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Study of Cassava Starch Layer on Zinc Anode by Electrochemistry Method for Zinc-air Fuel Cell System

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Abstract. In this study, cassava starch was prepared as conductive biodegradable material on zinc anode in zinc-air fuel cell system by using electrochemistry method. Successful formation of cassava layer on zinc anode was determined by its conductivity values by using four-point probe instrument and the enhancement of conductivity of anode after the deposition of cassava starch was proven. The optimization of conductivity study was further carried out in different concentrations of cassava. It was shown the increment about 30% from 0.079 to 0.105 Scm⁻¹ of conductivity values from original conductivity of pure zinc. Moreover, SEM analysis exhibits the morphology of cassava coated on zinc plate with distinct particle structure was observed, proving the successful formation of cassava layer via electrochemical method. Hence, the discharge profile analysis highlighted the composition of C3 of CS performed best performance in ZAFC system.

1. Introduction

An effective ways to support the global energy demands is by exploring the alternative energy [1]. By overlooking in exploring unlimited natural resources such as solar energy, hydropower and wind, but these natural resources yet are unstable and difficult to control [2]. Recently, to replace traditional fossil fuels, fuel cell technology has attracted massive attention as an alternative energy [3].

Fuel cells are electrochemical devices that convert chemical energy to electrical energy and heat. In fact, fuel cell is continuously operating batteries, which can generate electricity from fuel, such as hydrogen, and oxidant, such as air. However, even the fuel cells works like batteries, in principle of fuel cell, it cannot run down or require recharging like battery as long as fuel and oxidant are supplied [4-8]. For examples of fuel cell with properties shown in Table 1.

Table 1. Types of fuel cells

Fuel Cell Type	Mobile ion	Operating Temp.	Application
PEMFC	H ⁺	25°C - 100°C	Portable, stationary and vehicular
SOFC	O ²⁻	600°C- 1000°C	Stationary power, or as an APU
ZAFC	OH ⁻	700°C	Portable and vehicular power



To date, many attempts of researchers to modify the electrochemical and improve discharge capacity of ZAFC [9–12]. This is due to the ZAFC can operate in low-medium discharge capacity. A ZAFC system possesses the highest specific energy compare to the Zn-based alkaline batteries because of free supply of oxygen from the air that does not incorporated within the fuel cell [14]. This free oxygen application system will lower the cost of experiments [15].

In order to lead environmentally friendly consumption, the modification of the anode had been approached in this study by using natural polymer which is cassava starch to be applied on the anode. This is due to the cassava starch is one of the natural polymers that can be applied on the fuel cell system as it advantages of good physical and chemical properties [16]. There is few studies on cassava starch as a conductive agent in system [9, 15, 16].

Hence, this study focuses on the preparation of cassava starch as conductive biodegradable material on zinc anode for zinc-air fuel cell (ZAFC) system using electrochemistry method. To the best of our knowledge, this is the first report on fabrication of conductive layer on the anode based on electrochemistry approach.

2. Materials and Methods

Materials used such as pure Zn plate, pure cassava starch, and potassium hydroxide (KOH). Cassava layer was coated on Zn anode in different concentrations which are 66, 83, 100 and 116 g/L, denoted as C1, C2, C3 and C4, respectively. The electron acceleration voltage was standardised to this sample, 10 kV. The conductivity was tested using Four-point probe (4PP) with constant current 10 mA. The ZnC was discharged at a constant current of 10 mA at room temperature.

3. Results and Discussion

3.1 Physical observation

Fig 1 shows the images of off-white cassava layer that formed on Zn anode in different thickness by tuning a number of cycles (eg. 5, 10 and 15 cycles) during electrochemical analysis. It is expected that different thickness of cassava layer coated on the Zn will lead to different values of conductivity, which thicker layer could exhibit higher value of conductivity. Yet, the maximum number of cycles only 15 cycles to finally form at certain thickness until the coated crack and unable to coat on the Zn anode.

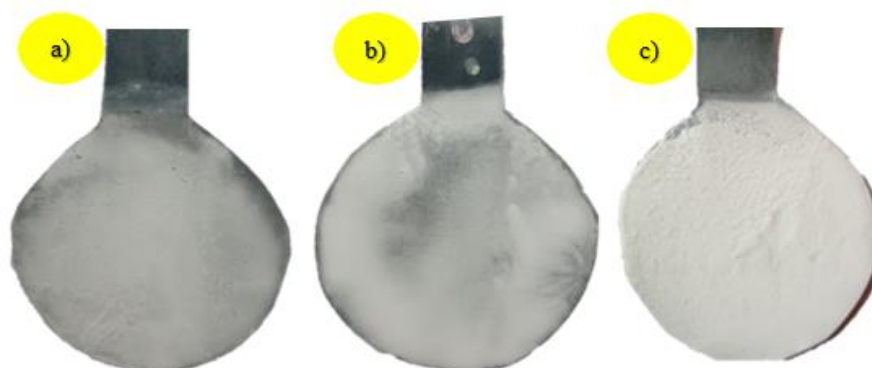


Figure 1. Cassava coated of Zn with different thickness of cassava layer (a) 5 cycles, (b) 10 cycles and (c) 15 cycles, respectively

3.2 Morphology analysis

Scanning electron microscopy (SEM) analysis was used to analyse the morphology surface of zinc plate, cassava powder and cassava-coated zinc plate. Fig.2 (a), the deposition of cassava particles was observed on the Zn, and so thus from b-e. Fig.2 (a) exhibits the surface morphology of cassava layer on the zinc before the sample was introduced for the discharge analysis.

Whilst, Fig. 2 (b-e) are the images of cassava coated on the Zn after performing the discharge. The cassava coating layer on zinc plate (ZnC) can be clearly seen from SEM morphology with different surface morphology compared. Cassava particle (c) deposited on the Zn has same structure particle in image (b).

However, different concentration of cassava starch gives different result of oxide. Clearly showed from (b), an oxide that found was in 'needle-like' shape, while (c) and (d) exhibited as 'sea-coral like' oxide and 'porous needle-like' form. Oxide happens due to the contact of KOH and ZnC itself [18]. The optimum concentration usage of KOH is 6M lead to corrosion happens in the system.

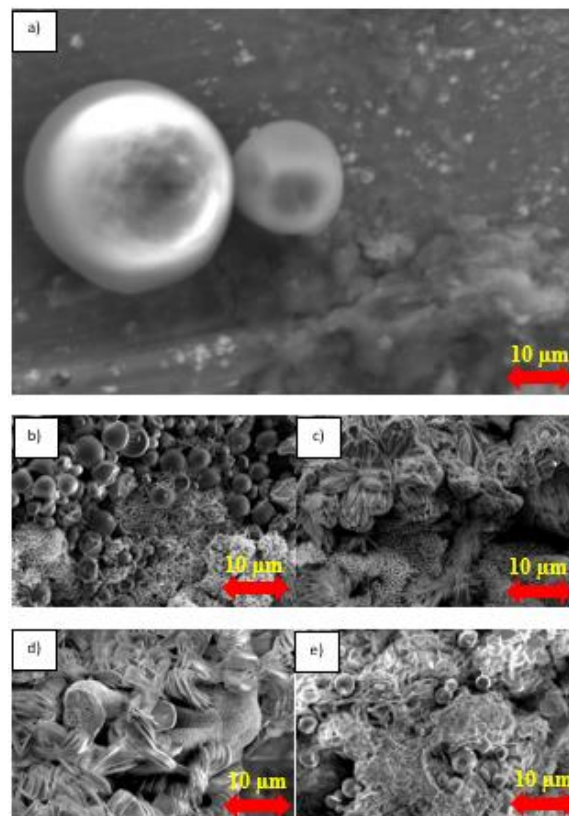


Figure 2. Morphology of (a) ZnC (b) C1, (c) C2, (d) C3 and (e) C4

The obtained observed image can be explained due to above reactions, which because of the effect of KOH concentration that have direct contact with cassava-coated Zn. As KOH concentration is optimum, the activity of the water decrease, resulting in a higher rate for reaction [15- 16]. Overall images proved that the cassava starch was coated successfully on Zn anode.

3.3 Conductivity

The obtained ZnC was fabricated in different concentration of cassava starch solution which are 66, 83, 100 and 116 g/L that denoted as C1, C2, C3 and C4 using electrochemistry method. Each samples was futher analysed for conductivity properties in order to confirm the fromation of cassava on zinc and the effect of thickness of that cassava coated on the conductivity value.

There was a study reported that higher concentration of cassava solution can conduct higher electricity due to the existence of higher amount of active ions that can increase the conductivity of Zn plate [21]. The trend is in accordance with the finding which, the conductivity values of cassava-coated zinc increases with the increase concentration of cassava solution. Figure 3 shows the conductivity plot of zinc plate and cassava-coated zinc in different concentrations (C1-C4).

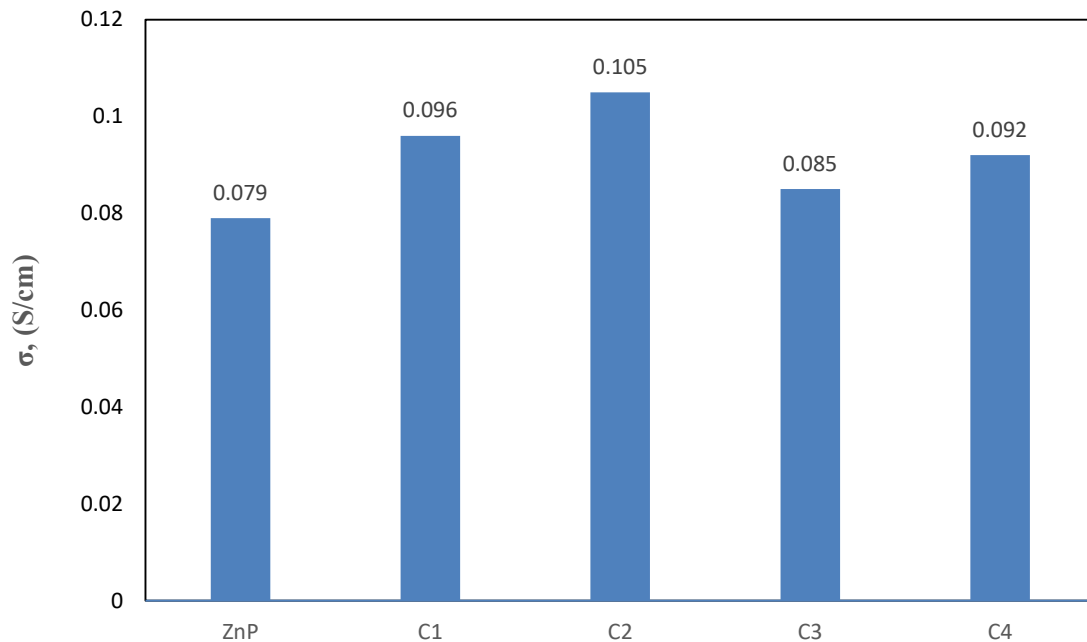


Figure 3. Conductivity values of the Zn coated cassava

It is shown in Fig 3, the result of conductivity ZnP recorded only 0.079 Scm^{-1} compared to after cassava-coated on the zinc, presented by C1, C2, C3 and C4 with value 0.096 , 0.105 , 0.085 and 0.092 Scm^{-1} , respectively. From this analysis, it proves that the cassava coating layer can enhance the conductivity of Zn plate from ZnP (0.079 Scm^{-1}) up to 0.105 Scm^{-1} of ZnC (C2). Thus, this result proved the conductivity of cassava itself and enhance the conductivity values of Zn anode after coating. Thus, the Zn coated with cassava in concentration of C2 gives the highest value of conductivity. The increment value of conductivity from without cassava (ZnP) to with cassava (represents by ZnC) was found increases by 30% of conductivity values.

Although the conductivity increases with increasing cassava concentration solutions, it was found that the conductivity decreases gradually beyond 96 g/L concentration of cassava used. This is because due to the gel solution of cassava starch was formed and achieved maximum liquid phase. It is impossible to coat cassava on Zn plate at concentration higher than 116 g/L.

3.4 Discharge

Discharge characterization was performed on ZnC employing C1, C2, C3 and C4 to study lifetime performances. Using ZAFC mould for each type, the ZnC was discharged at a constant current of 10 mA at room temperature. Figure 4 shows discharge profile of C1, C2, C3 and C4.

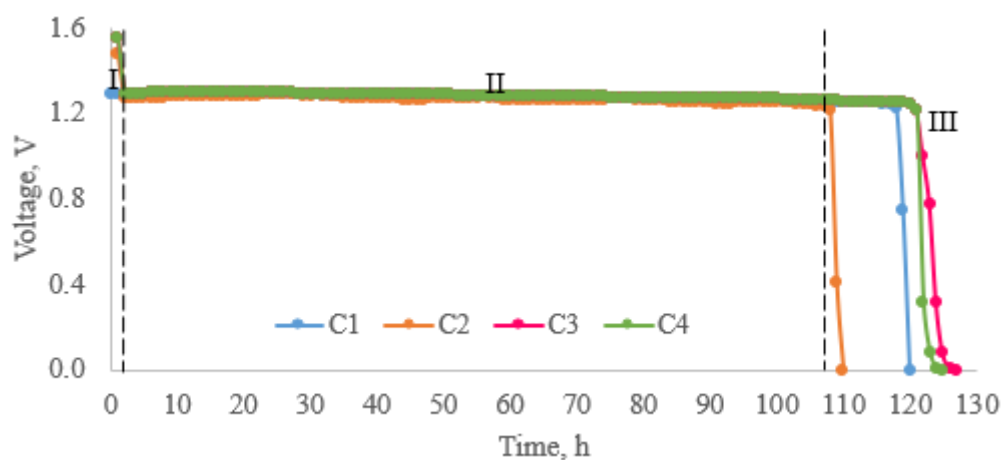


Figure 4. Discharge profile of C1, C2, C3 and C4

The optimum composition of C3 and C4 of CS employed in ZAFC, which promoted the best discharge profile, had a nominal voltage of 1.556 V. It was followed by ZAFC systems employing C1 and C2 with nominal voltages of 1.289 and 1.475 V, respectively. In Region I, there were small rapid initial dips in voltages at the early stages of discharge. The voltage fell less rapidly and become linear throughout Region II. This region is dominated by internal ohmic losses that caused by intrinsic resistance [22].

At one point, the voltages of the ZAFCs fell abruptly, reaching their lowest voltage as shown in Region III. This region is referred as a concentration loss caused by the depletion of reactants or active materials. Obviously, ZAFC with C2 of CS, exhibit shorter sustainability at only 108 h. Reactants with lower concentrations were more rapidly depleted, resulting poorer performance. Although, the ZAFC employing C2 and C3 was higher voltage, but they had different sustained value at 126 and 122 h, respectively. These results confirm that the optimum composition of C3 of CS performed best performance rather than C4 of CS as been employed into the ZAFC system.

4. Conclusion

Cassava has been found as valuable conductive material that have potential for zinc air fuel cell system. Overall results suggesting that the increment 30% of conductivity values from original conductivity of pure zinc (0.079) boosted to 0.105 Scm^{-1} with the application of cassava layer on zinc anode. The conductivity gives better performance of Zn with consistency till 126 hours of C3.

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