Improved ionic conductivity, potential window and dielectric strength in intercalated polymer nanocomposites

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Abstract. A nanocomposite solid polymer electrolyte has been synthesized using polyethylene oxide (PEO), sodium hexafluorophosphate ($NaPF_6$), and organomodified montmorillonite (DMMT) nano-clay, with an aim to improve the ionic conductivity, voltage stability window, transference number and dielectric properties. The DMMT intercalated PNCs exhibits an ionic conductivity of three order (~10^{-5} S cm^{-1}) higher as compared to the pure polymer (~10^{-8} S cm^{-1}). The DMMT based PNCs have ion transference number close to unity (0.99) and wide voltage stability window (~ 5 V). The dielectric constant and dc conductivity increases with nanoclay addition. The relaxation peak in loss tangent plot shift toward high frequency on nanoclay addition and indicates the decrease of relaxation time. The evaluated relaxation time $\tau_{\varepsilon'}, \tau_{tan\,\delta}, \tau_h, \tau_m$ are in good correlation with each other and exhibits minima for the nanoclay based PNCs which infers the faster segmental motion of polymer chain and supports the enhanced ionic conductivity.

INTRODUCTION

Development of the suitable source of energy that can replace the traditional sources has grabbed the attention of the researchers all over the world. Among energy storage devices, the battery is the suitable alternative source of energy. As electrolyte is the main component of the battery and is sandwiched between the electrodes. It must have good compatibility with both electrodes [1-2]. The present batteries are based on liquid or gel electrolyte that limits its operating range and faces many safety issues. To overcome the above issues, the solid polymer electrolyte (SPE) are suitable which comprise of a polymer host matrix with a salt dissolved in it. The ion migration in the polymer matrix is via the amorphous content. The SPE has low ionic conductivity due to crystalline nature. To increase the conductivity reduction of the crystallinity is the crucial approach. A number of strategies are adopted to reduce the crystallinity, (i) incorporation of plasticizer, (ii) dispersion of nanofiller, and (iii) addition of nanoclay [3]. The first two also improves the ionic conductivity, but ion pair formation issue still remains there. Therefore, the last one strategy is completely effective in order to suppress the ion pair formation. The nanoclay galleries accommodate the polymer chains inside them and anion stays outside the clay galleries, which favors the smoother cation migration. In intercalated polymer nanocomposites, the cation charge on the clay platelets acts as Lewis acid sites and compete with the cation to form complexation with a polymer chain. This enhances the clay gallery spacing and promotes cation migration as well as improves salt dissociation [4]. PEO is an attractive host polymer and is chosen due to the presence of electron donor ether group $(-\ddot{O}-)$ in polymer backbone, high value of dielectric constant (~4-5) and complexation ability with many salts. $NaPF_6$ shows superior properties than other sodium salt [5]. In the present paper, an attempt has been made to synthesize the polymer nanocomposite comprising of PEO as host polymer, $NaPF_6$ as salt and modified montmorillonite (DMMT) nano-clay. The effect of DMMT has been investigated on the ionic conductivity, voltage stability window, ion transference number, dielectric constant, loss tangent, ac conductivity and relaxation time ($\tau_{\varepsilon'}, \tau_{\tan\delta}, \tau_h, \tau_m$).

MATERIALS AND METHODOLOGY

All the polymer nanocomposites were prepared via the standard solution cast technique using polyethylene oxide (PEO; Aldrich MW 6×10^5 g/mol), as a host polymer, $NaPF_6$ (Aldrich) as salt and dodecyl-modified montmorillonite

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(DMMT) as nano-clay. The details of sample preparation and characterizations have been reported elsewhere [6]. The ionic conductivity was measured by impedance spectroscopy (IS; CHI760) in the frequency range of 1 Hz to 1 MHz with an ac signal of 10 mV across the cell SS|PNC|SS, where SS represents stainless steel blocking electrodes. The total ionic transference number (t_{ion}) was obtained by placing PNC film between stainless steel (SS) blocking electrodes and a fixed dc voltage of 10 mV was applied across the SS|SPE|SS cell using i-t technique. The voltage stability window of the PNC is measured by the linear sweep voltammetry technique. Then the impedance data is transformed into the dielectric constant, loss tangent, and complex conductivity. All plots were fitted with corresponding equations by Origin® 8 software to evaluate the relaxation time ($\tau_{\varepsilon'}, \tau_{\tan\delta}, \tau_h, \tau_m$). The equations used for fitting are reported somewhere in detail [6, 7].

RESULT AND DISCUSSIONS

IMPEDANCE SPECTROSCOPY ANALYSIS

Figure 1 shows the Nyquist plot of the prepared samples. It comprises of a semicircle at high frequency followed by a tilted spike at low frequency. The semicircle infers the bulk property (conduction due to ions only and immobilized polymer chains) of polymer nanocomposite while low-frequency spike is associated with double layer capacitance ate electrode-electrolyte interface [8-9]. The Nyquist plot was fitted by an equivalent circuit and comprise of a constant phase element (Q_1) in series with a parallel combination of another constant phase element (Q_2) and a resistor. The bulk resistance (R_b) is obtained from the intersection of semicircle at low frequency on the x-axis (shown by the arrow). The bulk resistance decreases with the addition of DMMT. Comparatively, DMMT based PNC demonstrates improved ionic conductivity (2.31×10^{-5} S cm^{-1}) and is three orders higher than pure PEO (figure 1 b). The increase in the conductivity is due to increased polymer flexibility, large free volume and enhanced amorphous content [10].

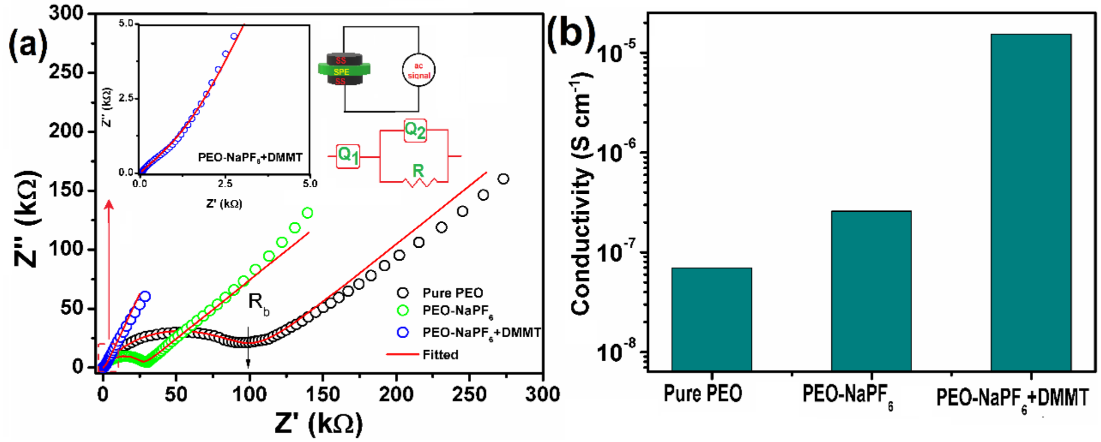

FIGURE 1: (a) Nyquist plot, and (b) conductivity variation for the various polymer nanocomposites.

ION TRANSFERENCE NUMBER AND LINEAR SWEEP VOLTAMMETRY MEASUREMENT

Figure 2 b & c shows the ion transference number measurement for the polymer salt system and DMMT based system respectively. The initial current ($i_{total=}$ i_{ionic}+ $i_{electronic}$) is due to ionic and electronic charge carriers and saturated current with time ascribed to the electronic current ($i_{electronic}$) only [5, 11]. It is observed that the ion transference number is close to unity and is higher for DMMT based PNC. This increase may be due to the interaction of ether group of PEO with Lewis acid sites of DMMT that enhances number of free charge carriers [12]. Figure 2 c shows the electrochemical stability window (ESW) of the DMMT based PNC. The voltage stability window is between -2.2 V to 2.9 V (~5 V) and is sufficient working voltage for battery applications. Beyond this voltage abrupt increase in current is associated with the breakdown of the electrolyte.

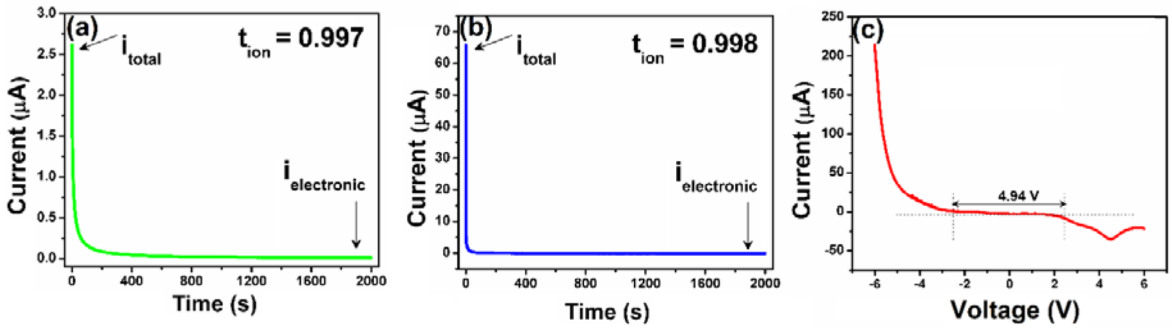

FIGURE 2: Ion transference number measurement for (a) polymer salt, (b) PEO-NaPF$_6$-DMMT, and (c) linear sweep voltammetry measurement of PEO-NaPF$_6$-DMMT polymer nanocomposite.

DIELECTRIC CONSTANT AND LOSS TANGENT ANALYSIS

Figure 3 a shows the variation of dielectric constant against the frequency for pure PEO, polymer salt and polymer salt+ DMMT nanocomposite. All the samples show the high value of dielectric constant at low frequency and are attributed to the localization of charge carriers and consequent charge accumulation at electrode/electrolyte interface. While a decrease of dielectric constant at high frequency is owing to the periodic reversal of applied field [13]. It is important to note that the dielectric constant increases at all frequencies on the addition of DMMT in polymer salt matrix and infers the enhanced polymer flexibility along with better salt dissociation. The solid line is the fitted plot and is in good agreement with a slight deviation at high frequency which is due to the dominance of the dielectric relaxation. The fitted parameters are summarized in Table 1. The increased dielectric strength and lowering of relaxation time is observed. The former one indicates the increased number of charge carriers and later one indicates the enhanced cation migration [14].

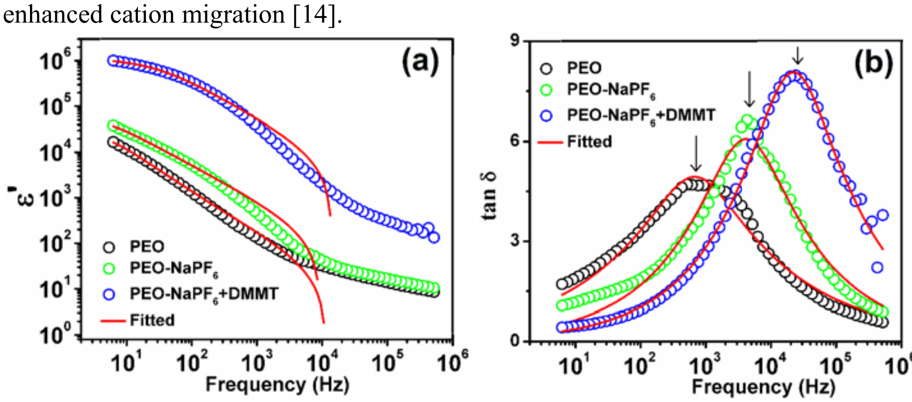

FIGURE 3: Plot of (a) dielectric constant, and (b) loss tangent against frequency for various polymer nanocomposites.

Figure 3 b shows the variation of the loss tangent against the frequency (@RT). The occurrence of loss peak at a particular frequency indicates the presence of relaxation. It may be observed that with the addition of salt peak shifts toward the high-frequency side, followed by a further increase with the addition of DMMT. This peak shift toward the high-frequency side indicates the decrease of relaxation time, reduction of crystallinity and supports the conductivity value. Also, the highest area under the loss tangent curve for the DMMT based PNC is observed, which indicates the highest ionic conductivity and is in good agreement with impedance study.

AC CONDUCTIVITY ANALYSIS AND RELAXATION TIME PLOT

Figure 4 a shows the variation of the σ_{ac} with frequency. It shows three characteristic regions, (i) low frequency electrode polarization region due to formation of space-charge layer, (ii) frequency independent plateau region at intermediate frequency associated with long-range ion migration (ascribed to the dc conductivity), and (iii) high frequency dispersion region associated with short-range ion migration or dipolar relaxation Addition of salt and DMMT shifts the plot toward +ve y-axis and confirms the enhancement in the dc conductivity (dotted line intercept at intermediate frequency) when compared with polymer-salt matrix. The dispersive region also shifts toward the high frequency on clay addition [6, 7]. This suggests that the DMMT plays an effective role in enhancing the dc conductivity and is attributed to the increased amorphous content. The solid red line is the fitted plot and is in absolute agreement to the experimental data in whole frequency.

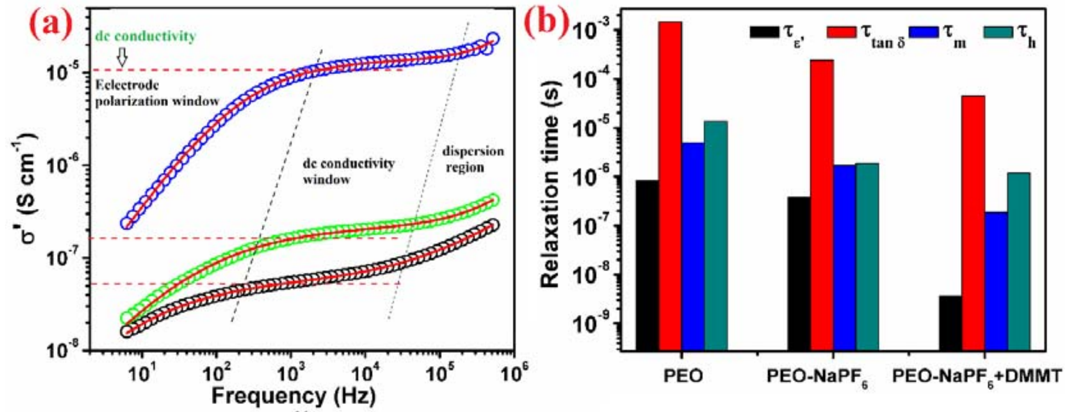

FIGURE 4: (a) Frequency-dependent real part of complex conductivity, and (b) variation of various relaxation time for polymer nanocomposites

The fitted parameters are summarized in Table 1 and value of exponent is less than unity. The dc conductivity obtained from the $\sigma\ vs.\ \omega$ plot matches with the bulk conductivity obtained from impedance study (Table 1).

Table 1. Relaxation time, conductivity and ion transference number for prepared polymer nanocomposites.

Sample Code	**Relaxation time**				**Conductivity (S cm-1)**		t_{ion}	C_{dl}
	$\tau_{\varepsilon'}$(ns)	$\tau_{\tan\delta}$ (ms)	τ_h (μs)	τ_m(μs)	bulk	dc	-	
PEO	828	1.48	13.3	4.94	6.97×10^{-8}	5.81×10^{-8}		0.02
PEO-$NaPF_6$	382	0.24	1.88	1.69	2.59×10^{-7}	2.21×10^{-7}	0.997	0.03
PEO-$NaPF_6$-DMMT	3.72	0.04	1.18	1.18	1.53×10^{-5}	1.42×10^{-5}	0.998	0.65

Figure 4 b shows the variation of relaxation time $\tau_{\varepsilon'}, \tau_{\tan\delta}, \tau_h, \tau_m$ for different system (Table 1). It may be noted that addition of DMMT lowers the relaxation time as compared the polymer salt matrix. It indicates the enhanced ion dynamics and is attributed to the faster polymer chain segmental motion due to disorder in polymer chthe ain. As clay galleries allows polymer chains to intercalate while blocks the anion that makes easier cation migration and hence the conductivity. The lowering of the relaxation time promotes fast ion migration, hence conductivity.

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REFERENCES

1. A. Bauer, J. Song, S. Vail, W. Pan, J. Barker, Y. Lu, Advanced Energy Materials, 1702869 (2018).
2. J. Kim, J. Lee, J. You, M. S. Park, Y. Yamauchi, J. H. Kim, Materials Horizons, **3**, 517-535 (2016).
3. A. Arya, A. L. Sharma, Ionics, **23**, 497-540 (2017).
4. Y. Ma, L. B. Li, G. X. Gao, X. Y. Yang, Y. You, Electrochimica Acta, **187**, 535-542 (2016).
5. A. Arya, A. L. Sharma, Journal of Solid State Electrochemistry, **1-21** (2018).
6. A. Arya and A. L. Sharma, Journal of Physics: Condensed Matter **30**, 165402 (2018)
7. A. Roy, B. Dutta, S. Bhattacharya, RSC Advances **6**, 65434-65442 (2016).
8. W. Liu, N. Liu, J. Sun, P. C. Hsu, Y. Li, H. W. Lee, Y. Cui, Nano Letters, **15**, 2740-2745 (2015).
9. A. Rai, A. L. Sharma, A. K. Thakur, Solid State Ionics, **262**, 230-233 (2014).
10. A. Arya, A. L. Sharma, Journal of Physics D: Applied Physics, **50**, 443002 (2017).
11. A. Das, A. K. Thakur, K. Kumar, Ionics, **19**,1811-1823 (2013).
12. Y. Zhang, Y. Zhao, D. Gosselink, P. Chen, Ionics, **21**, 381-385 (2015).
13. A. Arya, S. Sharma, A. L. Sharma, D. Kumar, M. Sadiq, Asian J Eng Appl Technol **5**, 4-7 (2016).
14. A. Arya, M. Sadiq, A. L. Sharma, Ionics, **24**, 2295-2319 (2018).