Sri Lankan Journal of Physics, Vol. 15 (2014) 45-51

INSTITUTE OF PHYSICS – SRI LANKA

Short Communication

Evaluation of a copper based gel polymer electrolyte and its performance in a primary cell

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Abstract

Portable electronic device industry is vastly developing over the last few years. As electrochemical batteries are suitable power sources for portable devices, demand for reliable and efficient batteries have also been increased. Since liquid electrolytes can cause several safety hazards due to leaking of the electrolyte, studies on gel polymer electrolytes have been able to attract many researchers. In this research work, a gel polymer electrolyte based primary cell was fabricated and discharge characteristics were studied. To prepare the gel polymer electrolyte, Polymethylmethacrylate (PMMA), Ethylene Carbonate (EC), Propylene Carbonate (PC) and Copper trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$ - CuTf) were used. Gel polymer electrolyte sample which contained 22.5% PMMA: 30% EC: 30% PC: 17.5% CuTf showed a conductivity of 2.34×10^{-3} S cm^{-1} at room temperature with an appreciable mechanical stability. Primary cell with Cu and Mg electrodes showed 1.73 V open circuit potential, 131 µA h capacity and 1.13 mA short circuit current.

Keywords: Gel polymer electrolytes; PMMA; primary cells; discharge characteristic; CuTf, DC polarization

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1. INTRODUCTION

As a diverse range of portable electronic devices are being introduced to the market, requirement of reliable power sources has also been increased. Although batteries are inherently simple in design, development has been progressing much slowly due to the lack of suitable electrode materials, electrolytes and difficulties in mastering of good interfaces between electrodes and electrolytes[1].

In batteries, electrolytes play the role as a medium which facilitates charge transfer between electrodes. Earlier liquid electrolytes were used widely for batteries but at present, gel polymer electrolytes (GPE) have received a global interest because they have many advantages such as free of internal shorting, no leakage of electrolytes and higher ionic conductivity over the liquid electrolytes[2]. Due to these characteristics, gel polymer electrolytes can be used in various electrochemical devices such as batteries, solar cells and super capacitors[3,4]. General concept of the structure polymer gel electrolytes are trapping liquid electrolyte solutions in polymer cages[5,6]. Polyacrylonitrile (PAN), polymethylmethacrylate, polyvinylidene fluoride (PVdF), polyethylene oxide (PEO) are commonly used polymers for synthesis of polymer gel electrolytes[7]. Ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) etc. can be used as solvents[2].

Although much attention had been paid on lithium based batteries, now it has been deviated towards alternative salts due to the drawbacks of lithium based devices, such as manufacturing difficulties, safety issues, and environmental issues connected with disposal[8]. Among alternative salts, Cu has great importance such as low toxicity, high availability, low cost and high safety. In this research work, a gel polymer electrolyte based on Polymethylmethacrylate (PMMA), Ethylene Carbonate (EC), Propylene Carbonate (PC) and Copper trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$ - CuTf) was considered and primary electrochemical cells were constructed in the configuration, Mg/PMMA:EC:PC:CuTf/Cu using Mg and Cu as electrodes. Discharge characteristics of the cells were studied under different loads.

2. EXPERIMENTAL

2.1 Materials

PMMA, EC (98%), PC (99%) (Aldrich) and CuTf (98%, ABCR) were used without further purification. Hot pressed method was used to prepare samples. First required amounts of PMMA, EC, PC and CuTf were weighed and stirred well by magnetically stirring. The mixture was heated at 60˚C for about one hour while stirring. Finally resultant hot mixture was pressed in between two well cleaned glass plates to get a thin homogeneous film and it was kept in a desiccator for about five hours. EC and PC weight ratio was fixed at 1:1 and PMMA concentration was changed to find out the composition which has the highest room temperature conductivity and optimum mechanical stability.

2.2 Ionic conductivity measurements

Circular films with about 14 mm diameter was sectioned out from the GPE film and assembled in a brass sample holder by sandwiching in between two stainless steel (SS) electrodes. Impedance measurements were taken in the frequency range from 0.01 Hz to 37 KHz and from room temperature to 60˚C using Metrohm Autolab M101 impedance analyser. The conductivity was calculated by the following equation;

$$\sigma = \frac{t}{R_b A} \qquad (1)$$

where *t* is the thickness of the GPE film, A is the area of the GPE film, R_b is the bulk electrolyte resistance and it was retrieved by using impedance plot.

2.3 Ionic transport number measurements

DC polarization test was done using stainless steel (SS) electrodes to find out the types of the charges responsible for the conductivity. The current flow through the sample was observed with the time by applying a 1 V bias voltage.

2.4 Mg/PMMA:EC:PC:CuTf/Cu cell fabrication and characterization

For the fabrication of Mg/PMMA:EC:PC:CuTf/Cu primary cell, well cleaned Mg and Cu disc shaped samples were used as electrodes and cells were assembled as shown in the Figure 1. Cells were prepared to observe the discharging characteristics under the loads of 1 MΩ, 10 MΩ and also under self-discharging.

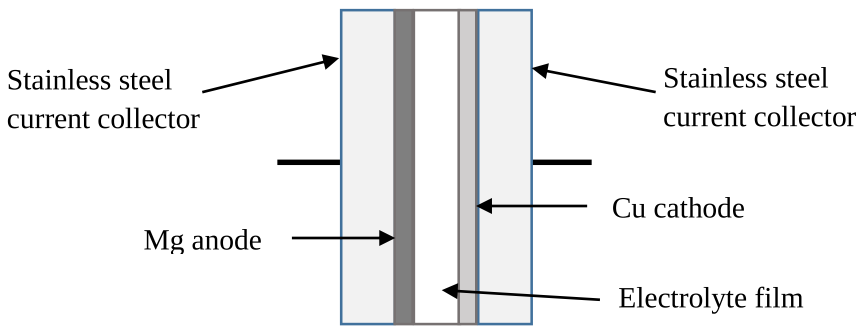

Figure 1: Configuration of the Mg/PMMA:EC:PC:CuTf/Cu primary cell

3. RESULTS

In order to find the sample composition having an appreciable ionic conductivity and a good mechanical stability, PMMA concentration was varied and the room temperature conductivity of the samples was measured. Impedance data were analyzed using the Non Linear Least Square Fitting method developed by B.A. Boukamp[9]. Figure 2 shows the variation of the room temperature conductivity with PMMA concentration of PMMA:EC:PC:CuTf gel polymer electrolyte films.

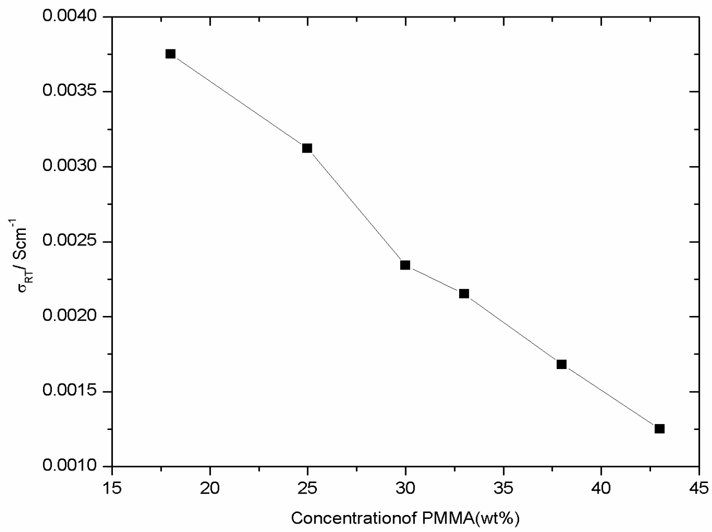

Figure 2: Room temperature conductivity variation of the Gel polymer electrolyte with PMMA concentration

Although first two samples showed higher ionic conductivity, both of them were in more or less the liquid form. Hardness of the samples had increased when PMMA concentration was increased, but the conductivity had decreased. Increasing of PMMA concentration may leads to increase the density of polymer structure. The structure of a gel polymer electrolyte is described as a liquid electrolyte encapsulated in polymer matrices. When polymer concentration in the gel polymer electrolyte increases, ion conduction paths may become tortuous disturbing ion motion. Due to this, ionic conductivity may go down[10]. The third sample which contained the next highest PMMA concentration was selected for further studies as it had shown both acceptable ionic conductivity and mechanical stability. Room temperature conductivity of that sample was 2.34×10^{-3} S cm^{-1}. Figure 3 shows the graph of current variation with time obtained from the polarization test with stainless steel electrodes.

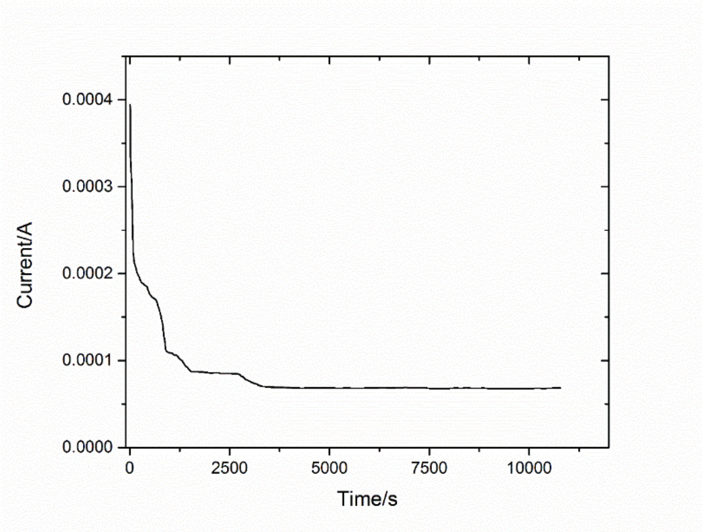

Figure 3: DC polarization curve of SS/GPE/SS cell with 1 V bias voltage

The sudden drop in current within first 3000 s time hints that more contribution for the conductivity is coming from ions than electrons. In other words, the sample is purely an ionic conductor. The calculated ionic transference number is 0.79. Mg/Gel polymer electrolyte/Cu primary cells showed an average open circuit voltage of 1.70 V and a short circuit current of 1.13 mA. Figure 4 shows the variation of open circuit voltage with time. During first 150 hours period, the drop of the open circuit voltage due to self-discharging is very small and hence it can be neglected. Even after 150th hour, voltage remains at a constant value showing the excellent stability.

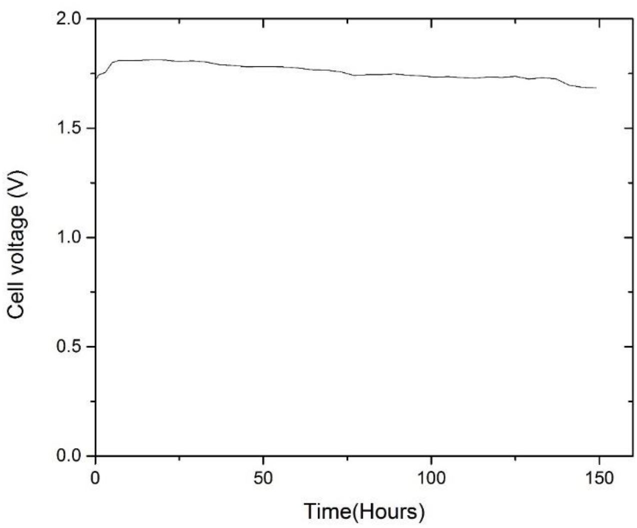

Figure 4: Self-discharge characteristic of Mg/PMMA:EC:PC:CuTf/Cu primary cell at room temperature

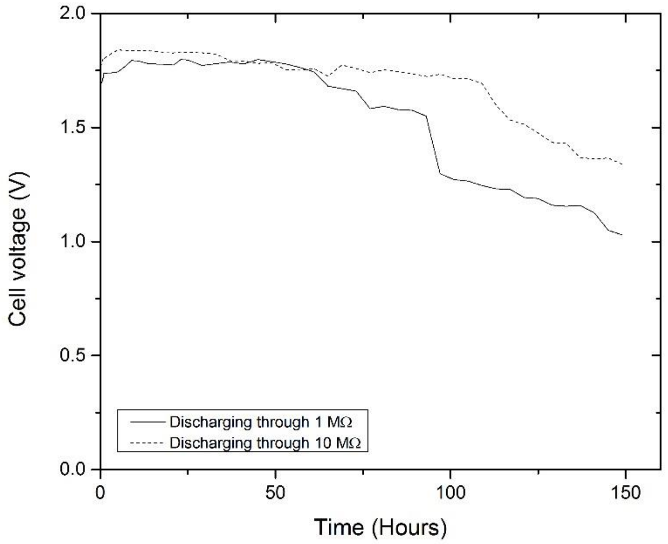

Figure 5: Discharge characteristic of Mg/PMMA:EC:PC:CuTf/Cu primary cells through 1 MΩ and 10 MΩ loads at room temperature

Discharge characteristics of cells under 1 MΩ and 10 MΩ loads at room temperature are shown in Figure 5. During first 60 hour (nearly) time period, voltage of both cells remain rather constant. After that, the voltage of the cell under 1 MΩ starts decreasing faster than the other cell. This can be accepted as because of the low resistance. As low resistances draw higher current flow, discharge through lower loads can be much faster than higher loads. An interesting feature is that even within the entire 150 hour period, the voltage reduction under 1 MΩ load is about 0.75 V. This is an indication of the fairly high stability of the cells though the open circuit voltage is small. Some voltage fluctuations are seen at the beginning for a small time period probably due to cell polarization[11]. The discharge capacity of the cell was calculated to be 131 μA h. Low discharge capacity may be attributed to the high internal resistance of the cell[12].

4. CONCLUSION

Gel polymer electrolyte which is containing 22.5% PMMA: 30% EC: 30% PC: 17.5% CuTf is having a good ionic conductivity of 2.34×10^{-3} S cm^{-1} which is suitable for applications. DC polarization test with stainless steel blocking electrodes suggests that the sample is purely an ionic conductor. Preliminary results on the primary cells with Cu and Mg electrodes are useful to further develop the performance of cells. Measures should be taken to avoid any unwanted reactions that are possible with electrolyte and electrodes.

ACKNOWLEDGEMENTS

National Research Council of Sri Lanka (NRC) is acknowledged for funding this research work under the grant no NRC-12-109.

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