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Investigation of a Zn Rechargeable Cell with an Ionic Liquid Based Polymer Electrolyte

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ABSTRACT

Due to the rapid increase of the energy demand, harnessing energy from renewable sources is a common trend. To tackle the major issues of these renewable sources with respect to their fluctuations, use of energy storage devices is of utmost importance. An enormous amount of research activities are being done to explore energy storage devices with attractive features. However, their cost and safety have to be addressed to make them attractive for present day thoughts on economical and environmental aspects. In this study, zinc/natural graphite cells were fabricated with 1-ethyl-3-methylimidazolium chloride/poly(vinylidene fluoride-co-hexafluoropropylene) gel polymer electrolyte and characterized through electrochemical impedance spectroscopy, open circuit voltage (OCV) test and cyclic voltammetry. It was found that the cell had an initial open circuit voltage of 1.1 V. Stability of OCV was quite satisfactory. Potential window of 0.1 V - 0.8 V and the scan rate of 10 mVs^{-1} resulted optimum performance. This cell is low cost and also, safe. With further modifications, the performance can be improved further.

Keywords: *gel polymer electrolyte, Zn rechargeable cell, electrochemical impedance spectroscopy, cyclic voltammetry*

1. INTRODUCTION

Globe is leaning towards various devices which require constant, continuous power for smooth operation. Many of them are powered by fossil fuels mainly. But, the depletion of fossil fuel and the excessive emission of carbon dioxide have paved the way for shifting towards alternative power sources mainly renewable such as solar and wind. However, due to their fluctuations, the need of energy storage devices became essential to assure uninterrupted power supply. For this purpose, cells and capacitors have been renowned as suitable energy storage devices. Among different types of cells, Li based cells have been widely accepted for their merits of high performance [1]. But, the safety issues with respect to the electrodes and the liquid electrolytes present in those Li cells have been seriously taken into consideration by the modern world and as such, so many initiatives have been launched to seek suitable alternatives in place of those toxic and unsafe materials [2]. Zn, Mg, Na cells based on polymer electrolytes are getting a rising attraction as they are capable of minimizing the cost and hazardous effects [3].

In this study, Zn/natural graphite cells were fabricated with the IL,1-ethyl-3-methylimidazolium chloride (1E3MICl) based gel polymerelectrolyte and characterized through electrochemical impedance spectroscopy, open circuit voltage (OCV) test and cyclic voltammetry. There are several novel features of the present study including use of Sri Lankan natural graphite (NG) which is low cost as well as safe and use of an ionic liquid (IL) based polymer electrolyte in place of toxic solvents in normal polymer electrolytes.

2. METHODOLOGY

2.1 Preparation of Electrodes

A Zn plate with purity of 99.9% (Sigma-Aldrich) was used as an electrode having 1cm^2 effective area. Sri Lankan natural graphite (NG) obtained from Bogala Graphite Lanka Ltd was sonicated in an ultrasonic homogenizer (Athena Technology) with acetone to form a homogeneous mixture. Then, the resulting slurry was evenly coated on a thoroughly cleaned fluorin doped tin oxide (FTO) glass plate and left to dry well.

2.2 Preparation of the Electrolyte

Poly(vinylidene fluoride-co-hexafluoropropylene)(PVdF-co-HFP) (average Mw ~400,000, Sigma-Aldrich) was dissolved in acetone by magnetic stirring. The ionic liquid (IL), 1-ethyl-3-methylimidazolium chloride(1E3MICl) (95%, Sigma-Aldrich) and the salt, zinc chloride ($ZnCl_2$)(98%, Sigma-Aldrich) were then added to that solution. Magnetic stirring was continued to obtain a homogeneous blend. The resultant mixture was casted on a cleaned glass substrate and left to form the IL based polymer membrane.

2.3 Fabrication of the Cells

Cells were fabricated by sandwiching the electrolyte in between Zn and NG electrodes.

2.4 Characterization of the Cells

OCV of the cell was measured just after fabrication and continued within three hours of time using a multimeter.

Electrochemical impedance spectroscopy (EIS) test for the cell was performed with Metrohm Autolab Impedance Analyzer M101 at ambient temperature within the frequency range of 0.05 Hz to 400 kHz range.

The cyclic voltammetry (CV) test was done on various potential windows and the window that results a good cyclic voltammogramme was chosen. Then, the optimum scan rate of the cell was determined by cycling at different scan rates. The specific capacitance, C_s was calculated using the equation,

$$C_s = \frac{\int (I/S)dv}{m} \qquad [1]$$

where $\int (I/S)dv$ is the area under cyclic voltammogram, m is the mass of anode and S is the scan rate of the process.

3. RESULTS AND DISCUSSION

3.1 Stability of Open Circuit Voltage (OCV)

Variation of OCV of the cell under study with time is given in Table 1. Initially value of OCV of the cell was around 1.1 Vand it shows a rapid declination over first few minutes. After about three hours, OCV value began to stabilize around 0.7 V. This final stable value can be considered as a good indicator for the stability of the cell. OCV is the measurement of the electromotive force of a cell, which is directly related to the state of charge [4]. Although OCV values can be used to determine and model the state of charge and the state of health of a rechargeable cell, which are considerably good measures of long term durability and usability, in this study OCV of a freshly fabricated cell was measured with respect to time to get an idea about the stability of the cell [5].

On the other hand, the stable OCV observed hints the absence of any parasitic reactions they may happen with time in the cell.

Table 1: The table of OCV vs

Time (min)	OCV (V)
0	1.1
0.5	1.0
1	0.9
2	0.8
5	0.8
10	0.8
15	0.8
30	0.7
45	0.7
75	0.7
120	0.7
180	0.7

3.2 Electrochemical Impedance Spectroscopy (EIS) Test

EIS is a frequency domain measurement which applies sinusoidal voltage to the system and measures the impedance [6]. Nyquist plot is the most common way to represent the EIS result as the imaginary part of the complex impedance with respect to the real part of complex impedance. Nyquist plot of a cell has three major features at different frequency regions. They are two consequent semi-circles at the high and middle frequency regions and a spike in the lower frequency range [7]. High frequency response shows the resistive properties while low frequency responses show more of the capacitive properties. Figure 1 shows the Nyquist plot for the cell within 0.05 Hz- 0.4 MHz range.

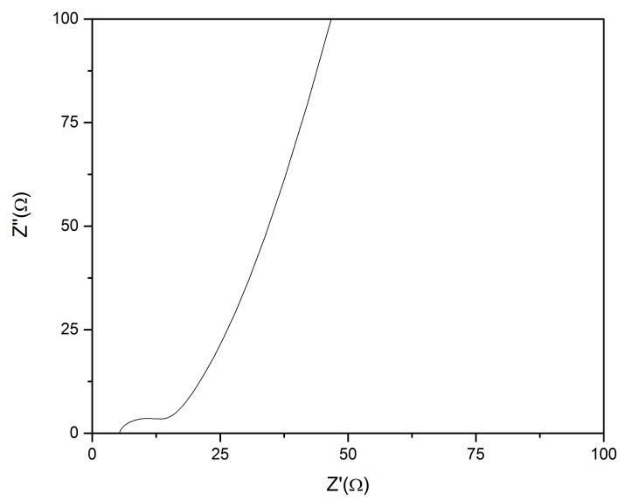

Figure 1: Nyquist plot for the cell within the frequency range 0.05 Hz- 0.4 MHz at ambient temperature

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Instead of two semi circles, only one at the mid frequency range is seen in the plot. This happens when the high frequency range is not sufficient. However, the first lowest intercept can be used to find the bulk electrolyte resistance. That value was found to be very small. This hints the fact that prepared polymer electrolyte is very suitable for the cell application. It is also seen that there are no additional features other than the ones mentioned theoretically. The absence of any parasitic reactions can be confirmed with this observation.

3.3 Cyclic Voltammetry

Figure 2 represents the cyclic voltammograms obtained for different potential windows with a scan rate of 10 mV s^{-1}. The minimum potential was kept at 0.1 V and the maximum value was varied starting from 0.5V. When the maximum value reached 1.2 V, cyclic voltammograms started to show some distortion at higher currents. Though the value of C_s increases with widening potential window as shown in Table 2, change of shape with the increase of current indicates the presence of unwanted reactions. Hence, 0.1 V - 0.8 V range was chosen as the suitable potential window which showed a specific capacitance of 2.85 Asg^{-1}. Since any kind of major peaks does not appear in the plot, it is possible to assume that redox reactions do not present in the device [8].

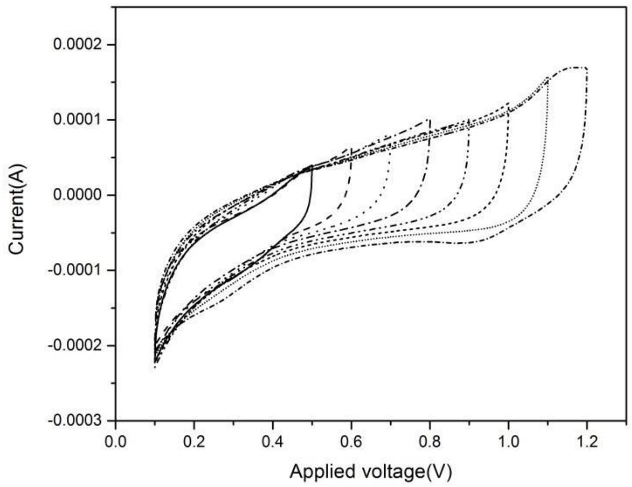

Figure 2: Cyclic voltammograms for different potential windows

With the selected potential window, cell was cycled under different scan rates to obtain the suitable scan rate that results a good C_s value. Resulted plots are shown in figure 3. When increasing the scan rate, the time period for reactions to happen decreases and with that there is a possibility for C_s to decrease (Table 3). But lower scan rates may have the potential to deposit and accumulate reactive substances on the electrode which may reduce the durability of the cell. The value of 10 mV s^{-1} was chosen as the optimum scan rate for the system considering the shape of the graphs as well.

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Table 2: Variation of specific capacitance (C_s) with the peak potential

Peak potential (V)	C_s (A s g^{-1})
0.5	1.33
0.6	1.71
0.7	2.20
0.8	2.85
0.9	3.42
1	4.27
1.1	5.27
1.2	6.41

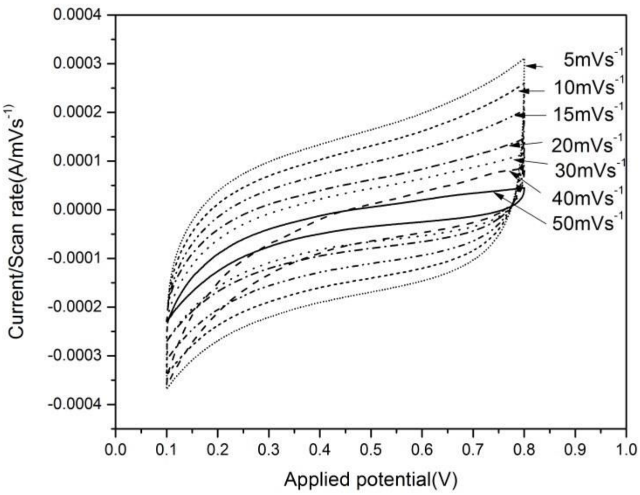

Figure 3: Cyclic voltammograms for different scan rates

Table 3: Variation of specific capacitance (C_s) of the cell with respect to scan rate

Scan rate (mV s^{-1})	C_s (A s g^{-1})
5	3.29
10	3.089
15	3.059
20	2.96
25	2.95
30	2.90
35	2.88
40	2.84
45	2.82
50	2.79

4. CONCLUSION

Zn/NG cell with the 1E3MICl/PVDF-HFP electrolyte was fabricated in the ambient temperature and had an initial OCV of 1.07 V, which was decreased into 0.73 V within 3 hours of time. Optimum potential window for the cell was found to be 0.1 V - 0.8 V range and the optimum scan rate was selected as 10mV s^{-1}. Further investigations are in progress to improve the performance of the cell.

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