



Characterization of conducting cellulose acetate based polymer electrolytes doped with “green” ionic mixture

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ARTICLE INFO

Article history:

Received 28 May 2012

Received in revised form 25 June 2012

Accepted 2 July 2012

Available online 31 July 2012

Keywords:

DES

Ionic conductivity

Complexation

Amorphous region

Li⁺ mobility

ABSTRACT

Polymer electrolytes were developed by solution casting technique utilizing the materials of cellulose acetate (CA), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and deep eutectic solvent (DES). The DES is synthesized from the mixture of choline chloride and urea of 1:2 ratios. The increasing DES content well plasticizes the CA:LiTFSI:DES matrix and gradually improves the ionic conductivity and chemical integrity. The highest conducting sample was identified for the composition of CA:LiTFSI:DES (28 wt%:12 wt%:60 wt%), which has the greatest ability to retain the room temperature ionic conductivity over the entire 30 days of storage time. The changes in FTIR cage peaks upon varying the DES content in CA:LiTFSI:DES prove the complexation. This complexation results in the collapse of CA matrix crystallinity, observed from the reduced intensity of XRD diffraction peaks. The DES-plasticized sample is found to be more heat-stable compared to pure CA. Nevertheless, the addition of DES diminishes the CA:LiTFSI matrix's heat-resistivity but at the minimum addition the thermal stability is enhanced.

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1. Introduction

In recent years, we are frequently being exposed to the awareness of “green” technology with plenty of informative sources. This consciousness was brought forward by keeping in mind the critical environmental problem associated with the utilization of synthetic polymer in the production of polymer electrolytes. The growing needs of polymer electrolytes to be used in a variety of electrochemical devices (Armand, 1986; Rajendran, Sivakumar, & Subadevi, 2004; Ratner & Shriver, 1988; Shriver et al., 1981; Siva Kumar, Subrahmanyam, Jaipal Reddy, & Subba Rao, 2006), especially in lithium polymer cells, urging for better development that are more environmental friendly. In conjunction to this, the natural types of polymers have been substituted with the synthetic types.

In this research work, cellulose acetate (CA) was chosen to build up the conducting membrane. CA has number of outstanding properties as listed are; (1) non-toxic nature, (2) availability of renewable resources, (3) low cost and (4) biodegradable (Averous, Fringant, & Moro, 2001; Wu, Wang, Li, Li, & Wang, 2009). The presence of polar functional groups in its polymer chain is an added advantage, which has high affinity towards the lithium ions and

plasticizing solvents (Ramesh & Lu, 2008). Up to date not much efforts were executed by researchers to develop the conducting membrane using the CA. The main obstacle that limits its wide utilization is attributed to its highly crystalline nature, which provokes the CA membrane to be insulated.

In the effort to overcome the above mentioned limitation, incorporation of suitable additives is potential to convert the highly crystalline region in CA matrix to amorphous for better ion conduction. As in this research, the initial approach to suppress the high crystallinity is done by embedding a type of ionic salt, LiTFSI into the CA matrix. This type of ionic salt is of special interest due to its large electronegativity and delocalization of charge (Ramesh & Lu, 2008). These successive properties contribute to the complete dissociation of LiTFSI in CA matrix forming free ions and retain in its ionic state throughout. The cations (Li⁺) will move along the polar functional group in CA matrix whereas the anions (TFSI⁻) modify the phase composition, both of these different charged ions exert significant influence in ionic conductivity (Ramesh, Tai, & Chia, 2008).

Further enhancement in ionic conductivity was done by incorporating DES in CA:LiTFSI matrix. The DES is a type of ionic liquid but since it is composed of a mixture of quaternary ammonium salt and hydrogen bond donors (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003) the term ionic mixture was adopted (Hou et al., 2008). In this present work, we synthesized an ionic solvent from the eutectic mixture of choline chloride and urea (Abbott et al., 2003). This type of ionic mixture gains interest due to its

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Table 1
The composition ratio of the designated CA:LiTFSI:DES polymer electrolytes.

Designation	Polymer electrolyte composition (CA:LiTFSI:DES) (wt.%)
Pure CA	100:0:0
CA-0	70:30:0
CA-20	56:24:20
CA-40	42:18:40
CA-60	28:12:60

unique properties including; (1) unusual solvent property that further dissolves the highly crystalline CA, (2) cheap in cost compared to pure ionic liquid due to the low cost of raw materials, (3) ease in the preparation method ignoring the purification process and no medium being required, (4) most of the formulations are non-toxic and (5) biodegradable (Hou et al., 2008; Jhong, Wong, Wan, Wang, & Wei, 2009; Zhang, Wu, Chen, Feng, & Bu, 2009).

The DES do possess an unusual solvent property owing to its high chloride ion concentration and its specific activity which is capable of breaking the bonding network between the oxygen (–O) and acetate (–Ac) atom in –OAc functional group. The bond disruption causes the oxygen atom to be unoccupied, thus permitting the Li⁺ ions mobility by forming a temporary co-ordination (Swatloski, Spear, Holbrey, & Rogers, 2002). Moreover, the incorporation of DES also displays high ionic conductivity as a result of its high mobility and high concentration of carrier ions (Abbott et al., 2003).

In this communication, we study the plasticizing efficiency of DES content in tailoring the insulating property of CA:LiTFSI polymer electrolytes by using various characterization techniques, namely ionic conductivity, complexation, structural conversion and thermal properties.

2. Experimental

2.1. Materials

The chemicals used to build up the non-plasticized matrix are cellulose acetate, CA ($M_w = 61,000 \text{ g mol}^{-1}$) and lithium bis(trifluoromethanesulfonyl)imide, LiTFSI, which were purchased from Aldrich and Fluka respectively. For the matrix plasticization, DES is synthesized using the starting materials of choline chloride and urea that were procured from Sigma. The N,N-dimethylformamide, DMF solvent that purchased from R&M Chemicals is used to prepare the polymer electrolytes solution.

2.2. Preparation of polymer electrolytes

2.2.1. Synthesizing method of DES

As an initial step, an appropriate amount of choline chloride and urea in 1:2 ratio was weighed in a small glass beaker. Then, the physically mixed solid state chemicals were heated up to a temperature of 50 °C, under a manual stirring using glass rod. The synthesis process is accomplished upon the complete dissolution of the solids mixture, which produces colorless viscous solution.

2.2.2. Thin film preparation

The DES plasticized matrix was prepared by dissolving an appropriate DES composition, as shown in Table 1, into the CA:LiTFSI matrix in the presence of 10 ml DMF. Then, the solution is stirred overnight to obtain a colorless homogeneous solution. The procedure continues by spreading the suspension on a clean Petri dish and left to dry in the oven at 55 °C. Upon casting, a mechanically stable and free standing transparent thin film is obtained. The casted thin films are stored in desiccator when not in use. This is to avoid the thin films from absorbing the moisture from air since it is made of hygroscopic materials. The ratio of CA:LiTFSI is fixed at 70:30

throughout the sample composition since this is the ratio combination that gives good property for the non-plasticized matrix in terms of its conducting nature and thermal profile.

2.3. Characterization technique

The developed DES-plasticized matrix is characterized in terms of electrical, structural and thermal properties.

2.3.1. Electrical characterization

2.3.1.1. Impedance spectroscopy. This analysis is performed by using the impedance spectrometer, which tests on the ionic conductivity of samples of freshly casted and aged. The ionic conductivity of the aged samples is studied for the storage time of 30 days with every measurement recorded with 10 days interval at room temperature.

Prior testing, the thickness of the thin films is measured by using the micrometer screw gauge. Then, the thin films with the known thickness are sandwiched between two stainless steel blocking electrodes (area of 4.9807 cm²) and tested using the HIOKI Model 3532-50 Hi-Tester. The measurements were recorded at room temperature over the frequency ranging from 50 Hz to 5 MHz with the amplitude of 10 mV.

The obtained impedance plot was used to find the bulk resistance (R_b) value to calculate the exerted ionic conductivity by substituting in Eq. (1):

$$\sigma = \frac{L}{R_b A} \quad (1)$$

where σ is the conductivity in S cm⁻¹, L refers to the thickness of thin film sample in cm, R_b is the bulk resistance in Ω obtained from Cole–Cole impedance plot whereas A represents the surface area of the stainless-steel blocking electrodes in cm².

2.3.2. Structural characterization

2.3.2.1. Fourier transform infrared (FTIR)-horizontal attenuated total reflection (HATR) analysis. The occurrence of complexation between the added chemical constituents in the matrix was analyzed by using Perkin–Elmer FTIR Spectrometer, Spectrum RX1, with the aid of HATR compartment. The FTIR spectra were recorded in the transmittance mode in the wave region ranging from 4000 to 600 cm⁻¹ with the resolution of 4 cm⁻¹.

2.3.2.2. X-ray diffraction (XRD) analysis. The structural alternations in the CA matrix upon doping with increasing DES content are studied using the Siemens D-5000 Diffraction System with the Cu-K α radiation of 1.5406 Å wavelength. The XRD patterns were recorded at the Bragg angles (2θ) ranging from 5° to 80° at room temperature.

2.3.3. Thermal characterization

2.3.3.1. Thermogravimetric analysis (TGA). Mettler Toledo analyzer that consist of TGA/SDTA851^e main unit and STAR^e software was used to analyze the thermal properties of polymer electrolytes. This analysis was performed on an approximate polymer electrolyte weight of 5 mg at the temperature ranging from 25 °C to 550 °C with the heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

3. Results and discussion

3.1. Ionic conductivity studies

The influence of DES content on the electrical properties of CA:LiTFSI:DES was evaluated over the storage period of 30 days and the variations are as presented in Fig. 1.

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