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

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A R T I C L E   I N F O
Article history:
Received 20 October 2014
Received in revised form 19 December 2014
Accepted 27 January 2015
Available online 28 January 2015

Keywords:
Solid polymer electrolyte
Starch-chitosan blend
Ammonium chloride
Proton battery
Electrochemical double layer capacitor

A B S T R A C T
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+) 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 conducting cathode 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 × 10–3 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 Prapat et al. [10], the conductivity of ~10 −8 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 characterization are reported and the highest conducting electrolyte is used in the fabrication of proton batteries and an EDLC.