dissolution method (PDCM).

wt% of PVP in P(VdF-co-HFP)-CeO ₂ membrane before removal	Residual wt(%) of PVP in the PDCM after the removal
10	0.003
20	0.001
30	0.007

2.2. Conventional Phase Inversion Composite Microporous Membrane Electrolytes (PICME). Phase inversion composite microporous membrane (PICM) was prepared by dissolving a certain amount of P(VdF-co-HFP) in NMP solvent with constant stirring to form a homogeneous solution. To this different wt% of CeO₂ (2–10 wt%) filler was added to the polymer solution and stirred continuously for 24 h. The resultant homogenous viscous slurry was cast on a newly cleaned glass plate with desired thickness by using doctor blade. This glass plate was then put into large excess of deionized water for 3–5 h to extract solvent and phase inversion occurred. Mean while, CeO₂ nanoparticles stayed in the polymer matrix during the phase inversion process. The resultant PICM was dried under vacuum pressure at 80°C for 6 h. Finally, dimensionally stable and solvent free PICM with thickness ranging from 70–100 μ m were obtained. These PICM were immersed in 1M LiClO₄ containing 1 : 1 (v/v) ratio of EC and DMC for 6 h to obtain their corresponding phase inversion composite membrane electrolytes (PICMEs).

2.3. Preferential Polymer Dissolution Composite Microporous Membrane Electrolytes (PDCME). Preferential polymer dissolution composite microporous membrane (PDCM) was prepared by dissolving a P(VdF-co-HFP) and different weight (%) of PVP (10, 20 and 30 wt%) in NMP with constant stirring to form homogenous solution. Then the optimized concentration of 8 wt% CeO₂ nanoparticles was dispersed into the polymer solution and stirred continuously for 24 h. The resultant homogenous slurry was spread on a newly cleaned glass plate and a desired thickness was made by doctor blade method. It was allowed to stay in air for few minutes at room temperature, followed by immersing the glass plate into deionized water at 40°C for 3–5 h to obtain PDCM with the removal of PVP, then it was peeled off from the substrate easily. The membrane was dried under vacuum pressure at 80°C for 6 h before and after the treatment. Residual wt% of PVP in the dried PDCM was found out by knowing the wt% of PVP before and after treatment [22] of the membrane from the Table 1. Finally, dimensionally stable and solvent free PDCM with thickness ranging from 70–100 μ m were obtained. These PDCM were immersed in 1M LiClO₄ containing 1 : 1 (v/v) ratio of EC and DMC for 6 h to obtain their corresponding preferential polymer dissolution composite membrane electrolytes (PDCMEs).

The surface morphology of PICM/PDCM was examined by means of JEOL-Field emission scanning electron

microscopy (FE-SEM) with an accelerating voltage range of 20 kV.

Thermal property of PICM/PDCM was investigated by Perkin Elmer—differential scanning calorimetry (Model: Pyris DSC-6) instrument. The measurements were carried out with the heating rate of 10°C/min at nitrogen atmosphere. Crystallinity of PICM/PDCM membranes was calculated from the following equation (1),

$$X_c = \left(\frac{\Delta H_m}{\Delta H_m^\Phi} \right) \times 100, \quad (1)$$

where ΔH_m^Φ is the crystalline melting heat of pure α -PVDF (104.7 J/g), ΔH_m is the heat of melting of P(VdF-co-HFP) based PICM/PDCM.

The porosity of these composite microporous membranes (PICM/PDCM) was measured by immersing the membrane into *n*-butanol for 1 h, weighing the membrane before and after absorption of *n*-butanol and then calculated the porosity using the following equation (2),

$$\text{Porosity } (\rho\%) = \frac{(W_a/\rho_a) \times 100}{(W_a/\rho_a + W_p/\rho_p)}, \quad (2)$$

where W_p is the weight of the dry composite membrane, W_a is the weight of *n*-butanol absorbed by the composite membrane, ρ_a is the density of *n*-butanol and ρ_p is the density of the dry composite membrane.

The electrolyte solution uptake of PICM/PDCM was measured as a function of soaking time in 1 M LiClO₄-EC/DMC (v/v = 1 : 1) for 6 h to obtain their corresponding PICME/PDCME. The electrolyte solution uptake by these membranes was calculated using the following equation (3),

$$\text{solution uptake wt}(\%) = \left[100 \times \frac{(W_f - W_o)}{W_o} \right], \quad (3)$$

where W_f and W_o are the weight of the wet and dry composite membranes (PICM/PDCM), respectively.

The electrolyte solution leakage test for these soaked PICM/PDCMs were carried out by placing the composite membrane electrolyte (PICME/PDCME) in between two filter papers and then squeezed by pressing with a 100 g poly (tetrafluoroethylene) sheet. The weight changes of the membranes containing electrolyte solution was measured every 10 min. We have applied the pressure of $\sim 133.322 \times 10^{-2}$ Pa (10^{-2} torr) to find out the electrolyte leakage studies. The electrolyte solution leakage of the PICME/PDCME was calculated using the following equation (4) described elsewhere [33]:

$$\text{solution leakage wt } (\%) = \left[\frac{(W_i - W_f)}{(W_i - W_o)} \right] \times 100, \quad (4)$$

where W_o is the weight of the dry composite membrane, W_i and W_f are the initial and equilibrium weights of the composite membrane after absorbing the liquid electrolyte, respectively.

To measure the ionic conductivity of PDCMEs and PICMEs, they were sandwiched in between two stainless steel nonblocking electrodes and the measurements were made using HIOKI—LCR Hi-TESTER at a wide frequency range of 10 Hz to 100 KHz at different temperatures ranging from 25 to 80°C. The ionic conductivity of both these PICME/PDCME was determined using conductivity equation; $\sigma = t/(A \times R_b)$ Scm⁻¹, where σ is the conductivity, t is the thickness of the membrane electrolyte, R_b and A are the bulk resistance and cross-sectional area of the membrane electrolyte, respectively. The electrochemical experiments were carried out under inert Argon gas atmosphere.

The interfacial stability of the PICME/PDCME was confirmed by fabricating the cell as Li/electrolyte/Li using EG & G—Electrochemical analyzer over a frequency range of 10 Hz ~ 100 kHz, with an amplitude of 10 mV, for different storage time.

The electrochemical stability window of both these electrolytes was determined by running a linear sweep voltammetry. It was performed by using a two-electrode cell in the configuration of Li/electrolyte/SS (Stainless Steel) in the potential range of 2.0 to 5.5 V versus Li/Li⁺ at a scan rate of 1.0 mVs⁻¹.

Finally, coin type lithium ion cells were assembled by sandwiching the PDCME/PICME in between a mesocarbon microbead (MCMB) anode and a LiCoO₂ cathode. The cell was assembled and then sealed under vacuum in a glove box filled with argon. The cell performance of the PDCME/PICME was evaluated galvanostatically using WonA Tech battery cycle life tester and its performance was compared between PDCME and PICME. At C/2 rate, the test was carried out with a constant current density of 0.25 mAcm⁻² and the cut-off voltage of 3.0 V and 4.2 V.

3. Results and Discussion

3.1. Morphology and Thermal Studies. The morphology of PICM and PDCM is shown in Figure 1. The top surface of PICM containing 8 wt% CeO₂ has shown a sponge like structure and its pores are very tiny and exhibits nearly 1 μ m while that on the bottom surface has shown compact structure and exhibit low degree of pores. The asymmetric distribution of pores appeared on both surface of the membrane can be clearly seen from Figures 1(a) and 1(b). The asymmetric structure is caused by different kinetics during the phase inversion between the two surfaces of the composite membrane. Thus, these two surface facing may differ in morphology to some extent [34]. Further, addition of CeO₂ filler (>10 wt%) on the polymer matrix leads to more rough surface by the growth of aggregates and becomes more compact structure [32]. On contrary, removal of 20 wt% PVP from the PDCM exhibits uniform honeycomb like structure with uniform microporous on both top and bottom surface (1 to 5 μ m) and is shown in Figures 1(c) and 1(d). On the other hand, during the preferential polymer dissolution process, a highly ordered pore structure (i.e., honey comb-like structure) was observed due to the removal of PVP additive from the composite matrices. It

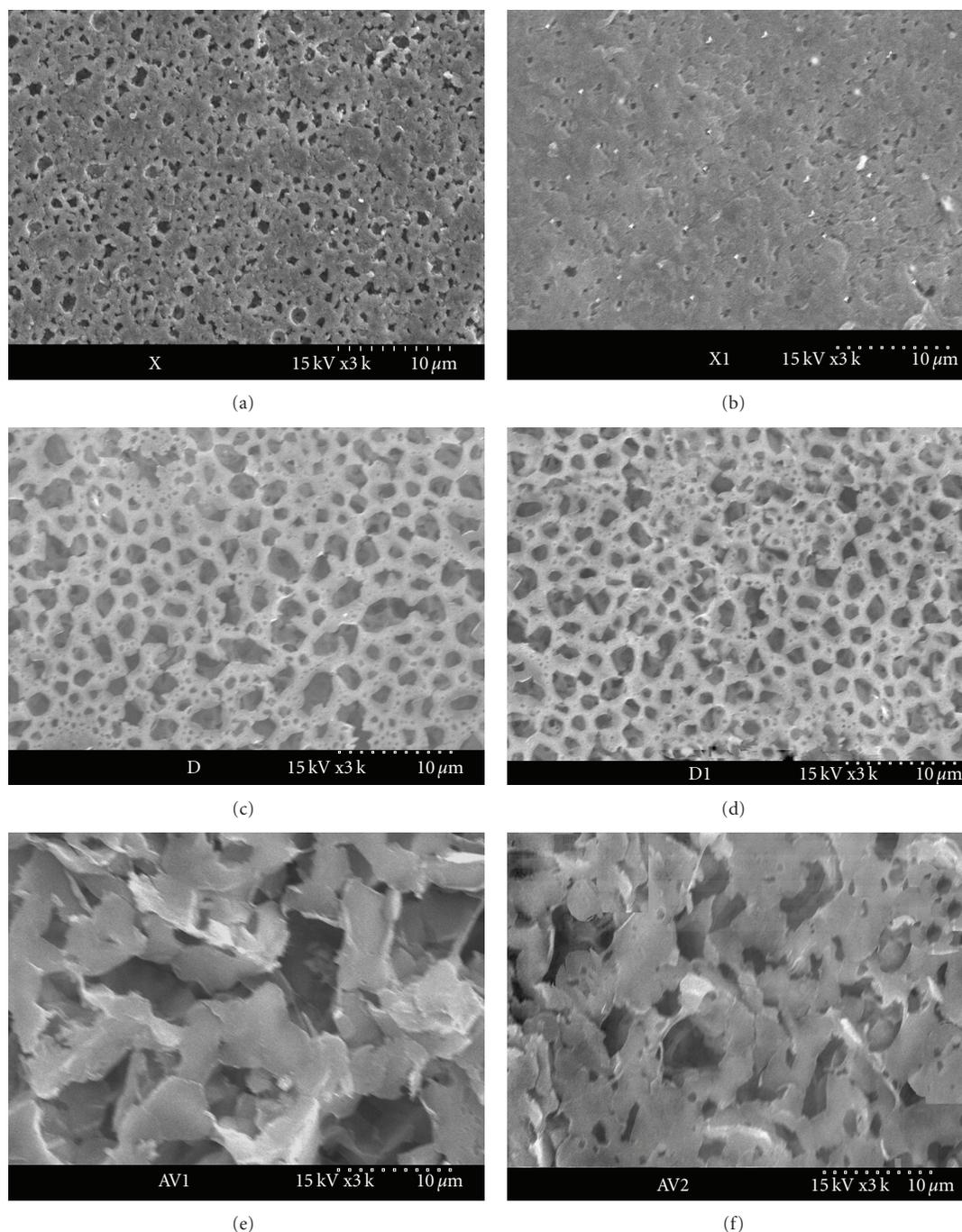


FIGURE 1: FE-SEM images of PICM with the addition of 8 wt% CeO_2 (a) top surface view (b) bottom surface view; PDCM with the removal of 20 wt% PVP from P(VdF-co-HFP)- CeO_2 /removal PVP matrix (c) top surface view (d) bottom surface view; PDCM with the removal of 30 wt% PVP from P(VdF-co-HFP)- CeO_2 /removal PVP matrix (e) top surface view (f) bottom surface view.

could also be an effective track for microporous structure formation on the polymer matrix with high porosity. 30 wt% PVP extracted PDCM showed quite different honey-comb like structure and also large voids were seen on the top and bottom surface (Figures 1(e) and 1(f)). The pore sizes were greater than 5–10 μm and microporous structure become sparser. The residual (negligible) wt% of PVP in the PDCMs was observed after removal of additives (Table 1). It indicates

that negligible wt.% of residual PVP was observed in the PDCMs. It confirms the effective removal of PVP by preferential polymer dissolution process during the treatment of deionized water.

Thermal properties of PICM are illustrated in Table 2. The nanoscale filler incorporation into the polymer matrix decreased the melting temperature ($T_m = 142.2^\circ\text{C}$), and heat of melting ($\Delta H_m = 25.17 \text{ J}\cdot\text{g}^{-1}$) with 8 wt% of

TABLE 2: Thermal and other physical properties of composite microporous membranes obtained by conventional phase inversion method (PICM).

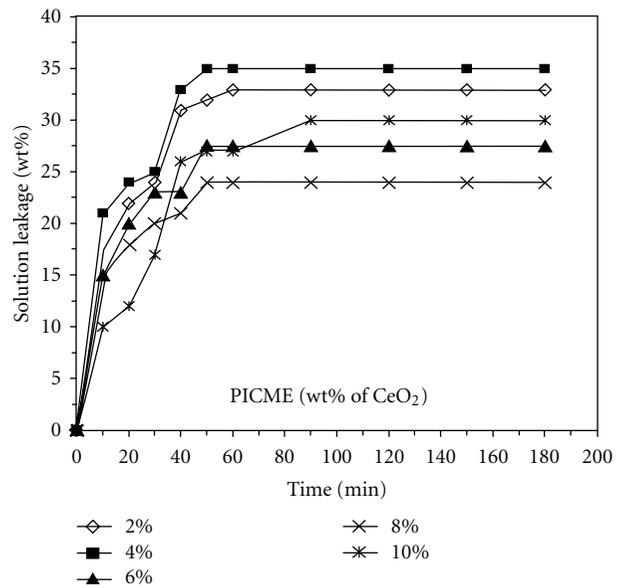
CeO ₂ (wt%)	PICM					
	T_m	ΔH_m	X_c (%)	ρ (%)	Electrolyte uptake (wt%)	Film strength
2	143.2	30.81	29.41	58	124	Good
4	143.1	28.72	27.43	63	132	Good
6	142.7	27.33	26.10	66	146	Good
8	142.2	25.17	24.04	72	150	Good
10	143.1	26.54	25.34	64	132	Good

CeO₂ filler content. Beyond this filler content enhanced the T_m (143.1°C) and ΔH_m (26.54 J·g⁻¹) due to filler aggregation on the polymer matrix. PDCM with removal of 20 wt% of PVP declined the melting temperature ($T_m = 142.1^\circ\text{C}$) and heat of melting ($\Delta H_m = 24.58 \text{ J}\cdot\text{g}^{-1}$) and are given in Table 3. Moreover, removal of PVP (10 and 20 wt%) on the PDCMs have no drastic changes in thermal properties.

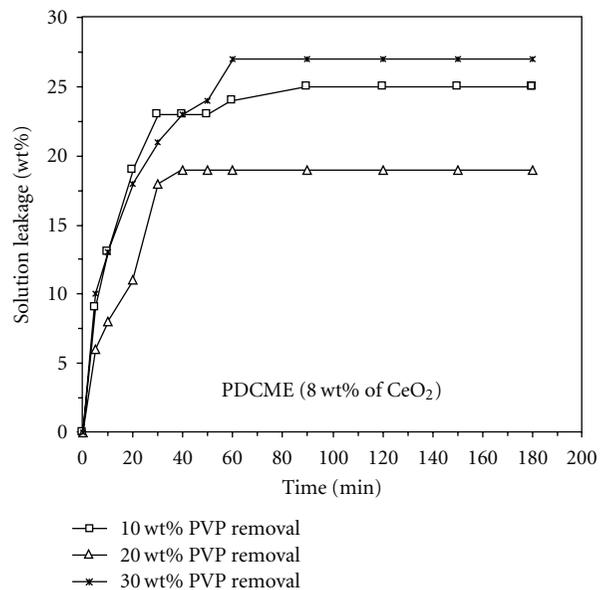
3.2. Porosity, Solution Uptake and Leakage Studies. The porosity values of PICM/PDCMs are given in Tables 2 and 3. It is quite obviously observed that in the case of PICMs, the addition of CeO₂ filler increases the porosity up to 8 wt% CeO₂. Beyond this filler content, porosity was decreased due to aggregation of filler on the polymer matrix [32]. But in the case of PDCMs, the removal of PVP increases the porosity from 79% to 87% continuously. The removal of 20 wt% PVP on the PDCM has the porosity of 85% with good film strength. Beyond this PVP removal, the porosity was higher to 87%, but microporous structure becomes sparser (Figures 1(e) and 1(f)).

Tables 2 and 3, clearly illustrates the electrolyte uptake of both PICM and PDCM even after 6 h. PICM reaches the maximum electrolyte uptake of 150 wt% at optimized CeO₂ (8 wt%) filler concentration (Table 2). But in the case of PDCM reaches maximum electrolyte uptake of 216 wt% with the optimum PVP (20 wt%) extracted membrane (Table 3). Beyond the optimum PVP removal in the PDCM decreased electrolyte uptake owing to the poor pore morphology (Figures 1(c) and 1(d)) and increased the solution leakage (28 wt%). Hence, optimum additive removed PDCME has enhanced liquid electrolyte uptake, due to higher affinity of filler towards the solvents of (EC/DMC) liquid electrolyte solution and also porosity.

The solution leakage of both PICMEs and PDCMEs was studied as a function of time is shown in Figures 2(a) and 2(b). The PICME with 8 wt% of CeO₂ was found to have less solution leakage of 24 wt% after 50min than all other PICME. The PDCME (removal of 20 wt% of PVP) showed very less solution leakage of 19 wt% even after 50min among over all studied membranes. This is due to the modification of rather uniform pores size causes more trapping of liquid electrolyte in the pore walls which helps to avoid solution leakage. But 30 wt% of PVP extracted PDCM has raised solution leakage of 28 wt% after 50min. This is because of macrovoids evident from the morphological studies (Figures



(a)

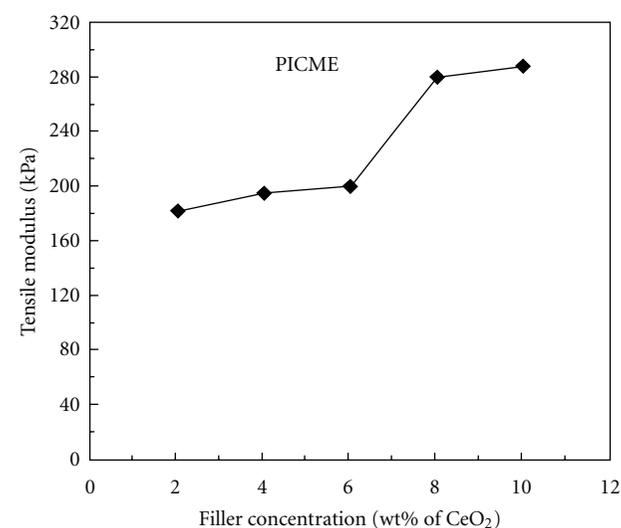


(b)

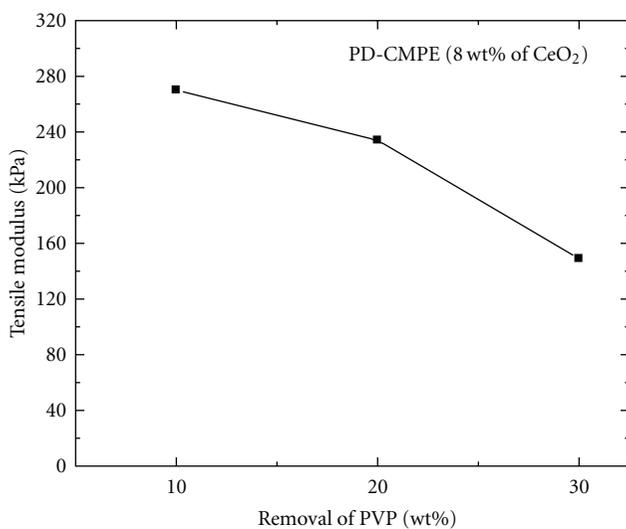
FIGURE 2: Solution leakage versus time of the polymer electrolyte (a) PICMs (b) PDCMs.

TABLE 3: Thermal and other physical properties of composite microporous membranes obtained by preferential polymer dissolution method (PDCMs).

Removal of PVP (wt%)	PDCM					
	T_m	ΔH_m	X_c (%)	ρ (%)	Electrolyte uptake (wt%)	Film strength
10	142.2	24.66	23.55	79	200	Good
20	142.2	24.58	23.47	85	216	Good
30	142.0	24.07	22.98	87	209	Moderate



(a)



(b)

FIGURE 3: Mechanical strength of (a) PICME (b) PDCME.

1(e) and 1(f) which results in fewer amounts of free liquid electrolyte stores in the composite membrane matrix and leads to decrease in ionic conductivity.

3.3. Mechanical Strength. Figure 3(a) shows the tensile strength of PICME as a function of filler content. Mechanical strength of the polymer electrolyte increased with filler

content. The reinforcement mechanism is attributed to the adhesion of inorganic filler to the macromolecular chain [35]. Tensile modulus values of the PICME samples enhanced from 184 kPa to 284 kPa (2 to 8 wt% CeO₂) followed by a small change in tensile modulus values 293 kPa for 10 wt% filler. Figure 3(b) shows the mechanical strength of PDCMEs. It indicates 10 and 20 wt% PVP extracted PDCME has a small loss in mechanical strength related to that of optimized PICME (8 wt% CeO₂), whereas in the case of 30 wt% PVP removed PDCME declined their mechanical strength (149 kPa) due to uneven macrovoids formation and phase separation.

3.4. Electrochemical Studies. The ionic conductivity of PICMEs increased linearly with 2–8 wt% of filler content and attained the maximum ionic conductivity of 2.5 mS·cm⁻¹ (Figure 4(a)). The enhancement of ionic conductivity would be expected due to CeO₂ which interacts with either or both the anion and cation thereby reducing the ion pairing and increases the number of charge carriers [30]. The addition of filler concentration diminish the conductivity, which implies that increased the dilution effect predominate and the conductivity decreases continuously [36]. From the DSC analysis it is found that the crystallinity was reduced due to enhanced polymer segmental motion and also lithium ion migration. Further, the PDCME has enhanced ionic conductivity value of 3.84 mS·cm⁻¹ (Figure 4(b)). It is suggested that PDCME obtained by the removal of 20 wt% of PVP has better performance for Li-ion batteries. In other words, Dey et al. [37] reported increase of amorphous region creates more free volume which enhances the motion of the ionic charge. The increase of conductivity up to 10 wt% ceria is due to Lewis acid-base interaction between filler and PEO. Generally, lithium ion migrates in two route: one route is move along the molecular chain of the polymer and other route is in the amorphous phase of polymer electrolyte [38], where former case is slow transport while the later case is fast. But in the case of PDCME, lithium ion migrates in three routes: one is moving on the microporous gel electrolyte medium, second one is amorphous phase of the polymer electrolyte and third one is filler acts as solid plasticizer to enhance the ion transport. Moreover, uniform microporous structure has enhanced the ionic conductivity.

The Arrhenius plot of Log σ versus 1000/T for the composite membrane electrolytes PICMEs and PDCMEs are shown in Figures 5(a) and 5(b). It is found that the PICME containing 8 wt% CeO₂ has higher ionic conductivity among the systems studied over the whole temperature range of 298–353 K. Moreover, the conductivity increased

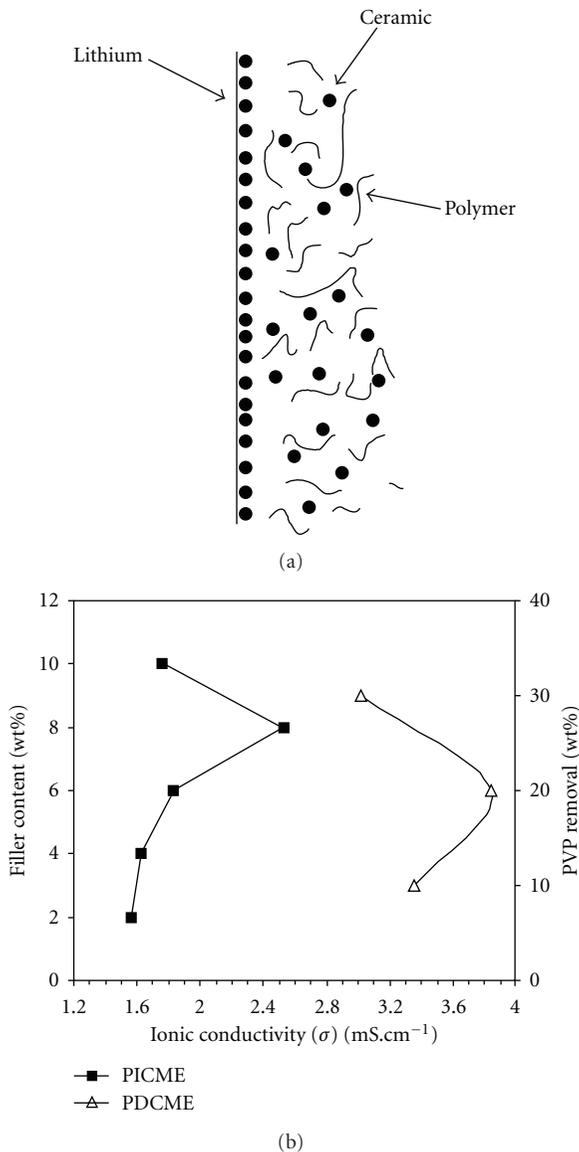


FIGURE 4: (a) The schematic representation of composite polymer electrolyte with the inert filler of nanosized particle (b) Ionic conductivity of (a) PICMEs and (b) PDCMEs at 25°C.

with increase of filler content up to 8 wt% CeO₂ and then decreases with further increase of filler content. In the case of PDCME found that the 20 wt% PVP extracted composite membrane electrolyte containing optimized filler content of 8 wt% CeO₂ has the higher conductivity among the systems studied. But 30 wt% PVP extracted PDCME showed low Log σ value with increase in temperature. It is attributed that the less solution uptake and the electrolyte solution may escape from the composite polymer matrix with increase in temperature. But, PDCME up to 20 wt% PVP extracted membrane was conformed that comparatively less electrolyte solution escape from the composite polymer matrix owing to the uniform microporous morphology.

The interfacial resistance as a function of time is shown in Figures 6(a) and 6(b) and their impedance values

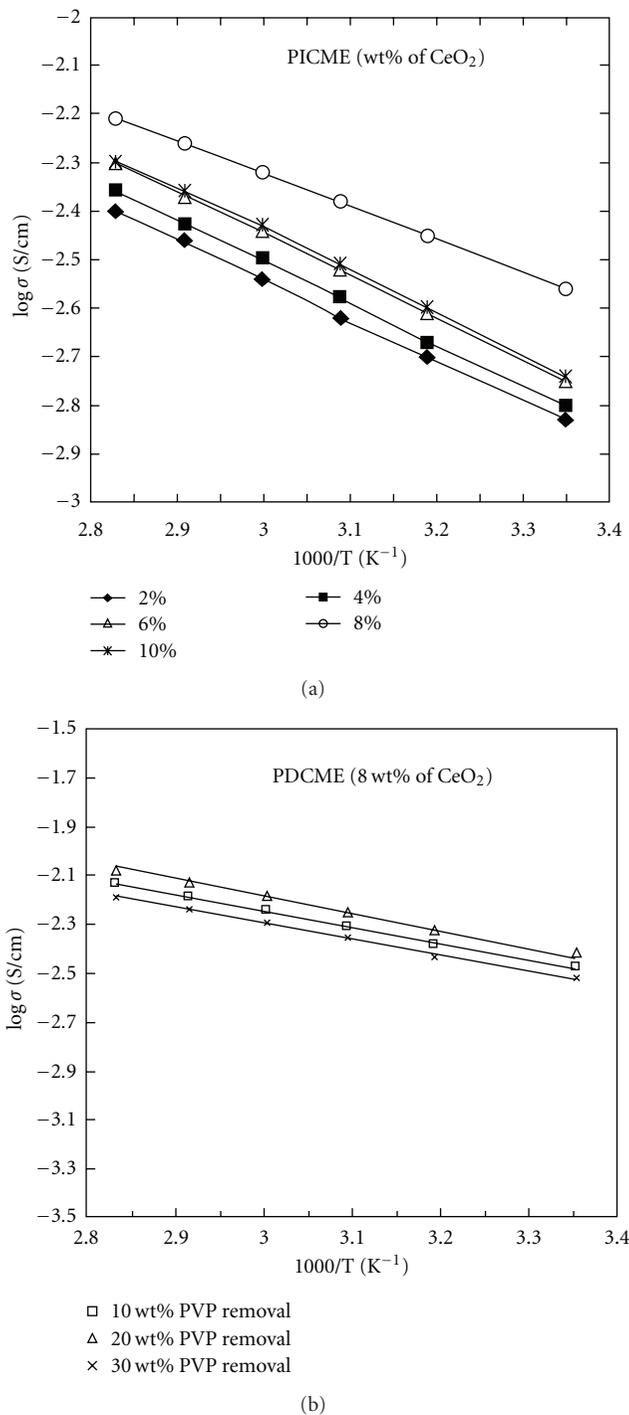


FIGURE 5: Arrhenius plot of (a) PICME with 8 wt% of CeO₂ and (b) PDCME with the removal of different wt% PVP.

were measured from Li/composite microporous membrane electrolyte/Li symmetrical cell kept at room temperature with different storage time. The interfacial resistance was increased gradually and declined with storage time for the PICMEs with 2–8 wt% CeO₂ contents and stabilized after 336 h (2week). It is attributed by assuming that initially slight

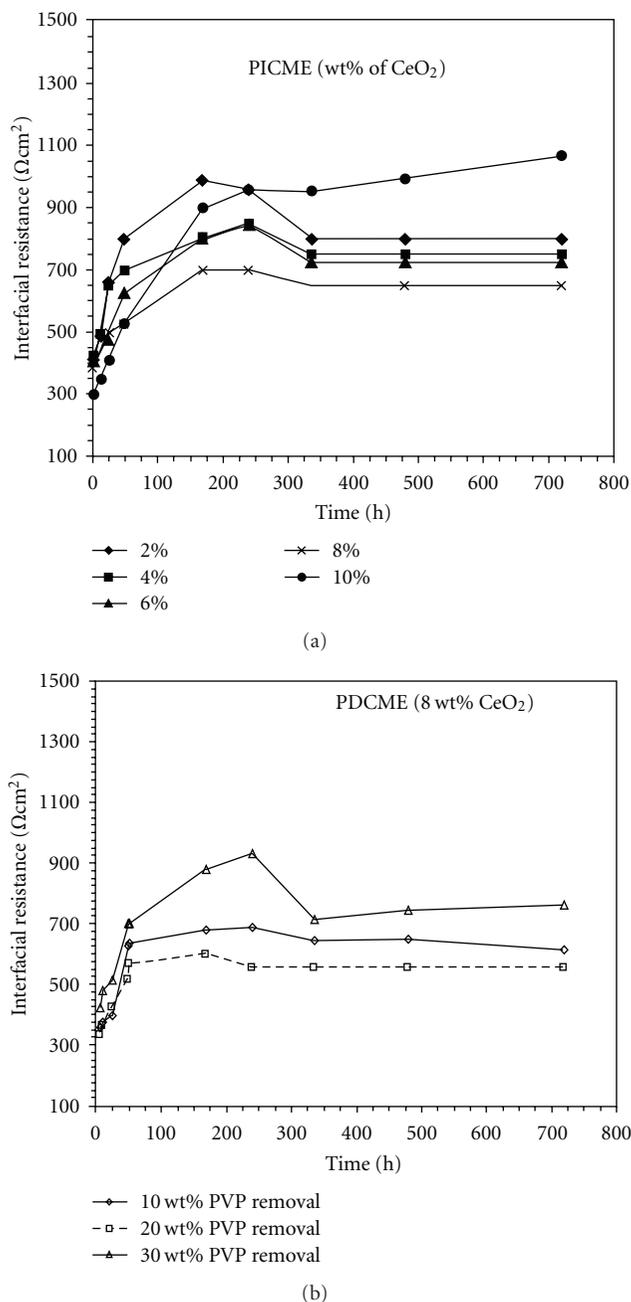


FIGURE 6: Interfacial resistance of the composite microporous membrane electrolyte (a) PICME and (b) PDCME.

passivation layer formed on the lithium metal electrode and the electrolyte solution exhibits more interfacial resistance.

Beyond 8 wt% CeO₂ filler content, the formation of insulating layer (passivation ceramic phase) was increased into the polymer matrix and also impede the electrode reaction. Generally, the higher interfacial resistance of the polymer electrolytes is based on the growth of passive layer on the lithium electrode surface and the degradation of physical contact between the polymer electrolyte and lithium electrode [12, 39]. At the higher filler content, initial interfacial resistance was declined and sharply increased

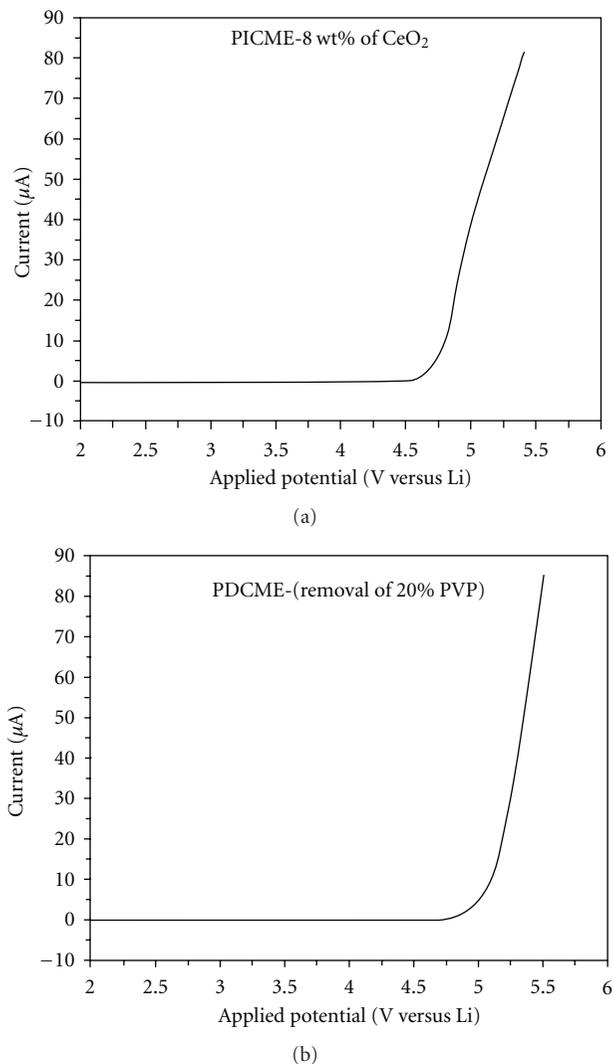


FIGURE 7: Linear sweep voltammetry of the polymer electrolyte (a) PICME and (b) PDCME.

with increasing time. This is due to the formation of thick passivation layer at the electrode surface is feasible at a higher volume fraction of a passive ceramic phase.

Figure 7 displays the current-voltage response by using SS (stainless steel) as a working electrode and lithium metal as a reference electrode measured between the potential ranges of 2.0 to 5.5 V at a scan rate of 1 mVs⁻¹. The onset current flow is associated with the decomposition voltage of the polymer electrolyte. In the decomposition of PDCME no electrochemical oxidation occurs when the voltage is below 4.9 V (versus Li/Li⁺) and the current sharply increases when the voltage is about 5 V (Figure 7(b)). Figure 7(a) shows the decomposition voltage of PICME is about 4.7 V (versus Li/Li⁺). Thus, the oxidation stability of the PDCME is suitable for high-voltage lithium-ion batteries.

A prototype MCMB/composite membrane electrolyte (PICME or PDCME)/LiCoO₂ coin type cell was fabricated to evaluate its cycling performance. LiCoO₂ is widely used

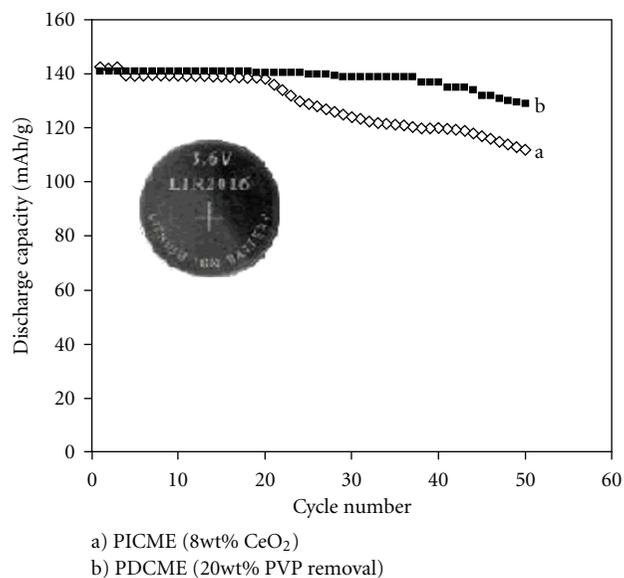


FIGURE 8: Discharge capacity as a function of cycle number for MCMB/electrolyte/LiCoO₂ cells at 25°C with discharge rate of C/2; (a) PICME and (b) PDCME.

as cathode material for conventional lithium ion batteries. The cell was subjected to cycle test with a cut off voltage of 4.2 V for the upper limit and 3.0 V for the lower limit. Figures 8(a) and 8(b) displays the curve of the discharge capacity versus cycle number. The cell with PICME has higher initial discharge capacity 142 mAh/g and declines faster during the cycling test (50th cycle, 18.4% capacity loss) when compared with PDCME (8% capacity loss) at the same cycle. The cell with PDCME delivered a discharge capacity of 141 mAh/g for the initial cycle at C/2 rate. The coulombic efficiency is more than 97% after 10 cycles, and the discharge capacity after 50th cycles is about 92% of its initial discharge capacity. Hence, PDCME showed relatively stable discharge properties, having little capacity fade under constant current and constant voltage conditions at the C/2 rate.

4. Conclusions

P(VdF-HFP)-CeO₂-based composite microporous membranes (PICM/PDCM) have been obtained by adapting conventional phase inversion (CPI) and preferential polymer dissolution (PD) methods. The higher solution uptake and porosity of preferential polymer dissolution composite membrane (PDCM) was achieved by extracting 20 wt% PVP from the composite matrixes and its corresponding PDCME has higher conductivity of 3.84 mS·cm⁻¹ at room temperature than PICME. These optimized PDCME exhibits stable interfacial resistance and provides better electrochemical stability window of 4.8 V with good cycling performance during the discharge at C/2 rate. These results confirmed that the PDCME is considered as the best candidate for the application of lithium-ion polymer batteries rather than PICME.

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