Performance of a rechargeable cell using an ionic liquid gel polymer electrolyte and natural graphite electrode

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Abstract. With the concepts of green environment and the priority given on economical aspects, a great deal of research activities has been diverted towards clean and low-cost device fabrication. Central focus was on eliminating the use of toxic and expensive materials like Li and different solvents. Application of ionic liquid-based gel polymer electrolytes (GPEs) and non-Li electrodes can address many shortcomings associated with liquid, solid and GPEs. In the present study, characteristics of a rechargeable cell with 1-ethyl-3-methylimidazolium trifluoromethanesulphonate-based GPE having Zn and Sri Lankan natural graphite electrodes have been investigated. For characterization, electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic charge discharge test have been performed at room temperature. The open circuit voltage of the cell was about 1V. Specific charge and discharge capacities of the cell were 4.66 and 2.99 mA h g⁻¹, respectively. Moreover, efficiency of the specific charge was 80.2% over 500 cycles, while efficiency of specific discharge was 92% over 1000 cycles. These results proved the suitability of the electrolyte and electrodes investigated in the present study to be used well in rechargeable cells.

Keywords. Rechargeable cell; ionic liquid; gel polymer electrolyte; specific charge; graphite.

1. Introduction

Due to the high demand for mobile and stationary applications, rechargeable cells for energy storage have received intense attention. In this context, Li rechargeable cells are widely used in a diverse range of applications including portable electronics, power tools and electric vehicles due to the highest theoretical energy density of Li metal [1]. However, safety issues, reactivity towards atmospheric oxygen and high cost of Li have prompted research activities to shift towards environmentally friendly, low-cost rechargeable cells. As a result, research activities have been directed on cells based on materials such as Zn, Al, Mg, Cu and Na [2,3]. In this scenario, Zn rechargeable cells have been greatly attracted because of their availability, low toxicity, low cost and less reactivity at ambient temperature.

Graphite is a natural resource which is eco-friendly and inexpensive. In Sri Lanka, there are graphite mines in several locations. But, it has been utilized mostly for industries like automobile and pencil manufacturing. Recently, an increasing attention has been paid to graphite for its use in electrochemical energy storage devices upon the realization of its potential to serve as electrodes at the global level. Some researchers have started studies towards fabricating natural graphite-based rechargeable cells [4].

In any electrochemical device, an electrolyte is a key component that plays a major role. Earlier, liquid electrolytes,

solid electrolytes and gel polymer electrolytes (GPEs) have been highly used for such devices [5,6]. However, they possess some drawbacks such as poor mechanical integrity, poor conductivity, toxicity, leakage and evaporation. To overcome most of them, ionic liquid (IL)-based GPEs have been identified as viable substitutes. ILs have excellent properties, such as good thermal and electrochemical stabilities, high ionic conductivity, negligible vapour pressure and non-flammability [7,8]. They have been successfully incorporated for the preparation of GPEs with a polymer and salt. This approach has opened the pathway to eliminate solvents in GPEs which are known to be very toxic and volatile.

In this work, a rechargeable Zn cell was fabricated using 1-ethyl-3-methylimidazolium trifluoromethanesulphonate (1E3MITF)-based GPE with poly(vinylidene fluoride)-co-hexafluoropropylene (PVdF-co-HFP) as the polymer host. Natural graphite in Sri Lanka and Zn were used as electrodes.

2. Materials and methods

2.1 Preparation of electrolyte

Electrolytes were prepared using a conventional solvent casting technique. PVdF-co-HFP (average MW 400,000), zinc trifluoromethanesulphonate (ZnTF, 98%) and 1E3MITF (98%) were used as received from Aldrich. The required

amount of PVdF-co-HFP was magnetically stirred with acetone at room temperature. Required amounts of ZnTF and 1E3MITF were added to the resultant mixture and magnetically stirred again overnight. Then, the homogeneous solution was poured into a glass Petri dish and it was kept in a vacuum desiccator to evaporate acetone. Finally, it was possible to obtain a thin, homogeneous and free standing films.

2.2 Preparation of electrodes

Pure circular-shaped Zn pellet was used as one electrode. It was polished and cleaned well with the use of acetone.

Natural graphite obtained from Bogala Graphite Lanka (Pvt.) Ltd., Sri Lanka and polyvinylidene fluoride (PVdF) (534,000 MW, Aldrich) were used as received. Graphite was initially heated for 8 h. Pre-heated graphite and PVdF were mixed with acetone using a homogenizer. The resulting mixture was applied evenly on the surface of a stainless steel dice and dried well.

2.3 Fabrication of rechargeable cell

The electrolyte film with a circular shape was sandwiched between a Zn pellet and a graphite + PVdF-coated dice. The assembly was loaded inside a brass sample holder.

2.4 Instrumentation

Open circuit voltage (OCV) was measured soon after fabrication using a digital multimeter.

The rechargeable cell was subjected to impedance measurements using a Metrohm Autolab Impedance Analyser M101. The frequency range was from 0.1 Hz to 400 kHz. It was repeated at different time periods.

Cyclic voltammograms (CVs) of the cell were recorded using a computer controlled Metrohm Autolab Impedance Analyser M101 at various scan rates and within various potential windows. Continuous CVs were obtained using the optimized scan rate and the potential window at room temperature.

Galvanostatic charge discharge (GCD) cycling characteristics of the cell was recorded at room temperature between the voltage range of 0.05 and 2.05 V.

3. Results and discussion

OCV was about 1 V. This is an acceptable value for low power requirements.

Electrochemical impedance data of a cell are a very crucial factor because they reveal many internal features. Nyquist plots of the cell with the configuration of Zn/IL-based GPE/graphite + PVdF measured at different time periods are shown in figure 1.

The first intercept on the real axis (Z') represents the bulk electrolyte resistance which greatly governs the performance

Figure 1. Nyquist plots for the Zn/IL-based GPE/graphite + PVdF cell as the function of time.

Figure 2. Bulk electrolyte resistance (R_b) variation as the function of time.

of any device. Also, it hints the level of ion conduction between the two electrodes. For a satisfactory device performance, R_b should remain constant with time.

Figure 2 shows the variation of R_b with time. Initially R_b was found to be 2.23 Ω. It decreased to 1.23 Ω during the storage period of 450 min as shown in figure 2. Only 1 Ω reduction has taken place during the time period of investigation. This is an evidence to prove the stability of the electrolyte in the cell. It also reveals that the electrolyte retains its properties which well proves the absence of any parasitic reaction with the electrodes. And also, the minimized leakage and evaporation can be conferred with this result. If those were present, R_b would drop drastically.

Figure 3. CVs obtained for different potential windows.

Figure 4. CVs obtained at different scan rates.

Figure 3 illustrates the CVs obtained by varying the potential window at room temperature.

The charging/discharging processes of the cell under study are associated with ion insertion and deinsertion into electrodes. During discharging, Zn ions move towards the graphite electrode, whereas during charging, they undergo the opposite reaction. The respective voltages at which the ion movements are taking place are represented by peaks in the CVs. According to figure 3, within the narrow potential windows, there were no peaks to be observed. When widening the potential window, peaks tend to appear gradually due to the initiation of cell reactions. The absence of these peaks at lower potential ranges suggests that reactions do not occur in these potential windows [9]. The maximum specific charge was obtained within the potential window, 0.05–2.05 V.

Figure 5. Variation of specific charge of the Zn/IL-based GPE/graphite + PVdF cell with time at a scan rate of 10 mV s^{-1} and within the potential window of 0.05–2.05 V.

Figure 4 represents CVs obtained at different scan rates. Voltammograms reveal that the respective capacity values have decreased upon increasing scan rates. Normally, cell reactions are taking place according to the scan rate. It is because cell reactions are involved with ions and ion movement occurs according to scan rates. When the scan rate is fast, ions do not get enough time to completely participate in cell reactions which results in lower capacity values. On the other hand, if the scan rates are too small, cell may undergo different irreversible reactions which do not contribute to capacity. The optimized scan rate was 10 mV s^{-1} and the corresponding specific charge was 4.6 mA h g^{-1} .

Figure 5 illustrates the variation of specific charge values of the Zn/IL-based GPE/graphite + PVdF cell at the optimized window and the scan rate.

At the initial stage, specific charge was 4.66 mA h g^{-1} and it was nearly constant during 500 cycles. The efficiency of the fabricated cell remains 80.2% over 500 cycles.

Figure 6 shows the variation of the discharge capacity of the rechargeable cell upon continuous cycling under continuous current.

The initial discharge capacity of the cell was 2.99 mA h g^{-1} . Small discharge capacity may be due to high internal resistance of the cell [10]. The efficiency of the discharge capacity over 1000 cycles was about 92%. This value confirms the absence of any unwanted reactions that may take place within the cell. Also, it can conclude that the cell is very stable over continuous cycling.

Zhang *et al* [8] have observed an increase in the initial discharge capacity in a cell and their conclusion is that upon continuous cycling, the electrolyte is exuded and it penetrates into the electrodes promoting ion conduction. However, this imposes a chance for the short circuit effect to take place. Our results do not show such increase. Rather, the discharge

Figure 6. Discharge capacity variation with the cycle number of the Zn/IL-based GPE/graphite + PVdF batteries.

capacity remains more or less constant. It may be because the GPE has no component to exude and as a result, discharge capacity does not increase. Due to the same reason, the cell investigated under the present study is having a low risk for short circuiting.

4. Conclusion

A rechargeable cell was fabricated with the configuration Zn/IL-based GPE/graphite + PVdF. The OCV was about 1 V. With time, bulk electrolyte resistance remained nearly constant. The optimum potential window for CV was 0.05–2.05 V and the optimum scan rate was 10 mV s⁻¹. Specific charge

and discharge capacities of the rechargeable cell was 4.66 and 2.99 mA h g⁻¹, respectively. Both CV and GCD tests prove the stability of the cell to sustain continuous cycling. Further developments are being carried forward to increase the performance of the device.

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