RESEARCH ARTICLE

Effect of the gel polymer electrolyte conductivity on the performance of Zn rechargeable cells

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Abstract: Gel polymer electrolytes (GPEs) have been extensively considered for various applications such as primary and rechargeable cells, super capacitors and electrochromic devices. Various strategies have been adopted to enhance their properties so as to develop efficient and effective devices. One such method is to increase the ionic conductivity of the electrolyte. In this study, attempts were made to study the variation of ionic conductivity with salt concentration of a GPE and to evaluate the dependence of performance on conductivity in a rechargeable cell. The composition was optimized by varying the salt concentration. The highest room temperature conductivity of 4.46×10^{-3} Scm^{-1} was obtained with the composition 50 PVdF : 100 EC : 100 PC : 80 ZnTf (by weight). The maximum ionic transference number was also obtained with this composition and it was 0.97. Four different cells were fabricated with four different salt concentrations and the best performance was observed with the cell having the GPE of the highest conductivity. This clearly proves that performance of the device depends on the conductivity of the electrolyte.

Keywords: gel polymer electrolyte, ionic transference number, discharge capacity, polyvinylidene fluoride.

INTRODUCTION

As per the growing demand in domains of portable electronics, transportation and stationary power storage, various types of rechargeable cells have received a great attention. Research community has strongly involved in developing and enhancing the performance of cells using different strategies to fulfill the demand (Kuo *et al*., 2002; Novak *et al*., 1997; Brandt, 1994). One such attempt is improving the properties of the electrolytes which ensure electronic insulation while allowing effective ion transport between electrodes (Palacin, 2009). This means that the ionic nature and ion mobility in electrolytes need to be improved. This can be circumvented by fine tuning the ionic conductivity because it is a result of interplay between the charge carrier concentration and their mobility (Jyothi *et al*., 2014). To achieve an appreciable conductivity, the salt concentration which plays a major role, needs to be optimized.

Many of the electrolytes that have been considered for rechargeable cells are of liquid form. They have exhibited inherent adverse effects such as leakage and evaporation. This has promoted the search for alternative electrolytes which are in solid form. Gel polymer electrolytes (GPEs) are one category of such solid electrolytes which are assumed to be having minimal drawbacks. It is assumed that these GPEs consist of a polymer network within which a liquid electrolyte is trapped (Pandey *et al*., 2011; Bandaranayake *et al*., 2016). In this case, polymer network provides the dimensional stability whereas salt concentration governs the conductivity. GPEs have been widely investigated for various applications including primary and rechargeable cells, super capacitors, electrochromic devices and solar cells.

At present, there exists a high demand for rechargeable cells due to the increasing demand for energy and power. Li rechargeable cells have received a tremendous attention for many years but their hazardous nature and the increasing cost have been well recognized now. As a result, attention of the scientific community has been focussed towards alternative anode materials such as Zn, Mg and Na (Sheha, 2013; Saleem, 2009). In this study, it was aimed to investigate the effect of the conductivity of the electrolyte on the performance of Zn rechargeable cells.

MATERIALS AND METHODS

Preparation of GPE samples

Polyvinylidene fluoride (PVdF), zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$ or

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ZnTF, ethylene carbonate (EC) and propylene carbonate (PC) were used as received from Aldrich. Required amounts of starting materials were weighed and mixed well using magnetic stirring. Samples were prepared in varying salt concentrations.

Characterization of GPE samples

A circular shape sample was cut from the electrolyte film. It was sandwiched in between two well cleaned stainless steel (SS) electrodes in a brass sample holder which is sealed by means of an O ring. Impedance data were gathered in the frequency range 4 MHz to 0.01 Hz. By placing the sample holder in a glass tube furnace, impedance data were taken from room temperature (28 °C) to 50 °C using a Metrohm 101 frequency response analyser and a Sibata glass tube furnace. The thickness (t) and the diameter (d) of the GPE samples were measured using a micrometer screw gauge. Using impedance data, Nyquist plots were drawn in between imaginary and real parts of impedance. The high frequency intercept value of the Nyquist plot was taken as the bulk electrolyte resistance, R_b. If the conductivity is σ,

$$\sigma = (1/R_b)(t/A) \tag{1}$$

where t is the thickness and A is the area of cross section of a GPE electrolyte sample.

Using a circular shape GPE film, DC polarization test was carried out for each sample at room temperature as per the procedure reported by us previously (Jayathilake *et al.*, 2014). DC polarization test data in terms of current and time was plotted and the resulting graph was used to calculate the transference numbers. In this study, Stainless Steel (SS) electrodes were used with the sample and they are acting as blocking electrodes. That means, they are blocking the ion movement while facilitating the electron movement. With such electrodes, at the beginning of the DC polarization test, current starts to decrease due to polarization of ions. A steady state current results thereafter due to the motion of electrons. From the polarization graph, it is possible to calculate the ionic transference number, t_i. If the initial current is I_i, constant current is I_o, ionic transference number (t_i) can be calculated as given in Equation 2 (Perera and Vidanapthirana, 2016).

$$t_i = (I_i - I_o)/I_i \tag{2}$$

Fabrication and characterization of cells in the configuration, Zn / GPE / polypyrrole (PPy) electrode

Fabrication of polypyrrole (PPy) electrodes was accomplished as reported by us earlier (Bandaranayake *et al.*, 2016). The thickness of the PPy electrode was 1 µm. The cells were assembled in the configuration Zn / GPE / PPy electrode inside a brass sample holder in an Argon filled glove box for each GPE having different salt concentrations. Constant load discharge characteristics of the cells were observed with a 1 kΩ resistor. Discharge characteristic curve was used to calculate the discharge capacity, C.

$$C = (\int Idt)/M \tag{3}$$

where $\int Idt$ is the integrated area under the discharge characteristic curve and M is the mass of the active material in the cathode (Sarangika *et al.*, 2014).

RESULTS AND DISCUSSION

Effect of salt concentration

Figure 1 illustrates the ionic conductivity variation with salt concentration at different temperatures. Ionic conductivity increases with salt concentration first and then, it reduces. Initial increase may be due to the augment of charge carrier concentration which assists conductivity greatly (Rosadi, 2015). As the salt concentration increases, the mutual distance between ions reduces significantly and ion-ion interactions become dominant. Therefore, at high salt concentrations, the stronger is ion-ion interaction which changes free ions to ion pairs or the higher aggregates. The samples are in quasi solid state. Therefore, the viscosities of the samples are playing a major role in governing the ionic motion. At higher salt concentrations, the viscosity of the samples can increase reducing the ionic motion.

Electrolyte with the composition of 50 PVdF: 100 EC : 100 PC : 80 ZnTf was taken as the optimum composition that shows the maximum room temperature conductivity of $4.46 \times 10^{-3} Scm^{-1}$. This value is higher than the values reported by G.G. Kumar and Sampath (2003).
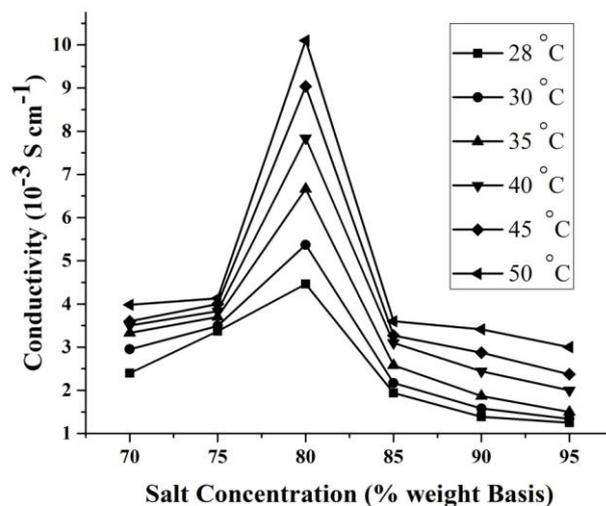
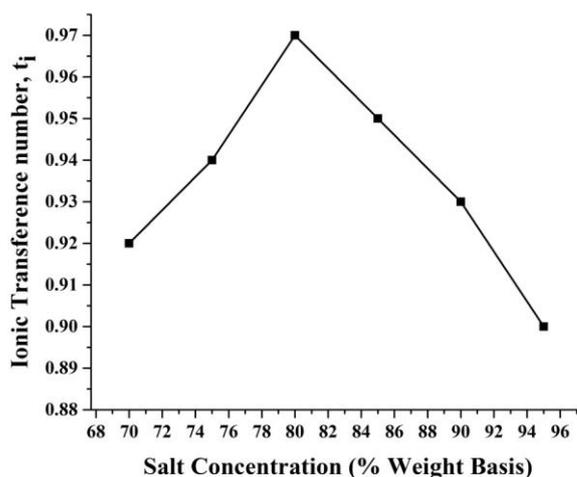**Figure 1:** Variation of conductivity at different temperatures and at different salt concentrations (by weight basis).

Figure 2: Variation of ionic transference number with the salt concentration of the GPE.

Ionic transference number measurements

Figure 2 illustrates the variation of ionic transference number with the salt concentration. As per this, all samples are having ionic transference numbers higher than 0.90. This is a good evidence to confirm the ionic nature of all samples. But, the important feature is that the sample which showed the highest conductivity (at salt concentration of 80 (weight basis)) is having the highest ionic transference number of 0.97. Even the ionic transference number is a measurement of the ion motion, it is not connected with the salt vidconcentration directly. At high salt concentrations, the quantity of charge carriers is high. But, their motion is not significant. It may be because at high salt concentrations, the formation of neutral ion species takes place and they are not mobile as free ions. Therefore, ionic transference number goes down at high salt concentrations similar to the ionic conductivity. This clearly proves the direct relationship between the ionic conductivity and the ionic transference number (Dey *et al.*, 2011).

Discharge characteristics of the cells of the configuration, Zn / GPE / PPy electrode

Figure 3 shows the discharge characteristics of the cells fabricated using GPE samples having different salt concentrations.
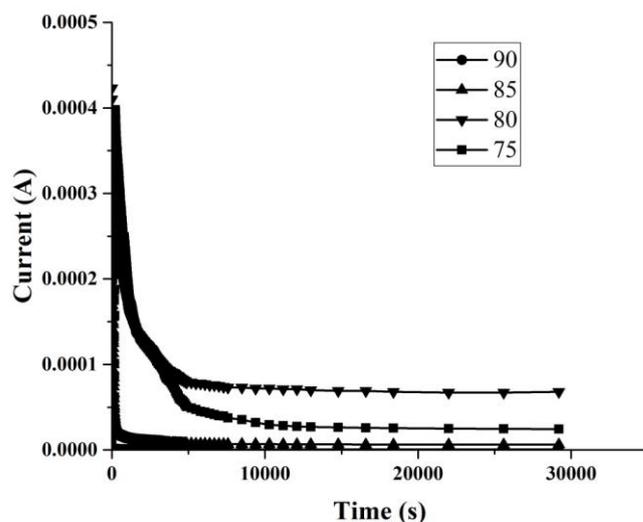
Figure 3: Discharge characteristics of the cells fabricated in the configuration, Zn / GPE / PPy. GPEs used have different salt concentrations (% weight basis).

Table 1: Calculated discharge capacities with the salt concentrations and the corresponding room temperature conductivities

Salt concentration (%weight basis)	Ionic conductivity at RT (28 °C) ($\times 10^{-3}$ Scm^{-1})	Discharge capacity (mAh/g)
70	2.4	375
75	3.37	490
80	4.46	1360
85	1.94	124
90	1.39	12
95	1.25	1.4

The cells fabricated with the salt concentrations, 75, 85 and 90 (weight basis) shows quick discharge characteristics. For the clarity of Figure 3, only the results of the cells fabricated with four salt concentrations (including the one having the highest conductivity) were included in the graph. The cell having the highest conducting GPE shows the maximum current plateau whereas the drop of the current is also rather slow.

Table 1 shows the calculated discharge capacities for the four cells. The highest discharge capacity is seen with the cell fabricated with the GPE having the highest conductivity. This proves the necessity of having a high conducting GPE to achieve better performance from cells.

CONCLUSIONS

It was noticed that salt concentration is playing a major role in determining the ionic conductivity of a GPE. In addition, ionic transference number is also found to be depending on the ionic conductivity and not on the salt concentration. Constant load discharge characteristics of Zn rechargeable cell in the configuration, Zn / GPE /PPy electrode evidences the fact that cell performance is having a dependency on the conductivity of the electrolyte. Hence, it can be concluded that composition of a GPE should be fine-tuned to obtain the optimum conductivity

and subsequently it results maximum performance in cells.

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