A novel gel polymer electrolyte based on Polymethylmethacrylate and Copper Trifluoromethanesulfonate

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ABSTRACT

Gel polymer electrolytes which have attracted a great attention for many electrochemical devices have been earlier considered with lithium salts. But, today, the problems of lithium in applications have diverted some research activities toward non lithium salts. In this study, a gel polymer electrolyte consisting with Polymethylmethacrylate, Copper Trifluoromethanesulfonate, Ethylene Carbonate and Propylene Carbonate was investigated for its electrochemical properties. It is a well known fact that Copper is lesser reactive than lithium and so environmental friendly. It is also easier to handle and store. The composition, 22.5% Polymethylmethacrylate/17.5% Copper Trifluoromethanesulfonate/30% Ethylene Carbonate/30% Propylene Carbonate (by weight) showed a room temperature conductivity of 2.34×10^{-3} S cm^{-1}. This value clearly proves that the system is quite suitable for ambient temperature applications. The sample was purely an ionic conductor having more contribution from anions ($t = 0.82$). Ionic nature further qualifies the sample for electrochemical applications. An electrochemical stability window up to 1.5 V was possible and it was seen that Cu plating and stripping process takes place on Cu electrodes though not on stainless steel electrodes.

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1. Introduction

It has been a well understood fact that polymer electrolytes are good substitutes for liquid electrolytes because they eliminate most of the drawbacks of liquid electrolytes such as volatility, corrosion, evaporation and less design flexibilities. But unfortunately, solid polymer electrolytes generally suffer from low conductivity at and below room temperature [1]. When attempts are made to increase the ionic conductivity, mechanical stability goes down. This hinders their suitability for applications. Therefore, tremendous research activities have been carried out to enhance their characteristics mainly by means of ionic conductivity and mechanical stability.

Gel polymer electrolytes (GPE) have been introduced to the world by Feuillade and Perche around 1975 [2] and have been extensively studied due to their promising ion conducting and mechanical properties which are not simultaneously available with solid polymer electrolytes. The most significant feature of gel polymer electrolytes is that a polymer network envelops a mixture of salt and solvent/s. In other words, a polymer network acts as a container to hold a liquid electrolyte. Due to this, gel polymer electrolytes exhibit higher ionic conductivities similar to liquid electrolytes and also mechanical properties same as to a solid polymer electrolyte. Polyacrylonitrile (PAN) [3,4], Polymethylmethacrylate (PMMA) [5] and polyvinyldinefluoride (PVDF) [6] are some of the polymers that have been commonly used for preparation of gel polymer electrolytes. At present, gel polymer electrolytes have been greatly investigated for their potential candidacy for many applications such as rechargeable cells [7], super capacitors [8], electrochromic devices [9] and solar cells [5,10,11].

Earlier, much attention was on gel polymer electrolytes based on lithium salts but at present, that trend has been diverted toward other cation based salts such as Cu, Mg, Zn and Na [12–14]. It is mainly due to the realization of some hazards of lithium that may arise with applications. In addition, plentiful existence as natural resources, low cost, more stability are some of the other features which have attracted multi valent cations for consideration. Different types of non lithium salts have been investigated with different polymers and some results predict that such systems are also bearing properties as well as performances similar to lithium based systems [13,15].

As per our knowledge, reports on gel polymer electrolytes prepared using Polymethylmethacrylate (PMMA) and Copper salts are quite rare anyway. Some have done studies with other polymers and Copper salts like Copper Trifluoromethanesulfonate [16,17].

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When comparing with lithium, Copper is lesser reactive and it is easier to handle. In this study therefore, proper preparation conditions such as temperature and time duration for the system, PMMA/Ethylene Carbonate (EC)/Propylene Carbonate (PC)/Copper Trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$ – CuTF), had to be determined beforehand to obtain mechanically stable and bubble free thin films. A composition that has an appreciable conductivity and a good mechanical stability and its electrochemical properties are reported in this preliminary work.

2. Materials and methods

2.1. Preparation of the electrolyte

PMMA (Aldrich), EC (Aldrich), PC (Aldrich) and CuTF (ABCR) were used as received. Required amounts of PMMA, EC, PC, and CuTF were weighed and the mixture was stirred magnetically while heating at 60 °C for 1 h. The hot, viscous mixture was then pressed in between two well cleaned glass plates and left in a vacuum dessicator overnight. It was then possible to obtain a mechanically stable film which was free from pin holes. Samples were prepared changing the amount of PMMA.

2.2. AC measurements of the samples

A circular shape sample was cut from the film and it was assembled in between two stainless steel (SS) electrodes in a spring loaded cell holder. Impedance data were gathered in the frequency range, 37 kHz–0.01 Hz by using a computer controlled Metrohm Autolab Impedance Analyser M101. Measurements were taken from room temperature to 60 °C. Thickness and diameter of the circular shape films were measured using a micrometer screw gauge.

2.3. Transference number measurements

As above, a circular shape sample was loaded in between two SS electrodes and was assembled in a spring loaded sample holder. By applying a potential of 1 V, the drop of current was measured as a function of time by using a computer controlled Metrohm Autolab Potentiostat M101. Another sample was assembled in between two Cu electrodes and the current drop across it was monitored as before.

2.4. Linear and cyclic voltammetry studies

A sample was sandwiched in between two SS electrodes and assembled in a spring loaded sample holder. Linear cyclic voltammetry study was performed in the potential range 0–1.6 V at the scan rate 1×10^{-3} V s^{-1}. A computer controlled Metrohm Autolab Potentiostat M101 was used to obtain the current variation with voltage. Using the same setup, cyclic voltammetry measurements were performed in the potential range −1 V to +1 V for cells in the configurations, SS/sample/SS and Cu/sample/Cu.

3. Results and discussion

3.1. AC impedance measurements of SS/GPE/SS cell

As per the Non Linear Least Square (NLLS) fitting method proposed by Boukamp, the general electrochemical impedance spectrum of a GPE with SS electrodes and the corresponding equivalent circuit is shown in Fig. 1 [18].

The high frequency semicircle corresponds to the bulk electrolyte and the second semicircle at intermediate frequency region corresponds to the SS/GPE interface. The spike represents
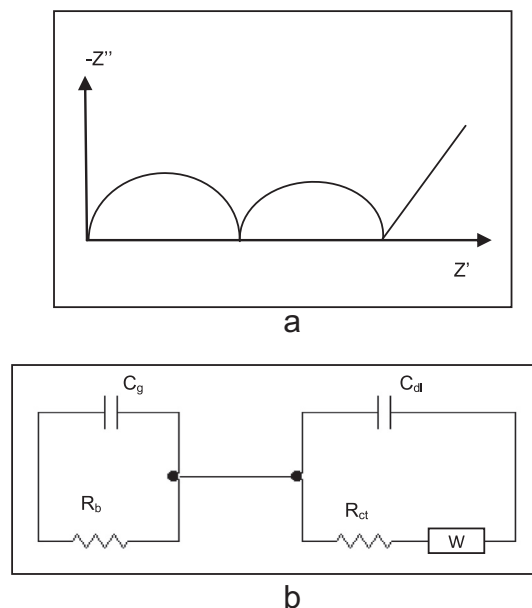

Fig. 1. (a) General Nyquist plot and (b) corresponding equivalent circuit for a symmetrical cell SS/GPE/SS cell.

the diffusion process. Accordingly, R_b, C_g, R_{ct}, C_{dl}, W refer to GPE resistance, geometric capacitance, charge transfer resistance, double layer capacitance and Warburg element (to represent diffusion).

One impedance spectrum obtained for the system under study is given in Fig. 2.

It does not consist with a high frequency semi circle as shown in inset of Fig. 2. It is due to the unavailability of the required high frequency range. So, the first intercept of the available semicircle was taken as the corresponding R_b. Conductivity, σ was calculated using the equation, $\sigma = (1/R_b)l/A$ where l is the thickness and A is the area of cross section of the sample.

3.2. Determination of the composition that results the highest room temperature conductivity

Several samples were prepared varying PMMA concentration and their room temperature conductivities were considered as
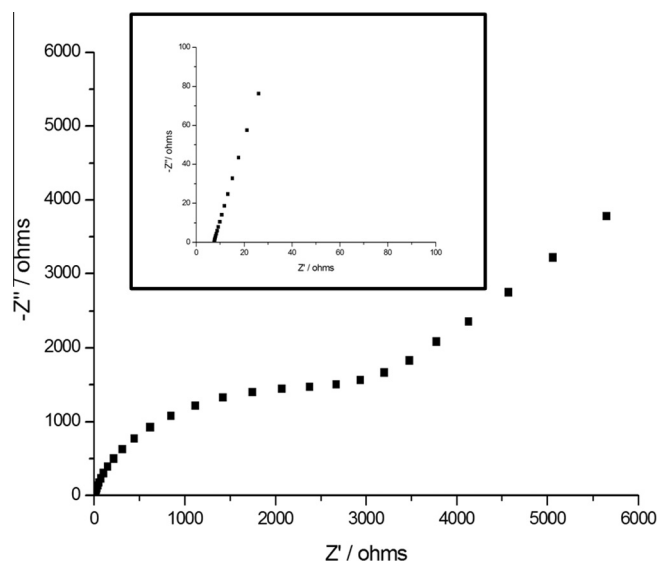

Fig. 2. A resulted Nyquist plot for the symmetric cell in the form of SS/GPE/SS. Z', Z″ refer to real and imaginary component of impedance respectively. High frequency region is expanded and it is given in inset.