

Research Article

Investigation on Electrochemical Performance of New Flexible Nanocomposite Poly(Vinylidene Fluoride-co-Hexafluoropropylene) Polymer Electrolytes

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This research paper as an article investigates electrochemical performance of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) flexible nanocomposite polymer electrolytes which have been prepared successfully with incorporation of zinc oxide (ZnO) nanofiller. First, nanofillers are incorporated in a polymer matrix to form the flexible nanocomposite PVdF-co-HFP polymer membranes (PI-CMPM), and it is obtained by phase inversion technique. Contact angles of PI-CMPM have achieved a maximum of 136°. After this procedure, it has been activated by using a 1.0 M LiClO₄ containing of DMC/EC (1 : 1 v/v ratio) electrolyte solution to get flexible nanocomposite polymer electrolytes (PI-CMPE). The optimized PI-CMPM has increased the electrolyte uptake by 150%. It reaches the maximum ionic conductivity value of 2.47 × 10⁻³ S cm⁻¹ at room temperature. Optimized PI-CMPE achieved a maximum transference number of 0.61, which may be further evidence for the ability to fabricate high-performance lithium ion polymer batteries.

1. Introduction

Several research groups are working and putting a lot of effort to fabricate lithium ion batteries. These batteries are of great interest due to an increasing demand for safe, light-weight, high-energy density, geometry, no memory effect, high single cell voltage, and next-generation batteries [1]. Lithium ion- (Li⁺-) conducting polymer electrolytes are one of the key interests to enhance the performance of batteries. Lithium ion movements progress continuously in the polymer electrolyte/separator between anode and cathode electrodes during the charging and discharging process. In the 1970s, solid-state PEO with alkali metals salt polymer electrolytes have received huge consideration [2–4]. For the past few years, PVdF-co-HFP-based polymer electrolytes such as solid [5], gel [6], blended [7], porous [8], and composite [9] are prepared to meet the electrochemical performance in

lithium ion batteries. Gozdz et al. [10–13] established the process of a porous polymer membrane by the PVdF-co-HFP polymer, and the electrolyte has been commercialized in plastic lithium ion batteries (PLiON) by using Telcordia Technologies. However, the prepared polymer membranes have faced inconvenience due to extraction of dibutyl phthalate (DBP) which also increases the cost of preparation. The porous polymer membrane has been activated by the liquid electrolyte. In general, liquid electrolytes can be obtained by dissolving the organic plasticizers, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC), and propylene carbonate (PC), with lithium electrolyte salts. These electrolytes show high conductivity in the order of 10⁻³ S cm⁻¹. But for long time usage, the organic liquid electrolyte solvents (DMC/DEC/EC/PC) may escape from the polymer membrane electrolytes, which causes a fall in ionic conductivity, and it is possible to damage electrodes and

other components. To overcome this issue, additions of dry inorganic filler are used to enhance not only the structure but also the conductivity and stability of the polymer [14]. Nanocomposite polymer membrane electrolytes prepared by inclusion of inorganic nanofillers such as TiO₂ [15–17], Al₂O₃ [18], ZrO₂ [19], SiO₂ [20, 21], MgO [22], and CeO₂ [23] on the polymer matrix to enhance the electrolyte performance.

This research article attempted to investigate a PVdF-*co*-HFP-ZnO flexible nanocomposite polymer membrane by a phase inversion technique. The membrane has been activated by soaking in a lithium salt (LiClO₄-DMC+EC) electrolyte solution to obtain a flexible nanocomposite polymer electrolyte (PI-CMPE). Thus, finally, the physical as well as electrochemical properties of PI-CMPE have also been successfully investigated.

2. Experimental Details

2.1. Materials and Its Pretreatment. Poly(vinylidene fluoride-*co*-hexafluoropropylene) PVdF-*co*-HFP (M.wt > 500,000) and lithium perchlorate (LiClO₄) were purchased from Sigma-Aldrich, USA. The polymer has been dried at 100°C in a vacuum oven under 10⁻³ Torr pressure for 24 h. Lithium perchlorate salt was dried at 100°C under vacuum condition for 10 to 12 h. Dimethyl carbonate (DMC) and ethylene carbonate (EC) were purchased from Sigma-Aldrich, USA. Plasticizer was used without further purification. N-Methyl pyrrolidone (NMP) was brought from (E. Merck, Germany).

2.2. Preparation of Flexible Nanocomposite Polymer Membrane and Nanocomposite Polymer Electrolyte. Flexible nanocomposite polymer membranes (PI-CMPM) were obtained by dissolving a conceived amount of PVdF-*co*-HFP in N-methyl pyrrolidone with constant stirring to obtain a homogeneous viscous solution. Nanoscale zinc oxide (ZnO) (13 nm) filler [24] is added to form a flexible PVdF-*co*-HFP-ZnOx nanocomposite polymer membrane. Various samples with different weight percentages of zinc oxide (ZnO) (*x* = 2, 4, 6, 8, and 10 wt%) nanofiller were added to the slurry; it was agitated constantly for 24 h. The doctor blade method was applied for the nanocomposite viscous slurry which was spread over a glass plate to make the desired thickness. Various compositions of the nanocomposite porous PVdF-*co*-HFP polymer membrane obtained by phase inversion technique were described elsewhere [7, 23]. Thus, ZnO nanofillers resided in the PVdF-*co*-HFP matrix during the phase inversion technique to form a flexible nanocomposite PVdF-*co*-HFP polymer membrane (PI-CMPM). The resultant flexible membranes were dried up under vacuum pressure at 80°C for 6-8 h. Finally, a mechanically stable and solvent-free PI-CMPM membrane was obtained. It has a thickness ranging from 60 to 100 μm; the PI-CMPMs were soaked in a 1 M LiClO₄ containing of DMC/EC (1:1 (v/v)) electrolyte for less than 6 h to obtain their corresponding phase-inversed flexible nanocomposite polymer electrolytes (PI-CMPEs). The prepared membranes are optimized and the physical as well as electrochemical characteristics are thus investigated.

2.3. Characterization of Flexible PI-CMPM by FE-SEM Studies. FE-SEM studies were carried out by means of JEOL Field Emission Scanning Electron Microscopy (FE-SEM) with step-up voltage range of 20 kV to investigate the surface morphology of PI-CMPM.

2.4. Contact Angle Studies of PI-CMPM. Water contact angle measurements have been carried out by using the sessile drop in dynamic mode at ambient temperature in a DataPhysics OCA20 device using ultrapure water as the test liquid [25–27]. Three measurements have been done in each sample and were performed at different locations, and the average contact angles were determined.

2.5. Electrolyte Solution Uptake Studies. The electrolyte solution uptake of PI-CMPM was calculated with respect to immersion time in 1 M LiClO₄ containing of DMC/EC electrolyte for 6 h to obtain the corresponding flexible nanocomposite polymer electrolytes [23]. The electrolyte solution uptake by these membranes was calculated using the following equation:

$$\text{Electrolyte solution uptake wt (\%)} = \frac{(W_f - W_o)}{W_o} \times 100, \quad (1)$$

where W_f and W_o are the weight of the wet and dry flexible nanocomposite polymer membranes (PI-CMPM), respectively.

2.6. Electrolyte Solution Leakage Studies. The electrolyte solution leakages examined for these immersed flexible PI-CMPMs were checked out by placing the flexible PI-CMPE in between two filter papers and then squeezed by pressing with a 100 g poly(tetrafluoroethylene) sheet [22]. Changes in weight of the flexible PI-CMPM electrolytes were observed at every 10 min time interval and applied ~ 133.322 × 10⁻² Pa pressure. The electrolyte solution leakage of the flexible PI-CMPE was calculated using the below formula [23]:

$$\text{Electrolyte solution leakage wt (\%)} = \frac{(W_i - W_f)}{(W_i - W_o)} \times 100, \quad (2)$$

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

2.7. Ionic Conductivity Studies. The ionic conductivity of flexible PI-CMPEs was investigated by sandwiching the PI-CMPE in between two stainless steel nonblocking electrodes [22]. Conductivity measurements were carried out by using a Hioki LCR HiTESTER 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 PI-CMPMs was calculated using the conductivity equation [23]:

$$\sigma = \frac{t}{(A \times R_b)} \text{ S cm}^{-1}, \quad (3)$$

where σ is the ionic conductivity, t is the thickness of the PI-CMPE, and R_b and A are the bulk resistance and cross-sectional area of the flexible PI-CMPE, respectively.

2.8. Interfacial Stability Studies. The interfacial stability of the PI-CMPE was investigated by assembling the cell as Li/PI-CMPE/Li using an EG&G electrochemical analyzer over a frequency range of 10 Hz~100 kHz, with an amplitude of 10 mV, for different storage times. The electrochemical experiments were carried out under an inert argon gas atmosphere.

2.9. Study of Electrochemical Stability. The electrochemical stability window of PI-CMPE 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 mV s⁻¹.

3. Result and Discussion

3.1. Mechanical Strength. Tensile strength of the PI-CMPMs is measured by adding ZnO nanofiller content on a PVdF-co-HFP matrix as shown in Figure 1. Mechanical strength of the PI-CMPMs is enhanced gradually by ZnO nanofiller content. Mechanism strength of optimized PI-CMPM (6 wt% ZnO) is shown as 243 kPa. It is noted that it has increased gradually from 131 kPa to 281 kPa. The reinforcement mechanism is confirmed by the sticking of the nanofiller to the macromolecular chain [28].

3.2. Morphology Studies. Morphology of the PI-CMPMs was performed by making use of the FE-SEM technique, and images of both cross-section views are shown in Figures 2(a) and 2(b). It illustrates that the optimized 6 wt% nanofiller-added flexible PI-CMPM has a highly porous structure with well-distributed honeycomb-like morphology when it has an average diameter of around 4 μm generated from the phase inversion technique (Figure 2(a)). In particular, these pores are highly open, continuous, and interconnected in the membrane, which is favorable for constructing a continuous Li⁺ transport pathway [29]. Optimized fillers improve the pores and give smooth morphology [30]. In contrast, the 10 wt% nanofiller-added PI-CMPM exhibits randomly uneven-distributed porous morphology with the average diameter of around 20 μm (Figure 2(b)). In addition, the self-aggregation of polymers is observed at the 10 wt% nanofiller-added PI-CMPM, ensuring the diminished compatibility of the interface between the electrolyte and the electrode. The optimized nanofiller-flexible PI-CMPE is significantly beneficial for better solvent uptake and less solution leakage, subsequently enhancing the electrochemical performance in lithium ion batteries.

3.3. Contact Angle Studies of PI-CMPM. Figure 3 shows the water contact angle of PI-CMPM with various wt% of ZnO nanofillers. The water contact angle is typically used as an indicator of hydrophilicity of the membrane; the smaller the contact angle, the higher the hydrophilicity and vice versa [25, 26]. It is obviously observed that the PVdF-HFP (118°)

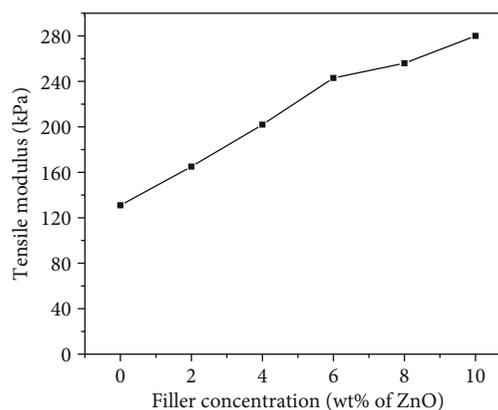


FIGURE 1: Mechanical strength of the flexible nanocomposite polymer membranes (PVdF-co-HFP+LiClO₄+ZnO) at room temperature with various wt% of ZnO (0, 2, 4, 6, 8, and 10 wt%).

membrane has a hydrophobic character. The water contact angle further increases with the increase of the ZnO nanofiller (134°) on the nanocomposite membrane. In agreement with the morphology results, PI-CMPM had excellent hydrophobicity with microporous morphology and also wettability in EC and DMC.

3.4. Studies of Electrolyte Solution Uptakes and Electrolyte Leakages. Figure 4(a) depicts the solution uptake of flexible nanocomposite polymer membranes. It is clearly seen that adding nanofiller on the PVdF-co-HFP polymer matrix has increased the solution uptake from 2 wt% to 6 wt%. Optimized (6 wt%) concentration of flexible PI-CMPM was found to have a high degree of solution uptake (210%) than the 8 wt% and 10 wt% filler concentration (Table 1). It indicates that higher electrolyte uptake was obtained at a better conductivity system saturated within 1 hr.

Figure 4(b) depicts the solution leakage of flexible PI-CMPE with respect to time. Electrolyte uptake decreases with the increase in nanofiller concentration > 6 wt% (Figure 4(b)); it agrees with the change in porosity [22]. The solution leakage also slightly varies with the nanofiller content and showed nearly the same change as in solution uptake studies.

As seen from the figure (Figure 4(b)), the optimized filler (6 wt% ZnO) concentration PI-CMPM was found to have less solution leakage of 28% even after 40 min. Pore size and its distribution were the vital factors of solution leakage. Hence, superior behavior of the polymer electrolytes exhibits a low solution leakage when compared with other electrolytes (>6 wt%).

3.5. Ionic Conductivity Studies. Ionic conductivity of the flexible PI-CMPEs was evaluated at ambient temperature by sandwiching between two stainless steel (SS) nonblocking electrodes, and the bulk resistance (R_b) was measured by using the LCR HiTESTER (AC-impedance analyzer). Nanofiller content up to 6 wt% gradually increases the ionic conductivity value to about 2.73 mS·cm⁻¹, higher than reported by Padmaraj et al. [30]. The improvement of ionic conductivity would be expected due to ZnO which interacts with both cations and anions thereby reducing the ion pairing and

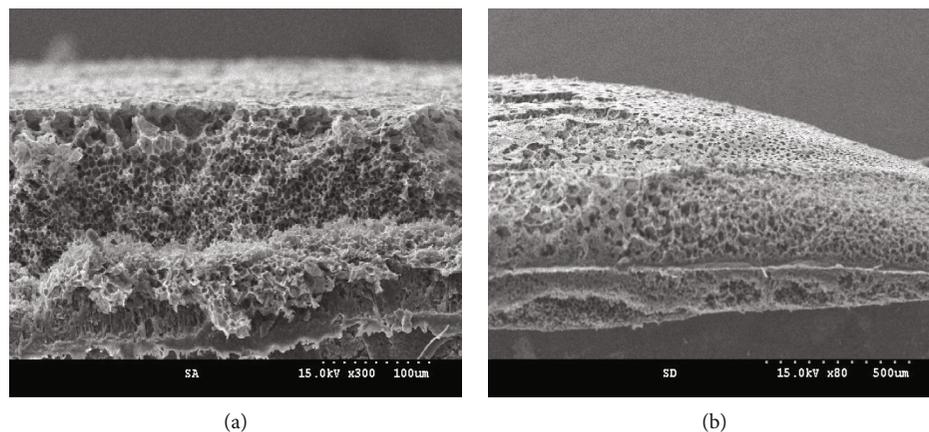


FIGURE 2: FE-SEM cross-section images. (a) PVdF-co-HFP nanocomposite polymer membranes with zinc oxide nanofillers ((a) 6 wt% and (b) 10 wt%).

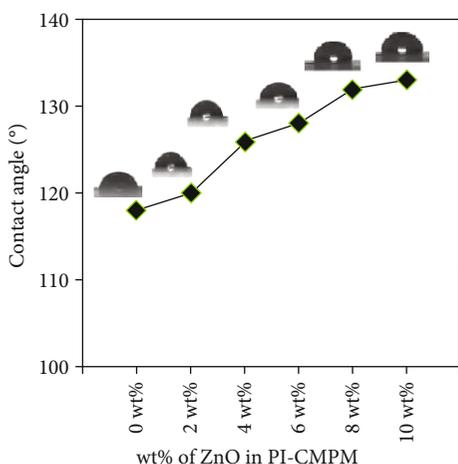


FIGURE 3: Contact angles of the PI-CMPM at room temperature.

increasing the number of charge carriers [23]. Further, addition of nanofiller content (8 wt%) decreased the ionic conductivity values and is shown in Figure 5(a). It indicates that at a higher concentration (>6 wt% ZnO), dilution effect predominates and ionic conductivity is decreased [31]. A similar result is also seen in the polymer electrolyte obtained by combining poly(ethylene oxide) with lithium salt and SnO₂ nanoparticles [32]. Figure 5(b) shows the schematic representation of lithium ion movement during the cell reaction and enhances the ionic conductivity during the electrochemical reaction.

3.6. Interfacial Stability Studies. Time dependence of the interfacial resistance was measured between the flexible PI-CMPE (PVdF-co-HFP+ZnO+LiClO₄ (DMC/EC) and lithium electrodes at room temperature using the impedance spectroscopy measurements. A cell was assembled for the impedance studies with a symmetrical Li/PI-CMPE/Li non-blocking cell at different storage times. It is evident from Figure 6 that interfacial resistance of optimized flexible PI-CMPE (6 wt% ZnO) increased from 355 to 847 Ω cm² with the storage time (720 h, i.e., 30days). However, interfacial

resistance between PI-CMPE (10 wt% ZnO) and the lithium electrode is higher than that of PI-CMPEs as shown in Figure 6 which may be due to changes in adhesion between polymer electrolytes and the lithium electrode [23].

A higher value of interfacial resistance in the PI-CMPE is due to growth of the passivation layer on the lithium electrode surface during the storage time which also indicates the degradation of physical contact between the lithium electrode and the electrolyte [33].

3.7. Transference Number. Figure 7 depicts the chronoamperometry profile for the better ionic conductivity system of the optimized flexible nanocomposite polymer (PVdF-co-HFP+6 wt% ZnO+LiClO₄ (DMC/EC)] electrolyte. From the figure, the initial current (I_0 , 39.9 μA) is measured, and it is monitored with respect to time (sec) until a steady state current is obtained, and the steady state current (I_s , 26.5 μA) is then measured after 3800 s with application of 10 mV DC polarization. This technique has proven to be applicable in circumstances where correction for the passivation layer is required [33]. The values of the lithium transference number for the PI-CMPE are summarized in Table 2. The lithium ion transference number of the PI-CMPE (optimized filler content) is achieved at a maximum of around 0.61, and its corresponding initial interfacial resistance and steady state interfacial resistance are determined by an AC-impedance analyzer before and after the chronoamperometry and are listed in Table 2. An increase in the interaction of the nanofiller and polymer and lithium salt electrolyte promoted a local relaxation and segmental motion. Thus, lithium ions migrated faster to form a favorable polymer network which in turn enhanced the mobility of lithium ions resulting in an increase of lithium ion transference number and also contributes to enhancement of ionic conductivity. Beyond this filler concentration in the polymer matrix, the transference number decreased due to accumulation of filler.

3.8. Electrochemical Stability Studies. Figure 8 shows the current-voltage response curve of the optimized flexible PI-CMPE. The potential is scanned between the ranges of 2.0 and 5.5 V vs. Li at the scan rate of 10 mV s⁻¹. The onset

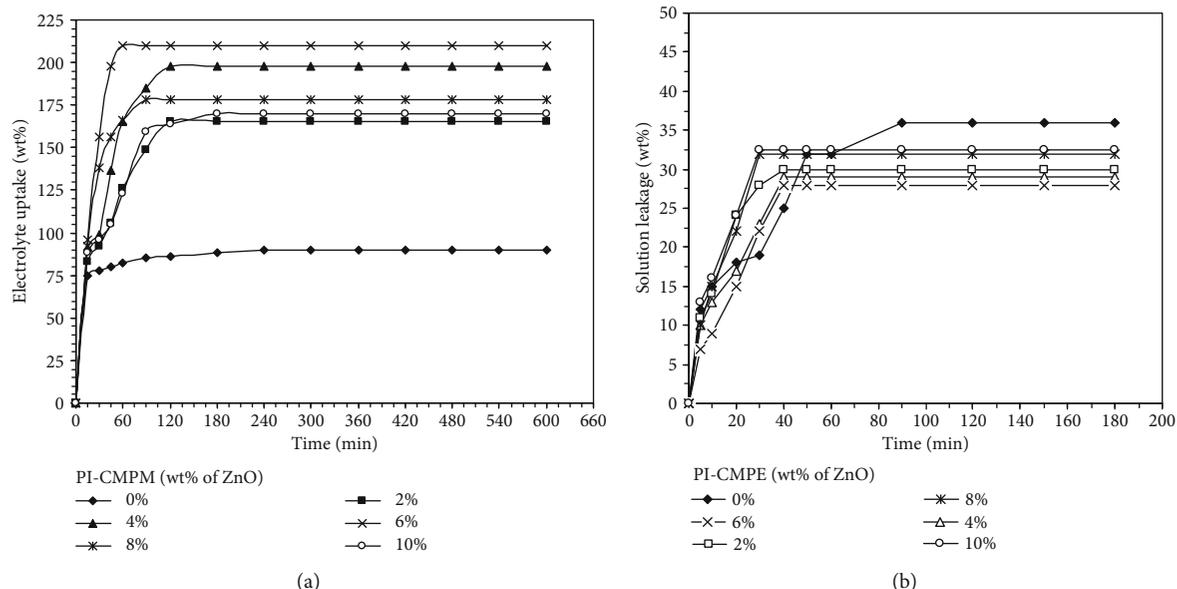


FIGURE 4: (a) Electrolyte uptake of flexible nanocomposite polymer membranes based on various wt% of ZnO (2, 4, 6, 8, and 10 wt%) on a PVdF-co-HFP matrix. (b) Solution leakage of the phase inversion nanocomposite polymer electrolytes (PVdF-co-HFP+LiClO₄+ZnO) at room temperature with various wt% of ZnO (0,2, 4, 6, 8, and 10 wt% nanofiller).

TABLE 1: Physical properties of PI-CMPM based on PVdF-co-HFP-ZnO.

S. no	ZnO (wt%)	Nanocomposite polymer membranes		
		Solution leakage (wt%)	Electrolyte uptake (wt%)	Film strength
1	0	37.2	90	Good
2	2	29.7	165	Excellent
3	4	29.1	198	Excellent
4	6	28.0	210	Excellent
5	8	32.6	178	Excellent
6	10	33.2	170	Good

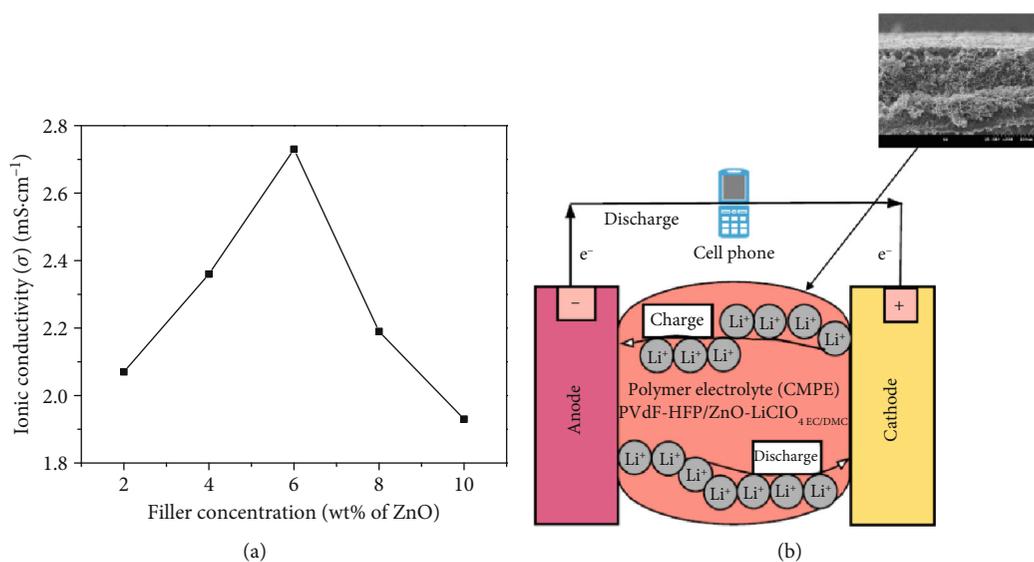


FIGURE 5: (a) Ionic conductivity of the PI-CMPEs at room temperature. (b) Schematic representation of a flexible nanocomposite polymer electrolyte in lithium ion polymer battery.

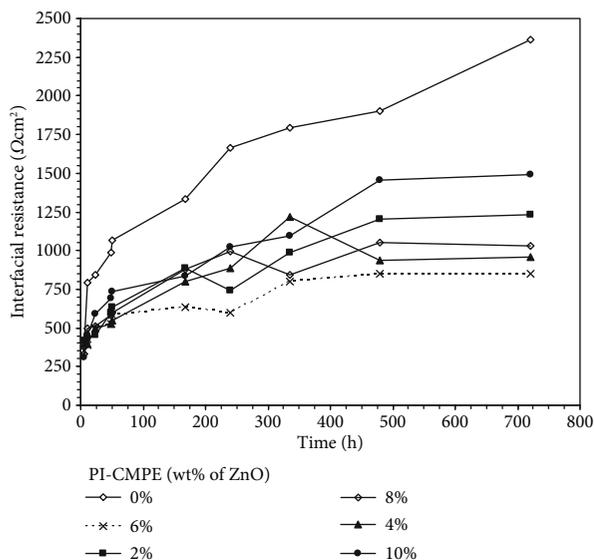


FIGURE 6: Interfacial resistance of PI-CMPEs.

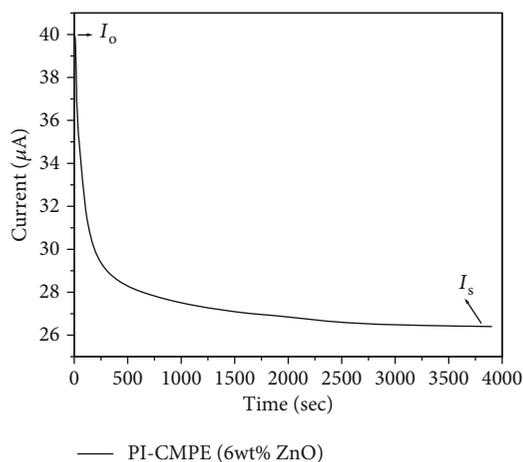


FIGURE 7: DC polarization curve of the optimum filler-filled PI-CMPE.

TABLE 2: Electrochemical properties of PI-CMPEs.

Filler content (wt%)	σ ($\text{mS}\cdot\text{cm}^{-1}$)	I_0 (μA)	I_s (μA)	R_0 (Ω)	R_s (Ω)	Time (sec)	T_+
0	1.27	42.3	26.7	258.93	497.86	5100	0.52
2	2.07	29.1	20.5	188.1	341.9	4000	0.55
4	2.36	33.7	24.3	181.5	324.0	3960	0.56
6	2.73	39.9	26.5	172.4	281.5	3800	0.61
8	2.19	50.2	20.6	153.5	289.9	3800	0.53
10	1.93	44.6	25.1	185.3	363.4	3800	0.51

current flow is associated with the decomposition voltage of the polymer electrolyte [34]. From the magnitude of the current response, the decomposition voltage is attained, high electrochemical oxidation does not occur when the voltage is below 4.6 V (vs. Li/Li⁺), and the current sharply increases

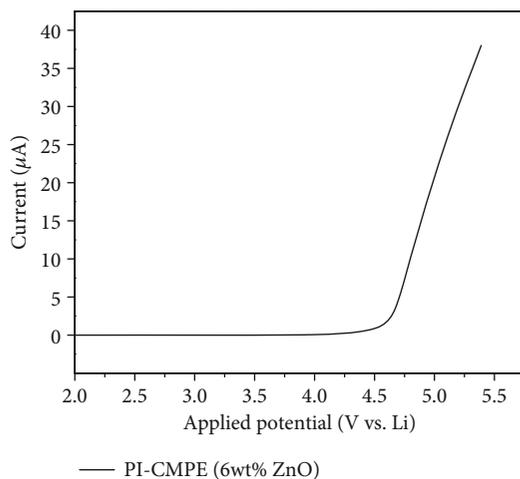


FIGURE 8: Linear sweep voltammetry of the PI-CMPE.

when the voltage is 4.7 V. The stability of the PI-CMPE is influenced partially by the weight percentage of the nanofiller content in the polymer electrolyte.

4. Conclusions

Flexible nanocomposite poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) polymer membranes (PI-CMPM) were prepared by phase inversion technique using N-methyl pyrrolidone as a solvent. Water contact angles of PI-CMPM have achieved a maximum of 136° to identify hydrophobicity. A flexible nanocomposite polymer electrolyte was obtained from their respective PI-CMPM when it was soaked in an electrolyte solution (1.0 M LiClO₄ containing of DMC/EC ($v/v = 1 : 1$)). The PI-CMPM mechanical strength has been increased up to 281 kPa. The optimized membrane increases the liquid electrolyte uptake of 150%. It may be further evidence that the prepared electrolyte is a good candidate to fabricate high performance lithium ion polymer batteries.

Data Availability

The data used to support the finding of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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