

PEO/STARCH-NANOCRYSTALS BASED SOLID POLYMER
ELECTROLYTE MEMBRANES FOR MAGNESIUM ION
CONDUCTING APPLICATIONS

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Abstract

PEO/SNCs based nanocomposite electrolyte membrane complexed with MgBr₂ salt (15 wt.%) was fabricated following conventional solution casting technique. The effect of incorporation of salt ions on microstructural properties of host matrix of PEO/SNCs were investigated by means of XRD, FTIR, DSC studies. The modifications in the nature of diffraction peaks and vibrational modes of nanocomposites revealed the formation of strong hydrogen bonding and cross links between SNCs and salt ions. A decrease of melting and glass transition temperatures of host matrix was observed as a result of salt doping. The complex electrochemical impedance measurements were carried out in the applied frequency range of 0.1 Hz – 1 MHz and in the temperature range of 303–373 K. The PEO/SNCs composite complexed with 15 wt.% salt showed room temperature ionic conductivity of 7.8×10^{-8} S/cm promising for soft electronics, solid state ionics and sensing applications.

Key words: solid polymer electrolytes, nanocomposites, bioorganic filler, starch nanocrystals (SNCs), electrical impedance spectroscopy, magnesium ionic conductivity, microstructural properties

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Introduction. In the pursuit of significant improvements in the field of flexible electronic devices, the development of advanced flexible battery technology is necessary to meet the requirements of next-generation devices with the required safety attributes [1]. In this context, liquid electrolytes based battery technology has been gaining remarkable attention by virtue of their cycling stability and high energy density [2]. However, due to continuous electrochemical interactions between liquid electrolyte and electrodes result in terms of depletion of electrolyte, generation of resistances at ‘electrode/electrolyte’ interfaces, which reduce the overall end performance of the battery and cause the dendrite-induced internal short circuits [3]. Currently, there is a continuous increase of publications on the fabrication of novel solid polymer electrolytes (SPEs) membranes for their effective utilization in super capacitors, fuel cells, energy storage devices and dye sensitized solar cells [4]. Specifically, SPEs are recognized as alternative liquid electrolytes by means of the inherent safety characteristics and prevention of dendritic deposition of the metal electrodes [5]. SPEs are easy to fabricate and are characterized by their lower cost, compatibility with large scale roll to roll manufacturing processes, light weight and superior mechanical toughness properties. The ideal SPEs are labelled by their high bulk ionic conductivity provided with fast shuttling capability metal ions (i.e. Li^+ , K^+ , Na^+ , Mg^{+2} ... etc.) across two electrodes in the architecture of the battery and mechanically, chemically inert during cycling processes [6]. Poly (ethylene oxide) (PEO) based solid polymer electrolyte membranes complexed with various alkali metal salts are gaining substantial significance in the fabrication process of advanced flexible SPE technology [7].

The development of polymer nanocomposites is prominently increasing as a multidisciplinary research field with promising results that could extend to the energy harvesting and various industrial applications [8]. In ‘polymer – inorganic nanoparticle’ systems interfaces play key role and they control the corroborations that polymer molecules can choose, the free energy of the polymer, which is fundamentally different from the bulk polymer. It is worth mentioning that the ‘polymer – nanoparticle’ interface is associated with the fundamental length-scale of the host polymer matrix, in which the order of the radius of gyration of polymer chain is [9]. In polymer nanocomposites, the complete matrix of the host polymer can be considered nanoscopically confined interfacial polymer and respective polymer chain conformations will tailor the characteristic properties such as glass transition temperature, relaxation behaviour and mobility of the polymer chains and thus supports for the enhancement of the mobile actions [10]. Currently biopolymers, extracted from natural sources, are gaining significant attention in academic and scientific sectors. Starch is one of the natural polymers and it is cost effective, environmentally friendly and biodegradable [11]. Significantly, the backbone of the starch contains abundance of hydroxyl groups, which have more affinity for other hydroxyl groups via hydrogen bonding. However, intrinsic starch films or membranes exhibit brittleness and high rate of water absorption, which

restrict their direct employment in wide-scale applications.

Lithium-ion rechargeable batteries (LIB) have been employed as reliable energy sources in different high end electronic devices and automotive applications because of their promising battery chemistries and desired high energy densities [12]. However, LIB technology is relatively cost effective, toxic, and besides lithium deposits are gradually decreasing and limited quantity of lithium is insufficient to fulfil the requirements of the humankind globally [13]. In addition, in the total architecture of Li-ion based rechargeable batteries, lithium metal anodes contribute to the higher capacity and lower reduction potential than intercalation anodes. Comparatively, Mg metal anodes offer high capacity of $3833 \text{ mA h cm}^{-3}$ vs. $2046 \text{ mA h cm}^{-3}$ for lithium, dendrite-free deposition, low reduction potential (-2.4 V vs. SHE), and 100% Coulombic efficiency in some electrolytes [14]. In comparison to lithium salts, magnesium salts are less reactive toward oxygen and water humidity, non-toxic, and easy to handle safely in open air. Hence research on Mg-battery technology is continuously gaining interest towards commercialization level as complementary to Li-ion battery technology. This shows impetus scope to search for the new rechargeable battery systems, which are environmentally-friendly and low cost. In this light, authors in the present study aimed to prepare PEO/SNCs and PEO/SNCs/MgBr₂ (15 wt.%) solid membranes and to investigate the effect of MgBr₂ salt doping on structural, thermal and ion conductivity properties by means of XRD, FTIR, DSC and EIS techniques. The current study is related to the solid state ionics applications of advanced biopolymer soft/solid composite materials.

Experimental and characterization. Poly (ethylene oxide) (PEO, viscosity average molar mass, $M_v = 8\,000\,000$ and containing 200–500 ppm BHT as inhibitor), magnesium bromide (MgBr₂, 98%), methanol solvent (99.8%)/potato starch and sulphuric acid (analytical reagent 98%) were purchased from Sigma-Aldrich. All these materials were used as received without further purification. Starch nanocrystals (SNCs) were prepared by acid hydrolysis of potato starch granules according to the method previously reported ANGELLIER et al. [15] and followed by a minor modification. Intrinsic PEO and PEO/starch composite electrolyte membranes were prepared using conventional solution casting method. In the first step, appropriate weight percentages of PEO material was dissolved in methanol solvent and the resultant solution was stirred magnetically for 10 h to get homogeneous PEO solution. Next, the appropriate weight percentages of prepared SNCs were dispersed into methanol solvent and sonicated for 30 min to prepare SNCs dispersed solutions of different concentrations. Later, ‘starch nanocrystal’ solutions were added in dropwise method to the PEO solutions and followed by magnetically stirring process for 8 h and ultra-sonicated for next 30 min. The resultant end homogeneous slurry solutions were transferred to petri dishes and allowed to dry in controlled environmental conditions to harvest free standing blend electrolyte membranes of the composition ‘PEO/SNCs (10 wt.%)’.

In the second step, MgBr_2 (15 wt.%) salt solution was added to the 'PEO/SNCs (10 wt.%) composite solution and continued to stir for 10 h and followed by ultrasonication for 30 min. The harvested membranes of thickness around 170 μm were stored in a vacuum sealed desiccator provided with silica gel to prevent the effect of moisture and to carry out further characterizations.

Structural modifications, as a function of SNCs doping concentrations and salt complexation, in matrix of PEO electrolyte membranes were examined by recording X-ray diffraction patterns at room temperature using Bruker D8 Advance diffractometer equipped with $\text{Cu K}\alpha$ radiation in Bragg's angle (2θ) range of $10\text{--}80^\circ$ with a constant step of 0.020 and counting time of 25 s/step. The effect salt complexation on vibrations modes associated with the PEO polymer were analyzed by Fourier transform infrared (FTIR) spectroscopic studies in the wavenumber region of $500\text{--}3500\text{ cm}^{-1}$ using a spectrometer Perkin Elmer, Spectrum 100. The thermal properties of all samples were studied using a Netzsch DSC 204 F1 Phoenix differential scanning calorimeter (DSC) under nitrogen atmosphere. In all thermal scans, weights of electrolyte samples loaded aluminum pans, empty aluminum pan (as reference) and lids were recorded. DSC thermograms of all electrolyte samples were obtained in the temperature range from -70°C to 300°C at a scan rate of $10^\circ\text{C}/\text{min}$. A potentiostat/galvanostat (SP-200, BioLogic) was utilized to record the impedance spectra in the frequency range of 0.1 Hz – 1 MHz. The electrochemical impedance spectroscopy technique was employed to estimate the room-temperature ionic conductivity values of all fabricated SPEs. In this case, the electrolyte membranes were sandwiched between two circular shaped aluminum electrodes ($1\text{ cm} \times 1\text{ cm}$) and the entire assembly was placed in closed chamber.

Results and discussion. The X-ray diffraction patterns for intrinsic and salt doped PEO/starch nanocomposites are presented in Fig. 1. PEO demonstrated two characteristic peaks at angular positions of 19.29° , 23.49° which are assigned to (1 2 0) and (1 1 2) crystal planes [PCPDF File no. 49-2200], respectively [16]. The relative sharpness and high intensity of the two characteristic peaks, which originated from the strong hydrogen bonding between polymer chains of PEO, confirm the semi-crystalline nature of PEO. As a result of doping of SNCs (10 wt.%) and MgBr_2 (15 wt.%) salt, significant changes bonding between polymer chains of PEO, confirm the semi-crystalline nature of PEO.

As a result of doping of SNCs (10 wt.%) and MgBr_2 (15 wt.%) salt, significant changes in terms of shift in position and decrease of height of the two characteristic peaks are visible. These observations suggest the decrease in percentage of crystalline portion in the matrix of 'PEO/SNCs' due to the maximum uptake of the salt. Figure 2 shows FTIR spectra recorded at room temperature for the intrinsic and salt doped composite samples.

The IR spectrum of intrinsic composite (PEO/SNCs (10 wt.%) showed all allowed characteristic modes of vibrations associated with PEO (Fig. 2) and all

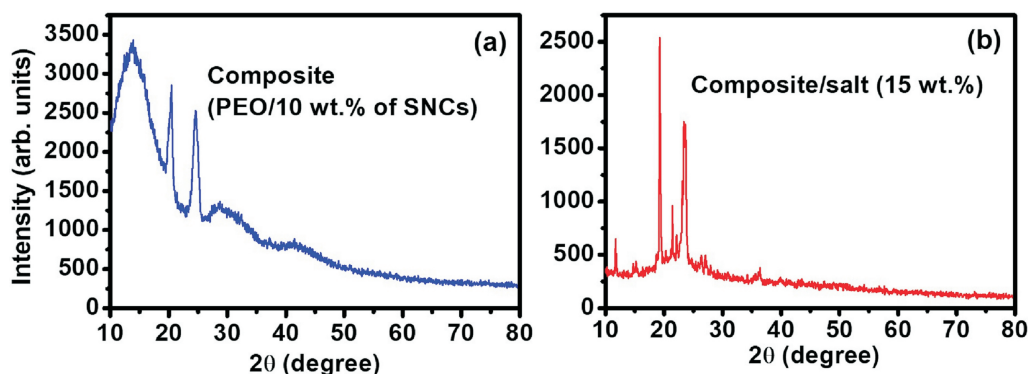


Fig. 1. X-ray diffraction patterns for composite (a) and salt complexed nanocomposite membrane (b)

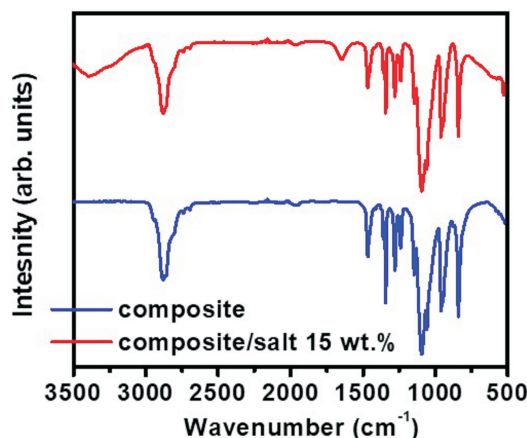


Fig. 2. FTIR spectra for intrinsic nanocomposite and salt doped nanocomposite membrane

allowed vibrational modes, which are in agreement with YOSHIHARA et. al [17]. Generally, the wavenumber region $800\text{--}1500\text{ cm}^{-1}$ represents significant fingerprint region associated with the backbone of PEO polymer and any changes in nature of the modes present in this region indicates destruction in the local helical structure of PEO. The IR spectrum of intrinsic composite showed characteristic modes at 841 cm^{-1} (CH_2 rocking), 943 cm^{-1} (C–O stretching), strong band at 1100 cm^{-1} (asymmetric C–O–C stretching). Significantly the asymmetric C–O–C stretching mode indicates the information of amorphous portion in the matrix of PEO and any changes in nature of the respective mode associated with the crystalline nature of PEO [17]. The decrease in intensity, slight shift in position of the absorption bands and peak broadenings of all characteristic modes of vibrations suggest the decrease of crystalline portion in the matrix of composite upon doping of 15 wt.% of salt (Fig. 2). This could be due to increase of amorphous portion in the matrix

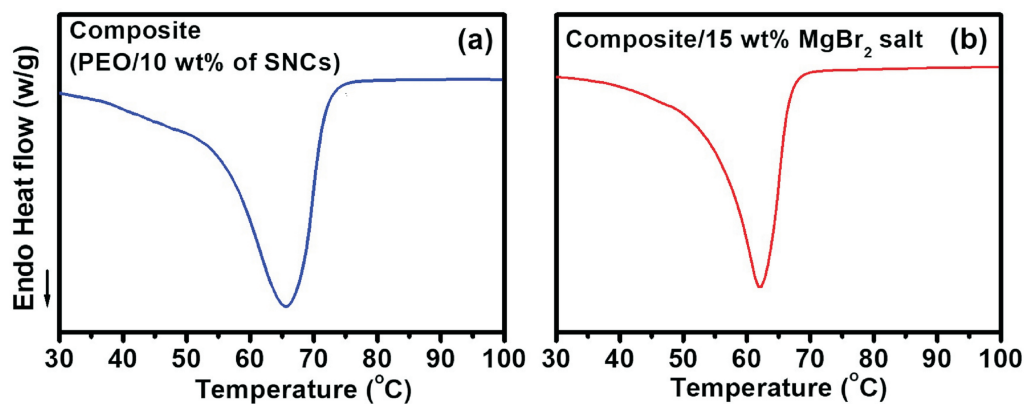


Fig. 3. DSC thermograms for composite (a) and salt doped composite systems (b)

of host matrix, which supports the increase in mobility of Mg^{+2} ions via hopping mechanism [18].

Thermal stability of the polymer systems is one of the prerequisites for electrolyte applications. Figure 3 shows DSC thermograms for the intrinsic and MgBr_2 salt (15 wt.%) doped 'PEO-SNCs (10 wt.%)' systems in the temperature range of -70 – 300 °C. The melting and glass transition temperatures of the nanocomposite host were estimated from the tip of endothermic peak and by extrapolating crystallization region, respectively. The estimated melting and glass transition temperatures for intrinsic composite were found to be 75.6 °C and 64.90 °C, respectively. As a result of doping of 15 wt.% of salt, the melting and glass transition temperatures were noticed to be decreased to 67.4 °C and 52.6 °C, respectively. The decrease of glass transition and melting temperatures represent the micro phase separation between soft and hard segments. It can improve the degree of freedom of the soft segments in the matrix of PEO and cause the decrease in crystalline portion and enhancement in visco-elastic properties and flexibility in the polymer chains of PEO.

Impedance measurements were carried out for the pure and salt doped nanocomposite systems in the applied frequency range of 0.1 – 1 MHz and temperature range of 30 – 70 °C. Figure 4 represents the Nyquist plots, for the investigated samples, in which a depressed semicircle at high frequency region (associates to the bulk resistance of the electrolyte membrane) and a tilted straight line at lower frequency region, which is attributed to the charge transfer resistance and capacitance of electric double layer generated at electrolyte/electrode interfaces [19]. The bulk resistance (R_b) of the electrolyte membrane was estimated by determining intersecting point of lower end of depressed semicircle with real impedance (Z_{real}) axis. The conductivity (σ) of the composites is evaluated from $\sigma = t/(R_b A)$ [20], where t is the thickness of the composite and A its active area. The estimated room temperature conductivity of intrinsic composite is 7.5×10^{-10} S/cm

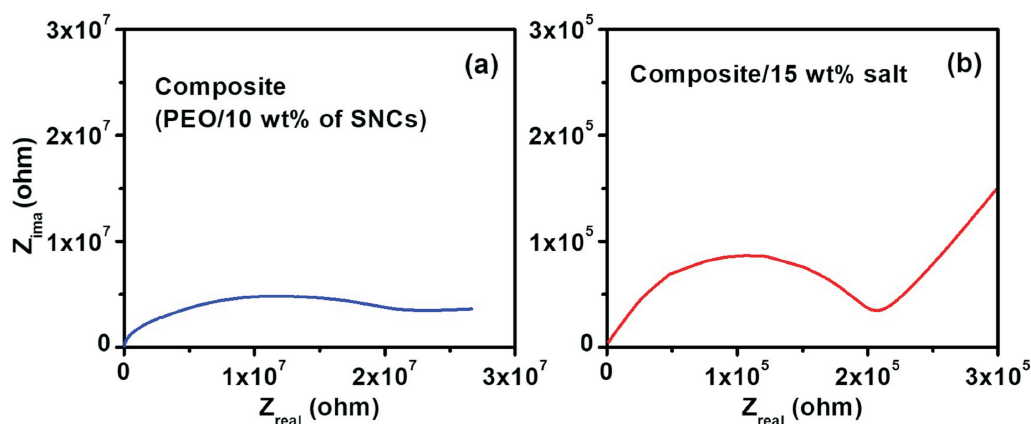


Fig. 4. Nyquist plots for composite (a) and salt doped nanocomposite systems (b)

and was found to be increased to 2.78×10^{-8} S/cm as a result of doping of 15 wt.% of MgBr_2 salt. In comparison to pure composite, salt doped PEO/SNCs (10 wt.%) composite exhibited fairly higher room temperature conductivity of 7.8×10^{-8} S/cm.

Conclusions. Starch nanocrystals incorporated PEO based solid electrolyte membranes were prepared using solution casting technique. The characteristic modifications in X-ray diffraction spectra and Fourier transform infrared spectra evidenced for doping of MgBr_2 salt (15 wt.%) ions into the three-dimensional matrix of PEO polymer and salt uptake by the host matrix. The decrease of melting and glass transition temperatures evidenced for the increase of flexibility in the host matrix, which supports the increase of mobility of the free ions. The XRD, FTIR and DSC studies reveal that, starch nanocrystals incorporated host matrix provides more ion conducting paths in the three-dimensional matrix. Further, impedance studies evidenced for structural relaxations in the host matrix and suggested that in comparison to intrinsic composite, salt doped composite demonstrated increased room temperature Mg^{+2} -ionic conductivity of 7.8×10^{-8} S/cm. The results from this study are of practical significance in relation to the use of these composites and related systems as materials for applications in energy storage devices, flexible bioorganic electronics, solid state ionics and sensors. Further charging/discharging, charge-sensing stress and CV studies are in progress.

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