SYNTHESIZE OF GEL POLYMER ELECTROLYTES FOR HIGH CONDUCTIVITY AND GOOD CYCLIC VOLTAMMETRY

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Abstract

Ionic conductivity for gel polymer electrolytes (GPE) are obtained and the polymers are used in zinc-air and tin-air batteries application. The gel polymer consists of methanesulfonic acid (MSA) as additives and polyacrylamide (PAAm) as host polymer. Objective of this work is to synthsize one GPE which gives a high conductivity and good cyclic voltammetry The PAAm-MSA gel electrolytes were prepared with different concentration of MSA. The chemical interaction between PAAm and MSA was studied by FTIR. Impedance spectroscopy technique has been employed to compare the ionic conductivity of these polymer electrolytes. The ionic conductivity of the PAAm ($\sim 10^{-2}$ S/cm) electrolyte increases by an order of magnitude to ~10-1 S/cm. It was observed that when 3.0 M of MSA is added into the host hydrogel polymer, the ionic conductivity is enhanced from 4.9×10^{-2} S/cm to 7.1×10^{-1} S/cm. The best GPE synthesized in this work is 3.6M PAAm-MSA.

Keywords: Gel polymer electrolytes (GPE), methanesulfonic acid (MSA), polyacrylamide (PAAm), Zinc-air batteries, Tin-air Batteries

1.Introduction

Metal-air batteries have gained great interest in this current era because of the new energy storage systems produced. Among the systems which have been extensively studied recently are Li-air [1], Zn-air [2], Mg-air [3] Al-air [4], Na-air [5] and Sn-air [6,7].

A suitable electrolyte would be chosen to combine with metal anode and an air-breathing cathode to fabricate the metal-air battery. Metal-air batteries are assembled in an open battery configuration method therefore the oxygen can be directly received from the surrounding air as a reagent thus contributing to their very high theoretical density [8]. The selection of a proper electrolyte system is a very important factor for a cell which should be given serious attention in order to obtain a good electrochemical performance from the cell. Good electrolyte selection is essential to achieve a better discharge capacity in metal-air batteries. High power applications need devices which have high ionic conductivities [7]. An electrolyte can be considered to be good when it can fulfil certain criterias. First, it must be chemically stable and to minimize the effect of interfacial resistance, it must possess the ability to rapidly form a passivation solid electrolyte interface layer. Ideally, it must be non-flammable, non-explosive in the event of a short circuit. Lastly, it also has to be nontoxic and cheap [9,10]. The development of the electrochemical devices have been proven to promising due to extensive research done on various polymer electrolytes. Research activities being conducted in this area are mainly devoted to the field of solid state electrochemistry. High ion-conducting materials are considered as the suitable candidates to fabricate the cells which are used for an energy conversion and storage applications. Among all the electrolytes, the polymer electrolytes are the preferred substance to be worked on in this digital era. It has been categorized into a few category such as plasticized polymer electrolytes, dry solid polymer electrolyte, composite polymer electrolytes and gel polymer electrolytes[11].

A better reliability compared with liquid type electrolyte is significantly giving the edge to gel polymer electrolyte (GPE) to be more attractive for the researchers to work on for metal-air batteries. Gel polymer electrolyte also has the advantage over solid type electrolyte with a higher ionic conductivity [12]. A Gel has the cohesive properties of solids and the diffusive transport properties of liquids, which makes the gel to have an outstanding liquid electrolyte retention ability. This advantages gives the gel it's special state of matter, therefore GPEs can effectively solve the security problem caused by liquid electrolyte leakage to a certain extent [13]., Subtances such as polyethylene oxide (PEO), polytetrafluoroethylene (PTFE), polymethyl methacrylate (PMMA), PVdF, polyacrylamide (PAAm) and polyacrylonitrile (PAN) diverse host materials have been employed for the GPE matrix [14-17].

Plasticizers are common additive in polymer electrolytes which increase polymer flexibility to ease segmental motion. These plasticizers also can act as the solvent that ease ion diffusion. Apparently both of these characteristics can improve conductivity of the electrolyte. The plasticizers used in a gel polymer electrolyte also must be suitable to give a good GPE and it can be categorized into 2 categories which are acidic plasticizers and neutral plasticizers [18]. Intrinsic conduction ability which acidic plasticizers have making it to be the common used in proton-conducting polymer electrolytes. Higher conductivity in the electrolyte can be achieved due to the proton dissociation from the plasticizers which can help in providing more conducting species in the system. Strong acids like phosphoric acid and sulfuric acid are some common examples of acidic plasticizers [19]. Studies done by Oishi et. al. related to sulfonic acid groups in hydrocarbon polymers show that MSA is a suitable polymer electrolyte because it is a super strong acid and with a Gibbs free energy (ΔG) of dissociation of 1,317 kJ mol^{-1} [20]. Hydrochloric acid and sulfuric acid have 0.35 and 0.44 S cm^{-1} conductivity respectively compared to 1.0 M MSA aqueous solution which has 0.30 S cm^{-1} and it produces a lower risk of corrosion compared to other mineral acids. MSA is an acid which had been proven to be a good conductive material and to add to that strength, it has good thermal stability, water miscibility and low toxicity [21]. In this present study, gel polymer electrolyte is prepared using polyacrylamide (PAAm) as polymer host material and methane sulfonic acid (MSA) is used as an additive. PAAm has a few beneficial properties and one of it is a higher water retention capability compared to PVA [22]. Electrochemical impedance spectroscopy (EIS) and Fourier Transformed Infra-red spectroscopy are used to characterize the PAAm-MSA gel polymer electrolyte with different molarity of MSA. Cyclic voltammetry (CV) were used to define the redox processes between GPEs and zinc or tin metal anode.

2.Methodology

Polyacrylamide (PAAm) (R&M Chemicals) with molecular weight (Mw = 5,000,000) added with methane sulfonic acid (MSA) (>98%, R&M Chemicals) are used to prepare gel polymer electrolytes (GPEs) of several polyacrylamide-methane sulfonic acid materials with different proportion of both substances. Approximately 48.5 ml distilled water is used to dissolve 1.25 gram of granular powder of PAAm and this mixture are stirred continuously for 24 hours until it becomes a homogeneous hydrogel at room temperature room 25 °C. After that to produce

3.0 M PAAm-MSA gel polymer electrolyte, 14.4 gram of MSA solution is added into hydrogel solution and stirred continuously at room temperature. In order to prepare similar gel polymer electrolyte at a different molarity, this process is repeated to produce 3.3 M, 3.6 M and 3.9 M by adding 15.8 g, 17.3 g, and 18.7 g of MSA respectively.

These synthesized electrolytes are subjected to go through the Electrical impedance spectroscopy (EIS) test and Fourier-transform infrared spectroscopy (FTIR) study. EIS method is used for conductivity measurement of GPEs which is carried out using Autolab PGSTAT 30 (Eco Chemie, B.V. Netherlands) with the frequency response analyser (FRA) module at room temperature. A frequency range of 10 Hz – 1000 MHz are used to obtain the bulk resistance (Rb) from the impedance spectrum which ia collected using the EIS test. The intercept at the real impedance axis in the Nyquist plot gave the bulk resistance value. Calculation of the ionic conductivity of PAAm-MSA GPEs are done using the following Eq (1) [6].

$$\sigma = \frac{t}{\mathrm{RbA}} \tag{1}$$

where σ is the conductivity, and t and A are thickness and surface area of the electrolyte. This analysis is conducted to investigate the interaction of polymer-acid in the gel electrolyte composition of the polymer electrolytes between 400 and 4000 cm^{-1} wavelength. Computer controlled potentiostat (Autolab PGSTAT 30 (Eco Chemie, B.V. Netherlands) is used to perform Cyclic Vaoltammetry measurement. The working electrode used in thie cell is Sn metal or Zn metal with dimension (1 cm x 1 cm) whereas the counter electrode is graphite and SCE (saturated calomel electrode) as reference electrode. Methanesulfonic acid based polyacrylamide (PAAm-MSA) gel polymer electrolytes with the molarity of 0.0 M, 3.0 M, 3.3 M, 3.6 M, and 3.9 M are analysed electrochemically. The potential range was cyclically scanned between 0 V and -0.8 V at 5 mV/s and 50mV/s scan rate.

3. Results and Discussion

3.1 Electrical Impedance Spectroscopy (EIS)

Ionic conductivity is certainly the most important parameter for polymer electrolytes. The effect of MSA on the ionic conductivity of PAAm GPEs was analyzed using EIS with the frequency response analyser (FRA) module technique. The Nyquist plots for PAAm-with different concentrations of MSA at room temperature are shown in Fig 1. Rb (resistance bulk) value can be obtained by the interception on the real axis from the Nyquist plot to calculate the ionic conductivity. The bulk resistance value and ionic conductivities of the GPEs are presented in Table 1. The data shows that the presences of MSA in the PAAm influence the ionic conductivity of the polymer electrolyte. The variations of conductivity of the polymer electrolyte as a function of MSA concentration are given in Fig 2. The ionic conductivity of the PAAm (~10^{-2} S/cm) electrolyte increases by an order of magnitude to ~ 10^{-1} S/cm with the addition of 3.0 mole MSA. The ionic conductivity increases from 4.91 x 10^{-2} S/cm for 0.0 mole MSA to 7.11 x 10^{-1} S/cm for 3.0 mole MSA. The maximum ionic conductivity is 8.47 x 10^{-1} S/cm at 3.6 mole MSA. The conductivity decrease when concentration of MSA increase. However, it shows that the MSA as an additive to polymer electrolyte enhances the ionic conductivity of electrolyte compare the other acids. Sumathi et al [23] reported that other researcher have focused on the mixtures of PAAm gels with strong inorganic acids such as H_3PO_3 or H_2SO_4 as additive which exhibited conductivities in range of 10^{-3} – 10^{-2} S/cm. In the present study, the ionic conductivity show good value in the range of 10^{-2} – 10^{-1} S/cm.

Table 1. The Rb values and the ionic conductivity of GPEs with different concentration of MSA

Concentration of MSA	R_b (Ω)	σ (S/cm)
0.0	2.865×10^{2}	4.919×10^{-2}
3.0 M	1.981×10^{1}	7.114×10^{-1}
3.3 M	1.845×10^{1}	7.638×10^{-1}
3.6 M	1.662×10^{1}	8.479×10^{-1}
3.9 M	1.876×10^{1}	7.512×10^{-1}

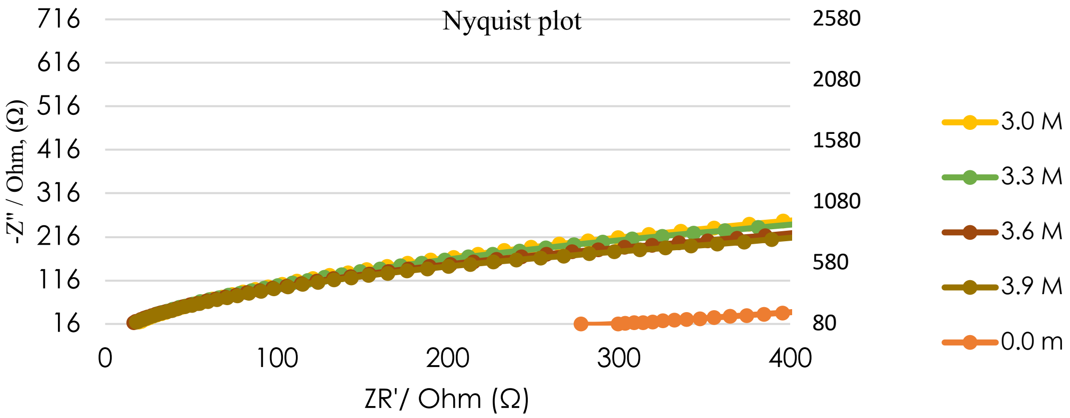

Figure 1. Nyquist plot with various concentration of MSA

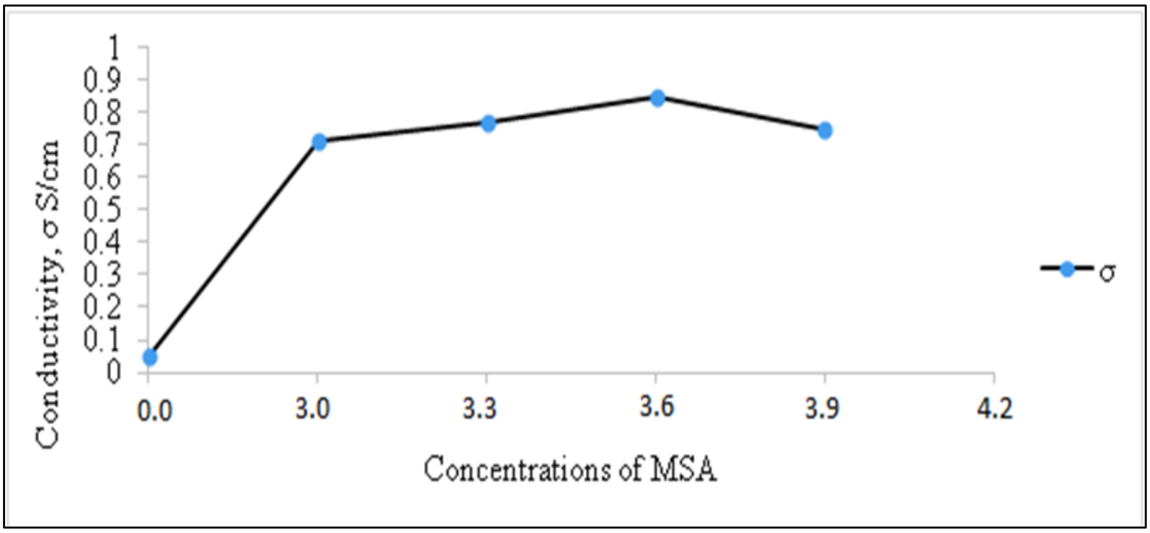

Figure 2. The variation in conductivity of PAAm-MSA GPEs with different concentration of MSA

3.2 Fourier-transform infrared spectroscopy (FTIR)

Fig 3. shows of spectra for polyacrylamide hydrogel. The weak of vibration around 3000 -3500 cm-1 is due to the OH group and NH group. The strong band stretching at 1740 cm^{-1}, 1368 cm^{-1} and 1217 cm^{-1} are arise from carbonyl group (C=O) [24] (Coates, 2000) due to the strong hydrogen bonding interaction between water molecule. According to Lehtonen [25], polyacrylamide is from amide group which contains (C=O) and (N-C) dipole. This dipole arises from covalent bonding between electronegative oxygen and nitrogen atoms and electro-neutral carbo atoms. However, the carbonyl group (C=O) has a stronger dipole than (N-C) dipole. This is due to the pi-bonding arrangement and the greater electronegativity of oxygen than nitrogen at the carbonyl group. The presence of a C=O dipole, and to a lesser extent the N-C dipole, allows amides to act as hydrogen bond acceptors. Meanwhile, the presence of N-H dipoles allow the amide to function as hydrogen bond donors as well [25]. Thus amides can participate in hydrogen bond from water as well as donate hydrogen bond to water. The oxygen and nitrogen atoms can accept hydrogen bonds from water molecule, while the N-H hydrogen can donate H- bonds to the water molecules. The polymer-acid interaction of the PAAm-MSA were shown in Figure 4. The vibration at 1648 cm^{-1} is due to the C=C stretch [26]. The vibration at 1177 cm^{-1} and 1044 cm^{-1} is due to the sulfonic acid SO_3H and sulfonic ion SO_3- [23].

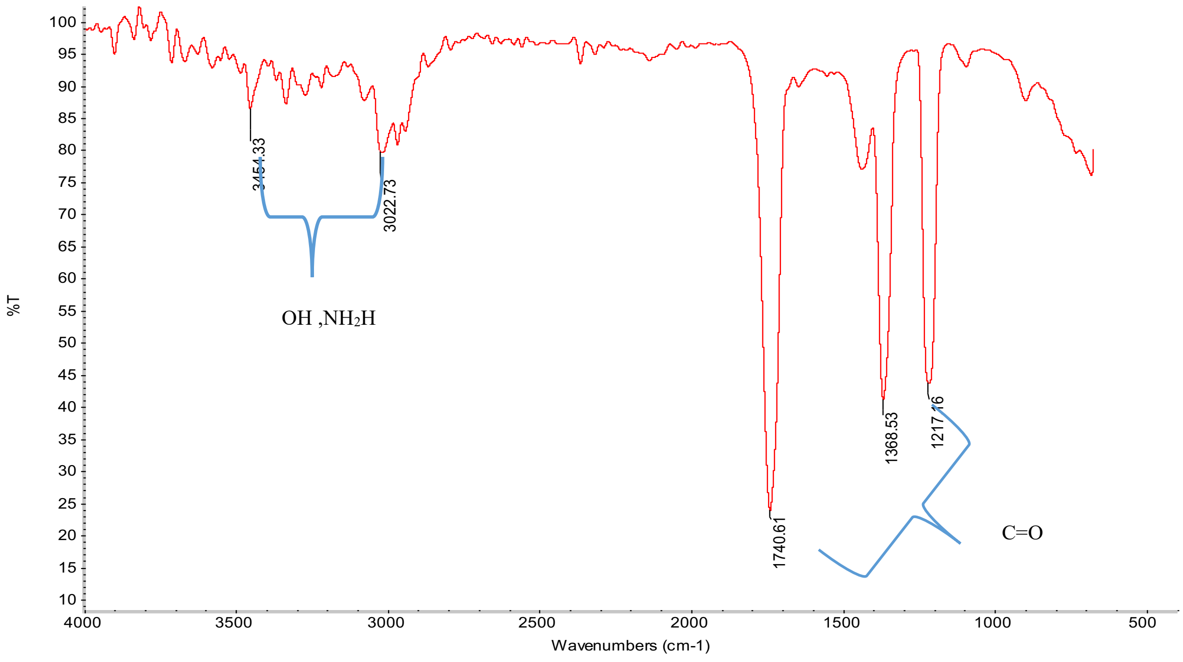

Figure 3. FTIR Spectra for PAAM-MSA 0.0 M

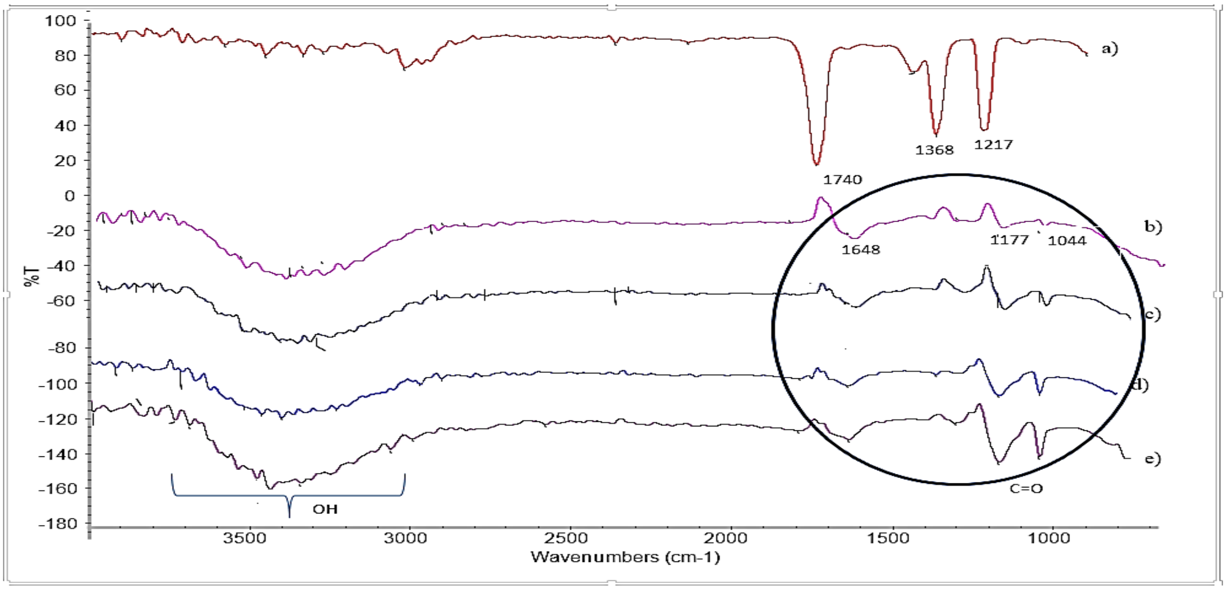

Figure 4. FTIR spectra for all concentration of MSA which is a) 0.0 M, b) 3.0M, c) 3.3 M, d) 3.6 M, e) 3.9M MSA

3.3 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was used to examined the reversibility of the tin and zinc redox activity using gel polymer electrolyte that consist different MSA concentration. Tin and zinc foil (1 cm^2) was used as working electrode and graphite electrode as counter electrode and SCE (saturated calomel electrode) as reference electrode. CV measurements were recorded starting at 0 V, going down in the reduction section to −0.80 V at a scan rate of 5mV and 50 mV/second, as shown in Figs. 5- Figs. 14. Starting at the potential of 0 V, to the negative side. At −0.80 V, the cyclic voltammogram flips to the oxidation scan. Corrosion process also occurred during CV process and Zn foil become Zn oxide faster compared Sn foil. Voltammogram of GPE PAAm-3.6 M MSA shows obvious loops of oxidation and reduction. This proves that the best GPE synthesized with the concentration of 3.6 M.

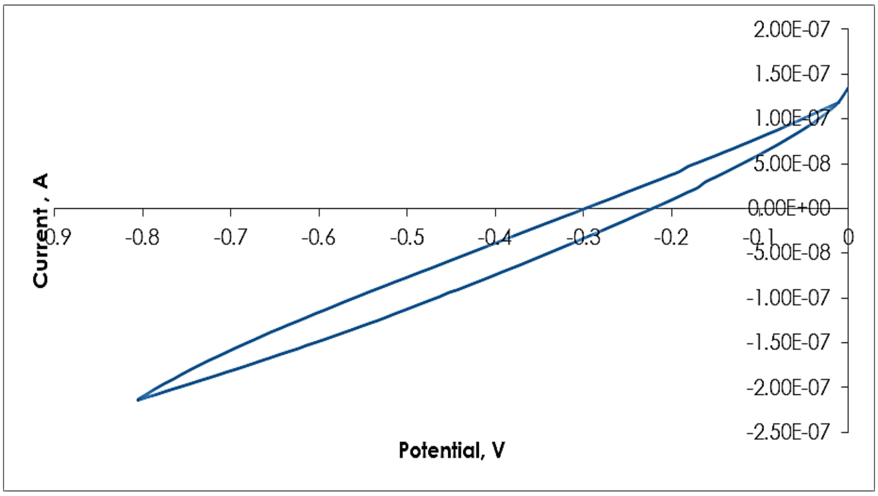

Figure 5. Cyclic Voltammetry for working electrode Sn metal in GPE PAAm-0.0 M MSA at 5 mV/s scan rate.

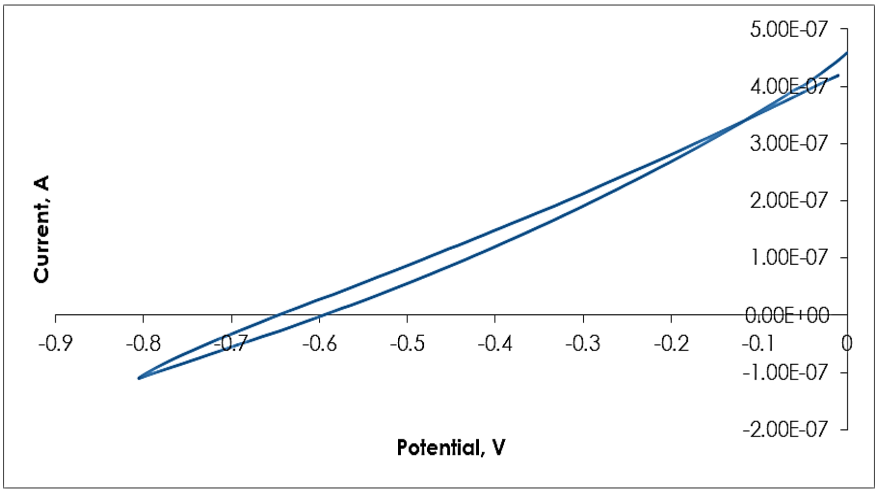

Figure 6. Cyclic Voltammetry for working electrode Zn metal in GPE PAAm-0.0 M MSA at 50 mV/s scan rate.

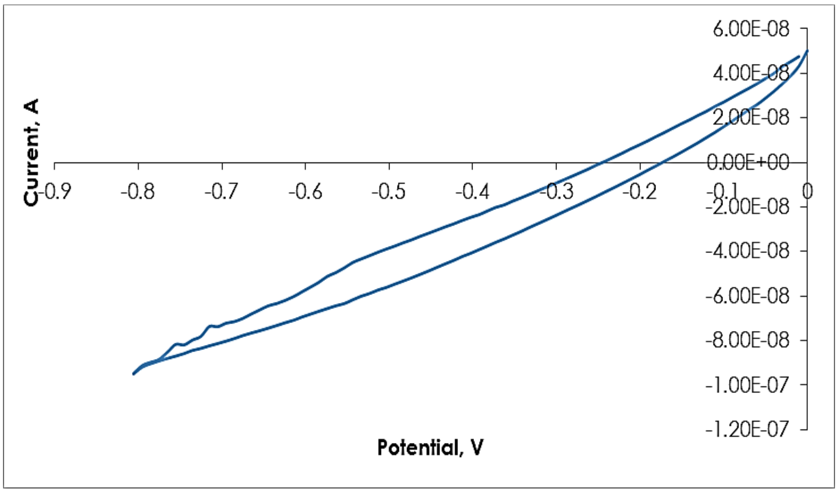

Figure 7. Cyclic Voltammetry for working electrode Sn metal in GPE PAAm-3.0 M MSA at 5 mV/s scan rate.

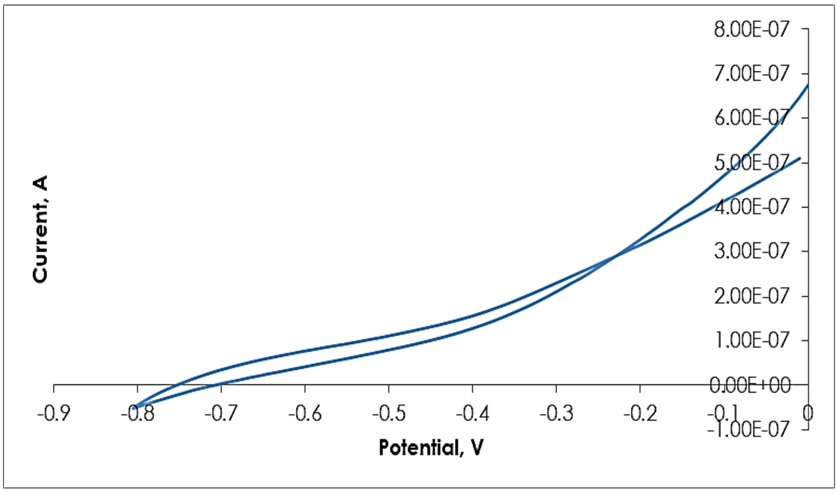

Figure 8. Cyclic Voltammetry for working electrode Zn metal in GPE PAAm-3.0 M MSA at 5 mV/s scan rate

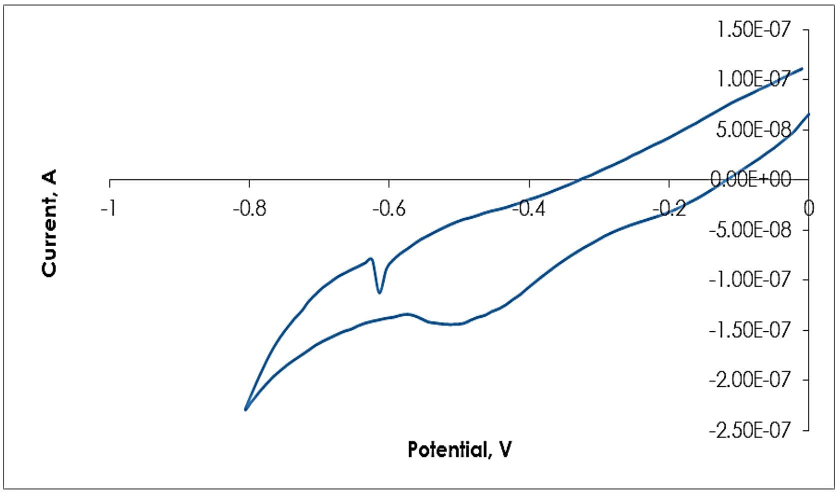

Figure 9. Cyclic Voltammetry for working electrode Sn metal in GPE PAAm-3.3 M MSA at 50 mV/s scan rate

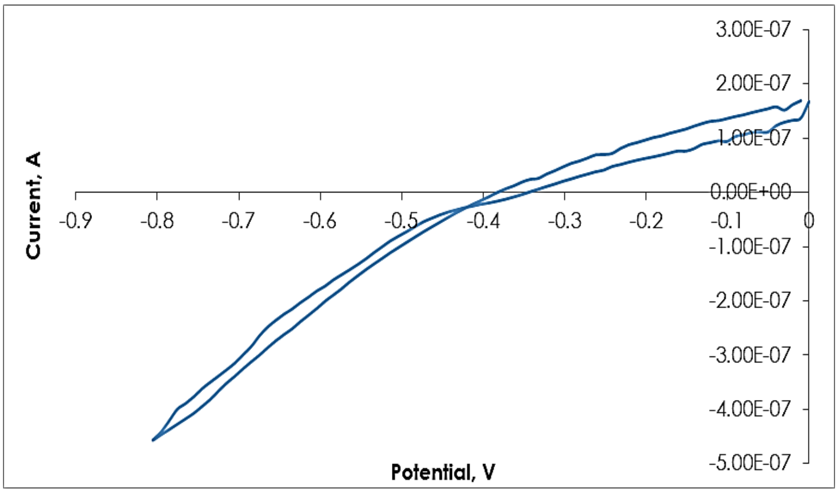

Figure 10. Cyclic Voltammetry for working electrode Zn metal in GPE PAAm-3.3 M MSA at 50 mV/s scan rate

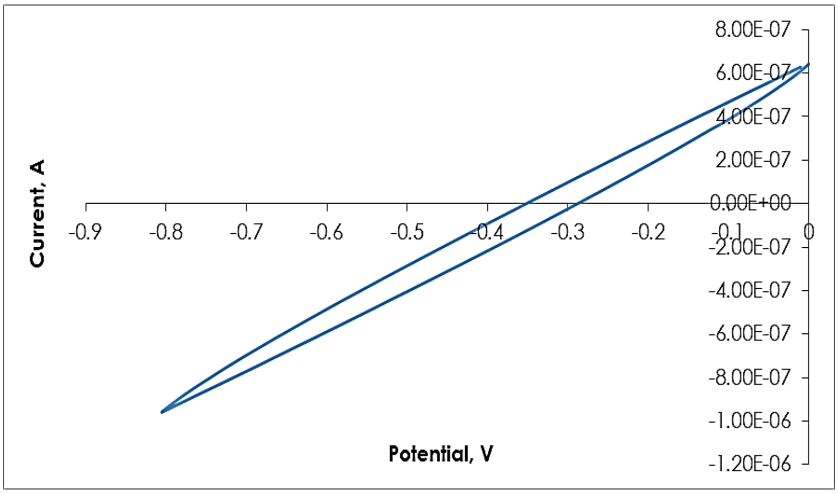

Figure 11. Cyclic Voltammetry for working electrode Sn metal in GPE PAAm-3.6 M MSA at 50 mV/s scan rate

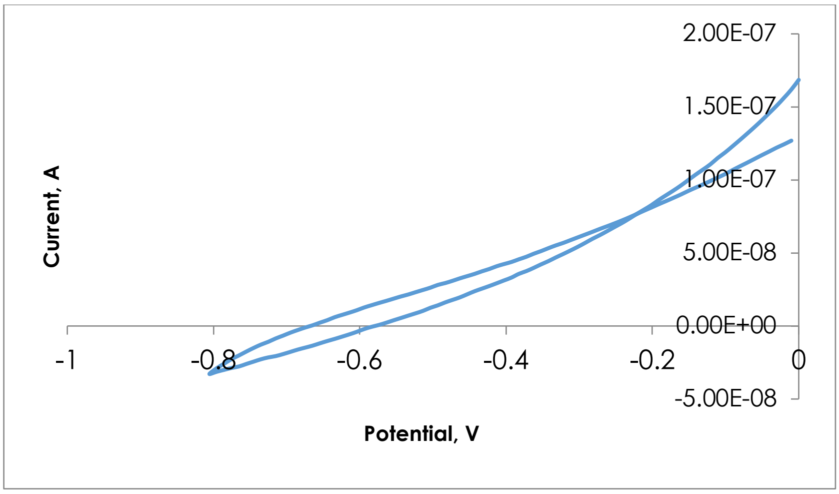

Figure 12. Cyclic Voltammetry for working electrode Zn metal in GPE PAAm-3.6 M MSA at 50 mV/s scan rate

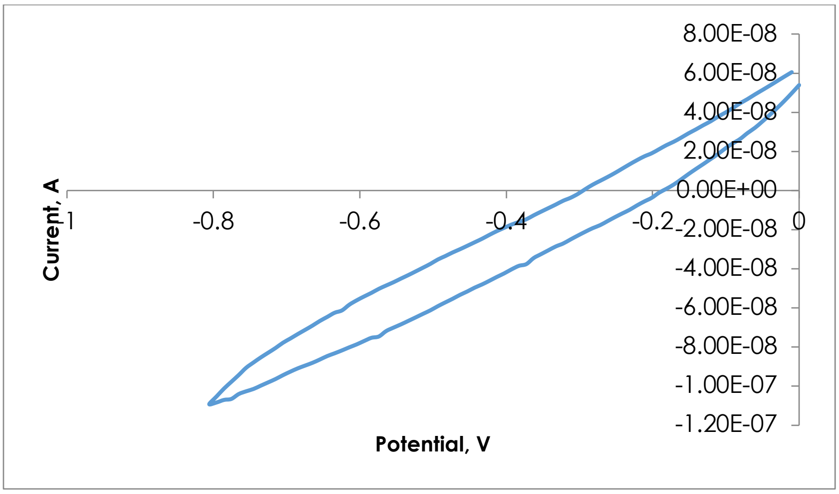

Figure 13. Cyclic Voltammetry for working electrode Sn metal in GPE PAAm-3.9 M MSA at 50 mV/s scan rate

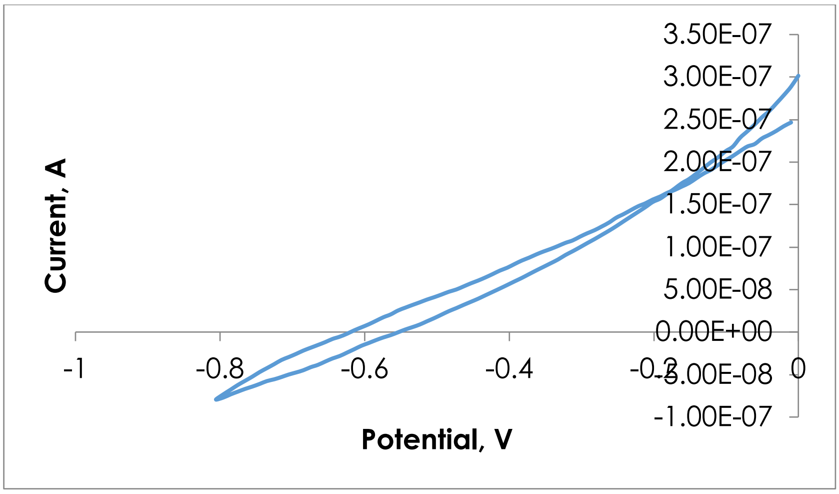

Figure 14. Cyclic Voltammetry for working electrode Zn metal in GPE PAAm-3.9 M MSA at 50 mV/s scan rate

4. Conclusions

The objective of this study was to investigate the ionic conductivity of the methane sulfonic acidic based polyacrylamide (PAAm-MSA) gel polymer electrolyte for tin and zinc-air batteries application. In the present study, the ionic conductivity show good value in the range of 10^{-2} – 10^{-1} S/cm which is the ionic conductivity of the PAAm (~10^{-2} S/cm) electrolyte increases by an order of magnitude to ~ 10^{-1} S/cm with the addition of 3.0 mole MSA. The ionic conductivity increases from 4.91×10^{-2} S/cm for 0.0 mole MSA to 7.11×10^{-1} S/cm for 3.0 mole MSA. The maximum ionic conductivity is 8.47×10^{-1} S/cm at 3.6 mole MSA and proves to be the best-synthesized GPE in this work. FTIR spectroscopic were conducted to define the water and acid interaction with host polymer PAAm. The spectra showed that the protonation occurred at the amine group.

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