

A Comparative Studies on Methanesulfonic and p-Toluene Sulfonic Acid Incorporated Polyacrylamide Gel Polymer Electrolyte for Tin-Air Battery

S. Sumathi, V. Sethuprakash, W. J. Basirun

Abstract—This study was focused on polymer electrolytes containing methanesulfonic acid (MSA) and p-toluene sulfonic acid (pTSA) mixed with polyacrylamide (PAAm) respectively. Impedance Spectroscopy technique has been employed to compare the ionic conductivity of these polymer electrolytes. The ionic conductivity of the PAAm hydrogel electrolytes increase upon adding the sulfonic acids. Ionic conductivity of PAAm-pTSA is higher than PAAm-MSA. The electrochemical performance evaluations were done with the tin-air cells discharge at zero current for 30minutes and at constant current density of 2.5, 5, 7.5, 10, 12.5 and 15mA/cm². The tin-air cell of PAAm-MSA produce higher specific discharge capacity compared to PAAm-pTSA. Open-circuit voltage measurement revealed a higher voltage for tin-air cell of PAAm-MSA which is 1.27V.

Keywords—Methane sulfonic acid, polyacrylamide, polymer gel electrolytes, p-toluene sulfonic acid.

I. INTRODUCTION

ONE of the great challenges in the twenty-first century is unquestionably energy storage devices such as batteries, fuel cells and capacitors, hence the rapid development of research in this field. The performance of these devices depends intimately on the properties of the electrolytes. Since Wright et al. [1], [2] discovered ionic conductivity in solid polymer electrolytes based on the complex of poly (ethylene oxide) (PEO) and alkaline metals salts, a lot of effort done on the electrochemical preparation of polymer electrolytes. Many kinds of polymeric hosts, such as poly (acrylonitrile) (PAN) [3], [4] poly (vinylchloride) (PVC) [5], poly (methylmethacrylate) (PMMA) [6], [7] and poly (vinylidene fluoride) (PVdF) [8]-[10] have been proposed as frame works of polymer electrolytes. Their ionic conductivities were reported between 10^{-4} and 10^{-3}Scm^{-1} at room temperature.

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Several strategies have been developed to improve the electrochemical performance of the polymer electrolytes. Among the strategies, chemical interaction between basic polymers and strong acids or polymeric acid had attracted the interest of researchers. Polymers bearing basic sites such as ether, alcohol, imine, amide or imide groups enable the establishment of hydrogen bonds with the acid which allows the acid undergoes to some extent dissociation. Another characteristic property of them is the dissociation of the acid where the proton is transferred from the acid group to the polymers with more basic groups. Many researchers have shown that the acid doped polymers exhibit conductivity less than 10^{-3}Scm^{-1} at room temperature[11]-[14]. Phosphoric acid, sulfuric acid, acetic acid, salicylic acid and oleic acid are some of the acids that have been introduced into the polymer electrolytes systems.

Sulfonic acids with the presence of hydrogen atom make the compound acidic with dissociation constants of $\sim 10^{-2}$.The effect of trifluoromethanesulfonic acid concentration on conductivity with polymethylmethacrylate (PMMA) as host polymer electrolyte has been studied [15]. The maximum ionic conductivity of $7.55 \times 10^{-3}\text{Scm}^{-1}$ has been observed in this study. Methane sulfonic acid (MSA) gained some commercial acceptability during the early 1980s and became a potential electrolyte for usage in tin, lead and tin-lead plating [16]. MSA has good thermal stability, water miscibility and low toxicity [17]. p-Toluenesulfonic acid (pTSA) is a white solid which can dissolve in water, alcohol and other polar organic solvents.

The effects of methane sulfonic acid and of p-toluene sulfonic acid on the conductivity behavior of polyacrylamide gel electrolytes were analyzed in this study. Polyacrylamide (PAAm) has a great ability to entrap water and produce gel-like characteristic which makes it a good candidate for forming gel polymer electrolyte [18]. It is a good proton conductors with conductivities exhibited greater than 10^{-2}Scm^{-1} at room temperature and increased up to 10^{-1}Scm^{-1} at 100°C [19]. On the other hand, polyacrylamide gel polymer electrolyte system was used to study the performance of direct borohydride fuel cell with different concentrations of KOH which exhibits $2.73 \times 10^{-1}\text{Scm}^{-1}$ at 6M KOH and the discharge capacities was in the range of 257.12-273.12mAhcm⁻² [18].

II. PROCEDURE

A. Preparation of PAAM Gel Polymer Electrolytes

Gel polymer electrolytes were prepared by using Polyacrylamide (Polyscience, INC), methane sulfonic acid (MSA) (>99.5%, Sigma-Aldrich) and paratoluenesulfonic monohydrate acid (pTSA) (>98.5%, Sigma-Aldrich). In order to prepare the gel polymer electrolytes 1.25g of PAAm were dissolved in 48.75ml distilled water and stirred continuously. 1.2g of MSA was added to the resulting homogenous solution and again was stirred continuously at room temperature to produce PAAm-0.5M MSA homogenous gel polymer electrolyte. This process was continued with 4.8g, 9.6g, 14.4g and 19.2g of MSA to produce 1.0M, 2.0M, 3.0M and 4.0M of MSA in 50ml solutions respectively.

PAAm hydrogel polymer electrolytes with pTSA were also prepared according to the primary procedure. 4.75g of pTSA were dissolved into the prepared PAAm hydrogel and stirred efficiently for 24 hours to achieve a homogenous mixture with 0.5M of pTSA. Stoichiometric amounts of 9.5g, 19g, 28.5g and 38g of pTSA were added to PAAm hydrogel to produce polymer electrolytes with 1.0M, 2.0M, 3.0M and 4.0M of pTSA respectively.

B. Electrical Impedance Spectroscopy (EIS) Study

Electrical impedance spectroscopy (EIS) studies were done to measure ionic conductivity of samples. The EIS were measured using Autolab PGSTAT 30 system (Eco Chemie, B.V.) at room temperature. The samples of gel polymer electrolyte with different concentrations of MSA and pTSA were connected to a frequency response analyzer (FRA) module. The bulk electrolyte resistance value (R_b), the intercept at the x-axis of the impedance plot, was used to calculate the ionic conductivity (σ) of polymer electrolytes. The equation below was used to calculate the ionic conductivity of each sample.

$$\sigma = l/R_b A$$

R_b = bulk resistance

l = thickness = 0.55cm

A = Area of contact between the gel and the electrode, $A = \pi r^2 = \pi(0.10\text{cm})^2 = 0.0314\text{cm}^2$.

C. Discharge Characteristic of Tin-Air Polymer Cell

Discharge characteristic of Tin-Air polymer cell were used to examine the application of this sulfonic acids gel polymer electrolyte in energy storage device, electrochemical device, Tin/air was assembled and tested. A tin film anode with an active area of 1.0cm^2 was used as working electrode. An air-cathode made of $\text{MnO}_x/\text{C}/\text{Ni}$ (ECT, UK) was used to test the discharge characteristic of tin-air polymer cell. About 25ml of the PAAm-3M MSA and PAAm-4MpTSA gel polymer electrolytes with highest conductivity value were transferred into a cylinder with a cathode attached to the bottom of it. A Tin film of $0.5\text{cm} \times 1.0\text{cm}$ (active area of 1.0cm^2) was immersed into the gel electrolyte. Two wires were connected to the tin anode and the air-cathode to complete the circuit which was connected to the Autolab PGSTAT 30 system (Eco Chemie, B.V.). The discharge characteristics of the tin-air

polymer cell were evaluated according to their OCV by running the cell in the open circuit condition for 24 hours at 25°C . The discharge profiles of the tin-air /PAA-MSA and tin-air/ PAAm-pTSA gel electrolytes cells were measured with the current flows of 2.5, 5.0, 7.5, 10 and 12.5mA.

III. RESULTS AND DISCUSSIONS

A. Electrical Impedance Spectroscopy (EIS) Study

Table I illustrated the bulk resistance values of the PAAm samples with different concentrations of MSA and pTSA acids. Ionic conductivities were calculated and tabulated by using the bulk resistance values (Table II). The variations of conductivity of PAAm gel polymer electrolytes prepared as the functions of MSA and PTSA acid concentrations were plotted in Fig. 1. Apparently the conductivity of PAAm hydrogel increase by one order of magnitude ($\sim 10^{-3}$ to $\sim 10^{-2}$) with 0.5M of MSA whereas the ionic conductivity increase by two orders of magnitude ($\sim 10^{-3}$ to $\sim 10^{-1}$) with the addition of for PAAm-0.5M pTSA into PAAm. There are several factors that influence the ionic conductivity such as ionic conducting species concentration, cationic or anionic types charge carries, the charge carries mobility and the temperature [20]. In this study, the increases in conductivity attributed to the increases in the number of mobile H^+ ions when acids were added. However, the ionic conductivity of PAAm-pTSA GPEs found to be higher than the PAAm-MSA GPEs. This is because the degree of dissociation of pTSA ($\text{pK}_a = -2.8$) is higher compared to MSA ($\text{pK}_a = -1.9$) which released more free H^+ ions into the polymer matrix.

TABLE I
BULK RESISTANCES OF THE SAMPLES WITH DIFFERENT CONCENTRATION OF ACIDS

Concentrations of acid in the electrolyte/x(M)	Bulk Resistance(Ω)	
	PAAm-xMSA	PAAm-xpTSA
0	13000	2000
0.5	1125	32.92
1.0	151	26.00
2.0	85	30.50
3.0	25	23.25
4.0	46	21.20

TABLE II
THE IONIC CONDUCTIVITIES OF GPEs WITH DIFFERENT CONCENTRATIONS OF ACIDS

Concentrations of acid in the electrolyte/M	Ionic conductivity of	
	PAAm-MSA system, $\sigma/\text{Scm}^{-1} \times 10^{-1}$	PAAm-pTSA system, $\sigma/\text{Scm}^{-1} \times 10^{-1}$
0	0.0135	0.0876
0.5	0.156	5.31
1.0	1.16	6.74
2.0	2.06	5.74
3.0	7.00	7.53
4.0	3.81	8.26

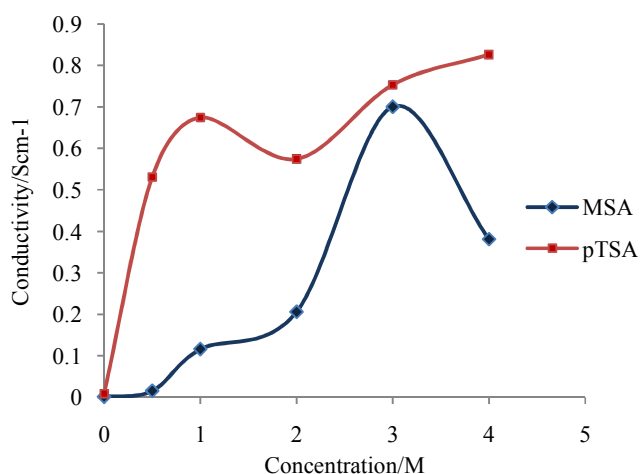


Fig. 1 Variations in ionic conductivity of PAAm-MSA and PAAm-pTSA GPEs

The ionic conductivity of PAAm-MSA polymer electrolyte increases with increasing acid content up to 3M and thereafter the conductivity decreases. This is due to the formation of neutral ion aggregates, which did not take part in conduction. The presence of ion aggregates at higher acid concentration was checked by mass action considerations by plotting a graph of $\log \sigma$ versus $\log C$ (concentration of acid). If the acid is strongly dissociated, plot of $\log \sigma$ versus $\log C$ should be a straight line and any deviation from straight line behavior shall indicate ion aggregation [21].

The variations of $\log \sigma$ versus $\log C$ for PAAm polymer electrolytes containing MSA and pTSA are shown in Fig. 2. PAAm-pTSA electrolyte's plots formed almost straight line compared with PAAm-MSA electrolyte plots which is an evidence of very minimum ion aggregations in the electrolytes. This was because of the presences of benzene ring in the sulfonate ions which could not bring the ions closer to one another. This led to a high conductivity of the electrolyte. The 4M of PAAm-pTSA polymer electrolyte exhibited the maximum ionic conductivity of $8.26 \times 10^{-1} \text{Scm}^{-1}$ at room temperature. On the other hand, the plot of $\log \sigma$ versus $\log C$ of PAAm-MSA electrolytes shows a strong deviation from straight line at higher concentration due to the ion aggregations. This reduces the conductivity from $7.0 \times 10^{-1} \text{Scm}^{-1}$ with 3M MSA to $3.81 \times 10^{-1} \text{Scm}^{-1}$ at 4M. However, the ionic conductivity given by the sulfonic acids in this study were higher than the values given by other acids as reported in the literature [12], [14], [22].

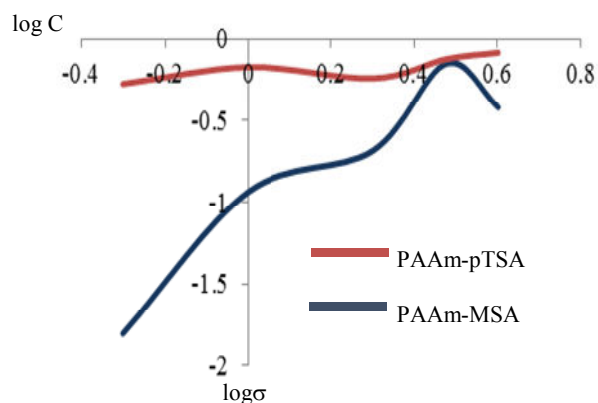


Fig. 2 Variations of $\log \sigma$ versus $\log C$ for Polymer Electrolytes

B. Discharge Characteristic of Tin-Air Polymer Cell

Discharge capacity was analyzed by using the tin-air cell. The highest conductivity of PAAm-MSA electrolyte and PAAm-pTSA electrolyte was $7.00 \times 10^{-1} \text{Scm}^{-1}$ and $8.26 \times 10^{-1} \text{Scm}^{-1}$ respectively. Open circuit voltage (OCV) remains constant without any significant drops during the course of the discharge for both of the systems which are visible in Fig. 3. They were about 1.27V for PAAm-MSA and 0.84V for PAAm-pTSA throughout the discharge process.

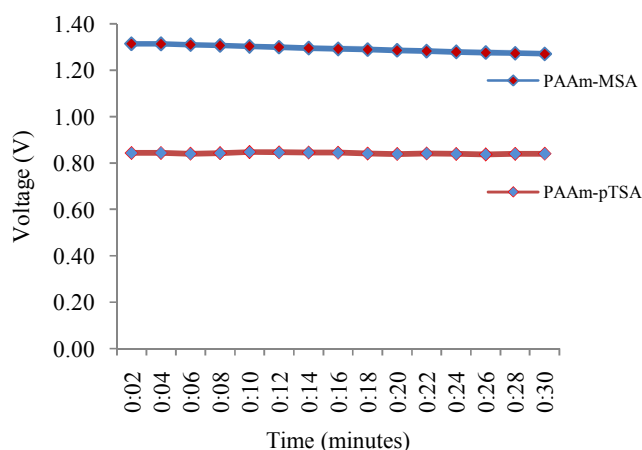
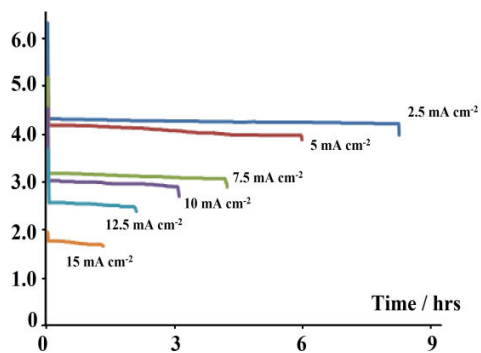
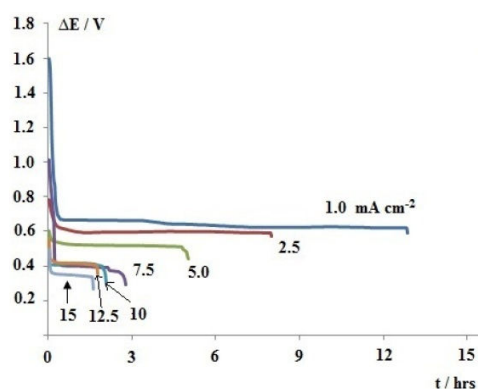


Fig. 3 OCV value for 30 minutes at room temperature

Comparison of discharge characteristic was made between PAAm-MSA and PAAm-pTSA gel polymers as the electrolytes in tin-air cells. It was done with different current flows. The results show that the cell potentials for PAAm-MSA remain constant with time until the capacity is fully exhausted. The discharge time of the cells decreases as the intensity of the current increases for both the system. Both of the cells remain constant for 8 hours with 2.5mA of current.



(a)



(b)

Fig 4 Discharge curves with different current density; (a) tin-air/PAAM-MSA, (b) tin-air/PAAM-pTSA

The capacity of the tin-air cell is determined only by the amount of the active tin metal in the anode since the capacity of the air electrode being infinite high because of the inexhaustible supply of oxygen in the atmosphere[23]. The specific discharge capacities for the cells at different current are listed at Tables III and IV. Fig. 5 shows the comparison of specific discharge capacities of Sn/O₂ cells between the PAAM-MSA and PAAM-pTSA as the gel electrolytes at different current flows. Ultimately, the Sn/O₂ with PAAM-MSA gel electrolyte battery system shows higher discharge capacities than the PAAM-pTSA battery system.

TABLE III
SPECIFIC DISCHARGE CAPACITIES OF TIN-AIR CELLS WITH PAAM-PTSA ELECTROLYTE AT DIFFERENT CURRENTS

Current (mA)	Discharge time/h	Capacity (mAh/g)
2.5	8.25	428
5.0	5.95	470
7.5	2.94	442
10	2.19	453
12.5	2.07	443
15	1.31	399

TABLE IV
SPECIFIC DISCHARGE CAPACITIES OF TIN-AIR CELLS WITH PAAM-MSA ELECTROLYTE AT DIFFERENT CURRENTS

Current (mA)	Discharge time/h	Capacity (mAh/g)
2.5	8.03	436
5.0	5.05	453
7.5	2.81	444
10	2.10	484
12.5	1.84	466
15	1.64	451

TABLE V
AVERAGE SPECIFIC DISCHARGE CAPACITY OF TIN/AIR CELLS WITH PAAM-MSA AND PAAM-pTSA POLYMER ELECTROLYTES

Tin/Air cell	Average specific discharge capacity (mAh/g)
PAAM-MSA	456
PAAM-pTSA	439

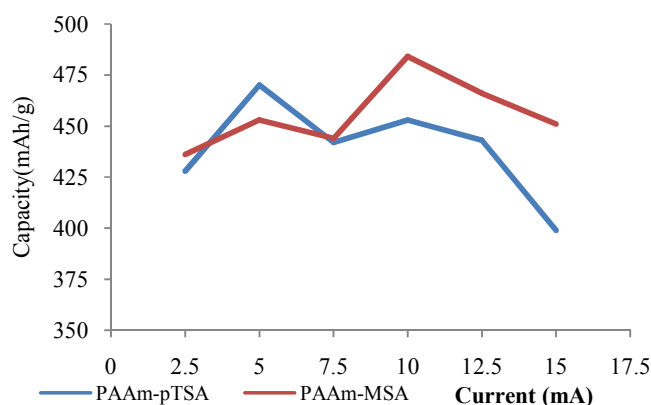


Fig. 5 Specific discharge capacities of Sn/O₂ cell at different current for PAAM-MSA and PAAM-pTSA

In Table V above, comparison between the average specific discharge capacities were calculated for Tin/air cell with PAAM-MSA gel polymer electrolyte and PAAM-pTSA gel polymer electrolyte. These values are comparably higher than the value determined in Lithium-air cells in the electrochemical studies of composited cellulose polymer gel electrolyte [24]. The Li-air cells exhibited 241.7mAhg⁻¹ at discharge current of 0.5mA and 61.9mAhg⁻¹ at discharge current of 1.0mA. The highest conductivity obtained by this electrolyte was 5.99 x 10⁻³Scm⁻¹.

The poly (vinyl alcohol)-LiBOB complexes polymer electrolytes for lithium-air cell system, exhibited specific discharge capacity of 263mAhg⁻¹ at 0.5mA current [25]. In the study done by Mohamad on the electrochemical properties of aluminum anodes in gel electrolytes-based, the highest capacity shown by aluminum-air battery was 105.0mAhg⁻¹ [26]. This value is much lower than the value produced by tin-air polymer system in this study. However, the discharge capacity shown by Zn-air battery with sago gel polymer is slightly higher than the value shown in this study which was about 505mAhg⁻¹ [27].

The results also revealed that the average specific capacity of Tin/air PAAM-pTSA cell is lower (439mAh/g) than the Tin/air PAAM-MSA cell (456mAh/g) although the PAAM-pTSA gel polymer electrolyte exhibited a higher ionic

conductivity than PAAm-MSA. This result proved that the PAAm-MSA gel polymer electrolyte exhibited better electrochemical performance in the tin-air cell with higher OCV value and higher specific discharge capacity when compared with PAA-pTSA. This could be explained by the presences of bigger structure of p-toluene sulfonic acid with benzene ring which prevent the diffusion of tin ions in the gel polymer electrolytes. Thus, the Tin is not fully utilized for the discharge reaction which is why the discharge capacity is lower when compared to the PAAm-MSA cell. Another reason that can be explained is the decreases in the O₂ flow into the PAAm-pTSA system. This was proved by the FESEM images taken on air-cathode after the complete discharge. The FESEM micrographs of the air-cathode are depicted in Fig. 6 (a) for PAAm-MSA system and Fig. 6 (b) for PAAm-pTSA system.

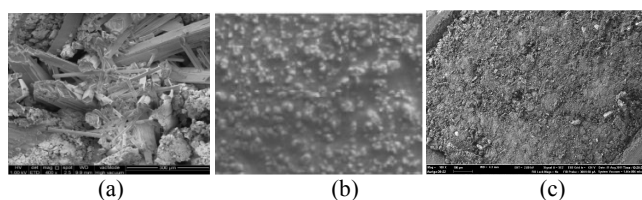
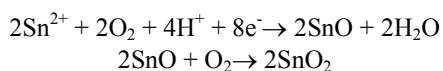


Fig. 6 FESEM images of air-cathode surface (a) before discharge (b) after complete discharge for PAAm-MSA polymer electrolyte system (c) after complete discharge for PAAm-pTSA polymer electrolyte system

The geometrical shapes of SnO and SnO₂ have been determined by FESEM imaging of the air-cathode after continuous discharge of the Tin-Air cell of PAAm-MSA system. The white spherical shaped objects indicated the presence of SnO and SnO₂ on the surface of the cathode. In Fig. 5 (b), the air-cathode surface was covered by the rod-like structure of SnO₂. The Sn²⁺ reacts with O₂ and the product SnO₂ are transported through the matrix and deposited at the air-cathode. The formation of SnO and SnO₂ at the air cathode during the discharge of the tin-air cell can be described by the following reactions:



According to Jian et.al decreasing in the O₂ flow will result in the increase in the super saturation of SnO₂ which is favorable for the growth of dendrites [28]. Thus, the developmental of SnO₂ (Fig. 6 (b)) dendrites in PAAm-pTSA system are due to the decreases in O₂ flow into the Tin-air cell.

IV. CONCLUSIONS

Studies were done on the different sulfonic acids added to polyacrylamide hydrogel electrolytes. The characteristic properties of the electrolytes have been analyzed by means of impedance spectroscopy. The increases in conductivity were significant for PAAm-pTSA polymer gel electrolyte. The ionic conductivity reached the maximum value of 8.23 x 10⁻¹ Scm⁻¹ with the addition of 4M of pTSA into the PAAm

hydrogel at room temperature. Maximum ionic conductivity of 7.00 x 10⁻¹ Scm⁻¹ was obtained at the addition point of 3M MSA into PAAm hydrogel.

The electrochemical studies of these electrolytes done by assembled tin-air cells had shown good electrical performance. The results revealed that although The PAAm-MSA gel polymer electrolyte gave lower ionic conductivity than the PAAm-pTSA electrolyte but it demonstrated better electrochemical performances. The OCV value of tin-air/PAAm-MSA cell was about 1.27V for 30 minutes compare with 0.84V for tin-air/PAAm-pTSA cell for the same range of time. It also had a steady discharge profiles for different currents flow with higher specific discharge capacity. The Tin-air battery cell with PAAm-MSA polymer electrolyte thus exhibited much better electrochemical cell performance in discharge capacity than that of the Tin-air cell with PAAm-pTSA polymer electrolyte.

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