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CONDUCTIVITY STUDY ON PLASTICIZED SOLID BIO-ELECTROLYTES CMC-NH¬4BR AND APPLICATION IN SOLID-STATE PROTON BATTERIES

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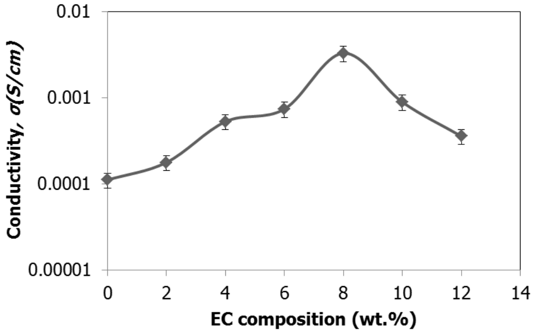
Graphical abstract



Abstract

This paper present the development of plasticized solid bio-electrolytes (PSBs) which has been accomplished by incorporating various composition of plasticizer namely ethylene carbonate (EC) with carboxy methylcellulose doped NH4Br via solution casting method. The plasticized polymer–salt ionic conduction of PSBs has been analyzed by electrical impedance spectroscopy. Plasticization using EC in PSBs system assists the enhancement of NH4Br dissociation and therefore increases the protonation process in the system. The highest ionic conductivity obtained for CMC–NH4Br containing with 25 wt. % NH4Br was achieved at 1.12 x 10-4 Scm-1 and improved to 3.31 x 10-3 Scm-1 when EC was added in PSBs system. The ionic conductivity-temperature for PSBs system was found to obey the Arrhenius relationships where the ionic conductivity increases with temperature. The solid-state proton batteries were assembled with the formation of Zn + ZnSO4.7H2O || highest conducting PSBs system || MnO2 and achieve with a maximum open circuit voltage (OCV) of 1.48 V at room temperature and showed good in rechargeablity performance with more than 10 cycles.

Keywords: Bio-electrolytes, ionic conductivity, solid-state proton batteries, discharge capacity

1.0 INTRODUCTION

Solid electrolytes based on polymer materials have acknowledged great attentions in electrochemical devices application due to their advantages [1]. In comparison to synthetic polymer, polymer natural based have been stated to be highly potential and suitable for expansion in polymer electrolytes system and this due to their good properties and low-cost materials [2, 3]. Amongst those types of biopolymer, carboxymethyl cellulose (CMC), a natural anionic polysaccharide which is widely used in many industrial and research sectors [4-6].

Generally, solid electrolytes based polymer-salt complexes are normally insufficient for the application in electrochemical device due to low in ionic conductivity [7]. In order to improve polymer electrolytes with high conductivity, several methods had been conducted such as polymer blending, copolymerization and addition of ceramic filler or plasticization in polymer-salt complexes. Plasticization is most common technique use by researchers in order to improve the conductivity of an electrolyte. Plasticizer such as ethylene carbonate, poly carbonate, dibutyl phthalate, dimethylformamide and poly ethylene has been reported for improvement in the mechanical stability of polymer-salt complexes sample in order to enhance the ionic conductivity [8-10]. Plasticizer play a role by assists the dissolution and dissociation of salt or dopant, hence increases transport properties of polymer electrolytes [11]. Moreover, the introducing of plasticizer in polymer-salts complexes can increase the amorphous content and lower the value of glass transition temperature (Tg) [12]. Previously, we have reported on CMC doped NH4Br system and have found that CMC incorporated with 25 wt. % NH4Br achieved the optimum conductivity value of 1.12 × 10−4 S cm−1 [13]. In this work, CMC doped 25 wt. % NH4Br plasticized with various amounts of ethylene carbonate (EC) is presented. The highest conducting sample in this work is applied in the fabrication of solid-state proton batteries.

2.0 METHODOLOGY

2.1 Preparation of Plasticized Solid Bio-Electrolytes

In this work, a series of plasticized solid bio-electrolytes (PSBs) films were prepared using solution casting technique contain with CMC (Acros Organics Co., D.S. 0.7, with average molecular weight is 90000) doped 25 wt. % NH4Br (due to the highest ionic conductivity from the previous report) [13] and addition of ethylene carbonate, EC (Sigma Aldrich Co.) in various amount. 2 g of CMC was dissolved in distilled water. Then, the CMC solution was added with 25 wt. % NH4Br and the mixture was stirred continuously until complete dissolution was obtained with homogenous solution. Various amounts with the interval of 2 wt. % of EC as shown in Table 1 were added. The solution was then poured into several glass Petri dishes and left to dry at room temperature for the films to form. The films then were kept in desiccators for further drying process.

Table 1 Composition and designation of PSBs sample

Composition of EC	Designation
0 wt.%	A25
2 wt.%	AE2
4 wt.%	AE4
6 wt.%	AE6
8 wt.%	AE8
10 wt.%	AE10
12 wt.%	AE12

2.2 Characterization of PSBs Films

The PSBs films were characterized by Electrical Impedance Spectroscopy (EIS) using HIOKI 3532–50 LCR Hi-TESTER in a frequency range between 50 Hz to 1 MHz from ambient temperature to 383 K. Samples were cut into a suitable size and placed between blocking stainless steel electrodes which was connected to EIS. The conductivity, σ was calculated using the following equation:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

The electrochemical stability window of the PSBs system was determined by means of linear sweep voltammetry (LSV) technique using Autolab Potentiostat for the highest conducting sample with 1 mVs−1 scan rate in a potential range of 0-2 V. The sample was sandwiched between stainless steel and manganese (IV) oxide (MnO2) electrodes, which was acted as working and counter electrodes respectively.

2.3 Fabrication and Characterization of Solid-state Proton Batteries

The highest conducting film in the PSBs system was used to fabricate the solid-state proton batteries. Anode and cathode pallet for the proton batteries were made by grounding a mixture and then pressed at 2 ton pressure for 10 min to form a pellet. The composition of the cathode and anode for proton battery is as follows:

Anode: Zn (Merck Co.)/ ZnSO4.7H2O (Merck Co.)/ PVdF (Sigma Aldrich Co.)/ acetylene black (Keijin Co.)

Cathode: MnO¬2 (Tosoh Co.)/ PVdF/ acetylene black/ highest conducting PSBs solution.

The highest conducting PSBs system was sandwiched between anode and cathode in a Teflon battery jig. The open circuit voltage (OCV) and their potential measurements were carried out with the assistance of a True RMS Multimeter. The fabricated battery was discharge at different constant current of 0.5 mA and 0.25 mA using Neware High Precision Battery Tester.

3.0 RESULTS AND DISCUSSION

The conductivity of the PSBs system at room temperature is shown in Figure 1. The composition dependence of ionic conductivity of sample A25 is also shown in the figure for the purpose of comparison. In the previous work, the best electrolyte composition was 75 wt. % CMC + 25 wt. % NH_4Br with the highest conductivity value of 1.12×10^{-4} Scm^{-1} [13].

Conductivity is observed to have an improvement in the case of plasticized system when 8 wt. % EC was added to the PSBs system, where the conductivity increases to a maximum value of 3.31×10^{-3} Scm^{-1}. Apparently, this observation was accounted by the efficiency of EC in dissociating NH_4Br in CMC matrix due to of the weakening the inter-ion Coulomb force between the anions and cations in NH_4Br, making availability of hydrogen conducting ions (H^+) to increase with increments in EC. It is believed that the addition of EC obtained a high ionic conductivity value due high dielectric constant value (ε = 89.6) of EC [14]. High dielectric constant value will weaken the Columbic force between cation and anion of the dopant; therefore more dopant can be dissociated [14, 15].

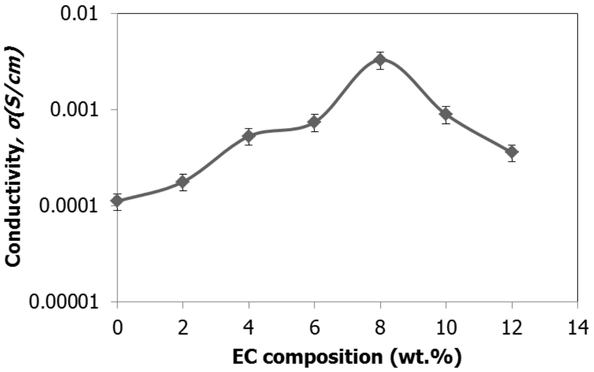


Figure 1 Ionic conductivity at room temperature as a function of EC composition

The variation an ionic conductivity of plasticized PSBs system as a function of temperature is shown in Figure 2. With addition of EC in sample A25, the conductivity increased with increasing of temperature for all samples which is clear that the plots of log σ versus 1000/T are linear, meaning that the conductivity follows an Arrhenius relationship. This increment may due to the availability of ionic mobility through the EC phase which entraps the residual solvents ensuing ionic mobility [16]. Hence, favors inter or intra-chain ion hopping and accordingly, the ionic conductivity of the PSBs system will be enhanced with the increase in temperature.

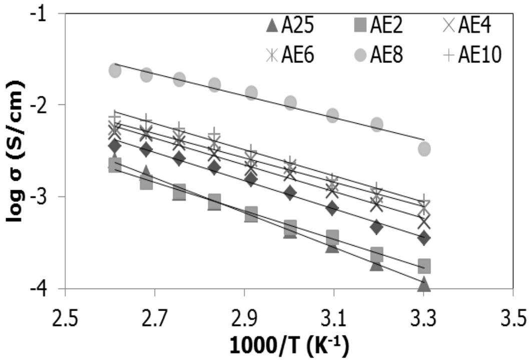


Figure 2 Temperature dependence of ionic conductivity for PSBs system

From the observation, it can be proved that the PSBs system in this work obey Arrhenius relationship where the conductivity mechanism is found thermally assisted [2, 13]. The Arrhenius relationship also has been observed by other researchers which were using same plasticizer in their electrolytes system [17, 18] and Arrhenian behavior can be expressed by:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \qquad (2)$$

where σ_o is a pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the temperature

Increasing in ionic conductivity is usually affected by the decrease in E_a value [5]. Buraidah *et al.* [19] reported the E_a value for the chitosan/NH_4I/EC polymer electrolytes system with sample containing plasticized with 45 wt. % EC which was the highest in conductivity sample and the E_a obtained was 0.22 eV. Although their system are different polymer used but similar plasticizer, the E_a value obtained for highest ionic conductivity based PSBs system is lower with 0.10 eV. Since the E_a of the plasticized system is lower than other research work, it is notable for practical applications especially in electrochemical devices [20]

The electrochemical stability (i.e. working cell potential range) of electrolyte system is an important parameter to be evaluated from their application point of view in electrochemical devices, such as batteries or other energy storage systems. The electrochemical stability of the PSBs system for sample AE8 has been studied using LSV technique, and its corresponding voltammogram is shown in Figure 3.

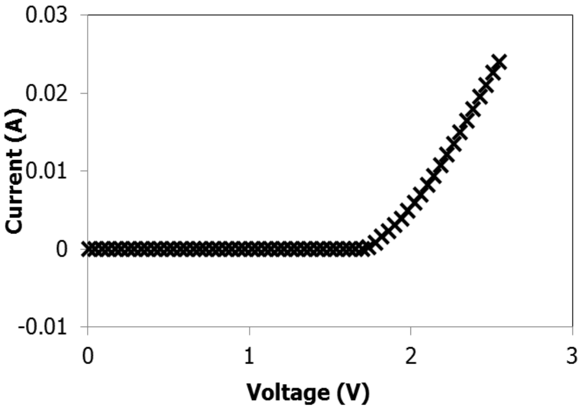


Figure 3 Linear sweep voltammetry for sample AE8 PSBs system

It can be observed that there is no obvious current through the working electrode from open circuit potential to 1.71 ± 0.01 V as shown if Figure 3, which corresponds to the plating of AE8 sample onto the stainless steel-MnO_2 electrode and this may be related to the decomposition of the sample. It increases gradually when the electrode potential is higher than 1.71 ± 0.01 V. In this present work, the experimental windows are kinetic, and may depend on processes occurring at the electrode [21], so the biopolymer electrolyte may breakdown at somewhat lower cell potential under differing conditions. The results revealed that the 1.78 ± 0.01 V and this imply that there is no decomposition of sample AE8 components at above this region. The decomposition voltage of methyl cellulose-NH_4NO_3 is reported by Suhaimi and co-workers to be ~1.5 V and the electrolyte was used in the fabrication of electrochemical devices [22]. From this results and observation, it shows that the highest sample for PSBs is compatible for application in proton battery, since the decomposition value standard of proton battery is about ~ 1 V [11].

3.2 Solid-state Proton Batteries Performance Study

The open voltage (OCV) performance of the fabricated battery contained with sample AE8 PSBs was measured at ambient temperature and is shown in Figure 4.

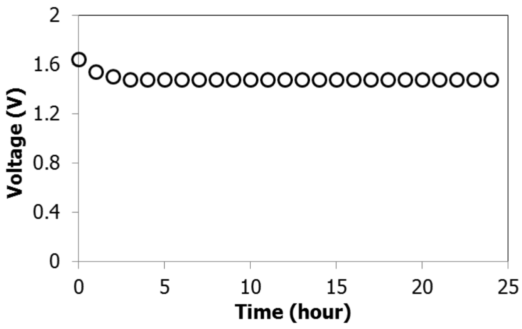


Figure 4 Open circuit voltage for BPSs solid-state proton battery system

It can be observed that there is a battery potential stay at the time of assembly where was higher in the first 1 h at 1.68 V and later stabilized at 1.48 ± 0.01 V with of battery potential drop of 9.75 %. This drop in OCV could be due to the oxidation of the Zn- electrode when the battery was self-discharged. Similar observation was also found by [23, 24] which correspond to their report based on proton batteries study. Figure 5 depict the discharge characteristic of assembled solid-state proton batteries at ambient temperature with different constant current.

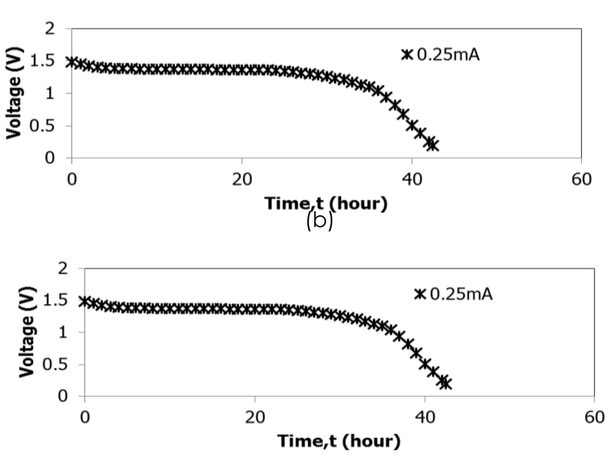


Figure 5 Discharge characteristics at different constant current for PSBs solid-state proton batteries

Based on Figure 5, it can be found that the initial voltage for solid-state proton battery system drop gradually before reaching a constant discharge plateau between 1.25 to 1.38 V for each constant current. Beyond the plateau region, voltage of the proton battery exhibited a rapid decrease within 1 to 3 hours before reach a cut-off voltage at 0.2 V. It looks that the proton battery for PSBs system discharged faster at higher constant current and this may due to the low diffusion rate (H^+) ions at sample AE8 based PSBs system, as observed by Selvasekarapandian *et al.* [24] in their work. The discharge performance of PSBs solid-state proton batteries at different constant current are presented in Table 2.

Table 2 Discharge performance for PSBs solid-state proton batteries

Cell Parameter	Measured values for discharge at	
	0.50 mA	0.25 mA
Discharge plateau time (hour)	11.80	36.8
Discharge capacity (mAh)	5.90	9.2
Current density ($mAcm^{-2}$)	0.31	0.16
Power density (Wkg^{-1})	1.36	0.96
Energy density ($Whkg^{-1}$)	16.04	35.33

Based on Table 2, it can be found that the solid-state proton battery for highest conducting PSBs system is more suitable for lower current applications. This is due to the internal resistance of the battery at intermediate load with the applied constant current [25].

To test rechargeablity performance, the solid-state proton battery PSBs system was charged with a constant current of 0.5 mA. The proton battery was discharge at 0.25 mA constant current with cutoff voltage of 0.8 V. This discharge current was chosen due to the better discharge capacity as observed from the discharge properties in Table 2. The characteristics of discharge-charge profile PSBs battery is shown in Figure 6.

It can be observed that from these figures, the potential voltage of the PSBs solid-state proton batteries system dropped after about a few hours and remain stable (plateau voltage) upon discharge at first 10 cycles and it becomes rapid thereafter. The longest charge-discharged cycle is identified at 6th cycle and this possibly may be due to the continuous supply of H^+ in electrolytes system. With addition of EC in CMC–NH_4Br complexes system, more ions due to H^+ would dissociate; this, in turn, increase the protonation of PSBs system and would influence the charge-discharge cycle when fabricated as the electrolytes of a solid-state proton battery. The discharge capacity of each cycle for PSBs solid-state proton batteries was calculated and plotted in Figure 7.

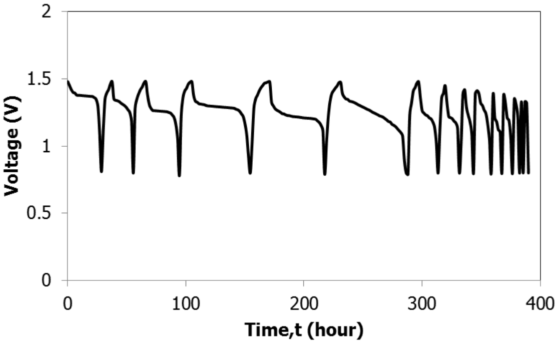


Figure 6 Discharge-charge curve of PSBs solid-state proton battery

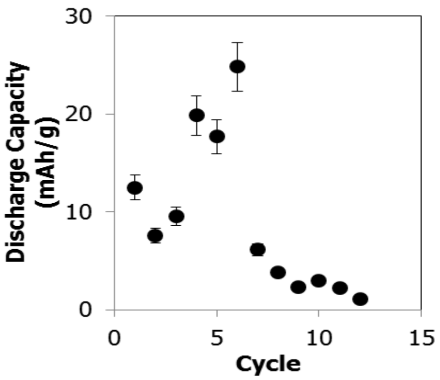


Figure 7 Discharge capacity for PSBs solid-state proton battery at different cycle

From Figure 7, it can be found that the longest discharge voltage-time with plateau voltage close to 1.28 V can be observed during the 6th cycle with discharge capacity is 24.25 mAh/g. The increment of discharge capacity is possible due to the good contact between electrode and electrolyte in battery system Shukor *et al.* [11] work. It would generate active materials at the surface of the electrodes to oscillate in $ZnSO_4.7H_2O$ discharge state thus, enhanced the performance in PSBs solid-state proton battery system. The results demonstrate possible application of this present plasticized bio-electrolyte based CMC-NH_4Br for solid-state proton battery applications and suitable for low current density applications [26].

4.0 CONCLUSION

In this work, CMC-NH4Br-EC plasticized solid bio-electrolytes (PSBs) system was successfully prepared with various amount of EC via solution casting technique. The ionic conductivity of the PSBs system was found to increase when EC was added and attain to optimum value at 3.31 x 10-3 Scm-1 with addition 8 wt. % EC. The temperature-ionic conductivity of the PSBs system exhibits Arrhenius relationship where the samples conductivity exclusively affected by the temperature with the highest conducting sample shown lower value of Ea with 0.1 eV. LSV measurement reveals that sample AE8 based PSBs system decomposed at 1.78 V, confirming the suitability in application for solid-state proton batteries. The solid-state proton battery has been fabricated with the formation of Zn + ZnSO4.7H2O || AE8 || MnO2 and achieve with an optimum open circuit voltage (OCV) of 1.48 V at room temperature. The battery displayed good in rechargeablity performance with more than 10 cycles and was found more suitable for lower current applications.

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