Performance of an all polymer supercapacitor

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Abstract— *Demand for power sources is getting increased day by day due to high usage of electronic equipment. Most widely used power sources are the batteries. However, when energy storage is considered, capacitors are in the forefront compared to batteries. An ultracapacitor, also called a supercapacitor, is an electrical component capable of holding hundreds of times more electrical charge quantity than a standard capacitor. This characteristic makes supercapacitor useful in devices that require relatively little current and low voltage. In some situations, a supercapacitor can take the place of a rechargeable low-voltage electrochemical battery. Supercapacitors are most commonly used in backup power applications because of their infinite lifespan. Due to the above reasons, work on supercapacitors is of high interest among the researchers. However, work on all polymer supercapacitors is less published. In the present study, performance of an all polymer supercapacitor is reported. Conducting polymer, Polypyrrole (PPy) was used as electrodes while a gel polymerelectrolyte (GPE) based on Polyvinylidene fluoride served as the electrolyte. Fabrication of the supercapacitor was done in the array of PPy : GPE : PPy. The capacitor was characterized using cyclic voltammetry tests, continuous galvanostatic charge-discharge tests and Impedance spectroscopy. Results showed that the fabricated supercapacitor was rather stable even though the obtainable capacity value was not very high.*

Keywords— *Supercapacitor, Conducting Polymer, Gel Polymer Electrolyte*

I. INTRODUCTION

Demand for power sources is getting increased day by day due to large usage of electronic equipments. Most widely used power sources are the batteries. However when energy storage is considered, capacitors are in the forefront compared to batteries [Kotz et al. (2000)]. A common capacitor is an electrical device that can deliver energy in an electric field between a pair of conductors or plates. Supercapacitors or the so called ultracapacitors lie in an intermediate state between batteries and conventional capacitors. They offer power densities higher than batteries and energy densities higher than normal capacitors [Meller et al. (2014)]. Due to the fast energy delivery, short charging time, high power capability and environmental friendliness, they have received a considerable global attraction [Zhang et al. (2009)]. Supercapacitors are already used in numerous applications such as portable consumer electronics, computer power backup, hybrid electric vehicles, medical equipment and space crafts [Miller et al. (2008), Simon et al. (2008)].

There exists two types of supercapacitors namely redox capacitors and electrochemical double layer capacitors based on the type of electrode material employed. For redox capacitors, conducting polymers or electroactive oxides are used as the active electrodes. For construction of electrochemical double layer capacitors, different carbonaceous materials are employed. Conducting polymers provide higher capacitance and higher power capability than carbon based electrodes [Naoi et al, (2008)]. Also, they have become attractive candidates for electrodes due to low cost, easy synthesis and environmental stability. Among the conducting polymers, much attention has been focussed on polyaniline and as such, a great deal of research work has been carried out taking polyaniline and its complexes as the electrodes [Zhu et al. (2011), Singu et al. (2014)].

In literature, most of the redox capacitors have used liquid electrolytes as the separator. Hence, they undergo crucial problems such as self discharge, corrosion, leakage and low energy density. To come across those, utilizing gel polymer electrolyte (GPE)s is a very suitable and a convenient option. This, on the other hand, leads to the concept of all polymer supercapacitors a reality.

In this research paper, it is reported about the fabrication of a redox capacitor based on a GPE and a conducting polymer as electrodes. The GPE consists with the polymer polyvinyldinefluoride (PVdF) and the conducting polymer is based on Polypyrrole (PPy). Performance of those super capacitors were evaluated using electrochemical impedance spectroscopy, cyclic voltammetry and galvanostatic charge discharge tests.

II. METHODOLOGY AND EXPERIMENTAL DESIGN

A. Preparation of the Polymer Electrode

The monomer Pyrrole (Aldrich) was distilled and stored under refrigeration prior to use. Polypyrrole (PPy) film was electrochemically polymerized on to a Fluorine doped tin oxide (FTO) glass galvanostatically using a three electrode set up. Ag/AgCl and Pt electrodes were served as reference and counter electrodes respectively. The monomer concentration was 0.1 M. Sodium Dodecylbenzenesulfonate (SDBS), (Aldrich) of the concentration, 0.05 M was used as the salt. Thickness of PPy film was maintained at 1 µm.

B. Preparation of the GPE

GPE based on Polyvinylidenefluoride (PVdF) (Aldrich), Zinc Trifluoromethanesulfonate (Zn $(CF_3SO_3)_2$ – ZnTF) (Aldrich), Ethylene Carbonate (EC) (Aldrich) and Propylene Carbonate (PC) (Aldrich) was used as the electrolyte. Starting materials were magnetically stirred well and heated at 130 ^{0}C for 15 minutes. The hot mixture was pressed in between two glass plates to obtain a bubble free thin film [Jayathilake et al. (2015)].

C. Fabrication of Supercapacitor

Supercapacitor was fabricated using two PPy films deposited on FTO glass pieces having an area of 1 cm^2 as electrodes and a GPE having same area as the electrolyte or the separator. Structure of the supercapacitor was in the form of PPy:DBS / PVdF:EC:PC:ZnTF / PPy:DBS.

D. Characterization of Supercapacitor

Electrochemical Impedance Spectroscopy (EIS) tests were carried out in the frequency range 400 kHz to 0.01 Hz. Impedance data were analyzed using Non – Linear Least Square fitting program. The capacitance of the redox supercapacitor was calculated selecting a lower frequency and using the equation, $C = -1/2\pi fZ''$ where f is the linear frequency and Z” is the corresponding imaginary value.

Cyclic voltammetry tests were carried out for the supercapacitor in the potential range 0.5V - (-0.4) V using a computer controlled potentiostat / galvanostat. One electrode served as the working electrode, the other as both the counter and reference electrodes. Using cyclic voltammogram, the charge, Q involved in the redox reactions were calculated by the area of the graph of differential capacity (C_d) versus potential. Here, $C_d = i/s$ where i is the current and s is the scan rate. The capacitance was found by using the equation, $C = Q / 2\Delta V$ where ΔV is the potential window.

Continuous galvanostatic charge and discharge tests were carried out to check their ability to withstand long term cycling. The supercapacitor was first galvanostatically discharged to 0.0 V, immediately subjected to a galvanostatic charge up to 0.5 V. The maximum charge and discharge currents were set to 25 µA. Using the charge discharge curves, the discharge capacitance of the supercapacitor was calculated using the equation, $C = i(\Delta t/\Delta V)$ [Ramya et al. (2013)].

For each test, specific capacitance was determined by dividing the capacitance value by the weight of the electrodes.

III. RESULTS AND DISCUSSION

An impedance plot obtained is shown in Fig.1.

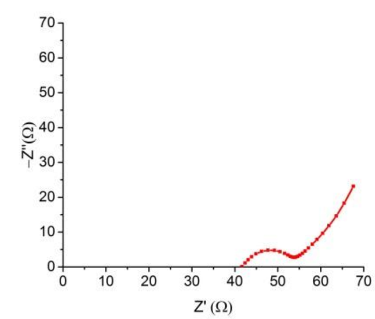

Fig. 1 Impedance plot obtained for the supercapacitor in the frequency range 400 KHz to 0.01 Hz

In general, at the high-frequency region of the impedance plot, there should be a semi circle representing the electrolyte. But, in the resultant impedance plot, it was not possible to observe that semicircle. It may be due to insufficient high frequency range. The semi circle appeared in the impedance plot at the intermediate frequency range represents the charge transfer resistance at the electrode-electrolyte interface. Corresponding equivalent circuit which is a RC parallel circuit gave a small resistance value indicating that the charge transfer resistance is small and electrochemical system under study is kinetically fast. At the low-frequency region, a tilted spike was observed which can be attributed to capacitive behavior of the electrodes. For pure capacitive behavior, the spike should be parallel to imaginary axis of the impedance plot. The resulting tilted spike can be attributed to the diffusion control process of the supercapacitor. The specific capacitance of the capacitor was calculated at the frequency of 0.01 Hz and it was 1.35 F/g.

Cyclic voltammetry was used to characterize the capacitive properties of the supercapacitor. Cyclic voltammetric scans were performed in the potential range from -0.4 to 0.5 V with the scan rate of 10 mV/s because it was reported that within this potential window, high conductivity and good electrochemical reversibility of PPy can be maintained [Vidanapathirana et al. (2002)]. The cyclic voltammogram (CV) obtained is shown in Fig. 2.

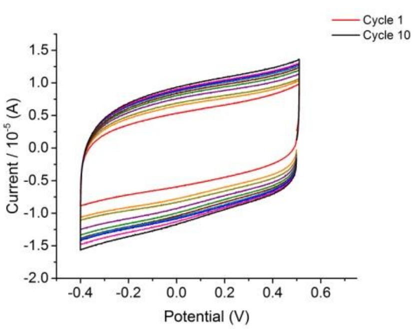

Fig. 2 Cyclic voltammogram curves for the supercapacitor. Scan rate 10 mV/s

The shape of the CV closely resembles a rectangle showing its ideal capacitive behavior [Tripathi et al. (2013)]. In addition this rectangular cyclic behavior exhibits that the charge discharge response is highly reversible. The obtained cyclic voltammograms show featureless characteristics. It is an indication of the constant electron transfer rate between the electrode and gel electrolyte. Even upon continuous cycling, the rectangle shape exists without any change and this indicates that capacitive behavior as well as fast switching rate of ions at the sites of electrolyte-electrode interfaces do not get disturbed with time.

The specific capacitance values calculated for cycle number 1 and 10 from the CV were 0.85 and 0.99 F/g. This shows that upon cycling capacitor tends to undergo the full electrochemical reactions and also it may be due to the possible improvement in interfacial properties with the use of highly flexible gel polymer electrolyte which offers the liquid like properties.

Charge–discharge characteristics of the capacitor are shown in Fig 3.

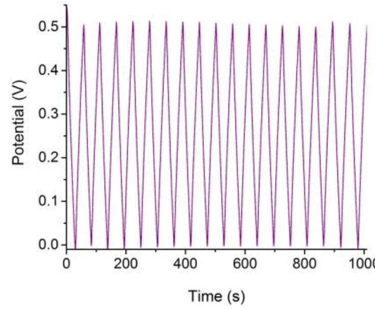

Fig. 3 Charge-discharge performance of the super capacitor at the constant current 25 µA

The discharge characteristics are found to be almost linear which symbolizes the capacitive behaviour of the super capacitors. The initial sudden change in voltage response with respect to time while charging and discharging has been found due to ohmic loss across the internal resistance of the capacitors. The small ohmic drops of the discharge curves suggest that there exist a lower ion diffusion resistance and less obstruction of the ion movement. One of the most important and special features of the supercapacitors when compared with rechargeable cells is their good reversibility for large number of charge discharge cycles [Hashmi et al. (2005)].

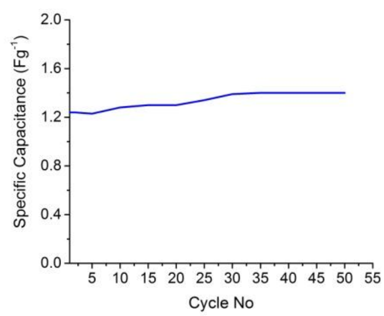

Fig. 4 The variation of capacitance with cycle number

Fig.4 shows the variation of capacitance with cycle number as per the galvanostatic charge discharge test. Initially, the capacitance value has increased upon cycling. This may be due to irreversible charge consumption due to some reactions associated with possible oxidation and reduction of loosely bound surface groups at the electrode electrolyte interface. After few cycles, the capacitance has reached a more or less constant value indicating the stabilization of redox reactions. The average specific capacitance value calculated from this galvanostatic charge-discharge tests was 1.35 F/g.

IV. CONCLUSION

An all polymer supercapacitor was successfully fabricated using conducting polymer PPy as electrodes and with Polyvinylidenefluoride based GPE. With the three characterization techniques, it was possible to obtain near equal specific capacitance values. This elucidates the fact that the specific capacitance obtained is unique for the electrode electrolyte combination selected for the present investigation. And also, this is clear indication that all three techniques are suitable for characterization of supercapacitors. From the cyclic voltammetry and galvanostatic charge discharge tests, it was noticed that the supercapacitor is rather stable even though the specific capacitance was not very high. Investigations are being carried out to optimize the performance further.

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Prof. Vidanapathirana graduated from University of Peradeniya in 1993 with a B.Sc.(Special) Degree in Physics. He completed his Ph.D. in the field of Solid State Physics from the same University under the sandwich Ph.D. programme with Technical University of Denmark in the year 2000. Presently he is serving as a Professor in the Department of Electronics, Wayamba University of Sri Lanka. His research interests are on conducting polymers and their applications. He is a member of the Polymer Electronics Research group of Wayamba University of Sri Lanka.