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Electrical characterization of corn starch-LiOAc electrolytes and application in electrochemical double layer capacitor

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ABSTRACT

Corn starch based solid biopolymer electrolytes doped with lithium acetate (LiOAc) and plasticized with glycerol are prepared by solution cast technique. In unplasticized system, the maximum room temperature conductivity of $(2.07 \pm 0.53) \times 10^{-5}$ S cm^{-1} is obtained by the electrolyte consists of 75 wt.% starch and 25 wt.% LiOAc. In plasticized system, addition of 30 wt.% glycerol to the highest conducting unplasticized electrolyte has further increase the conductivity up to $(1.04 \pm 0.10) \times 10^{-3}$ S cm^{-1}. Results from X-ray diffraction (XRD) explain that the enhancement of conductivity is contributed by the degree of crystallinity of electrolytes. Linear sweep voltammetry (LSV) shows that the highest conducting plasticized electrolyte is stable up to 2.1 V. The highest conducting plasticized electrolyte is used in the fabrication of an electrochemical double layer capacitor (EDLC). The EDLC is characterized using cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. From CV, the specific capacitance (C_s) of fresh EDLC is calculated to be 33.00 F g^{-1} at scan rate of 0.5 mV s^{-1}. The value of C_s increases as the scan rate decreases. From the charge-discharge measurement, the value of C_s is almost constant at $\sim$ 33.31 F g^{-1} for 1000 cycles.

1. Introduction

The potential application of solid polymer electrolytes (SPEs) in electrochemical devices is an interesting issue due to some advantages including the ease of fabrication, free of leakage and good electrode-electrolyte contact [1,2]. Recently, research on new materials from renewable sources as the possible electrolyte's host has grown vigorously, since synthetic polymers are obtained from finite sources [3]. Natural polymers are well known for their biodegradation properties, richness in nature and low cost [4]. The use of natural polymers in electrolytes could overcome the main shortcoming of synthetic ones, which are mostly insoluble in the solvents [5]. Many natural polymers have been used as polymer host in electrolytes, such as chitosan [6], cellulose derivatives [7], pectin [8] and natural rubber [9,10]. Among the natural polymers, great attention has been paid to corn starch. Starch is a mixture of amylose (poly-α-1,4-D-glucopyranoside) and branched amylopectin (poly-α-1,4-D-glucopyranoside and α-1,6-D-glucopyranoside) where it is regenerated from carbon dioxide and water by photosynthesis in plants [11]. Starch is completely biodegradable and it has good solubility and superior steel adhesion properties [12–15]. Starch is able to form mechanically stable films while starch based SPEs exhibit good opto-electrochemical characteristics [14,15].

It has been reported that ions are favorably mobile in the amorphous phase since their motion is assisted by polymer segmental motion [16–18]. The addition of salts to the polymer matrix can increase the percentage of amorphous nature of the polymer [19]. Ibrahim et al. [20] suggested that the incorporation of lithium hexafluorophosphate ($LiPF_6$) to polyethylene oxide (PEO) based SPE transforms some of the portion of PEO to an amorphous phase. However, the commercial $LiPF_6$ salt is very sensitive to moisture and thermally unstable [21]. Lithium salts such as lithium tetrafluoroborate ($LiBF_4$) [22–24], lithium arsenate ($LiAsF_6$) [25] and lithium triflate ($LiCF_3SO_3$) [26,27] have been studied as dopant in polymer electrolytes to improve the performance of electrochemical devices. Yahya and Arof [28] reported that lithium acetate (LiOAc) doped chitosan electrolyte exhibits a conductivity of $\sim 10^{-6}$ S cm^{-1} at room temperature. In the application of electrochemical devices, an electrolyte with a high conductivity value is required so that the device can deliver a good performance. SPEs based on only polymer and salt are normally insufficient for the application in electrochemical devices. Hence, researchers have tried to increase the conductivity by introducing other additives to

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the polymer-salt matrix. Plasticization is an effective technique to increase the conductivity of an electrolyte. Plasticizer assists the dissolution and dissociation of salt, hence increases the number density of ions [29]. The incorporation of plasticizer can increase the amorphous content of the polymer-salt complexes and lower the value of glass transition temperature (T_g) [30–32].

Electrochemical double layer capacitors (EDLCs) are devices in which energy is stored via charge separation across the blocking electrode-electrolyte interface [33]. Compared to batteries, EDLCs have identical electrodes, longer life times, high cyclabilities, and high-power density [34]. There are many reports on the use of SPEs in the fabrication of EDLCs [35–37]. In this work, EDLC was fabricated using the highest conducting plasticized electrolyte. The charge-discharge performance of the EDLC was recorded at a constant current density of 0.1 mA cm^{-2} at room temperature.

2. Experimental

2.1. Preparation of electrolytes

2 g of corn starch (Brown & Polson) were dissolved in 50 ml of 1% acetic acid and heated at 80 °C for 20 min. After the solutions cooled to room temperature, different concentrations of LiOAc (Aldrich) were then added to the starch solutions to prepare the starch-LiOAc (unplasticized) system. Different amounts of glycerol (SYSTERM) were added to the highest conducting unplasticized electrolyte solution for the preparation of starch-LiOAc-glycerol (plasticized) system. All homogeneous solutions were cast into different plastic Petri dishes and left to dry at room temperature. The dry samples were then kept in a desiccator filled with silica gel desiccants for further drying. The compositions and designations of all electrolytes in unplasticized and plasticized systems are tabulated in Tables 1 and 2, respectively.

Table 1
Composition and designation of electrolytes in unplasticized system.

Starch:LiOAc composition (wt.%)	Designation
100:0	U0
95:5	U1
90:10	U2
85:15	U3
80:20	U4
75:25	U5
70:30	U6
65:35	U7

Table 2
Composition and designation of electrolytes in plasticized system.

U5: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

2.2. Electrolytes characterization

2.2.1. Electrochemical impedance spectroscopy (EIS) measurements

Impedance measurements were conducted using HIOKI 3532-50 LCR Hi-tester from room temperature to 368 K in the frequency range of 50 Hz to 5 MHz. The electrolytes were sandwiched between two stainless steel electrodes of a conductivity holder. The value of bulk resistance (R_b) was determined from the Cole-Cole plots. Conductivity (σ) was calculated using the following equation:

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

where d is the thickness of the electrolytes and A is the electrode-electrolyte contact area.

2.2.2. X-ray diffraction (XRD) analysis

X-ray diffractograms were recorded using Siemens D5000 X-ray diffractometer. X-ray of 1.5406 Å wavelengths were generated by a Cu Kα source. The 2θ angle is varied from 5° to 80° at a resolution of 0.1°. The degree of crystallinity (χ_c) of the electrolytes was calculated using:

$$\chi_c = \frac{A_c}{A_T} \times 100\% \quad (2)$$

where A_c and A_T are the areas of crystalline and total hump, respectively. The areas of crystalline and total hump were determined using OriginPro8 software.

2.3. Voltammetry measurements

Linear sweep voltammetry (LSV) was performed using Digi-IVY DY2300 potentiostat to study the electrochemical stability window of the highest conducting plasticized electrolyte at room temperature. Stainless steel was used as working, counter and reference electrodes in a three-electrode configuration. LSV measurement was carried out at a scan rate of 5 mV s^{-1}. Measurement was done at room temperature.

2.4. Preparation of electrodes

13 g activated carbon (RP20, manufactured by Kuraray, Japan), 2 g poly(vinylidene fluoride) (PVdF) and 1 g carbon black (Super P) were mixed in 60 mL N-methylpyrrolidone (NMP) (EMPLURA) and stirred until a homogeneous slurry was obtained. The homogenous slurry was then doctor-bladed on an aluminum foil and heated at 60 °C. The dry electrodes were kept in a desiccator filled with silica gel desiccants for further drying.

2.5. EDLC fabrication and characterization

The highest conducting electrolyte was sandwiched between two carbon electrodes using perspex plates. CV of the EDLC was obtained at room temperature at different scan rates using Digi-IVY DY2300 potentiostat. Specific capacitance (C_s) is the amount of electric charge stored for given amount of electric potential per unit mass [38,39]. The values of C_s from the CV measurement were calculated using [40,41]:

$$C_s = \int_{V_1}^{V_2} \frac{I(V)dV}{2(V_2 - V_1)mv} \quad (3)$$

where $I(V)$ is the current, (V_2-V_1) is the potential window, m is mass of active material and v is the scan rate. The galvanostatic charge-discharge characteristics of the EDLC were carried out using Neware battery cycler. The EDLC were charged and discharged at a constant current density of 0.1 mA cm^{-2}. The values of C_s from the galvanostatic charge-discharge cycling were calculated from the linear part of the discharge curves using:

$$C_s = \frac{i}{m}\left(\frac{1}{s}\right) \quad (4)$$

where i is the constant current and s is the slope of the discharge curve. The specific capacity (Q) refers to the amount of charge passing through outer circuit during charge-discharge process per unit