

STARCH/MgSO₄ SOLID POLYMER ELECTROLYTE FOR ZINC CARBON BATTERIES AND ITS APPLICATION IN A SIMPLE CIRCUIT

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Abstract: Solid polymer electrolytes based on starch and magnesium sulphate were prepared via a casting method. The solid polymer electrolyte (SPE) films were an amorphous phase and the XRD analyses confirmed the coexistence of peaks for the materials mentioned. The films seemed to be coarse, as clarified by SEM, and the surface was evenly shaped. Sample of 35 wt.% MgSO₄ showed the utmost ionic conductivity ($8.52 \times 10^{-5} \text{ Scm}^{-1}$). The open circuit voltage (OCV) results for the fabricated cells can maintain a voltage of above 1.4 V for 14 days, by using the as-prepared films. The electrochemical preliminary results revealed that the as-prepared SPE has the ability to be employed in all-solid-state zinc-carbon battery.

Keywords: Sustainability, starch, magnesium sulphate, solid polymer electrolyte, all-solid state battery.

Introduction

All solid-state battery has been a subject of great practical importance due to the interest in the improvement of solid-state electrochemical devices (Sequeira & Santos, 2010; Arya & Sharma, 2019). Attention in this field began after Wright and co-workers reported that the electrical conductivity existed in polyethylene oxide doped with alkali metal salts (Hallinan & Balsara, 2013). The SPE without ionic salts was commonly identified to have poor performance at ambient temperature, which is one of its disadvantages as compared to the current conventional liquid/hybrid electrolytes (Dillip *et al.*, 2008; Hassan & Noruddin, 2018). Currently, several studies on SPE doped with selected ionic salts were conducted and the studies had excellent results. For the example, in PEO-LiClO₄-based systems, the maximum ionic conductivity of $1.56 \times 10^{-3} \text{ Scm}^{-1}$ at 80°C was gained with 10wt.% of poly(cyclotriphosphazene-co-4,4-sulfonyldiphenol) (Jiawei *et al.*, 2011), whereas for the PVA systems, the optimum ionic conductivity can reach up to $1.50 \times 10^{-3} \text{ Scm}^{-1}$ (Francis *et al.*, 2016).

So far, the greatest ionic conductivity obtained for the PVC systems was around $4.39 \times 10^{-4} \text{ Scm}^{-1}$, which resulted from the addition of 30wt.% lithiumbis-(trifluoromethanesulfonyl) imide, (LiTFSI) (Ramesh & Ng, 2011). The successful work had proven that high ionic conductivity can be obtained easily, and the elasticity of SPE can be well maintained by adjusting the dopant content in polymer system (Choi & Park, 2001; Rajendran *et al.*, 2004; Hassan & Arof, 2005; Feng *et al.*, 2005; Zhang *et al.*, 2011; Pandey *et al.*, 2011; Ramesh & Ng, 2011; Hassan & Ting, 2018). An advanced study on new SPE films is essential to explore their potential application as well as their possibility to be used in energy storage devices.

Starch contains two types of macromolecules, amylose and amylopectin and are also considered as a natural semi-crystalline biopolymer. Being a renewable, low cost, biodegradable, and high availability biopolymer are advantages that come from natural things (De Leon *et al.*, 2014). Numerous research works have confirmed starch as a host polymer and its bare ionic conductivity may possibly be enhanced if incorporated with applicable ionic

salts (Li *et al.*, 2011; Cheng *et al.*, 2015; Lin *et al.*, 2016; Kim *et al.*, 2018). The similar results were also obtained for MgSO_4 whereby some researchers had reported that a polymer-based complex with MgSO_4 has satisfactory ionic conductivity and are engaged as electrolyte in all solid-state battery fabrication, making viable for advance investigation by incorporating it with another polymer (Jian, 2015; Basha *et al.*, 2016; Basha *et al.*, 2018).

In 2018 and 2019, the SPE-based on starch- MgSO_4 was successfully prepared (Hassan *et al.*, 2018; Hassan & Azimi, 2019). The investigations were focused on morphological, structural and transport properties of the SPE. However, study on the electrochemical performance of the as-prepared SPE has not yet been established. This part of the study is very important in any study on SPE to assure that the claimed SPE can be proven to function when it is fabricated together with anode and cathode electrodes in a battery fabrication. Still, most of the previous works mentioned above were not put as a vital aspect in this field.

In this study, a new polymer electrolyte film was prepared with a starch complex with MgSO_4 and was used as the dual functioning material (as a separator and an electrolyte) in zinc-carbon battery fabrication.

Materials and Methods

Experimental Preparation

The detailed explanations for solid polymer electrolyte were recorded in works of Hassan *et al.*, 2018; Hassan & Azimi, 2019. Concisely, the solutions were prepared by dissolving starch powder into glycerine-distilled water solvent. Then, the mixtures were added with MgSO_4 at different weight percentage, wt.% (0 wt.% to 45 wt.%). The mixed solution was constantly stirred using magnetic stirrers until it turns into a homogenous solution. Later, the mixtures were placed in different petri dishes and left for evaporation process to take place and form the solid state films. Then, to diminish the water element, the films were relocated in

desiccators for a definite period. To note here, the experimental procedures were carried out at ambient temperature.

Solid Polymer Electrolyte Characterization

X-ray diffraction (XRD) technique was used to determine the crystallinity of the sample (Tufail *et al.*, 2019). The XRD patterns were collected in the range of $2\theta = 10^\circ$ to 80° via a Miniflex II diffractometer. The configuration and composite development in the film were examined by a Thermo Nicolet Avatar FTIR spectrometer. It instantaneously accumulates spectral data in a wide-ranging spectral of 4000 to 675 cm^{-1} with 4 cm^{-1} spectra resolution. The spectrometer is equipped with an attenuated total reflection (ATR) adjunct by a germanium crystal. The film was placed on the germanium crystal and infrared light was distributed over the film and the graph was sketched. To examine the influence of MgSO_4 on starch surface morphology, scanning electron microscopy (SEM) was employed to observe the surface images of the sample. It was carried out using the Model JEOL JSM-6360LA device with an acceleration voltage of 20kV. The image was taken for selected magnification of x5000. Through this procedure, the nature of the film could be directly observed to see whether it is in an amorphous or crystalline state.

Electrochemical Measurements

The anode (MnO_2) and cathode (Zinc) electrodes were taken from the battery available in the market. Firstly, the battery was disassembled to remove its separator and relocated with the active materials into another container. Next, the zinc plate was transformed into a cylindrical shape and layered with the prepared solid polymer electrolyte that had been cut into a suitable size (5cm x 8cm). Then, the cathode material was inserted into the zinc container with a carbon rod. In this case, the carbon rod was used as the current collector. The overall cell fabrication illustration is depicted in Figure 1. The cells were prepared for electrochemical analysis and were fabricated in the open air without any special equipment. The cells were slowly discharged at various currents up to $50\mu\text{A}$

with a Neware battery cycler over the voltage range of 0.1-1.5 V. The cells were also tested on a simple electronic circuit to know its real capability of providing the power supply to the circuit. Figure 4 shows the way the circuit was built in a laboratory by using a few electronic components, namely a step-up transformer, 2k Ohm resistor, BC transistor and led.

Results and Discussion

Figure 2 illustrates the image of the film, XRD pattern, FTIR spectra and SEM micrograph of the starch-MgSO₄ SPE film of 35wt.% MgSO₄ with conductivity of $8.52 \times 10^{-5} \text{ Scm}^{-1}$ (Hassan *et al.*, 2018). Briefly, the film based on this complexation (Figure 2a) could only be formed with up to 45wt. % of ionic salt, in film excess was hard to produce due to its low rigidity (Hassan & Ting, 2018). The SPE films

would become more crystalline when more salt was added. The XRD pattern (Figure 2b) of the film was recorded from $2\theta = 10^\circ$ to 80° . As can be seen in the pattern, with the addition of MgSO₄, there was no significant change and the film had a definite likeness and its presence was greatly in amorphous phase (Hassan *et al.*, 2018). However, a peak located between 15° and 30° was clearly noticeable in the diffraction pattern, relative to the MgSO₄ peak. The discovered XRD showed that the complex film was inclined to be moderately amorphous than the crystalline phase. Besides, the existence of MgSO₄ did not prominently affect the patterns due to low crystalline of polymer and it being partly crystalline. This result also revealed that the coexistence of peaks for the investigated materials ratified their complexation in solid polymer electrolyte film (Hashimi *et al.*, 1990;

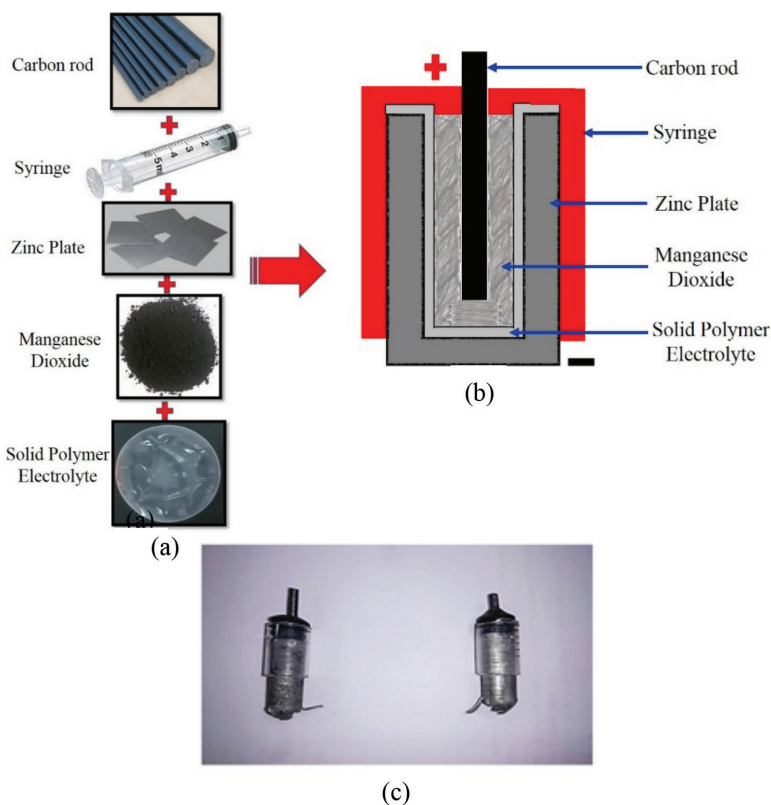


Figure 1: (a) List of materials used for cell assembly, (b) a schematic diagram of Zn-carbon cell and (c) a real fabricated cell

Sekhon *et al.*, 1995; Joshi & Sinha, 2006; Parvathy & Jyothi, 2019).

The FT-IR spectra starch-MgSO₄ complex film is displayed in Figure 2c. The major bands displayed at 3285 cm⁻¹, 2937 cm⁻¹, 2868 cm⁻¹, 1641 cm⁻¹, 1380 cm⁻¹ and 1006 cm⁻¹ were attributed to the starch (Navarchian *et al.*, 2015; He *et al.*, 2016; Mukurumbira *et al.*, 2017]. However, no peak was detected for MgSO₄. As discussed here (Hassan *et al.*, 2018) the addition of MgSO₄ had shifted the specific peak of MgSO₄ and confirmed that, in this case, the chain-reaction (or addition) polymerisation process was successfully achieved. Figure 2d shows the scanning electron micrograph image of starch-MgSO₄ film. The SPE film has some agglomeration surfaces with a circular shape, which seems to become jointly flat and the pores structure obviously appeared at a specific area of the sample. These pores had an estimated diameter size in the range of 20 nm to 70 nm and were thought to have special properties in which one of them could contribute in enhancing the electrical properties of the films (Angell, 1992; Li *et al.*, 2014).

The result of the electrochemical measurement is presented in Figure 3. Figure 3a

illustrates the open-circuit voltage of a fabricated cell. The voltage of the cell was 1.50V at early measurement and dropped to 1.43V for 14 days monitoring, which was almost 4.7% reduction. By looking at the preliminary discharge profiles of the cell (Figures b and c), it can be determined that the cell has the capability to supply current of up to 50μA for 65 minutes. These reasonable results were obtained for the constructed small cell size in this work.

To get a real performance of the as-prepared cell, a simple electronic circuit was developed by using a few electronic components, and its circuit diagram is as shown in Figure 4. The circuit was created by using the following components: a resistor (500-2000 Ohms), a transistor (NPN type), a transformer, a led (red colour), a breadboard, and some wires for linking every mentioned component in the laboratory. The connection should be exactly like the diagram as shown in the figure. In this investigation, the cell would be connected to the positive and negative terminals of the circuit.

According to Smith, (2015), there were some steps that showed the way the circuit worked. In the beginning, the transistor was in the off state. A small quantity of electricity flowed

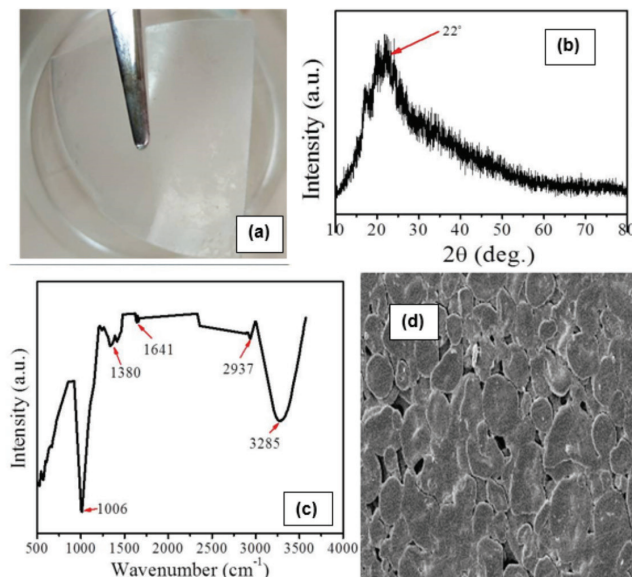


Figure 2: a) A starch-MgSO₄ SPE film (35 wt.% MgSO₄), b) XRD pattern of SPE film, c) FT-IR spectra of SPE film and d) SEM micrograph of SPE film

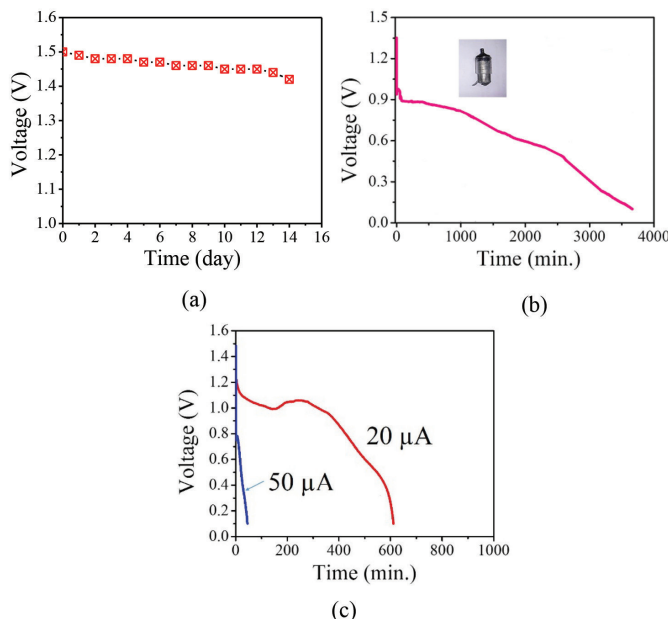


Figure 3: (a) Open circuit voltage of zinc-carbon cell; the discharge profiles of zinc-carbon cell at different current density (b) 5μA, (c) 20μA and 50μA

through the first coil of the resistor towards the transistor base. The collector-emitter passage was discreetly opened. Electricity was currently capable of moving via the number two coil and also through the transistor collector-emitter network. During this time, a greater amount of electricity was induced by the magnetic field in the first coil and it was produced by the growing quantity of electricity in the second coil. The transistor base started to collect the induced electricity from the first coil and the collector-emitter channel was open in a wide range.

More electricity was permitted to move via the second coil and through the transistor collector-emitter channel. Then, when the transistor base was saturated and the collector-emitter channel was entirely open due to repetition of action from the previous steps, the huge amount of electricity would flow to the number two coil and through the transistor at a maximum magnitude. Due to this, the high magnetic field of the second coil is produced due to the development of a lot of energy. Subsequently, the electricity in the second coil was saturated, and the induced electricity in the

first coil was stopped, and thus there was no more electricity to flow through the base of the transistor. With the low amount of electricity flowing into the transistor base, the collector-emitter channel began to shut-down.

As a result, there was a small amount of electricity to move via the number two coil. The negative amount of electricity in the first coil was obtained when the induction from the low amount of electricity in the second coil caused less electricity to flow into the transistor base. The repetitive actions of previous steps occurred continuously and may result in the transistor having almost no electricity passing through it. At this moment, the stored energy in the magnetic field of coil number two is in a low state. However, this large amount of energy was still built up and needed to move to someplace. This energy caused the output voltage of the coil to spine. Once the stored electricity cannot flow into the transistor, it needs to flow via the led. The output voltage at the coil was accumulated to a certain voltage whereby it can flow to the load and be dismissed.

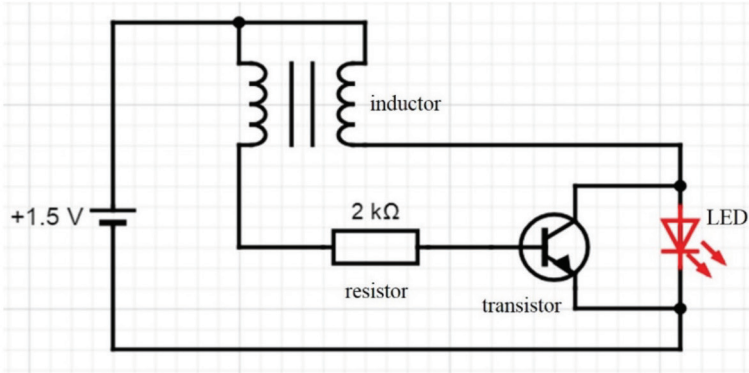


Figure 4: A booster electronic circuit diagram

Figure 5 demonstrates the electronic circuit which was connected to the as-fabricated zinc-carbon cell by using the as-prepared solid polymer electrolyte. The completed circuit with no connection to the negative terminal of the cell was shown in Figure 5a. From this circuit, the led (small image of the led) was not lighted. In Figure 5b, the negative terminal of the circuit was connected to the negative terminal of a cell which allowed the led to light up. To note, the as-fabricated cell was prepared almost 3 months before, and incredibly it could still supply power to the circuit. This initial result proved that the as-prepared solid polymer electrolyte had good capability not only in Zn-carbon batteries but also possibly in other related electrochemical device applications.

Conclusion

Starch-MgSO₄ solid polymer electrolyte with conductivities of the order of 10⁻⁶-10⁻⁵ S cm⁻¹

at ambient temperature was prepared. It was found that the electrolyte indicated excellent mechanical flexibility as well as decent chemical and electrochemical stabilities. The optimal mixture of starch-MgSO₄ was 1:0.55 and this electrolyte enabled the study to form a uniform and homogeneous polymer film. By contrast, the film was highly amorphous. Solid-state Zn-carbon cells by using the prepared polymer electrolyte were assembled and examined. The results demonstrated good electrochemical features. It showed that the starch-MgSO₄ solid polymer electrolyte with a mixture ratio of 1:0.55 was applicable in Zn-carbon batteries.

Acknowledgements

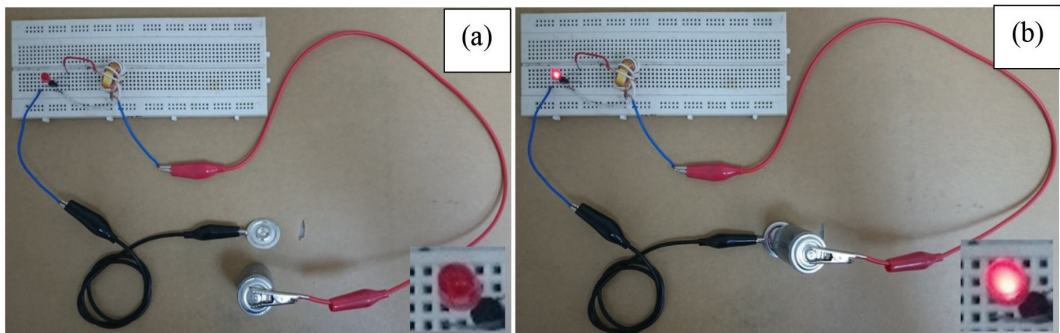


Figure 5: A cell is tested in a real situation using the developed circuit

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