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Nano composite solid polymer electrolytes based on biodegradable polymers starch and poly vinyl alcohol

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ABSTRACT

An attempt has been made to prepare nano composite solid polymer electrolytes by adding nano fumed silica in different weight ratios in a polymer matrix composed of biodegradable polymers Starch and Poly Vinyl Alcohol (PVA) to get high ionic conductivity with good mechanical strength. Fourier Transform InfraRed spectroscopy (FTIR) was used to confirm the complexation and interaction of the nano filler with the polymer matrix. From the FTIR investigations it could be established that the formation of C—O—Si bonds by nano fumed SiO_2 with Starch and PVA lead to the crucial structural modification that finally increase the conductivity of the sample. Dielectric and frequency dependent measurements substantiate the sharp increase in number of charge carriers as the major factor contributing to the enhancement of the conductivity for 3 wt% nano fumed silica. Electric modulus studies confirmed the ionic nature and indicate absence of electrode polarization in the system. Maximum ionic conductivity $\sim 10^{-3}$ S/cm could be realized for 3 wt% silica at ambient condition.

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1. Introduction

The brilliance of Wright marked the genesis of a new class of materials called the Solid Polymer Electrolytes (SPEs) and was recognized as the prospective candidates for advanced electrochemical device and replacement of liquid electrolytes [1]. SPEs synergize the mechanical strength and flexibility of the solid state with the high ionic conductivity of the liquid state. The synergy of the aspects of the solid and liquid states in a single system make SPEs ideal for the compact and lightweight devices of the modern age. Realization of ionic conductivity comparable to the liquid electrolytes in the solid state is the prime focus in the field of SPEs. To achieve this goal a sizeable number of new polymer systems and some effective methods to tailor the properties of existing polymer salt complexes have emerged in course of time. Addition of ceramic nano fillers in a polymer salt complex is one of the methods which has gained a noticeable attention in recent years. The resulting system is termed as Nanocomposite Solid Polymer Electrolyte (NCPE). Among various ceramic fillers Nano fumed silica has been recognized as an efficacious filler material for NCPEs in a considerable number of reports. Evolution of a three dimensional network facilitates ion motion causing increase in conductivity in nano fumed silica based NCPEs [2,3]. In addition to improvement in ionic conductivity addition of fumed silica also renders higher mechanical strength to the polymer electrolyte films [4]. On the other hand concurrent literature based on new polymer systems reveals the increasing interest toward the natural or biopolymers. It has been established that the biopolymers posses mechanically adhesive nature and provide good electrode/electrolyte contact. In addition natural abundance and eco friendly nature of the biopolymers are factors that augment their versatility [5,6]. Starch

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is one such biopolymer which has always intrigued researchers and technologists. The fundamental architecture of Starch comprises of two polymers of glucose–linear amylose and a highly branched amylopectin. Amylose molecules consist of 200–20,000 glucose units which form a helix as a result of the bond angles between the constituent glucose units. Amylopectin is a highly branched polymer containing short side chains of 30 glucose units attached to every 20–30 glucose units along the chain. Amylopectin molecules may contain up to two million glucose units [7]. Recent literature on SPEs contains a significant number of reports on application of Starch for solid polymer electrolyte applications [8–12]. Structural studies made on starch have affirmed that starch from almost all species contain water in its structure[13] which favors ion conduction and promotes dissociation of salts to the maximum extent [9]. However these advantages of Starch are often veiled by some flaws that limit its use. Some of the drawbacks are brittles of films, large water absorption, low mechanical strength etc. One way to overcome these shortcomings that has been devised is the blending of Starch with other biodegradable polymers like PVA [7]. It is a versatile synthetic biodegradable polymer that has been reported numerous times for SPE applications Starch and PVA are reported to be miscible with each other via the formation of hydrogen bond [14,15]. In the fabrication of Starch/PVA blends a vital role is played by crosslinkers and plasticizers. Plasticizers reduce the brittleness and glass transition temperature of Starch based films which are fundamental requirements for obtaining higher conductivity. Glycerol has been widely reported to be a fruitful plasticizer in Starch based films. Recent report made by Tiwari et al. has established that Glutaraldehyde is not only an efficacious crosslinker but also helps in attaining higher conductivity in Starch based films [9].

The motivation behind the present work is to explore the improved and desirable structural and electrical properties of a blend of Starch and PVA incorporated with nano fumed silica and Lithium Bromide (LiBr) as salt. The outcome of the different investigations encourages the utilization of Starch/PVA blend as potential material for electrochemical devices.

2. Experimental details

Starch Soluble (Himeedia Pvt Limited India, Botanical source Potato) [16] Polyvinyl Alcohol (Mw. 125,000) and Lithium Bromide (S.D. Fine Chemicals Boisar Mumbai India), Glycerol (Qualigen Fine Chemicals India), Glutaraldehyde (Merck India) were used for the preparation of solid polymer electrolyte films. Nano Fumed silica of average particle size 14 nm was obtained from Sigma Aldrich. Solid Polymer electrolyte films were prepared by solution casting method [8]. Starch and PVA in 60:40 ratio by weight were dissolved in 150 ml triply distilled water at 90 °C using magnetic stirring. After stirring for about 2 h Glutaraldehyde and glycerol were added to the viscous solution. Glutaraldehyde and glycerol in 60:40 ratio to each other constituted 30 wt% of the total weight of the sample. The content of LiBr salt was fixed at 5 wt% and a homogenous solution was formed. Fumed silica nano particles were added in 1, 2, 3 and 4 wt% and samples were designated as **S-0 (ii) S-1 (iii) S-2 (iv) S-3 (v) S-4**. The final solution was poured in plastic petri dishes and left at room temperature for solvent evaporation. Films of uniform thickness around 500–600 μm were chosen for characterization.

2.1. Characterizations

2.1.1. Fourier Transform InfraRed spectroscopy (FTIR)

FTIR spectra for the Starch/PVA nanocomposite polymer electrolytes with different contents of silica were carried out in the wave number region 4000–400 cm^{-1} at room temperature from a Perkin Elmer Spectrophotometer with an accuracy of 1 wave number. FTIR is used to obtain information about the structure of the nano composite solid polymer electrolyte film.

2.1.2. AC conductivity

Films of average thickness ~500 μm coated with silver paste were chosen for electrical measurements. [17]. Impedance data were recorded by sandwiching the films between two similar brass electrodes. Novo control Impedance analyzer operating in the frequency range 50 Hz–1 MHz was used to record the electrochemical impedance data. Temperature dependent Impedance data was recorded by placing the sample holder in temperature controlled furnace in the temperature range 303–363 °C with an accuracy of 5 °C.

2.1.3. Bulk conductivity

Electrical conductivity of the polymer electrolyte films with temperature and nano fumed silica content was recorded using the following expression.

$$\sigma_{dc} = \frac{1}{R_b}\left(\frac{d}{A}\right)$$

where d is the thickness of the polymer electrolyte film and A is the area of cross section. R_b is the bulk resistance of the film and is obtained from the intercept of the Nyquist plot on the real part of complex impedance plot.

2.1.4. Dielectric studies

The dielectric parameters ϵ' and ϵ'' were calculated from the impedance data using the following expression were obtained from the Z′–Z″ [18]

$$\varepsilon' = \left(\frac{1}{\omega C_0}\right)\left(\frac{Z''}{Z'^2 + Z''^2}\right)$$

$$\varepsilon'' = \left(\frac{1}{\omega C_0}\right)\left(\frac{Z'}{Z'^2 + Z''^2}\right)$$

where Z' and Z'' are the real and imaginary parts of impedance, ω is the angular frequency in Hz and C_0 is the free space capacitance obtained from the expression.

$$C_0 = \varepsilon_0(A/d)$$

where A is the electrode–electrolyte contact area and d is the thickness of the sample, ε_0 is the permittivity of free

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