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Studies on Polymer Blend Electrolytes for Redox Capacitors

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Abstract:- Cobalt cobaltite based redox supercapacitor has been fabricated using the polymeric gel electrolyte comprising of poly vinylidene fluoride co-hexafluropropylene (PVdF-HFP)-polymethyl methacrylate (PMMA)-sodium thiocynate (NaSCN) as salt. The fabricated redox supercapacitor has been characterized by using cyclic voltammetry and charge-discharge techniques. The capacitance value of the cell has been observed to be in the range of 69 mF cm^{-2} which is equivalent to single electrode specific capacitance of 8.5 F g^{-1}. The energy and power density of the cell has been found to be of the order of 1.2 Wh kg^{-1} and 0.2 kW kg^{-1}. The coulombic efficiency of the cobalt cobaltite based capacitor cell have been observed (closed to 95%) due to application of highly flexible gel electrolyte which is showing liquid like properties.

Keywords:- Redox capacitors, Gel Polymer Electrolyte, PVdF-HFP, PMMA

I. INTRODUCTION

Electrochemical capacitors are regarded as ideal storage devices to meet the urgent needs in electric and electronic devices, such as hybrid electrical vehicle-based green transportation, backup energy sources, since they have high power density and long cycle life [1-2]. However, compared with batteries, supercapacitor usually provides lower energy density and exhibits higher self discharge rates which make it impossible to be simply a substitute for batteries in commercial and industrial applications. The performance of the supercapacitor is closely related with the electrode and electrolyte. As far as electrode is concerned, to date, activated carbon [3-4], amorphous hydrous ruthenium oxide ($RuO_2.xH_2O$) [5-6], manganese oxide [7], nickel oxide [8], cobalt oxide [9] and conducting polymers like polypyrrole [10] have been extensively used as an electrode material for electrochemical capacitor. Among the metal oxides, the noble metal oxides such as ruthenium oxide have been found to possess high energy storage capabilities having large specific capacitance and excellent cyclic reversibility. However, due to lack of abundance and high cost inhibits its use for commercial applications. Therefore efforts have been made to find the substitute of this material.

Co_3O_4 (Cobalt cobaltite) is widely used in many fields such as catalyst, solar cells, microelectronics, and lithium ion batteries. Although it's cyclic reversibility is not that good but it has been suggested as a promising electrode material for supercapacitors because of its good pseudocapacitive performance, low cost, good corrosion stability [11]. Chuan et al. fabricated cobalt oxide by sol gel process and they obtained specific capacitance of 291 F g^{-1} [11].

Most of the redox supercapacitor reported in the literature is based on liquid electrolytes [12] which offer well known disadvantage of bulky design, corrosion, self discharge, electrolyte leakage etc. Therefore, major attention has been devoted globally by researchers to construct solid state supercapacitor based on polymer/gel electrolyte [13]. The all solid-state redox supercapacitor are not widely reported except the few recent reports which include the capacitor with different gel/polymer electrolyte for example PVdF-HFP-EC-PC-$TEABF_4$ [14], PVA-H_3PO_4 [15] etc.

The present paper reports preliminary studies on redox supercapacitor using cobalt cobaltite electrodes and polymeric gel electrolyte comprising of poly vinylidine fluoride-co-hexa-fluropropylene (PVdF-HFP)-polymethyl methacrylate (PMMA)-sodium thiocynate (NaSCN). The performance characteristics of the fabricated cell have been done by using cyclic voltammetry and charge-discharge analysis.

II. EXPERIMENTAL DETAILS

2.1 Materials Preparation

The polymeric gel electrolyte comprising of PVdF(HFP)-PMMA-NaSCN was prepared by using standard "Solution Cast Technique". PVdF(HFP) with an average molecular weight of $1.3x10^5$, PMMA with an average molecular weight of $1.2x10^5$, was purchased from (Sigma Aldrich) and inorganic salt NaSCN (Loba chemie) were used in the present study. All the chemicals were dried before use. Different composition of

NaSCN, PVdF(HFP), PMMA were dissolved in DMF (Merck) and mixed together. The resultant solution was stirred and heated continuously at 60 ^{0}C for 10 hours until the mixture gets homogenous and becomes gelly in nature.

The preparation method of cobalt cobaltite (Co_3O_4) based electrode is as follows. Slurry of cobalt cobaltite and PVdF-HFP in the ratio 90:10 (w/w) in the common solvent, acetone was prepared by a thorough mixing. Fine films of electrodes were coated by spraying the slurry on carbon cloth (Ballard, USA) followed by heating them at 100 °C for 10-12 hours. The capacitor cell was fabricated by sandwiching the gel polymer electrolyte between two symmetrical electrodes.

2.2 Electrochemical measurements

The bulk electrical conductivity of gel electrolyte was evaluated using complex impedance spectroscopy at room temperature by using computer controlled LCR HI TESTER (Model 3522-50, Hioki, Japan) in the frequency range from 1 Hz to 100 kHz. The signal level was kept at 10 mV.

The linear sweep voltammetry was carried out by using computer controlled CHI 608C, CH Instruments, USA. The capacitance values from this technique were evaluated by using the relation:

$C = i / s$ (1)

Where ‘i’ is the current and ‘s’ is the scan rate. The charge-discharge characteristics of the capacitor cell were evaluated at constant current. The discharge capacitance ‘C’ was evaluated from the linear part of the discharge curves using the relation:

$C = i\Delta t / \Delta V$ (2)

Where ‘i’ is the constant current and Δt is the time interval for the voltage change of ΔV. The coulombic efficiency ‘□’ was calculated by using the equation:

□□□□ t_D / t_C x 100 % (3)

Where t_D and t_C are the galvanostatic discharge and charge time respectively.

III. RESULTS AND DISCUSSIONS

3.1 Electrochemcial Characterization of Gel Polymer Electrolytes

The compositions of polymeric gel electrolyte PVdF(HFP)-PMMA- NaSCN was first optimized in order to get both substantially conducting and mechanically stable and flexible materials. Fig 1 shows the variation of ionic conductivity of PVdF (HFP) - PMMA - NaSCN [1M] polymer blend electrolytes systems. It can be seen from the figure that the ionic conductivity of the polymer blend electrolytes initially increases upto 20 wt% of polymer blend concentration thereafter it decreases upto 50 wt% of the polymer blend. The maximum conductivity of the PVdF(HFP) [80wt%] - PMMA [20wt%] - NaSCN [1M] polymer blend electrolytes at room temperature has been observed to be 4.54×10^{-2} S cm^{-1}. This order of higher conductivity has been achieved due to the proper interaction of PVdF(HFP)-PMMA and NaSCN salt. Higher conductivity in polymer blend electrolyte system could be attributed to the higher amorphicity due to steric hindrance. Higher amorphous region provides more free volume to the mobile sodium ions, which in turn give rise to higher conductivity to the electrolytes system.

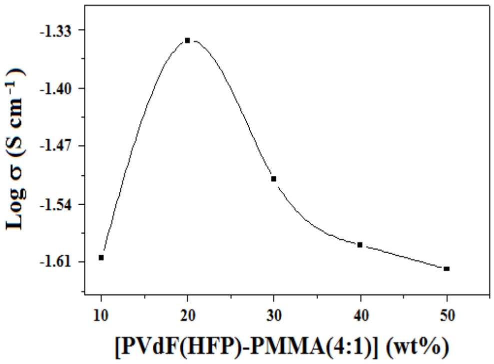

Fig.1 Variation of ionic conductivity for blend polymer gel electrolyte PVdF(HFP)-PMMA-NaSCN as a function of different wt% of polymer blend concentration.

The capacitor cell of following configuration has been constructed with cobalt cobaltite (Co_3O_4) electrode with optimized polymeric gel electrolyte:

Cell A: Co_3O_4 | PVdF HFP-PMMA-NaSCN | Co_3O_4

3.2 Cyclic voltammetric tests

Fig 2 shows the linear sweep cyclic voltammogram for the capacitor cell A at a scan rate of 10 mV sec^{-1}. The obtained cyclic voltammogram curve is considerably different from an ideal rectangular shape, indicating that capacitance mainly results from pseudocapacitance, which is caused by the fast and reversible faradic redox reactions of electroactive material. As can be seen from Fig.2 there is an increase in voltage difference between oxidation and reduction peak, it may be due to the polarization of electrode and also due to rapid reversible redox reaction occurred at the interface of electrode electrolyte material.

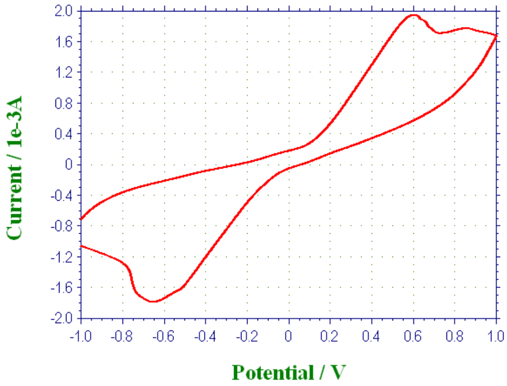

Fig.2: Cyclic voltammogram of redox capacitor cell A.

3.3 Charge-discharge tests

The capacitor cell has also been tested with the constant current charge-discharge methods. The typical charge-discharge characteristic of the capacitor cell is shown in Fig. 3.

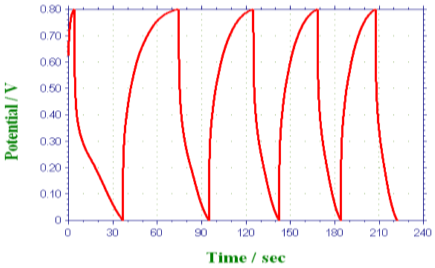

Fig.3: Charge-discharge curve of redox capacitor cell

The entire cell was charged upto 0.8 V. It has been observed that the charge-discharge curves are not linear indicating that the capacitance performance is not purely electric double-layer capacitance, which is in agreement with cyclic voltammogram curve in Fig. 2. There are two variations ranges as is displayed in the plot of potential versus time, which may be due to pseudocapacitance performance arisen from the electrochemical adsorption-desorption or redox reaction at the electrode-electrolyte interfaces. A linear variation of potential versus time is observed, which indicates pseudocapacitance rooted in the charge separation that took place between the electrode and the adjacent electrolyte interface. 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 cell. The internal resistance of the cell has also been estimated from this loss. The value of discharge capacitance C_d, internal resistance R_i and coulombic efficiency η are listed in Table 1. The energy density and power density has also been calculated for capacitor cell A and are listed in Table 1. Although the energy density value is comparatively lower than rechargeable batteries, but power density value make such supercapacitor device attractive from application point of view.

Table 1: Typical charge-discharge characteristics of redox capacitor cell at current density of 5 mA cm^{-2}.

Cell	**R_i (Ω cm^2)**	**Discharge capacitance, C_d**		**Working voltage (V)**	**Energy density (Wh kg^{-1})**	**Power density (kW kg^{-1})**
		(mF cm^{-2})^a	**(F g^{-1})^b**			
A	78	69	8.5	0.8	1.2	0.2

IV. CONCLUSIONS

In the present paper cobalt cobaltite (Co_3O_4) based electrode has been prepared and its capacitive behavior has been investigated. Based on all studies like cyclic voltammetry and charge-discharge that are performed it has been observed that capacitance of Co_3O_4 mainly results from pseudocapacitance. The gel electrolyte PVdF-HFP-PMMA-NaSCN shows the maximum conductivity of 4.5 x 10^{-2} S cm^{-1} at room temperature and has been found to be suitable electrolyte for their use in redox supercapacitor. The cell show the capacitive behavior with capacitance value of 69 mF cm^{-2} which is equivalent to single electrode specific capacitance of 8.5 F g^{-1}. The energy and power density of the cell has been found to be of the order of 1.2 Wh kg^{-1} and 0.2 kW kg^{-1}. The coulombic efficiency of the cobalt cobaltite based capacitor cell has been observed (closed to 95%) which may be due to application of highly flexible gel electrolyte which is showing liquid like properties.

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