Investigations on Poly (ethylene oxide) (PEO) – blend based solid polymer electrolytes for sodium ion batteries

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Abstract. Polymer blend electrolytes based on Polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP), complexed with NaIO4 salt and Graphene oxide (GO) are investigated in the present report. The electrolytes are prepared by a facile solution cast technique. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) are employed to study the influence of ion–polymer interactions on the micro structural properties of blend electrolytes. Measurements of electrical conductivity of the blend polymer complexes have been performed by using complex impedance spectroscopy in the frequency range 1 Hz - 1 MHz and within the temperature range 303 K – 343 K. A study on electrical conductivity properties of GO doped ‘salt complexed electrolyte’ systems is presented.

1. Introduction
Solid-state polymer electrolytes (SPEs) have attracted great attention by the researchers in the field of rechargeable metal-ion battery applications, to overcome a great deal of drawbacks of conventional liquid electrolytes especially related to safety issues originating from their high volatility and flammability [1]. Currently, Li – ion battery technology has been widely employed in energy supply & storage systems due to their high energy density values compared to all other battery chemistries. However, the high cost, decrease of abundance, environmental impact and safety limitations concerning to Lithium materials impede their widespread implementation in future battery technologies [2]. Therefore, there is urgent necessity to search for alternative energy storage system technology capable of complementing the Li-ion battery technology. Amongst the accessible battery chemistries, sodium (Na) based rechargeable batteries (SIBs) have recently captured much attention because they are environmentally friendly, non-toxic, low cost and earth abundant materials.
Substantial research, development, and demonstration efforts are currently in progress to replicate the performance of well-established Li-ion batteries with sodium ion batteries [3].

Polyethylene oxide-based polymer electrolytes have been employed extensively for battery applications since Armand et al. have demonstrated the feasibility of using PEO as a potential ion conductive electrolyte [4]. PEO is one of the widely investigated host polymer for synthesizing solid polymer electrolytes (SPEs) for alkali metal ion-conducting batteries due to its high electrochemical stability, good solvation power, complexation and ion dissociation abilities. Several researchers have reported about various sodium salts complexed PEO based polymer electrolytes for sodium ion battery applications [5]. It is worth to mention that, below the melting temperature (≈ 330 K) pure PEO electrolytes consist of both semi-crystalline and amorphous regions, as well as intermediate regions at the crystalline/amorphous interphase. The semi-crystalline nature of PEO leads to both amorphous and crystalline phases at room temperature, which subsequently limits its ionic conductivity [6]. The suppression in the degree of crystallinity of the polymer chains improves their mobility, thereby leading to better ionic conduction. Therefore, ionic hopping is believed to be predominant in amorphous rich PEO based electrolytes [7]. The most straightforward approach to overcome this problem is to modify the PEO matrix in order to decrease its degree of crystallinity. One of the most promising alternate choices of enhancing the amorphous phase in PEO based electrolyte systems is blending of PEO with suitable higher amorphous polymer. Polyanion pyrrolidone (PVP) has been identified as a compatible partner to PEO which exhibits higher order amorphosity. PVP demonstrates high glass transition temperature, mechanical and thermal stabilities, provided the carbonyl group (C = O) in PVP enables to form different complexes of alkali metal ion salts at wide range of concentrations. In particular, reinforcement of nanometer sized materials with polymer electrolyte systems can modify their microstructural properties and enhance their electrochemical performances [8].

Blending of PEO based polymer electrolytes with nano dimensional carbon materials is a novel perspective approach to improve their electrochemical applications, especially for secondary batteries, ionic conductors, and supercapacitors energy storage systems. Graphene oxide (GO) has been recognized as one of the unique carbon materials because of its multiple oxygen-containing functional groups, which could enable it to be well dispersed in polar solvents and can improve the mobility of the mobile ions and lead to the improvement of the ion conductions in polymer electrolyte systems [9]. In the present report, authors described about preparation of graphene oxide (GO) doped PEO/PVP blend system complexed with sodium periodate (NaIO₄) salt by using solution casting technique and discussed about microstructural and conductivity properties of prepared electrolytes.

2. Experimental
PEO of molecular weight 5 × 10⁶ and PVP of molecular weight 3.6 × 10⁵ were procured from Aldrich and employed without any further purification to prepare PEO/PVP solid state blend electrolytes. Sodium periodate salt (NaIO₄, Sigma Aldrich) and graphene oxide (GO of 2 mg/mL, dispersion in H₂O, Sigma Aldrich) were used as dopants and methanol (Aldrich) was used as a solvent. PEO/PVP blend electrolyte films of thickness 150 μm were prepared by following conventional solution cast technique. Appropriate amounts of PEO and PVP polymers were dissolved in methanol solution and followed mechanical stirring at room temperature for 10 hours to get uniformity & miscibility of the polymers. In the meanwhile, different weight percentages (wt%) NaIO₄ salts were dissolved separately in methanol solution and added to pre-prepared viscous PEO/PVP polymer solutions to obtain NaIO₄ salt complexed ‘PEO/PVP/NaIO₄ (x%)’ (x% = 0, 5, 7.5, 10) polymer electrolytes. To study the influence of graphene oxide, GO solution was sonicated for 15 minutes and added appropriate amount to ‘PEO/PVP/NaIO₄ (10 wt%)’ electrolyte solution to prepare ‘PEO/PVP/NaIO₄(10 wt%)/GO(0.4 wt%)’ electrolytes. To harvest free-standing polymer electrolyte films, obtained viscous solutions were poured into polypropylene dishes and the solvent (methanol) was allowed to evaporate slowly at room temperature. All electrolyte films were vacuum dried at 45°C to remove traces of methanol.
solvent and kept in desiccators filled with silica gel desiccants for several hours before being characterized to avoid any traces of moisture.

The structural properties of blend electrolytes were analysed by recording X-ray diffraction patterns in the 2θ range of 10° – 80° with a constant step 0.02°, counting time 35s/step on a Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. To understand complexation of additives with the host polymer blend, FTIR measurements were carried out in nitrogen atmosphere to record transmittance spectra in the wavenumber range of 400–4000 cm⁻¹ and with an optical resolution of 2 cm⁻¹ using ‘Bruker, model Vertex 70’ spectrometer. Scanning electron microscopy (Philips 515 digitalized)measurements were performed to understand the modifications in surface morphological features of blend electrolytes as a function of complexation NaIO₄ salt and doping of GO. Ionic conductivity measurements were carried out by a. c. impedance measurements using Biologic potentiostat/galvanostat (SP – 200) from room temperature to 343 K in the frequency range of 1 Hz to 1 MHz. During the measurements, electrolyte films were sandwiched between two copper electrodes which were assembled in a temperature controlled furnace.

3. Results and Discussion

3.1. Microstructural properties

![Figure 1](image_url)

**Figure 1.** XRD spectra for pure, NaIO₄ complexed and GO doped PEO/PVP blend electrolytes: (a) PEO/PVP pure blend, (b) PEO/PVP/NaIO₄ (5 wt%), (c) PEO/PVP/NaIO₄ (7.5wt%), (d) PEO/PVP/NaIO₄ (10wt%), (e) PEO/PVP/NaIO₄ (10 wt%)/GO(0.4 wt%).

Figure 1 represents XRD patterns of pure blend (PEO/PVP) and its complexes with NaIO₄ salt at different concentrations and GO (0.4 wt%) doped ‘PEO/PVP/NaIO₄ (10 wt%)’ blend electrolytes. The diffraction pattern of pure blend (PEO/PVP) displays intensity diffraction peaks at 2θ =19.3° and 2θ =23.4° (figure 1(a)) corresponding to characteristic crystalline peaks of PEO, which originates from
the ordering of polyether side chains and strong intermolecular interaction between PEO chains through the hydrogen bonding [10]. The gradual decrease in intensity and increase of breadthness of the diffraction peaks as a function of complexation of NaIO₄ salt (figure 1(b) – (d)), reveal the decline in crystalline nature of blend electrolytes. This could be due to strong interaction of dissolved NaIO₄ salt with host polymer matrix and intermolecular interaction among the polymer chains of blend electrolytes, which lead to increase of amorphous phase in polymer blend electrolytes. It is note that (as evidenced from figure 1e) the intensity of characteristic XRD peaks corresponding to PEO further decreased by doping of 0.4 wt% of GO to PEO/PVP/NaIO₄(10 wt%) electrolyte system. This evidences for further increase of amorphous portion in salt complexed electrolytes by the addition of GO, which favors for enhancement of mobility of the mobile charge ions in the polymer electrolytes and leads to an increase in the ionic conductivity [11].

**Figure 2.** FTIR spectra for pure, NaIO₄ complexed and GO doped PEO/PVP blend electrolytes.

FTIR measurements are carried out for salt complexed and GO doped polymer blend electrolytes (as shown in figure 2) to understand their complexation properties such as ion–polymer interactions, intermolecular interactions, and their miscibility. The lower wavenumber region of 800 cm⁻¹ – 1000 cm⁻¹ provides information about modifications in local structure of host polymer due to the interaction of the salt with polymer backbone. The vibrational modes present at 845 cm⁻¹ and 947 cm⁻¹ are accountable for CH₂ rocking motion with a little C–O stretching motion and C–O stretching motion with some contribution from CH₂ rocking motions, respectively (figure 2(a)). The intensities of two characteristic bands at 845 cm⁻¹ and 947 cm⁻¹ are associated to helical structure of PEO [12]. Considerable decrease in intensity of bands at 845 cm⁻¹ and 947 cm⁻¹ evidences for distortion in helical configuration of backbone of PEO polymer as a function of salt complexation. It gives the information of decrease in crystallinity and miscibility of ions with matrix of PEO/PVP blend. The small band present at 1350 cm⁻¹ signifies the amorphous portion in PEO matrix, whose intensity increased with
the increase of salt concentration. It evidences for increase of amorphous portion in the matrix of PEO polymer. In the FTIR spectra, the presence of all allowed vibrational modes and co-existence of well resolved respective band positions corresponding to ether oxygen groups (C–O–C) of PEO and carbonyl groups (C=O) of PVP are in congruent with previous reports in the literature and confirm the presence of PEO, PVP and their miscibility in resultant blend electrolyte films [13-15]. FTIR spectrum for GO doped ‘PEO/PVP/NaIO₄ (10 wt%)’ blend electrolyte film (figure 2(d)) displays a broad absorption band at around 3300 cm⁻¹ due to typical carbonyl or carboxyl groups present in the GO structure [16]. As evidenced SEM studies, the surface of pure blend electrolyte (figure 3(a)) is observed to be relatively rough and composed with micro-void and cracks, which signifies the crystalline nature. The formation of micro-voids over surfaces films is due to rapid evaporation of the solvent during the preparation of polymer blends.

Figure 3. SEM images for NaIO₄ salt complexed and GO doped PEO/PVP electrolytes: (a) PEO/PVP blend, (b) PEO/PVP/NaIO₄ (10 wt%), (c) PEO/PVP/NaIO₄ (10 wt%)/GO (0.4 wt %)

Apparently, surfaces of the blend electrolyte films become smooth upon increasing of complexing salt concentration as shown in figure 3b. This indicates the increase in percentage of amorphous portion in the matrix of blend electrolytes due to random distribution and dissociation of salt. Significantly, the GO doped salt complexed polymer electrolytes demonstrated relatively smoother surface topology (figure 3(d)), it can be attributed to enhanced portion of amorphous region in the matrix of resultant salt complexed blend electrolyte due to addition of Graphene Oxide.

3.2. Conductivity studies
Figure 4 shows Nyquist plots at room temperature for PEO/PVP polymer blend electrolytes complexed with NaIO₄ salt at various concentrations. In the plots, presence of depressed semicircles indicates non Debye nature of the polymer electrolytes and each semicircle represents the bulk resistance (Rₜ) of the respective electrolyte [17]. Nyquist plots are fitted with semicircle and the respective bulk resistance (Rₜ) of each polymer electrolyte is estimated from the point of intersection of higher end of semicircle with the real (Z’ = Rₜ) axis [18]. The ionic conductivity (σ) of electrolyte films is estimated from following equation.

$$\sigma = \left( \frac{t}{R_p \times A} \right)$$  

where t and A represent thickness and area of the polymer electrolyte, respectively. The estimated room temperature conductivity of pure PEO/PVP blend electrolyte is 2.24 X 10⁻⁹ S/cm and found to be increased to 1.57 X 10⁻⁷ S/cm as a result of increase in salt concentration to 10 wt%.
Figure 4. Nyquist plots at room temperature for NaIO₄ salt complexed PEO/PVP blend electrolytes:
(a) PEO/PVP blend (b) PEO/PVP/NaIO₄ (5 wt%), (c) PEO/PVP/NaIO₄ (7.5 wt%), (d) PEO/PVP/NaIO₄ (10 wt%).

Figure 5. Arrhenius plots for NaIO₄ salt complexed and GO doped ‘PEO/PVP blend’ electrolytes:
(a) PEO/PVP pure blend, (b) PEO/PVP/NaIO₄ (5 wt%), (c) PEO/PVP/NaIO₄ (7.5 wt%), (d) PEO/PVP/NaIO₄ (10 wt%), (e) PEO/PVP/NaIO₄ (10 wt%)/GO (0.4 wt%).
This could be due to maximum PEO/PVP electrolyte uptake and enhanced coordination interactions of ether oxygen atoms of PEO or/and carbonyl oxygen atoms of PVP with Na$^+$ cations. This leads to increase amorphous content in PEO/PVP electrolyte and favour for increase of ionic conductivity [19]. As a result of GO (0.4 wt%) doping, the intercept of higher end semicircle corresponding to ‘PEO/PVP/NaIO$_4$ (10 wt%)’ electrolyte’ on the $Z^l$ - axis tends move towards lower value as shown in inset of figure 4. The respective room temperature conductivity of ‘PEO/PVP/NaIO$_4$(10 wt%)/GO(0.4 wt%)’ electrolyte is found to be increase to $1 \times 10^{-6}$ S/cm. This increase in Na$^+$-ion conductivity is due to the nature of graphene oxide that has a lot of oxygen-containing functional groups such as carboxylic acid, epoxy and hydroxyl, which can improve charge carrier mobility and promote ionic conductivity. The large number of functional groups in GO enables it to dissolve more efficiently in methanol and distribute homogeneously in PEO/PVP electrolytes. This could facilitate the mobility of mobile charge ions and leads to increase in ionic conductivity [20].

Figure 5 illustrates the variation in electrical conductivity of pure, salt complexed and GO doped polymer blend electrolytes as a function of temperature in the range 303–343 K. Evidently, the linear variation of resultant curves represents Arrhenius – type of thermally activated process by satisfying the following equation.

$$\sigma_{dc} = \sigma_0 e^{(-E_a/KT)},$$

where $\sigma_0$, $E_a$, K and T represent the pre-exponential factor, activation energy, Boltzmann constant and absolute temperatures, respectively. As a function of temperature, ionic conductivities of complexed blend electrolytes are increased due to enhanced polymer segmental mobility.

4. Conclusions

PEO/PVP blend electrolyte films complexed with NaIO$_4$ salt and doped with Graphene Oxide (GO), have been prepared by using conventional solution cast technique. The presence of characteristic X-ray diffraction peaks at 19.3$^0$ and 23.4$^0$ indicates semicrystalline nature of the pure blend electrolytes. Upon increase in salt concentration and inclusion of GO, decrease in intensity of diffraction peaks indicates increase of amorphous portion in the blend electrolytes due to strong interaction of dissolved additives with matrix of polymer electrolytes. In FTIR spectra, the coexistence of functional groups & vibrational bands corresponding to PEO and PVP reveals their uniform miscibility in blend electrolyte film and variation in the environment of the functional groups due to completion of salt and addition of GO. Surface smoothness of the blend electrolytes increased as a result of inclusion additives, which suggests the improvement in amorphous region in the matrix of polymer blends. The room ionic conductivity blend electrolytes increased with increase in salt concentration and found to be maximum of $1.57 \times 10^{-7}$ S/cm for PEO/PVP/NaIO$_4$ (10 wt%). Upon inclusion of 0.4 wt% GO, resultant room temperature conductivity further increased to $1 \times 10^{-6}$ S/cm, which signifies the improvement in flexibility of blend electrolytes due to interaction of GO with matrix of blend. Temperature dependent conductivity studies reveal increase in segmental motion, which supports for the enhancement of ionic conductivity in amorphous rich electrolytes.

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