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SHORT COMMUNICATION

Zn/Natural graphite rechargeable cell with an ionic liquid based gel polymer electrolyte

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Abstract: There is an urgent need to fulfill the hunger for energy in an efficient and a safer way. In this context, non-Lithium based energy storage devices have received a noticeable interest. A prime attention has been given on electrolytes as many of the devices are composed with liquid electrolytes which have been later identified as having various problems. Gel polymer electrolytes (GPEs) are considered as viable substituents for liquid electrolytes because they exhibit liquid like conductivities while retaining good mechanical stabilities. To further improve the safety aspects of GPEs, nowadays many studies have been performed with ionic liquids (ILs) in place of solvents on GPEs. The present study was carried out to fabricate a Zn rechargeable cell with natural graphite (NG) cathode and an IL based GPE. The IL, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (1E3MITF) with the polymer poly(vinyl chloride) (PVC) and the salt zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2 - \text{ZnTF}$) were used in preparing the GPE. The electrochemical properties of the GPE were evaluated using electrochemical impedance spectroscopy (EIS) and DC polarization test. The maximum room temperature conductivity of the electrolyte was $3.06 \times 10^{-4} \text{ S cm}^{-1}$. Conductivity of the electrolyte was highly contributed by ions. The cell of the configuration, Zn / GPE / NG was characterized using cyclic voltammetry (CV) test. Initial specific charge was about 2.25 mA h g^{-1} and during 50 cycles, it had reduced down to 2.15 mA h g^{-1} . Moreover, satisfactory stability was observed during CV test. Further studies are in progress to improve the cell performance.

Keywords: rechargeable cell, ionic liquid, gel polymer electrolyte, electrochemical impedance spectroscopy, cyclic voltammetry test.


INTRODUCTION

In the present world, there is an enormous collection of electrical appliances being used for various activities ranging from home to the entire society. As a result, the demand for electrical power is increasing at an alarming rate. To fulfill that demand, not only electrical energy generation but also storage is essential. As the world is moving towards electrical energy generation via renewable sources, availability of storage sources has become essential to supply an uninterrupted power.

Since time immemorial, rechargeable cells and capacitors have been renowned as excellent energy storage devices (Ramesh, *et al.*, 2013). With respect to rechargeable cells, Li based cells have received the highest demand in the market with their significant performance (Park *et al.*, 2010, Cheng *et al.*, 2016). But, with the current pursue towards green environment and also due to economic constraints, a diversion is being taken place from Li cells. As such, a considerable amount of research activities are in progress to develop environmental friendly, low cost non Li based cells (Wang *et al.*, 2017, Liu *et al.*, 2014). Zn has received a tremendous attention as a viable substitute for Li. Many have reported about Zn based cells with satisfactory performance (Kravchyk *et al.*, 2017). Natural graphite (NG) is another material that receives a gradual attraction for applications in the energy and power field today. Being a natural resource, it is non-toxic and low cost. Anyhow, it is regretted that NG has not yet been utilized for scientific purposes to add a proper value. Since long ago, liquid electrolytes have been playing a key role in almost all devices. Upon identification of their demerits, many have initiated research activities on other types of electrolytes. Among them, gel polymer electrolytes (GPE) have been identified as a suitable substitute for liquid electrolytes mainly because of their quasi solid state nature having liquid like conductivities. In general, a GPE consists with a polymer, a salt and solvents. It is assumed that the salt and the solvent mixture are encapsulated within the polymer matrix so as to provide sufficient conductivity and mechanical stability. A large number of polymers such as poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF) and poly(acrylonitrile) (PAN) have been used to fabricate GPEs with notable performance (Kim *et al.*, 2001). Compared to those polymers, polyvinylchloride (PVC) is another polymer host which has not been widely considered.

With respect to solvents, a large number of different solvents have been employed for GPEs. But, by now, it has been realized that the presence of solvents carries some demerits for the safety of GPEs (Kumar *et al.*, 2011, Karmakar and Ghosh, 2011, Sapri *et al.*, 2017). Hence, many research activities have been launched to explore suitable substitutes for solvents. In this regard, ionic liquids (ILs) have been identified as reliable substitutions

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for those volatile solvents (Wang *et al.*, 2017). In addition, they are known as green solvents due to the key features of nonvolatility and exceptional solvation properties and disability to evaporate into air (Sapri *et al.*, 2017). As a result, ionic liquids (IL) based GPEs have been obtaining a substantial attention nowadays (Xu *et al.*, 2005, Kumar *et al.*, 2011).

ILs are room temperature molten salts with bulky asymmetric organic cations and inorganic anions. GPEs prepared with ILs possess several alluring features such as wide electrochemical window, non-flammability, non-toxicity and large liquid phase range (Pandey, 2010).

Present study is based on conducting properties of an IL based GPE and its performance in a Zn/NG cell. Performance of the cell was characterized using cyclic voltammetry technique. Before employing in the cell, conducting properties of the GPE were analyzed.

MATERIALS AND METHODS

To prepare the GPE, polyvinyl chloride (PVC), zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$ – ZnTF) and 1-ethyl-3-methylimidazoliumtrifluoromethanesulfonate (1E3MITF) were used as received from Aldrich as the polymer, the salt and the IL respectively. Required amounts were weighed and mixed using tetrahydrofuran (THF, Aldrich) for about 8 hours. The homogeneous mixture was poured in a petri dish and kept under ambient atmosphere for 24 hours allowing solvent evaporation. Thereby, it was possible to obtain a thin, bubble free electrolyte film.

The electrolyte film having a diameter of 1 cm was loaded in between two stainless steel (SS) electrodes in-side a brass sample holder. Impedance data were gathered from room temperature to 55 °C using a Metrohm impedance analyser. DC polarization test was carried out for a cell of the configuration, SS / electrolyte / SS under a DC bias voltage of 1 V. Current variation through the sample was

monitored with time.

Graphite electrodes were prepared by mixing graphite and polyvinylidene fluoride co hexafluoropropylene (PVdF-co-HFP, Aldrich) using acetone. The resulting slurry was spread on a SS dice and allowed to dry well. A disc shaped Zn electrode was cut from a Zn sheet purchased from Aldrich. The cell was assembled in the configuration, Zn / IL based GPE / graphite inside a sample holder. Then, the cell was cycled at the scan rate of 10 mV s^{-1} using a three electrode electrochemical cell. Zn was used as the reference and the counter electrodes whereas the graphite electrode was served as the working electrode. Voltage-current measurements were taken using a computer controlled Metrohm potentiostat at room temperature.

RESULTS AND DISCUSSION

Conductivity (σ) values of the GPE were calculated using the Eq. (1)

$$\sigma = (1/R_b) t/A \quad (1)$$

where R_b is the bulk electrolyte resistance, t is the sample thickness and A is the sample cross section area [Lieu *et al.*, 2013]. Fig. 1 illustrates the variation of conductivity with temperature.

Room temperature conductivity was $3.06 \times 10^{-4} \text{ S cm}^{-1}$. This is a satisfactory value for ambient temperature applications. For a system based on PVC and lithium perchlorate, a conductivity value lower than this ($3.7 \times 10^{-7} \text{ S cm}^{-1}$) has been reported [Ahmad *et al.*, 2008]. This highlights the better performance of the Zn salt. One feature which is very clear from the results is that upon increasing the temperature, the conductivity increases. This is due to the increase of the motion of ions which become energetically rich with rise of the temperature (Yu *et al.*, 2007). Accordingly, the charge transport can be assumed to be a thermally agitated process. Also, the salt and IL dissociation at high temperatures might be beneficial

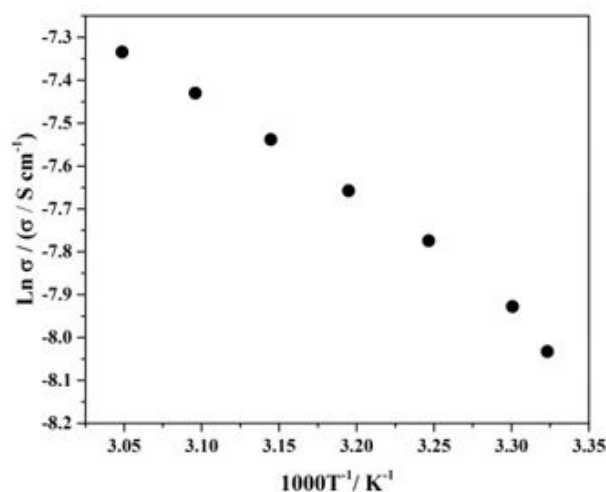


Figure 1: Variation of conductivity of the gel polymer electrolyte (GPE) with inverse temperature.

to the migration of charge carriers leading to a higher conductivity. Conductivity behavior with temperature follows a nonlinear variation suggesting that conductivity mechanism can be explained by Vogel Tamman Fulcher behaviour as given in Eq. (2).

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

where A is the pre exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, T is the absolute temperature and T_0 is the equilibrium glass transition temperature (Tafur *et al.*, 2015). This observation evidences the assistance of conductivity by the polymer segmental motion via forming free volume changes with temperature (Karmakar and Ghosh, 2011).

Fig. 2 depicts the DC polarization curve showing variation of current with time when the GPE was assembled in between two SS electrodes at room temperature.

Initially, there is a quick and fast drop of current. It is followed by a continuous current plateau very closer to zero. At the beginning, ions tend to polarize and a large current can be seen. With time, motion of ions is blocked

by SS electrodes as they are acting as blocking electrodes for ions and as a result, current decreases rapidly. Finally, only the electron movement exists. The constant current is mainly due to these electrons (Lieu *et al.*, 2013). The ionic transference number, t_i was calculated using the Eq. (3).

$$t_i = (I_t - I_s) / I_t \quad (3)$$

Here, I_t is the initial current and I_s is the steady state current. t_i was found to be 0.98. This indicates that the conductivity of the sample is mostly due to ions (Kravchyk *et al.*, 2017). The ionic contribution of this system is higher than the system reported by Sapri *et al.* (2017). They have found a t_i value of 0.95 for the system having PEO and NaCF₃SO₃. A possible reason for this difference might be an influence of the different polymers in the two systems as well as the difference of valance of Na and Zn. The cyclic voltammograms (CVs) obtained for the cell upon continuous cycling are shown in Fig. 3.

All CVs exhibit nearly equal shape at each cycle. This discloses the absence of any parasitic reaction that may take place upon continuous cycling. If such reactions

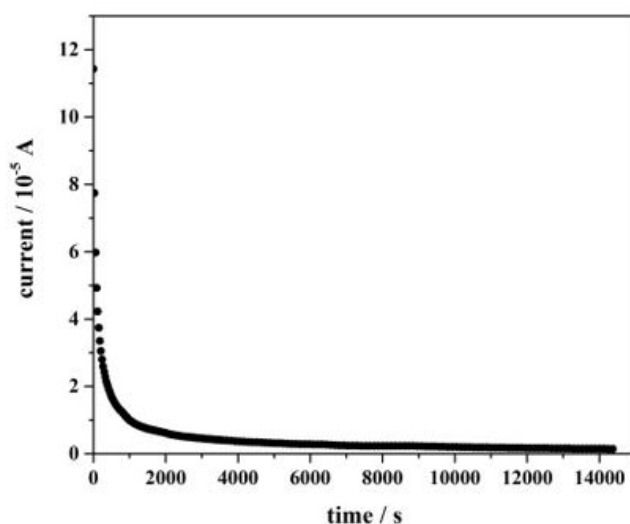


Figure 2: Current variation with time for the configuration SS/GPE/SS under 1V DC potential.

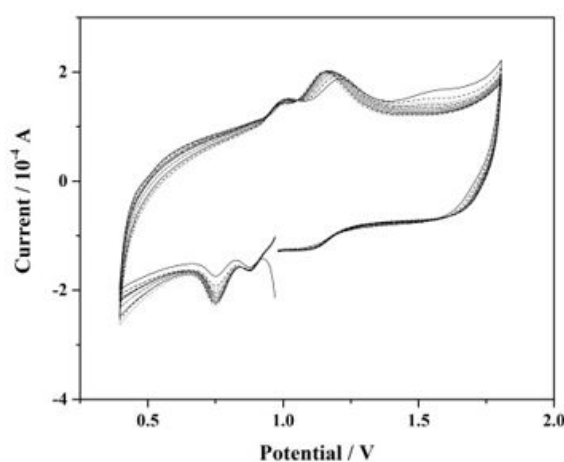


Figure 3: Continuous cyclic voltammograms obtained for the cell, Zn / IL based GPE / graphite.

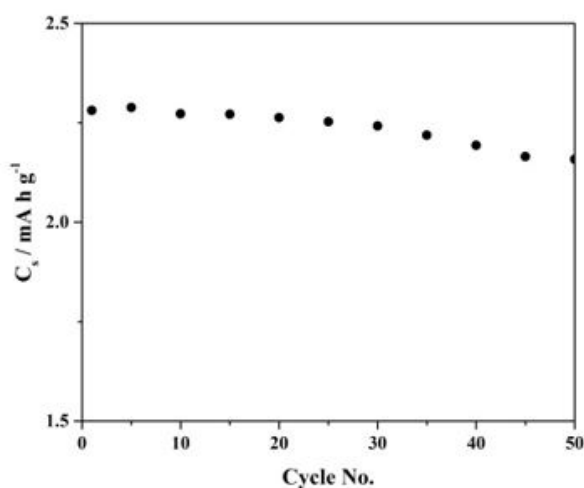


Figure 4: Capacity variation of the cell with cycle-number.

had taken place, shapes of CVs could have been changed among different cycles. In addition, the shapes of CVs take the form of deviated rectangles. In general, it is a well-known fact that for electrochemical double layer capacitors (EDLCs) having two carbon based electrodes, CVs have the rectangular shape (Das *et al.*, 2017). Deviated rectangular shape evidences that the cell under study may exhibit capacitive properties, if the required conditions are made available. Liu *et al.* have observed the cell-capacitor or the so called hybrid nature of a device having the similar configuration considered in the present study (Liu *et al.*, 2017). The peaks in the CVs represent the potentials at which ion exchange takes place. During the charge and discharge processes, two peaks are seen for each process. This hints the possibility of the movement of two types of ions. In the present system, it can be assumed that Zn^{2+} and $CF_3SO_3^-$ ions may take part for charge discharge processes. Fig. 4 shows the variation of capacity (C_s) with the cycle number.

The capacity fade is seemed to be rather slow.

The initial capacity was about 2.25 mA h g⁻¹. During 50 cycles, it had reduced down to 2.15 mA h g⁻¹. The percentage of reduction is about 4.44% which is quite low. This is a good evidence for the stability of the cell towards continuous operation. Moreover, this is an indication for the stability among electrode/electrolyte components (Liu *et al.*, 2017) The reduction, even though in a small amount, may be due to the deterioration of the electrolyte.

CONCLUSIONS

IL based GPE prepared in the present study shows a room temperature conductivity in the order of 10^{-4} S cm⁻¹. It is having a dominant ionic conductivity. The cell fabricated in the configuration, Zn / GPE / graphite shows a satisfactory cycling ability. Results showcase the compatibility of materials in the cell. Further studies are in progress to improve the cell performance.

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DECLARATION OF CONFLICT OF INTEREST

The Authors declare that there is no conflict of Interest.

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