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2-Hydroxyethyl cellulose as natural binder in electrodes for solid-state proton battery: Construction and preliminary results

M. A. Ramlli[1], Yu K. X.Yu[2], Y. W. Siew[2] and M. I. N. Isa[1]*

[1]*Advanced Nano Materials (ANoMa) Research Group,*
Advanced Materials team, Ionics State Analysis (ISA) Laboratory,
School of Fundamental Science, Universiti Malaysia Terengganu,
21030 Kuala Nerus, Terengganu, MALAYSIA.
[2]*School of Ocean Engineering, Universiti Malaysia Terengganu,*
21030 Kuala Nerus, Terengganu, Malaysia.

Affordable and greener materials were extensively studied in electrode fabrication for Li-ion based batteries but less interest was shown to proton battery. Hence, in this work, a methodology on preparing a natural based binder for proton battery was reported. 2-Hydroxyethyl Cellulose (2HEC) was chosen to replace PVDF commercial binder in electrode for ZnSO4|MnO_2 proton battery configuration. SEM image shows good surface formation for both anode and cathode with good porous structure. OCV result shows that the cell improved the stable voltage of reference cell of 0.7 V to 0.9 V after 24 hours. The first discharge of the cell took 6 hours and 49 minutes at 0.005mA and shows good potential for rechargebility test.

Keywords: Electrode, solid proton battery, cellulose, natural binder, water-soluble

I. INTRODUCTION

Binder in electrode is equally essential thing to study in order to achieve a good performance electrode when compared to active material, conductive material and current collector [1]. However, it is surprisingly that not many works devoted to investigate the effectiveness of a binder material in an electrode fabrication especially in solid proton battery. In composite electrode fabrication, binder is the most crucial thing to ponder because it maintain the physical of the electrode and holds together all the materials with the current collector. Without a good binder material that have strong adhesion, the electrode materials can easily fall apart and eventually lead to the decrease of overall performance. In addition, binder also needed to possess a good electric network to provide a good cycling performance [2]. Mostly, in the fabrication of proton battery, many researchers adopting the use of Polyvinylidene fluoride (PVDF) because it is the current commercial binder used in many battery productions [3]. PVDF, uses n-methyl pyrrolidone (NMP) as solvent which is a hazardous and highly volatile organic sol-

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*Corresponding author:ikmar_isa@umt.edu.my vent that can impose a threat to human being and environment if not handle carefully [4]-[5]. Moreover, PVDF and NMP was very expensive material to begin with and this can hinder the goal on to produce a cost effective electrode for many researchers.

In order to discard the usage of hazardous solvent, many types water-soluble binder that are cheaper and safer has been studied such as alginate, carboxymethyl cellulose (CMC), polyacrylic acid (PAA), alginate and many more water-soluble derivatives [6]-[7],[3]. However, to the best of our knowledge, these binders were studied mostly for Li-ion based batteries and not for proton battery especially with ZnSO4|MnO_2 proton battery. Therefore, in this paper we introduced a water-soluble binder material that is more affordable and safer to the environment for proton battery configuration. For this work, a cellulose derivative was chosen because it is the most abundance material on earth and relatively easy to find known as 2-Hydryethyl cellulose (2HEC). Commercially, 2HEC was popularly used as emulsifier in various food, cosmetics and pharmaceutical products. Throughout this paper, we document a procedure to fabricate new composite electrode using 2HEC as alternative natural binder to PVDF and the preliminary results

II. MATERIALS AND METHODS

A. Anode preparation

Both zinc powder (Zn) and zinc sulphate heptahydrate ($ZnSO_4 \bullet 7H_2O$) battery grade were bought from EMSURE, Germany and Timcall Graphite and Carbon supplied the conductive carbon black. 2-hydroxyethyl cellulose (2HEC) powder with average Mv∼90000 was bought from Sigma-Aldrich. The ratio of anode material used is 82:13:4 for active material, binder and conductive material respectively with total weight of the anode material is 19.5625 g. Binder solution was prepared by dissolved 2HEC in 50 ml distilled water. Then, active and conductive material were mixed in a planetary ball mill (stainless steel vial and ball) at 500 rpm for 90 minutes. After that, all the anode material were mixed slowly into the binder solution to prevent the formation of air bubbles. The slurry stirred at 1200 rpm until a consistent slurry was obtained. Copper (Cu) foil was prepared as current collector for anode by cutting it to suitable sizes. Then, spread the anode slurry uniformly onto the Cu foil by using a stainless steel blade. Masking tape was used as track for better spread of the slurry. The coated Cu foil were dried in oven at 100°C for 1-2 hours. A perfectly dried anode will have smooth surface without any phase separation or cracks. All samples were kept in a dry box to prevent from contamination

B. Cathode preparation

Cathode materials used in this work were manganese dioxide (MnO_2) as active material, 2HEC as binder and carbon black as conductive material. MnO_2 (battery grade) was bought from Sigma-Aldrich. The total weight and ratio used for cathode fabrication is the same as anode where 82:13:4 for active material, binder and conductive material respectively. Cathode were prepared the same as anode. Binder solution were prepared, and then mixed with MnO_2 and carbon black. The slurry was magnetically stirred at 1200 rpm. Aluminium foil was used as current collector for cathode. The slurry was spread uniformly onto the aluminum foil using stainless steel blade and masking tape was used as track for better spread of the slurry. The drying process was done in oven at 100°C and all samples were kept in dry box to prevent contamination.

C. Solid biopolymer electrolyte preparation

The solid biopolymer electrolyte (SBE) used in this work was based on a work done by [8]. The materials used are carboxymethyl cellulose (CMC) and ammonium chloride (AC). Firstly, dissolved 2 gram of CMC in distilled water, then doped with 16 wt. % of AC. Stir the solution until homogenous then pour the solution into Petri dish and dried in oven at 50 °C for 14 hours.

D. Single proton cell fabrication

In order to test the performance of the new electrodes, a single proton cell was fabricated with the configuration of $Zn{:}ZnSO_4.7H_2O{:}CB|SBE|MnO_2{:}CB$. The schematic diagram of the fabricated single proton cell was depicted in Figure 1. Here, the electrodes and SBE were cut into a disc shape with 2 cm diameter and active area of 3.1416 cm^2 and sandwiched in between the stainless steel inside the Teflon jig. The proton cell undergo an Open Circuit Voltage (OCV) for at least 24 hours to allow the self-discharge of the cell until a stable voltage is obtained. The OCV test was carried out by using True RMS multimeter with a computer interface.

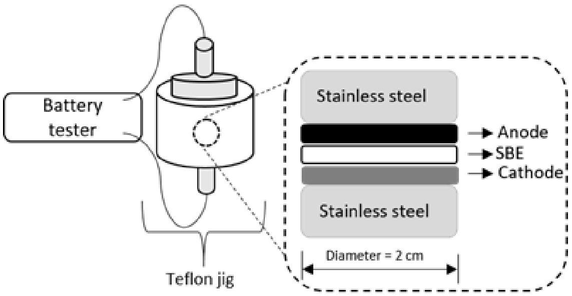

Figure 1. Schematic of single proton cell inside Teflon jig for testing

E. Scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDX)

Scanning Electron Microscope (SEM) with Energy-dispersive X-ray Spectroscopy (EDX) was used to investigate the surface morphology and the dispersion of the known material on the electrodes. The model used for this work is JOEL JSM-6360LA.

F. Cell performance

The performance of fabricated single proton cell was done by using Neware High Precision Battery Tester. The discharge current were set to 0.005 mA. The maximum charging voltage was set to 0.9 V and the discharge voltage was set to 0.1 V. The list of performance parameters determined for the cell can be referred to Table 1.

III. RESULTS AND DISCUSSIONS

Figure 2a) and 2b) shows the successfully fabricated cathode and anode that uses 2HEC as natural binder respectively. On the other hand, Figure 2c) shows the example of bad coating that after drying process. The cracked electrode was due to the excess of solvent while casting [9]. From this work, the most crucial step in fabricating the electrodes is to obtain a good slurry with good consistency. This is because, if the slurry have too much solvent the coating usually cracked after drying process, while lacking of solvent will produced a too porous coating that can easily peeled off from the current collector. The surface morphology of the electrodes was observed using SEM at x100 magnification and depicted in Figure 3. From the figure, SEM image showed good dispersities of the material and both the anode and cathode exhibits a porous-like surface morphology. In electrode fabrication, a good dispersity of the material can contributes in better cycling capabilities of the cell [2]. A porous like structure can also improve the electrochemical reversibility by providing more reaction sites and help in ease the movement of ions in between the electrode-electrolyte [2].

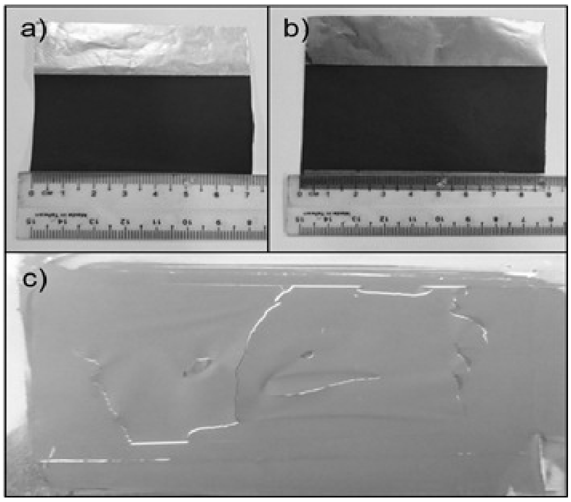

Figure 2. Fabricated electrode that uses 2HEC as binder; a) Cathode; b) Anode and c) Cracked coating

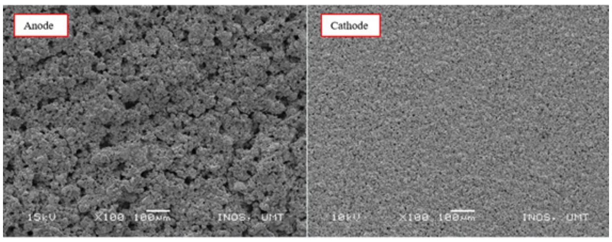

Figure 3. SEM image of anode and cathode at x100 magnification.

A single proton cell was fabricated using electrodes and SBE by cutting into disc shaped

Table 1. Performance parameters

Performance parameter	Equation	Equation
Voltage drop (%)	$V_D = \frac{V_o\text{-}V_{oc}}{v_o} \times 100$	(1)
Internal resistance Ω	$r_{in}= \frac{V_{oc}\text{-}V_{nv}}{I}$	(2)
Power density (Wg^{-1})	$P=\frac{V^2 nv}{r^{in} W}$	(3)
Energy density (Whg^{-1})	$E=P \times t$	(4)
Current density (A/cm^2)	$I_d = \frac{I}{A}$	(5)
Discharge capacity (mAh)	$Q=I \times t$	(6)

Where; V_o= Initial voltage from OCV test, V_{oc} = final voltage from OCV test, V^2nv = Nominal voltage for one cycle, I= Current applied, A= Area of the cell (cm^{-2}), t= time taken for one cycle (hour), W= Weight of the cell

with a diameter of 2 cm and sandwiched together in a Teflon jig. The ability of the cell to self-discharge over time was done by performing the OCV test for at 24 hours at room temperature. A single proton cell fabricated by Ahmad (2017) [Development and characterization of enhanced carboxymethyl cellulose - ammonium chloride as solid polymer electrolytes in rechargable proton cell] Unpublish raw data. was used as reference with the same configuration of $ZnSO_4.7H_2O|SBE|MnO_2$. The difference between the current proton cell and reference proton cell is the type of binder used, where current cell used 2HEC while reference cell used PVDF and both cell used the same SBE. Although it is to be noted that, the reference cell was compared using the data obtained by Ahmad (2017) [Development and characterization of enhanced carboxymethyl cellulose - ammonium chloride as solid polymer electrolytes in rechargable proton cell] Unpublish raw data only and not by fabricating a new cell from her work. Figure 4 shows the plot of OCV in a function of time for current proton cell and reference proton cell for 24 hours at room temperature. From the plot, the initial voltage for current work cell was 1.43 V and the reference cell was 1.34 V at room temperature. For the current cell, the value dropped gradually for the first eight hours of OCV test and stabilized at 0.9 V after 12th hours of OCV test with 37% voltage drop. Same pattern showed by the reference cell where the voltage decreased gradually by time but later stabilized at 0.7 V. From the OCV results, current cell shows slight improvement where the stable voltage has increased from 0.7 to 0.9 V at room temperature.

The possible electrode reactions were presented in Table 2 [10]-[11]. During discharge, electrons (e^-) were released by the oxidation of zinc and the protons (H^+) were supplied by zinc sulphate with the potential value of (∼0.76 V)

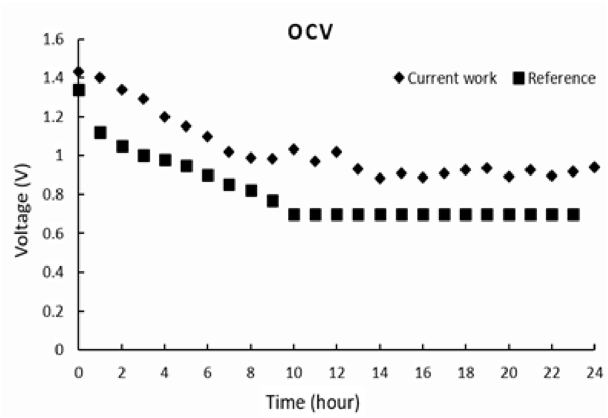

Figure 4. OCV as a function of time for current work and reference cell by [12]

and (∼-0.82V) respectively. Meanwhile at cathode, the reduction process of manganese dioxide yielded a potential value of (∼1.22 V). Hence, overall potential value of the electrochemical reactions could be summarize by Cell potential, E°cell = E°reduction E°oxidation = 1.28 V. From first assembled, the cell recorded a whopping 1.43 V but later stabilized at 0.9 V after 24 hours of OCV with 37 % of voltage drop. The large voltage drop can be related to the oxidation that occurred at anode and also can be due to the internal resistance of the cell and also can be resulted from the low conductivity of the SBE itself [13].

The performance parameter of the cell was calculated and recorded in Table 3. The cell rechargebility was investigated using battery tester and the graph of first time discharge voltage in a function of time (hour) was plotted in Figure 5. The cell was discharge at constant ∼0.005mA ± 0.002mA, the minimum voltage was set to 0.1 V and maximum charge voltage was set to 0.9 V. The first time discharge of the cell took about ∼7 hours before it reaches the minimum voltage. Here, there are no plateau region was observed, but the cell was steadily discharge at the given current. Figure 6 shows the rechargebility profile of the cell for the first 10 cycle. From the first time discharge to the second discharge, a huge significant reduction in time was observed, but after that, the cell shows relatively almost the same profile. For now, we did not discover any reason for the huge different of discharge time between the first and second time discharge just yet. Table 4 summarized the rechargebility profiles for each cycle. From the table, it can be seen that the cell took an average of ∼12 (±1) seconds to charge and 75 seconds to discharge where 2nd cycle took the longest time to discharge. It also can be seen that the discharge time of the cell gradually reduced by each cycle with a small fluctuation on 6^{th} and 7^{th} cycle and then continue to decrease for the next few cycles.

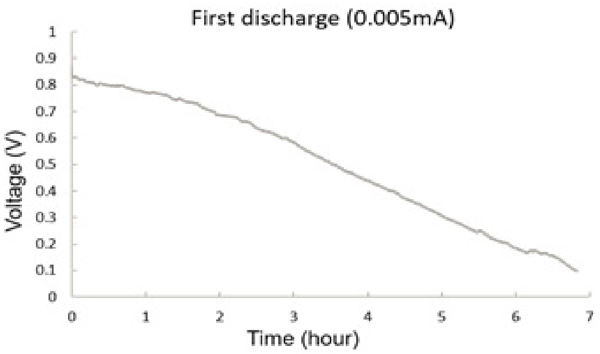

Figure 5. Plot of first time discharge of the cell over time (0.005mA)

Table 2. Possible electrode electrochemical reactions for Zn+ZnSO4|MnO_2

Electrode	Electrochemical reactions	Potential value (V)
Anode	$Zn \rightarrow Zn^{2+} + 2e^{-}$	~0.76
	$ZnSO_4.7H_2O \rightarrow 7H^{+} + 7OH^{-} + ZnSO_4$	~(0.82)
Cathode	$MnO_2 + 2e^{-} + 4H^{+} \leftrightarrow Mn^{+} + 2H_2O$	~1.22
Overall	$Zn + ZnSO_4.7H_2O + MnO_2 \leftrightarrow Zn_3SO_4{\bullet}5H_2O{\bullet}2(OH) + Mn(OH)_2$	~1.28

$$\text{Cell potential, } E^{\circ} cell = E^{\circ} reduction \text{ - } E^{\circ} oxidation \quad (7)$$

$$1.22 \ \ [-0.76 + (-0.82)] = 1.28 \text{ V}$$

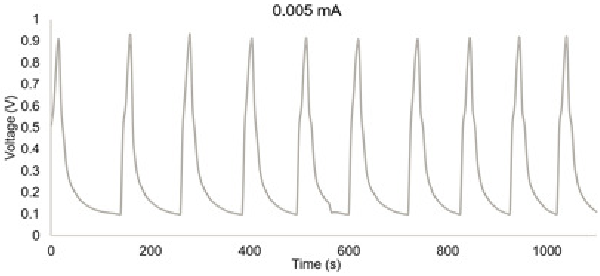

Figure 6. Rechargebility profile at 0.005mA at room temperature

Table 3. Performance parameter of the cell at 0.005mA

Performance parameter	Value
Weight (g)	0.171
Area (cm^2)	3.141
Voltage drop (%)	37
Internal resistance (Ω)	6
Power density (Wg^{-1})	0.7334
Energy density (Whg^{-1})	4.76
Current density (mA/cm^2)	1.591
Discharge capacity (μAh)	32.4 (first discharge)

Table 4. Time taken for the cell to charge-discharge until 10^{th} cycle with discharge capacity

Cycles	Time taken (s)		Discharge capacity
	Charge	Discharge	(μAh)
2^{nd}	13	97	1.347
3^{nd}	13	96	1.333
4^{th}	12	82	1.138
5^{th}	12	76	1.055
6^{th}	12	90	1.25
7^{th}	11	78	1.083
8^{th}	12	72	1.00
9^{th}	12	68	0.9444
10^{th}	12	66	0.9166

IV. SUMMARY

Having the option to replace PVDF in electrode fabrication with natural materials is a bliss for every researchers. This can reduced the overall fabrication cost and increased the safety value of the electrode. Therefore, this paper has demonstrated the preparation of composite electrode fabrication process using 2HEC as natural binder in electrode for Zn+$ZnSO_4$|MnO_2 configuration solid proton cell. SEM images summarized the porous-like structure and evenly distribution of the materials on the anode and cathode. Fabricated proton cell with 2HEC as binder shows improvement in OCV voltage and displays a good rechargebility profile. This paper has documented the preliminary results of the capability of 2HEC as natural binder in electrode for proton cell.

V. ACKNOWLEDGEMENT

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