

SOLID BIOPOLYMER ELECTROLYTES BASED ON CARBOXYMETHYL CELLULOSE FOR USE IN COIN CELL PROTON BATTERIES

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Abstract: The solid biopolymer electrolyte (SBE) system has been formed by introducing various compositions of oleic acid as ionic dopant into carboxymethyl cellulose via solution casting techniques. The highest conductivity achieved at room temperature is $2.11 \times 10^{-5} \text{ S cm}^{-1}$. The coin cell proton battery were fabricated with the configuration of $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \mid \text{SBEs} \mid \text{MnO}_2$ for the highest conductivity SBEs. The open circuit voltage (OCV) of the fabricated proton battery with the best performance is 0.87 V at ambient temperature. The discharge characteristics of the cell have been studied at different currents, and the cell remained stable for more than 15 h for low current ($\sim 0.03 \text{ mA}$), thus making it suitable for low current density applications.

Keywords: Solid biopolymer electrolytes, ionic conductivity, proton battery, open circuit voltage.

Introduction

Energy storage has embraced a wide range of energies, technologies, scales and applications. Energy can now be stored in chemical, electrical, kinetic, potential or thermal media. Among existing energy storage technologies, batteries are one of the most established means of storing electricity in the form of chemical energy (Zul *et al.*, 2015). Batteries have a long history of consumer usage after the invention. The development of modern batteries as a form of energy storage can be traced back to Galvani in the 1970s (Dell & Rand, 2001). In the 1800s, Volta outlined the design of a device that could produce a constant current from the proper assembly of dissimilar metals, which became known as “Voltaic pile” (Asimov, 1982). Further development of battery systems were then initiated in the 1950s.

The concept of polymer-based batteries, which was introduced almost three decades ago (Novák, 1997), has recently gained interest, mainly due to the possibilities

of manufacturing flexible and environmentally friendly devices. The first prototype for a polymer battery was a polyaniline (PANI) pellet electrode battery with a capacity of 13 mAh g^{-1} , introduced in 1968 (Li *et al.*, 2015). An all-polymeric solid state battery was established in 1981, based on doped polyacetylene electrodes and a polyethylene oxide based electrolyte (Ali *et al.*, 2005).

Solid biopolymer proton batteries play an important role in the development of new high energy density batteries due to their unique properties such as easy thin film formation, process ability, light weight and elasticity. Therefore, solid state polymer batteries are possible alternatives to the classical secondary battery systems (Isa & Samsudin, 2016; Gurunathan *et al.*, 2003). Hence, this present study focuses on conductivity studies of carboxymethyl cellulose (CMC) by doping with oleic acid (OA) based solid biopolymer electrolytes (SBEs) and its potential application in coin cell proton batteries.

Methodology

Preparation and characterization of CMC-OA SBEs

The development of CMC-OASBEs is following the previous work reported in (Chai & Isa, 2013). CMC was obtained from Acros Organic Co. (purity >99.9%) without further purification. 1 g of CMC was mixed with distilled water and stirred until it was completely dissolved. Different weight percentages (wt.%) of OA (R & M Marketing, purity 99%) were dissolved in ethanol, then added to the CMC solution and stirred until it became homogeneous. The mixtures were then cast into petri dishes and dried in an oven at a constant temperature of 333 K. The films were then kept in desiccators for further drying. The SBE films were analysed via Electrical Impedance Spectroscopy model HIOKI 3532-50 LCR Hi-Tester at various frequencies of 50 Hz to 1 MHz. The films were cut into a fitting size of a 2 cm diameter circle and placed between two stainless-steel blocking electrodes of the sample holder which connected to the LCR tester. The software controlling the measurement recorded the real and imaginary impedance at various frequencies. The bulk impedance (R_b) value was obtained from the plot of negative imaginary impedance ($-Z_i$) versus real part (Z_r) of impedance and the conductivity of the samples were calculated following Yusuf *et al.* (2014) and Buraidah *et al.* (2010).

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

where A = area of SBE–electrode contact and t = thickness of the SBE films.

Fabrication and characterization of coin cell proton battery

The highest conducting CMC-OA SBE was cut into a circular of 2 cm diameter which fits into the coin-cell casing for proton battery fabrication. To make an anode for the battery, a mixture of 34% of Zn, 28% of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 4% of PVdF and 34% of acetylene black were mixed and grounded together. Then, the mixture was pressed at 10 MPa to form pellet. The

same procedure was employed in preparing the cathode composing 80% of MnO_2 , 5% of PVdF, and 15% of acetylene black. The highest conducting SBE was sandwiched between the anode and cathode in a coin cell casing as shown in Figure 1. The total cell weight is 0.30 (± 0.01) g. The open circuit voltage (OCV) of the battery was monitored for 24 h by using Digital Auto-ranging True RMS Multimeter. The battery was tested for charge-discharge characterization using Neware High Precision Battery Tester. The battery containing the highest conductivity of CMC-OA SBE was studied at 0.01 mA, 0.03 mA and 0.05 mA of constant currents. Additionally, the batteries were tested at elevated temperatures of 323K, 343K and 363K. Several parameters such as the cell capacity, Q was calculated using Equation 2, whereas energy density, E and power density, P of the cell were computed following Equation 3 and 4.

$$Q = It \quad (2)$$

$$E = QV \quad (3)$$

$$P = E/t \quad (4)$$

Here, t is the discharge time, I is the current of the cell and V is the voltage.

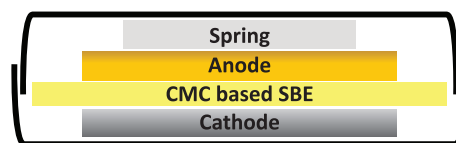


Figure 1: Schematic diagram of proton battery fabricated

Result and Discussion

Conductivity study of CMC-OA SBEs

The highest conductivity at room temperature calculated using Eq. 1 is $2.11 \times 10^{-5} \text{ S cm}^{-1}$ for sample containing 20 wt.% of OA as shown in Figure 2. Starting from 0 wt.% SBE, the conductivity started to increase until 20 wt.% CMC-OA SBE. It can be attributed to the complexation between the COO^- of CMC and H^+ of OA as proven in the FTIR analysis from the previous work (Chai & Isa, 2013).

On the other hand, it can be observed that the conductivity started to decrease with addition of more than 20 wt.% of OA. This behaviour can be explained by association of ions at higher OA concentration which leads to the formation of

ion clusters and thus the mobility are decreased which similar to the work done by previous researchers (Azzahari *et al.*, 2016; Samsudin *et al.*, 2014; Selvasekarapandian *et al.*, 2005).

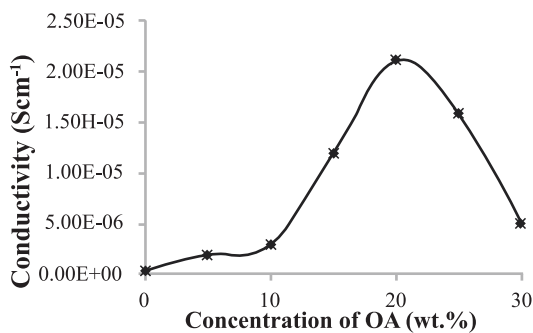


Figure 2: Room temperature ionic conductivity of CMC- OA

As we have reported previously (Chai & Isa, 2013), the relationship between conductivity and temperature of the SBEs are naturally Arrhenius behaviour. The thermal properties results of CMC-OA SBEs shows a good fit of $R^2 \sim 1$ for each sample in the series. This indicates that ionic conductivity of the SBEs obeys the Arrhenius law and it is suggested that the system is thermally activated which similar to

the work done by previous researchers (Pradhan *et al.*, 2007; Yahya *et al.*, 2006; Ali *et al.*, 2005; Ramesh & Arof, 2001).

Battery characteristics

The open circuit voltage (OCV) characteristic of the coin cell proton battery was measured at room temperature is shown in Figure 3.

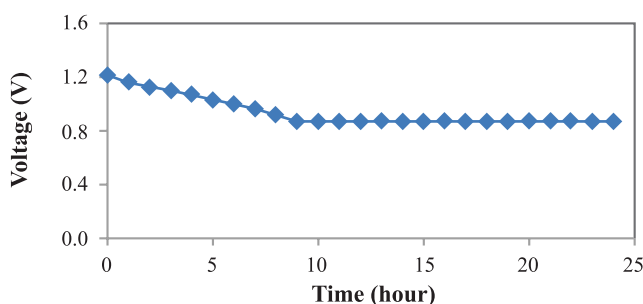


Figure 3: The graph OCV against time of OA-20 for 24 h

Table 1: Possible anode and cathode reaction for SBEs solid-state battery

Anode reaction	Cathode reaction	E_o (V)
$Zn \rightarrow Zn^{2+} + 2e^-$		0.7618
$ZnSO_4 + 7H_2O + 2e^- \rightarrow Zn + SO_4^{2-}$		-0.7993
	$MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O$	1.2240
	Overall reaction	1.2615

It can be observed that the initial voltage of the cell was 1.22 V. It drop rapidly in first 11 hours and it maintained at 0.87 V thereafter with % of voltage drop of 28.7%. The drop in OCV is due to the oxidation of the negative Zn electrode when the cell self-discharged (Isa & Samsudin, 2016; Mishara *et al.*, 2012; Selvasekarapandian *et al.*, 2005). The chemical reaction that takes place in the proton cell is shown as Table 1 similar to the work done by Mishra *et al.* (2012). The overall reaction should provide the cell with $E_o = 1.2615$ V. However in this work the cell gave a voltage of $E = 0.87$ V, which is about 31%

lower than the theoretical cell voltage. The cell was lower than the overall reaction due to the ionic conductivity of OA-20 SPE that achieved was $\sim 10^{-5}$ S cm^{-1} . According to Samsudin *et al.* (2014) and Subhan and Arof (2004), the value of ionic conductivity of electrolyte around $\sim 10^{-4}$ S cm^{-1} is more suitable for battery applications and comparable with electrolytes commonly used in the fabrication of proton batteries. The summarized results for CMC-OA proton battery at different constant current is presented in Table 2.

Table 2: Discharge properties of CMC-OA proton battery

Cell Parameter	Measured values for discharge at		
	0.01 mA	0.03 mA	0.05 mA
Discharge plateau time (hour)	1	15	1.6
Internal resistance (k Ω)	7.00	2.33	1.40
Discharge capacity (mAh)	0.01	0.45	0.08
Current density (mAcm $^{-2}$)	0.009	0.026	0.043
Battery capacity (x 10 28 mAhkg $^{-1}$)	1.10	49.40	8.78

Based on the Table 2, it can be inferred that the proton battery for CMC-OA SBE was more suitable for lower current applications. This is due to the internal resistance of the CMC-OA proton battery at intermediate load with the applied constant current. Moreover, the addition of CMC-OA SBE solution in cathode increased the period of performance (stability) as there was a copious supply of H $^+$ ions available from the CMC-OA SBE at lower discharge current (Bansod *et al.*, 2007). To further study the effect of temperature on discharge of the

proton battery, the current used was 0.03 mA. The fabricated proton battery was undergoing the discharge characteristics at 0.03 mA at the selected temperature which are 323K, 343K and 363K (Figure 4).

From Figure 4, the longest discharge curves obtained is at 343K compared to the others temperature (303K, 323K and 363K). Since the ionic conductivity of CMC-OA SBE increases with temperature, more ions are available for conduction and thus more ions are

able to intercalate and de-intercalate between the two electrodes. Hence, the battery gives a longer discharge time at elevated temperature (Samsudin *et al.*, 2014; Bansod *et al.*, 2007).

Nevertheless, the discharge curve of the fabricated proton battery reduces at higher temperature (363 K). This can be attributed due to the degradation of the CMC-OA SBE.

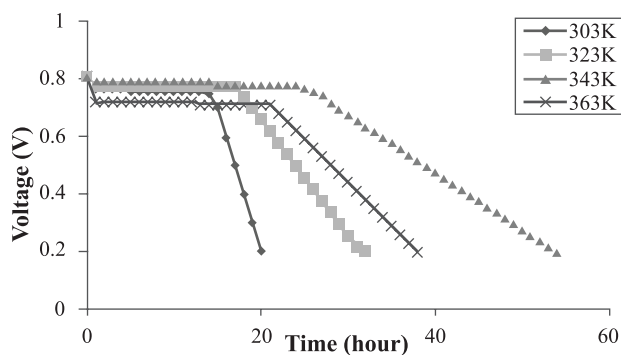


Figure 4: Discharge characteristics at 0.03 mA at elevated temperature

Conclusion

The new invention coin cell proton battery with the configuration of Zn | SBE | MnO₂ for the highest conductivity of CMC-OA SBE has been successfully developed. The battery gave an average open circuit voltage of 0.87 V and found suitable for low current drains or low load resistance. It's also had good agreement with the discharge properties during heat treatment. These results imply that CMC based SBEs suggest the possible practical application of the present electrolytes in the fabrication of solid-state batteries.

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