

Hydrogen ion conducting starch-chitosan blend based electrolyte for application in electrochemical devices



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ABSTRACT

This paper reports the characterization of starch-chitosan blend based solid polymer electrolyte (SPE) system and its application in electrochemical double layer capacitor (EDLC) and proton batteries. All the SPEs are prepared via solution cast technique. Results from X-ray diffraction (XRD) verify the conductivity result from our previous work. Scanning electron microscopy (SEM) analysis shows the difference in the electrolyte's surface with respect to NH₄Cl and glycerol content. From transference number measurements (TNM), transference number of ion (t_{ion}) of the electrolytes shows that ion is the dominant conducting species. Transference number of cation (t_+) for the highest conducting electrolyte is found to be 0.56. Linear sweep voltammetry (LSV) result confirms the suitability of the highest conducting electrolyte to be used in the fabrication of EDLC and proton batteries. The EDLC has been characterized using cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. The open circuit potential (OCP) of the primary proton batteries for 48 h is lasted at (1.54 ± 0.02) V, while that of secondary proton batteries is lasted at (1.58 ± 0.01) V. The primary proton batteries have been discharged at different constant currents. The secondary proton battery has been charged and discharged for 40 cycles.

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1. Introduction

Proton conducting electrolytes have long been recognized as the initiative to lithium ion conductors in electrochemical device applications [1–3]. This is because of the small radius of proton (H⁺) makes it suitable for better intercalation into the layered structure of cathode [4]. For battery application, most of the proton conducting electrolytes are electrochemically decomposed at ~1 to ~2 V compared to Li⁺ electrolytes (~4 V) [5–9]. However, due to the low cost of electrode and electrolyte materials used for proton batteries as well as no safety issues associated with them, proton batteries appear as a good alternative for low energy density battery applications [4,10].

Strong inorganic acids such as phosphoric acid (H₃PO₄) [11] and sulfuric acid (H₂SO₄) [12] have been used as proton donor for proton conducting electrolyte. Since the present work is dealing with polymer electrolyte, such inorganic acids are not an option. This is because polymer-inorganic acid complexes suffer from chemical degradation and mechanical integrity causing them unsuitable for practical applications [13]. Ammonium salts such as ammonium thiocyanate (NH₄SCN) [14], ammonium nitrate (NH₄NO₃) [15,16] and

ammonium chloride (NH₄Cl) [17,18] have been reported to act as the proton donor for polymer electrolyte. Starch-NH₄NO₃ electrolyte achieved the highest room temperature conductivity of 2.83 × 10⁻⁵ S cm⁻¹ [16]. Report by Polu and Kumar [18] shows that polyethylene glycol (PEG)-NH₄Cl electrolyte obtained a room temperature conductivity of 9.58 × 10⁻⁷ S cm⁻¹. According to Pratap et al. [10], the conductivity of ~10⁻⁵ S cm⁻¹ is low for battery application. The authors reported that the conductivity of polyethylene oxide (PEO)-ammonium perchlorate (NH₄ClO₄) electrolyte is enhanced to ~10⁻⁴ S cm⁻¹ when plasticized with propylene carbonate (PC), in order to use the electrolyte in proton battery. From our previous work [19], starch-chitosan-NH₄Cl plasticized with 35 wt.% glycerol (P7 electrolyte) obtained the highest room temperature conductivity value of (5.11 ± 1.60) × 10⁻⁴ S cm⁻¹, which is suitable for battery application.

In the development of electrochemical double layer capacitor (EDLC), many materials have been used as electrode active material like carbon aerogel [20,21], manganese oxide (MnO₂) [22], graphite [5,23] and activated carbon [24–26]. However, activated carbon is preferred due to its outstanding properties such as high surface area, low cost, high conductivity and good chemical stability [26]. Our previous work focused on the electrical characteristics of the electrolytes [19]. In this work, further characterizations are reported and the highest conducting electrolyte is used in the fabrication of proton batteries and an EDLC.

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Fig. 1. Transparent and free standing starch-chitosan based film.

2. Experimental

2.1. Electrolytes preparation

From our previous report [27], the blend of 80 wt.% starch and 20 wt.% chitosan has been found to be the most amorphous blend compared to other ratio of starch-chitosan. Thus, in the present work the blend of 80 wt.% starch and 20 wt.% chitosan is chosen to serve as the polymer host. A total of 0.8 g of corn starch (Brown & Polson) was dissolved in 100 ml of 1% acetic acid (SYSTEM) at 80 °C for 20 min. After the solution cooled to room temperature, 0.2 g of chitosan (>75% deacetylated, procured from Sigma Aldrich) was then added to the solution and stirred until homogenous solution was obtained. For the preparation of starch-chitosan-NH₄Cl (salted) system, different amounts of NH₄Cl (R&M Chemicals) were added to the starch-chitosan solutions and stirred until complete dissolution. For the preparation of starch-chitosan-NH₄Cl-glycerol (plasticized) system, different amounts of glycerol (SYSTEM) were added to the highest conducting salted electrolyte solutions and stirred until complete dissolution. All homogenous solutions were cast onto plastic Petri dishes and left to dry at room temperature to form film. The dry films were then kept in desiccators filled with silica gel desiccants for further drying process. The physical appearance of the films is demonstrated in Fig. 1. The compositions and designations of all electrolytes in salted and plasticized systems are tabulated in Tables 1 and 2, respectively.

2.2. Characterization of electrolytes

2.2.1. X-ray diffraction (XRD)

X-ray diffractograms were carried out by Siemens D5000 X-ray diffractometer in the range of $5^\circ \leq 2\theta \leq 80^\circ$ at a resolution of 0.1°. X-rays of 1.5406 Å wavelength were generated by a Cu K α source. The degree of crystallinity (χ_c) values of the electrolytes were

Table 1

Composition and designation of electrolytes in salted system.

(Starch-chitosan):NH ₄ Cl composition (wt.%)	Designation
100:0	S0
95:5	S1
90:10	S2
85:15	S3
80:20	S4
75:25	S5
70:30	S6
65:35	S7
60:40	S8

Table 2

Composition and designation of electrolytes in plasticized system.

S5:glycerol composition (wt.%)	Designation
95:5	P1
90:10	P2
85:15	P3
80:20	P4
75:25	P5
70:30	P6
65:35	P7
60:40	P8
55:45	P9

calculated using:

$$\chi_c = \frac{A_c}{A_T} \times 100\% \quad (1)$$

where A_c and A_T are the areas of crystalline and total hump, respectively. In this work, the investigation of the degree of crystallinity is focused in the region of $5^\circ \leq 2\theta \leq 50^\circ$ where crystalline and amorphous phases of starch, chitosan and starch-chitosan blends can be observed [28,29].

2.2.2. Scanning electron microscopy (SEM)

The surface morphology of the electrolytes at room temperature was studied using ZEISS EVO MA10 scanning electron microscope. Before SEM studies, the electrolytes were coated with a thin layer of gold using SC7620 mini sputter coater to prevent electrostatic charging on the electrolytes. SEM studies were done at 2000 \times magnification.

2.2.3. Transference number measurements

The transference number of ion (t_{ion}) was determined using Wagner's dc polarization technique [30]. A cell consists of the electrolyte sandwiched by two stainless steel electrodes was polarized using V&A Instrument DP3003 digital dc power supply at 0.20 V at room temperature. The dc current was monitored as a function of time. The same method was used to determine the transference number of cation (t_+). The electrodes were prepared by mixing 0.40 g manganese (IV) oxide (MnO₂) (Sigma-Aldrich), 0.04 g activated carbon (RP20, manufactured by Kuraray, Japan) and 0.08 g polytetrafluoroethylene (PTFE). The mixture was

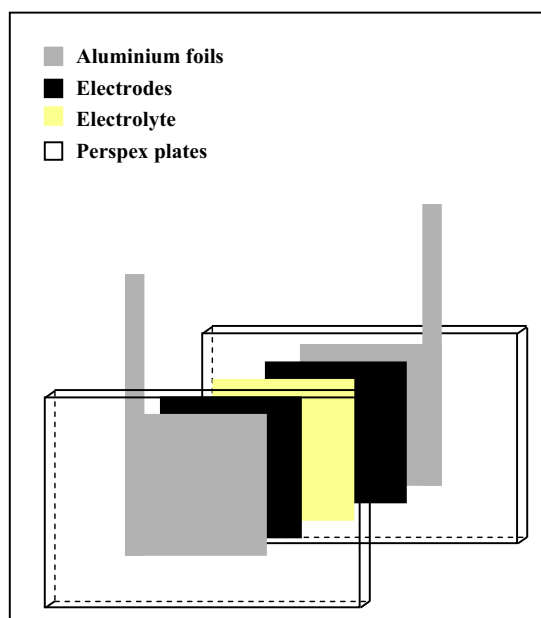


Fig. 2. Schematic diagram of EDLC fabrication.

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