Magnesium rechargeable cells based on PVdF gel polymer electrolyte

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Introduction

Gel polymer electrolytes (GPEs) have received a keen interest as an excellent substitute for liquid electrolytes due to anticipation of several advantages such as no leakage, no corrosion and easy preparation. They are basically consisting of a salt solvent mixture encapsulated in a suitable polymer matrix (Osman, *et al.* 2012). Due to the satisfactory conducting and mechanical properties, they have been extensively considered as suitable electrolytes for various applications such as rechargeable cells (Kumar *et al*, 2003) super capacitors (Tripathi *et al*, 2013) and electrochromic devices (Wu *et al*, 2012). Plentiful of investigations have been carried out on applications with Li based GPEs but now attention has been focused towards other cation based GPE mainly due to some problems associating with lithium. As such non lithium based devices have come forward getting more interest. Use of magnesium in place of lithium would be very convenient as it possesses various important characteristics such as low cost, substantial abundance, more stability than lithium and low toxicity (Pandey *et al*, 2011). This paper reports about employing a magnesium based GPE in a magnesium rechargeable cell.

Methodology

Polyvinylidenefluoride (PVdF), Ethylene carbonate (EC), Propylene carbonate (PC) and Magnesium trifluromethane sulfonate (MgTf) purchased from Aldrich were used as received. Appropriate amounts of EC, PC and MgTf were mixed by magnetically stirring for about 2 hours. Required amount of PVdF was added and stirring was continued for another 10 minutes. Then, the mixture was heated at 120 ^{0}C for 30 minutes. The resultant homogenous hot mixture was pressed in between two well cleaned glass plates to obtain a thin GPE film. A circular pellet of GPE was sandwiched in between two stainless steel (SS) electrodes and it was loaded inside a brass sample holder which is sealed by means of an O ring. Diameter and thickness of the sample were measured using a micrometer screw gauge. AC Impedance data were gathered by using Metrohm Autolab M101 impedance analyzer in the frequency range 0.01 Hz - 0.1 MHz. Temperature was varied from room temperature to 60 ^{0}C by placing the sample holder inside a Sibata glass tube furnace. Cyclic Voltammetry studies were performed by placing an electrolyte sample in between two Mg electrodes. Three electrode electrochemical setup with a working electrode, a counter electrode and a reference electrode was employed for the study. Scan rate used was 5 mV/s. A cathode having Polypyrrole (PPy) polymerized in the presence of Dodecylbenzenesulfonate (DBS) was prepared as reported before (Perera *et al*, 2008). The cells in the configuration, Mg / GPE / PPy : DBS were assembled and their charge discharge behavior was monitored. Cells were subjected to charge and discharge between the potential values 0.5 V and 2.0 V. They were first discharged galvanostatically and then charged galvanostatically. When the required potential has reached, further potentiostatic charge was done till the current drops to 10%.

Results and Discussion

The selected electrolyte composition, 0.5 PVdF: 1 EC: 1 PC: 0.7 MgTf (by weight) showed a room temperature ionic conductivity of 1.97×10^{-3} S cm $^{-1}$. The graph of ln (σT) vs 1000/T is depicted in Fig.1. It shows two features namely,

i. conductivity increases with temperature

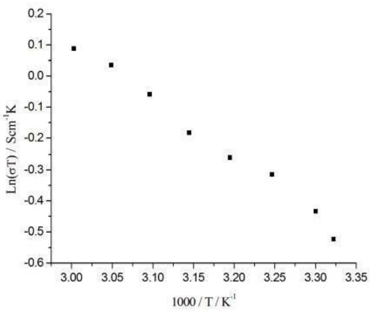

Fig. 1 Variation of conductivity with inverse temperature

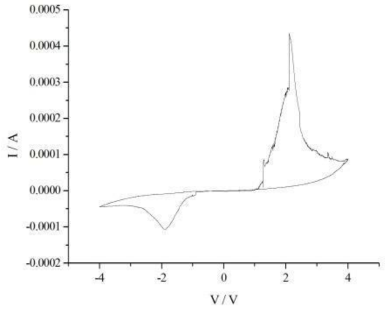

Fig. 2 Cyclic Voltammogram obtained with Mg electrodes

ii. temperature dependence of ionic conductivity shows non-linear behavior that follow the Vogel-Tamman-Fulcher (VTF) equation as given in below.

$$\sigma = AT^{-1/2}\exp(-E_a / k(T - T_0))$$

where *A* is a constant, E_a is the activation energy for conduction, k is the Boltzmann constant, T0 is the equilibrium glass transition temperature and T is the temperature.

These features are observed generally for high viscous electrolytes or for much amorphous polymeric systems. The increase in conductivity with temperature has been reported as due to a hopping mechanism between coordinating sites, local structural relaxations and polymer segmental motions (Rajendran et al 2006).

Cyclic voltammogram in Fig. 2 has one anodic peak at 2.0 V and a cathodic peak at -1.9 V. They evidenced the fact that mobile species in this electrolyte is Mg ions. The two peaks correspond to the reaction

$$Mg \leftrightarrow Mg^{2+} + 2e^{-}$$

This is related to reversible plating (reduction) and stripping (oxidation) of Mg ions (Kumar et al 2010). Anodic peak is appearing for stripping and cathodic peak is appearing for plating. Even the peak currents associated with anodic and cathodic peaks are not equal in magnitude, the voltammogram qualitatively suggests that reduction and oxidation processes are taking place in the system.

Average open circuit potential of the cell in the configuration, Mg / GPE / PPy : DBS was 1.6 V. Following cathodic and anodic reactions can be suggested as taking place during charging and discharging.

At anode: $Mg \leftrightarrow Mg^{2+} + 2e^{-}$

At cathode: $2PPy^{+}DBS^{-} + Mg^{2+} + 2e^{-} \leftrightarrow (PPy^{0}DBS)_{2}Mg$

Conclusions

GPE of the composition, 0.5 PVdF: 1 EC: 1 PC: 0.7 MgTf (by weight) has a room temperature ionic conductivity of 1.97×10^{-3} S cm^{-1}which is very convenient to be used for ambient temperature applications. Cyclic voltammetry study shows that Mg ions are mobile in the electrolyte. Cells of the configuration, Mg / GPE / PPy : DBS are suitable to be used for low power requirements.

Acknowledgement

Assistance provided by National Research Council, Sri Lanka (NRC 12-109) is highly acknowledged.

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