Fabrication and evaluation of a Sri Lankan graphite based rechargeable battery

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Abstract— *Renewable sources such as solar, wind and tidal have been recognized as suitable low cost and environmental friendly solutions for energy production. To store their energy to meet the continuous demand of power, energy storage devices are of utmost importance. Batteries and capacitors are the two main storage devices use commonly. At present, there is a huge concern over their safety as well as their price. This paper reports about fabrication and evaluation of a Zn and graphite based battery that uses a gel polymer electrolyte (GPE) instead of a liquid electrolyte. Graphite was mixed with polyvinylidenefluoride as a binder in the weight ratio 85 % : 15 %. GPE was consisted with polyvinylidenefluoride, ethylene carbonate, propylene carbonate and zinc trifluoromethanesulfonate. Hot pressed method was used to prepare the GPE. Assembling of the battery was done inside an Ar filled glove box. The open circuit potential was found to be about 1.03 V. Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) techniques were used to analyse the performance of batteries. The capacity values were satisfactory and the capacity fade over continuous cycling was rather low. With the CV test as well as the GCD, it was noted a sudden drop of capacity initially. But, after some cyclings, the rate of reduction has decreased. It may be due to material stabilization, electrolyte - electrode interface formation. No parasitic effects or resistive layer growth was observed in the impedance plot. Further studies are being carried out to improve the performance further.*

Keywords— **Rechargeable batteries, Gel polymer electrolyte, Cyclic Voltammtery.**

I. INTRODUCTION

To meet the future challenge of supplying energy in a reliable way, renewable sources such as solar, wind and tidal have enormous potential [Budischak, et al. (2013)]. But, to maintain a continuous supply, energy storage devices are essential. They are so critical to effectively level the cyclic nature of renewable energy sources. Since time immemorial, batteries and capacitors have been grouped as the two main energy storage devices [Xiong, et al. (2014)]. Even today, they are the key powering enablers in numerous applications ranging from transportation to consumer electronics. Batteries store more energy than capacitors and hence they are being used for instances where high energy is required. Primary batteries can be used only once and secondary or the rechargeable batteries can be charged to use many times. Today, much attention is on rechargeable batteries due to the provision of reuse after recharge. Li, Li ion, nickel metal hydride are some of the rechargeable batteries commonly used in applications [Scrosati, et al. (2010), Lu, et al. (2013)]. Even after several charging cycles, they have to be disposed. Nowadays, there is a great concern with their environmental friendliness specially at the stage of disposal as well as their cost. As such, several strategies have been introduced such as replacing hazardous materials like Li, employing non liquid electrolytes and using low cost materials. In that line, Zn, Mg, Na have been identified as some of the suitable alternatives to use for the anode instead of Li [Sheha, (2013), Weerasinghe, et al. (2016)]. Also, they are proven to be cheaper than many of the anode materials. As far as Sri Lanka is concerned, much attention should be given for the safety issues. Being a small island, the disposal of hazardous materials is a threat for the well-being of not only the humans but also for the flora and fauna. In Sri Lanka, there are a large number of natural resources and among them, graphite has been identified as a good electrode material for rechargeable batteries. Due to the inherent drawbacks of liquid electrolytes, many research groups have focused their attention on gel polymer electrolytes (GPEs) which are showing liquid like ionic conductivities with quasi solid state properties. They are consisted with a polymer network, salt and solvent/s. Due to their excellent properties, they have been investigated for various applications including batteries, capacitors, solar cells and electrochromic devices [Jayathilake, et al. (2014)]. In this paper it is described about a rechargeable battery fabricated using a GPE, a graphite cathode and a Zn anode. This is a kind of an environmental friendly, low cost battery which may be able to compete with the other rechargeable batteries in the market. Also, this type of a battery configuration has not been studied before as per our literature review. The use of Sri Lankan graphite with a GPE is a novelty in the study. If it is possible to develop the battery to get satisfactory performance, there will be a value addition to a Sri Lankan natural resource in the field of energy.

II. METHODOLOGY AND EXPERIMENTAL DESIGN

A. Preparation of the gel polymer electrolyte

Polyvinylidene fluoride (PVdF) (Aldrich, 99%), ethylene carbonate (EC), (Aldrich, 98%), propylene carbonate (PC) (Aldrich, 99%) and zinc trifluoromethane sulfonate ($Zn(CF_3SO_3)_2$) (Aldrich, 99%) were used without further purification. Required amounts were weighed and magnetically stirred for some time. Then, heating was done at 120 $^{\circ}$C for 30 minutes. The resulting hot viscous mixture was pressed in between two well cleaned glass plates and on cooling, it was possible to obtain a thin, flexible film.

B. Preparation of the graphite based electrode

Graphite sample which was received from Bogala Graphite Lanka PLC was used as received. It was mixed with PVdF in the weight ratio 85 % : 15 %. A homogenous slurry was prepared using acetone. It was then deposited on a stainless steel dice.

C. Fabrication of the battery

A circular shape electrode was cut from Zn received from Aldrich. An electrolyte film of the same shape and area was cut and it was sandwiched in between the Zn electrode and the graphite electrode. The cell was housed in side a brass sample holder. All the fabrication procedures were carried out in side an Ar filled glove box.

D. Evaluation of the performance of the battery

Firstly, the open circuit potential was measured. Cyclic Voltammetry test was done using the Zn electrode as the reference and counter electrodes and graphite electrode as the working electrode with a Metrohm 101 potentiostat. The scan rate used was 5 mV/s. Cycling was done in the potential window 0.1 V to 1.6 V for 800 cycles continuously. Continuous galvanostatic charging and discharging of the battery was carried out in the potential range 0.1 V to 1.4 V. The constant current used was 120 x 10^{-6} A. Measurements were taken for 1500 cycles. Impedance data were collected in the frequency range 400 kHz to 0.01 Hz at the room temperature using a Metrohm 101 Impedance Analyser.

III. RESULTS

Open circuit potential was 1.03 V. Fig. 1 shows the cyclic voltammograms obtained for the battery at cycles 1,50,100,250 and 800.

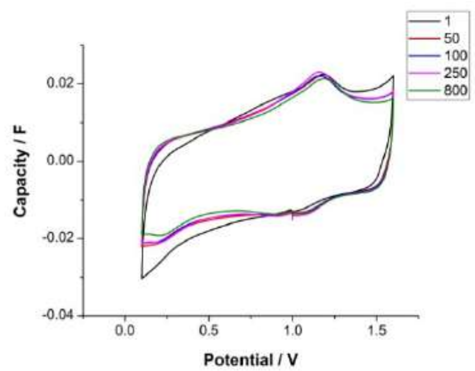

Figure 1. Cyclic Voltammogramms obtained for the battery of the configuration, Zn / PVdF : EC : PC : $Zn(CF_3SO_3)_2$ / Graphite at different cycles

Initial charging and discharging cycles obtained for the battery are shown in Fig. 2.

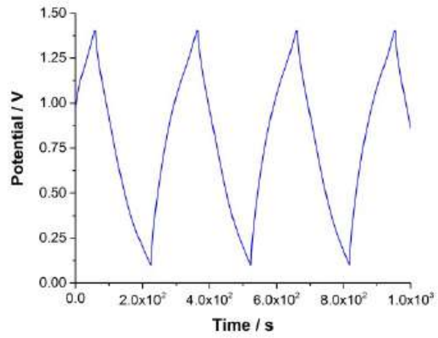

Figure 2. Initial charge discharge cycles of the battery of the configuration, Zn / PVdF : EC : PC : $Zn(CF_3SO_3)_2$ / Graphite under a constant current of 120 x 10^{-6} A

Fig. 3 shows the variation of discharge capacity with cycle number.

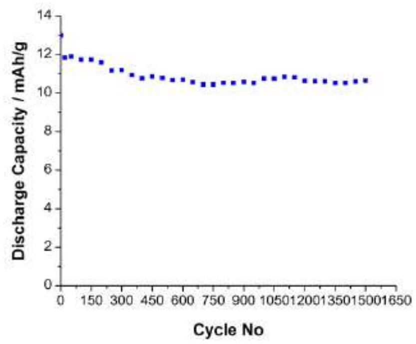

Figure 3. Discharge capacity variation with the cycle number for the battery of the configuration, Zn / PVdF : EC : PC : $Zn(CF_3SO_3)_2$ / Graphite under a constant current of 120 x 10^{-6} A

Fig. 4 shows the Nyquist plot drawn using the impedance data.

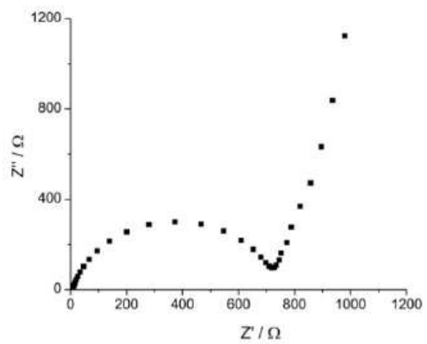

Figure 4. Nyquist plot for the battery of the configuration, Zn / PVdF : EC : PC : $Zn(CF_3SO_3)_2$ / Graphite obtained at room temperature

IV. DISCUSSION

In cyclic voltammogramms**, c**athodic peak appears at the potential 1.09 V. This is due to the plating of Zn on the cathode [Kuo, et al. (2002)]. Stripping of Zn can be seen on the reverse scan as the anodic peak at 1.18 V. Anodic and cathodic peaks appear at near equal potentials. This proves the proper functioning of the battery. There are no other visible peaks. This can be used to express that the battery has sufficient electrochemical stability to allow safe operation without undergoing any unwanted reactions. Capacity at 1^{st} cycle was about 27.6 mAh/g where as it was 25.6 mAh/g at 800^{th} cycle. It was noted that after several initial cycles, the capacity has reached a continuous value and the reduction upon continuous cycling is very low. This is a good indication for the absence of any unwanted, parasitic reactions. If such reactions were present, it can expect a considerable reduction of capacity. Also, it is evidenced that battery gains some maturity after several cycles. Due to that, a slight capacity decrease is observed at initial cycles followed by nearly steady capacity with increasing cycle number. At each cycle, the shape of the cyclic voltammogram remains unchanged. This is due to the wide electrochemical stability of the GPE used in fabricating the battery. If it were not stable, sudden current increments may take place disturbing the shape of the cyclic voltammogram.

In Fig. 2, identical charge discharge pattern can be seen at each cycle. This is a good indication to prove the absence of unwanted reaction. Also, it should be highlighted the negligible IR drop at discharge. If it were present, there would be a drastic sudden potential drop at discharge cycles.

The initial discharge capacity was about 13 mAh/g and 11 mAh/g at 1500^{th} cycle. Initially, a sudden drop of discharge capacity can be seen. But, upon continuous cycling, the drop of discharge capacity has reduced. The reduction of capacity may be attributed to material stabilization, electrolyte – electrode interface formation as observed in cyclic voltammogramms. [Aliahmad. et al, (2013)]. Also, the potential may drop initially due to polarization build up effect which affects the capacity [Agrawal, et al, 92013)]. From the cyclic voltammograms, the available charge during both charging and discharging processes are calculated as the capacity. But, in galvanostatic charge discharge, only the discharge capacity is calculated. Cyclic Voltammetry results show a capacity value of 27.6 mAh/g for the first cycle. The discharge capacity obtained from galvanostatic charge discharge test for the initial cycle is 13 mAh/g which is nearly the half from the capacity value present with cyclic voltammetry test. This is an indication for the comparability of the two tests.

In general, the high frequency, mid frequency and low frequency regions of a Nyquist plot are attributed to the properties of the bulk electrolyte, charge transfer at the interface and capacitive behavior **[**Westerhoff. et al, (2016)]. The high and mid frequency regions are governed by the ionic motion in the system [Larfaillou,et al, (2016)]. At high frequency region, a semi circle should appear representing the bulk electrolyte. In this plot, it is absent due to the unavailability of required high frequency. The bulk electrolyte resistance was found from the first intercept on the real axis and was about 3 Ω. The second semicircle was used to calculate the corresponding charge transfer resistance and it was about 720 Ω. The low frequency region is governed by the electrode polarization. The spike at the low frequency region represents a capacitive behavior. It is expected that at low frequency region, charges tend to accumulate on the electrodes. Because of this, a capacitive behavior is present. If the pure capacitive nature was available, the spike is parallel to the imaginary axis. Tilted spike is due to some facts such as uneven surface of electrodes and diffusion controlled behavior. Data clearly confirms the absence of any parasitic effects or any formation of resistive layers.

V. CONCLUSION

A battery of the configuration Zn/PVdF : EC : PC : $Zn(CF_3SO_3)_2$ / Graphite : PVdF was successfully fabricated. Open circuit potential was 1.03 V. Initially, battery needs to mature by stabilizing the materials and forming good interfacial contacts between the electrolyte and electrodes. Capacity fade over continuous cycling is low. And also, GPE is rather stable with the electrode materials. Results obtained with CV test, continuous charge discharge test as well as with impedance test, prove the absence of parasitic reactions that disrupt the proper performance of the battery. The bulk electrolyte resistance is very low. This is an indication for the high ionic conductivity of the GPE used for the present study. This type of battery can be used for low power requirements with the benefits of the low cost and the safety. Further studies are being progressed to improve the performance.

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