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Influence of the performance of Gel Polymer Electrolyte (GPE) with the addition of SiO_2 and Carboxy Methyl Cellulose (CMC) for Zinc-Air Batteries (ZABs)

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Abstract. PVA is a non-toxic, semi-crystalline polymer with good hydrophilicity that is also simple to produce. Consequently, PVA is strongly suggested as a potential material in GPE synthesis. GPE was created by converting the host polymer Poly-Vinyl Alcohol (PVA), which was utilized as a matrix and expanded when exposed to a 6M KOH solution. The thermal stability, mechanical toughness, and electrochemical toughness of GPE have all been proven to be improved by SiO_2. SiO_2 works as a plasticizer and crosslinker to make GPE more elastic. It also tends to make PVA more amorphous, which is predicted to make GPE more absorbent to 6M KOH. The SiO_2 surface's hydroxyl groups offer water-resistance characteristics that enable the zinc-air battery to operate at its best. It has been demonstrated that cellulose may significantly enhance the structure of GPE, which is more amorphous, and is anticipated to be able to raise the GPE's ionic conductivity value. The highest GPE-3 ionic conductivity is 6.288 mS/cm meanwhile the highest GPE-6 ionic conductivity is 5.645 mS/cm and the highest GPE-0A ionic conductivity is 0.997 mS/cm.

Keywords: *GPE; PVA; SiO_2; CMC; ZABs.*

1 Introduction

Electrolytic polymer gel (GPE) is an electrolyte gel containing a polymer matrix. It is currently considered an effective solution to replace the currently available liquid electrolyte in zinc-air batteries. Most of the problems that occur when batteries use liquid electrolytes are that the electrolyte is toxic, corrosive, unsafe, and there is always a danger of a leak if the battery is or is physically damaged. In addition, liquid has a tendency to accelerate the formation of dendrites which develop due to repeated recharge cycles and eventually lead to battery failure. It is hoped that replacing the electrolyte with GPE can improve the performance of the zinc-air battery.

Therefore it is necessary to replace this liquid electrolyte by using GPE. GPE comes from a polymeric material whose function is to minimize the volume of

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cell electrolyte and maintain the contact area with the zinc anode particles which will have an impact on high ionic conductivity and improve the performance of the battery. Another outstanding advantage is the reduced mobility of the zinc anode which minimizes the formation of dendrites during the battery charge reaction process and minimizes the movement of $Zn(OH)_4^{2-}$ ions towards the cathode during the battery discharge reaction process. The GPE contact with the cathode must also be considered so that the battery charge-discharge reaction continues optimally. GPE can act as a separator [1],[2].

Poly-Vinyl Alcohol (PVA) is a promising candidate material to become a polymer host polymer because of its ability to provide good optical, mechanical and electrochemical properties. PVA is also a semi-crystalline polymer with high hydrophilicity, easy to prepare, non-toxic [3]. so that PVA is highly recommended as a promising material in GPE synthesis. GPE was synthesized from the host polymer Poly-Vinyl Alcohol (PVA) which was used as a matrix which would expand when exposed to 6M KOH solution [2]. SiO_2 has been shown to improve the thermal stability, mechanical strength and electrochemical strength of GPE [4]. SiO_2 functions as a plasticizer and crosslinker which increases the elasticity of GPE, SiO_2 tends to increase the amorphous area of PVA which is expected to increase the area so that the absorption ability of 6M KOH to GPE will be higher. The hydroxyl groups on the SiO_2 surface have water-resistant properties that allow the zinc-air battery to work optimally. However, the excess SiO_2 additive will reduce the size of the PVA chain and the size of the GPE matrix which results in reducing the absorption of 6M KOH into GPE [5].

CMC (Cellulose) is the most abundant biopolymer on earth because it is very common in plant cell walls [6]. Cellulose has been shown to be able to comprehensively improve the structure of GPE which is more amorphous and is expected to be able to increase the value of the ionic conductivity of the GPE. Low concentrations of cellulose (0.5-2%) in water form a semi-stable gel. GPE based on cellulose hydrogel. The general properties of cellulose include: Abundant availability, Safe, Non-toxic, High ability to stick [7]

2 Preparation of Cu-plate

First prepare two Cu plates (2×1) cm^2, then put the Cu-plate in 3M HCl aquous to get rid of surface oxides [8] then do ultrasonication at 25℃ within 10 minutes after the ultrasonication process washing the all-Cu plates using aqua demineralization until pH ~ 6.5. Dry the Cu plate after that apply silver paste (1×1) cm^2. Diagram of the process for producing Cu-plate can be seen in Figure 1 below. Otherwhise microscopic differences in the surface color of the Cu plate on the Cu plate before being prepared with the Cu plate after being prepared can be seen in Figure 2 below. In Figure 3 is the shape of the Cu-plate used in this study.

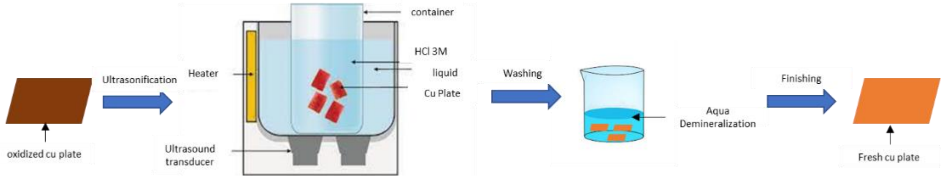

Figure 1 Diagram of the process for producing Cu-plate.

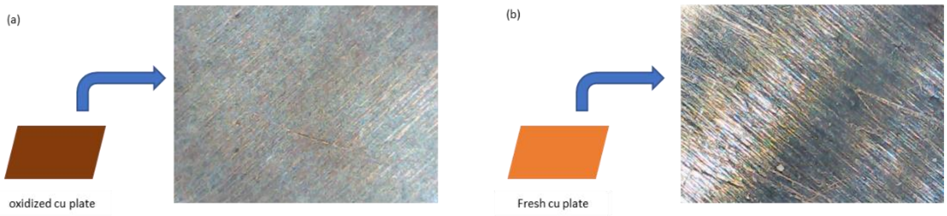

Figure 2 (a) Cu plate is oxidized and (b) Cu plate has been prepared in 2000 times camera magnification.

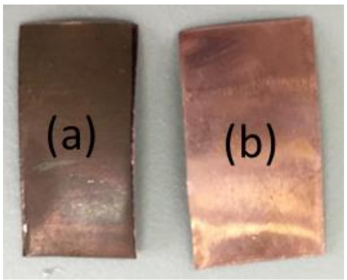

Figure 3 (a) Cu-plate is oxidized and (b) Cu plate has been prepared

3 Preparation of Gel Polymer Electrolyte (GPE)

To synthesize GPE, variations in the weight composition of SiO_2 (0.06 : 0.15) g, 0.45 grams of cellulose (CMC) and 3 grams of PVA are required. Mix these three ingredients into 60 mL of denionized water (aquadest) and stir for 2 hours at 50 ^{o}C and rpm=400. After it becomes homogeneous, pour the GPE into the mold and wait for it to dry. Dried GPE was then soaked in 6M KOH solution for 7 days. calculating the GPE ionic conductivity of each sample through the Eq. (1)

$$\delta = \frac{L}{A \times Rb} \tag{1}$$

Where L, A, and Rb represent the thickness, area of GPE between two Cu-plate, and bulk resistance of GPE [5]. Using SiO_2 as a crosslinker, Figure 4 depicts a probable process for how a hydrogel is created between CMC and PVA.

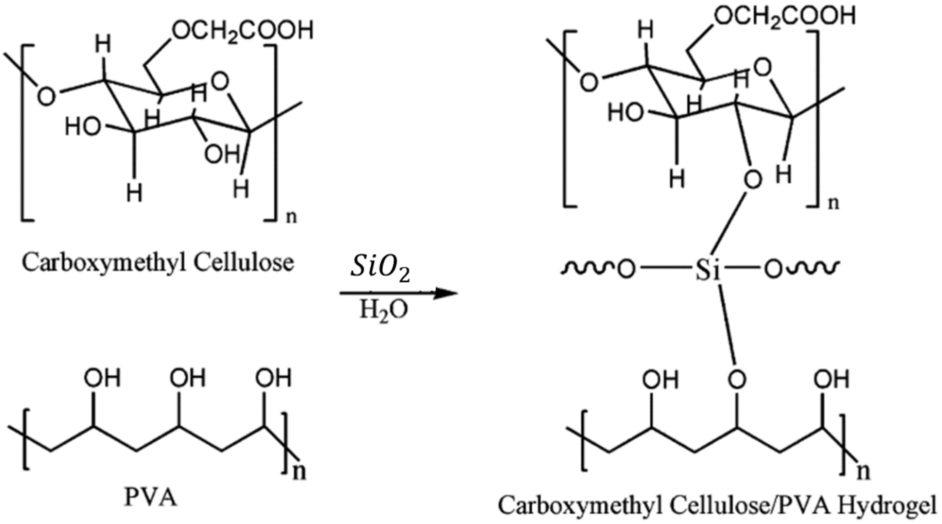

Figure 4 Diagrammatic representation of the synthesis of PVA/CMC hydrogel utilizing SiO_2 as a crosslinker (adapted by [9])

4 Assembly Cu-plate and GPE symmetrical cell

Assembly process of electrolyte polymer gel using Cu plates. The sonified Cu plates were taken along with the GPE sample (1×1) cm^2 which had been soaked in 6M KOH aquous for 2 days, then the surface of the GPE was dried using filter paper. Paste it carefully on the Cu-plate that has been smeared with silver paste after that attach the symmetrical cells with plastic wrap and then tape.

Figure 5 Cu-plate and GPE symmetrical cell.

5 Result and discussion

The Figure (6) below shows the ionic conductivity values of GPE at various test times.

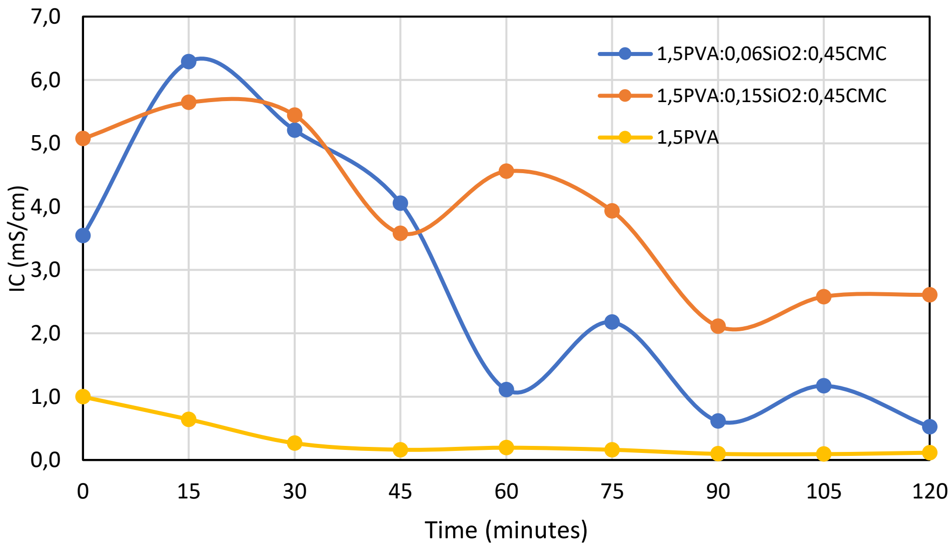

Figure 6 GPE ionic conductivity at a frequency of 0.1 Hz-100 kHz

Table 1 Ionic conductivity values in GPE samples with time variation

1.5PVA:0.06SiO$_2$:0.45CMC		**1.5PVA:0.15SiO$_2$:0.45CMC**		**1.5PVA**	
time (minutes)	**IC (mS/cm)**	**time (minutes)**	**IC (mS/cm)**	**time (minutes)**	**IC (mS/cm)**
0	3.541	0	5.073	0	0.997
15	6.288	15	5.645	15	0.641
30	5.207	30	5.444	30	0.266
45	4.054	45	3.580	45	0.162
60	1.108	60	4.557	60	0.194
75	2.175	75	3.930	75	0.161
90	0.613	90	2.111	90	0.097
105	1.171	105	2.579	105	0.093
120	0.524	120	2.609	120	0.115

Figure 6 above is GPE ionic conductivity at a frequency of 0.1 Hz-100 kHz from testing a time of 0-120 minutes with 15 minutes intervals which are more clearly presented in Table 1. The highest GPE-3 (1.5 PVA : 0.06 SiO$_2$: 0.45 CMC) grams ionic conductivity is located at 15th minutes meanwhile the highest GPE-6 ionic conductivity is also located at the 15th minutes and the highest GPE-0A ionic conductivity is located at the 0th minutes. At a certain value CMC (gelling agent) can optimally absorb OH- electrolyte so as to provide optimum GPE ionic conductivity value [10]. With the addition of SiO$_2$ (crosslinker) it can improve the GPE structure by bonding CMC mass with PVA so that additional SiO$_2$ with a certain level can maintain the electrochemical performance of zinc-air batteries [5]. It is known that the physical properties of PVA (binder) are hydrophilic polymers, inert, and have relatively few side effects on the performance of zinc-air batteries [3].

The GPE-0A (1.5 PVA) grams composition without the addition of CMC and SiO$_2$ as gelling agents and crosslinkers respectively had the lowest GPE ionic conductivity values due to the small amount of OH$^-$ absorbed into the PVA during immersion. Whereas GPE-3 (1.5 PVA : 0.06 SiO$_2$: 0.45 CMC) grams and GPE-6 (1.5 PVA : 0.15 SiO$_2$: 0.45 CMC) grams have higher ionic conductivity due to the high OH$^-$ absorption due to the addition of CMC in GPE-3 and GPE-6. The addition of SiO$_2$ plays an important role in the consistency of GPE keeping OH$^-$ in order to remain in the GPE seen in the 60th minute GPE-6 tends to be more stable in ionic conductivity because SiO$_2$ as a crosslinker between CMC and PVA is able to maintain the consistency of the GPE structure more durable so that the movement OH$^-$ tends to be more stable than GPE-3 and GPE-0A.

6 Conclusion

the effect of adding SiO_2 and CMC to GPE was able to increase the OH- ionic conductivity in the GPE. So it is expected that the OH- ionic conductivity in the GPE is able to provide zinc-air battery performance which is more durable than without the addition of SiO2 and CMC to the GPE.

Acknowledgements

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