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RESEARCH ARTICLE OPEN ACCESS

Performance and Evaluation of V_2O_5 Thin Film Electrode for Electrochemical Supercapacitor: Effect of Electrolytes

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ABSTRACT
In this study,V_2O_5 thin film electrodes were prepared by simple and inexpensive Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The electrochemical capacitors performances of V_2O_5 thin film electrode were tested by different electrolytes viz. KCl, NaOH, KOH, and K_2SO_4. The electrochemical capacitor performances were examined by using cyclic voltammetry and galvanostatic charge-discharge method. The specific capacitance and stability observed to be best in K_2SO_4 electrolyte. The specific capacitance of 310 F/g has been obtained in 0.5M K_2SO_4 solution at a scan rate 10mV/s within the potential window -0.2 to 0.6V. Specific energy of 21.34 Wh/kg and specific power of 13.34 kW/kg and cycle stability retention 91.25% was observed.

Keywords **-** V_2O_5, Thin films, Cyclic voltammetry, Supercapacitor, Charge-discharge

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I. INTRODUCTION

Conventional energy sources are reducing day by day and trouble of the energy is becoming more and more crucial. The researchers are attracted towards the search of the novel energy sources which are more sustainable and eco friendly. Utilization of renewable energy is the most reasonable option for sustainable development. Solar energy has amazing potential as energy source; but its irregular availability limits its uses. This problem can be defeated by use of efficient and effective energy storage systems [1]. Therefore the researchers provoked to work on development of superior energy storage device with the intention that energy can be stored as and when it is available and it can be used later as per requirement [2].

Supercapacitor or Electrochemical Capacitor (EC) has been identified over fifty years and taken into account as one of the potential energy storage system. Supercapacitor is an energy storage device holding a property of long life cycle and high power density. Supercapacitor possesses higher energy density than electrostatic capacitor and higher power densities than batteries. Simultaneously it shows fast charge-discharge capability and long cycle life [3-9].

Supercapacitor can bridge the gap between batteries and electrostatic capacitors.

The electrode is the significant part of the electrochemical capacitors (ECs); therefore the electrode material is the important factor to determine the properties of ECs. Vanadium is resistant to corrosion because of formation of surface film oxide. At room temperature they are not affected by water, acids or air. V_2O_5 and VO_2 have been identified as electrode material for EC due to their low cost, abundance, and their potential pseudocapacitive characteristics [10-15]. V_2O_5 has attracted much attention for EC or Supercapacitor applications because of its extensive multifunctional properties [16]. V_2O_5 has highest oxidation state (saturated oxide), and therefore the most stable one, in the V-O system [17]. Vanadium oxide store energy like EDLC and also shows electrochemical faradic reactions between electrode material and ions [18].

The electrolyte is a crucial part of Supercapacitor. The electrolytes used in the electrochemical capacitors must acquire a wide range of potentials of electrochemical stability, maximum possible decomposition voltage. The resistivity of the electrolyte used and size of the ions from the electrolyte that diffuse in and out of the pores of the micro-porous electrode determines the resistance of the electrochemical capacitor cell. These days, the types of Supercapacitor could be usually divided into aqueous and non-aqueous systems based on the electrolytes utilized. For the

non-aqueous systems, the working voltage range is wider than that for the aqueous electrolytes. But high production cost, high viscosity, low electrical conductivity, and high equivalent series resistance (ESR) are all drawbacks for non-aqueous electrolytes. Considering above parameters, aqueous electrolytes appear to be a more correct choice for Supercapacitor utilized in some particular circumstances. Organic electrolytes have a higher resistance, but the successive power reduction is usually compensated by the increase in higher cell voltage. This is generally not a trouble for an aqueous electrolyte, such as KCl, NaOH, KOH and K_2SO_4 with the resistivity of 1- 2 Ω.cm. Aqueous electrolytes have less resistance, are cheaper and easier to purify, but they bound the cell voltage to typically 1 V, and hence limiting the maximum reachable power [19]. Furthermore, the acidic electrolytes have the trouble of corrosion of electrode due to the acidic nature.

II. EXPERIMENTAL

2.1 Solution Preparation

Analytical reagent grade (AR) chemical (VCl_3: 99+ Merck Germany) was used for preparation of precursor solution. The V_2O_5 thin films were deposited on SS (202 grade) stainless steel substrate. Grade 202 stainless steel is a type of Cr-Ni-Mn stainless. It possesses low nickel and high manganese stainless steel. The toughness of grade 202 at low temperatures is excellent. SS 202 possesses good corrosion resistance, toughness, high hardness and strength, which is helpful in making a device.

Before the deposition of V_2O_5 thin films, SS substrates were cleaned with detergent and distilled water and dilute nitric acid and then washed by double distilled water and further ultrasonicated for 10 minutes then dried and used for deposition. While optimizing preparative parameters like precursor solution concentration, dipping time and number of cycles were varied to procure good quality of V_2O_5 thin films. The optimized parameters were as follows : 0.25 M VCl_3 in HPLC water, pH~1.5 was adjusted by HNO_3 drops, precursor solution temperature was maintained constant at 65^0 C. V_2O_5 films were deposited from the cationic precursor of 0.25 M VCl_3 in HPLC water and addition of HNO_3 to make pH ~ 1.5 and the 0.1 % H_2O_2 as anionic precursor. Double distilled water was alternately placed in between the beakers containing cationic and anionic precursor solutions. Cleaned SS substrate was immersed into the cationic solution of VCl_3 for 40s, where vanadium ions were adsorbed on the substrate surface which was then rinsed with double distilled water for 15 s to remove loosely bounded vanadium ions from the substrate. The substrate was then immersed in anionic precursor (0.1% H_2O_2) solution for 20 s where the oxygen ion reacted with pre-adsorbed vanadium ions on the SS substrate to form V_2O_5 film. This was then rinsed with double distilled water for 15 s to remove un-reacted species from the substrate. This forms one cycle. After about 40 such cycles the good quality of film was obtained.

2.2 Electrochemical Study:

Supercapacitive performance of SILAR deposited V_2O_5 thin film electrodes. The cyclic voltammetry (CV) was considered to be perfect tool to designate the capacitive behavior of any material. The supercapacitive performance of V_2O_5 thin film electrode was measured on Automatic Battery cycler WBCS3000. The V_2O_5 film electrode synthesized by SILAR technique was cycled from -0.2 V to 0.6 V at different sweep rates in different electrolytes. Films coated on SS substrate each with an area 1 cm^2 were employed as working electrode. Saturated calomel electrode (SCE) served as the reference electrode while platinum electrode as counter electrode.

The cyclic voltammetry measures the current density against fixed potential range (potential window). The potential is applied between the reference and working electrode and faradic current is measured between the working and counter electrode.

All electrochemical experiments were carried out at room temperature and all potential values given below refer to a saturated calomel electrode (SCE). In supercapacitor study of V_2O_5 thin film electrode in K_2SO_4 electrolyte the correct charge/discharge curve was obtained in between -0.2 to 0.6 V/SCE potential.

The cyclic voltammetry (CV) experiments were performed to determine the specific capacitance of the V_2O_5 electrode in electrolyte. The capacitance 'C' of film was calculated from the relations

$$C = \frac{I}{(dV/dt)} \text{..... ..(1)}$$

Where, 'I' was the average current in amperes and (dV/dt) was the scan rate in mV/s. Similarly the interfacial capacitance (Ci) was obtained by dividing the capacitance by respective electrode area in the electrolyte.

$$Ci = \frac{C}{A} \text{……..……(2)}$$

Where 'A' is the area (1 cm^2 in this study) of electrode dipped in the electrolyte. The specific capacitance (Cs) of the electrode was obtained by dividing the capacitance by the weight of V_2O_5 electrode dipped in the electrolyte.

$$Cs = \frac{C}{W} \ldots\ldots\ldots\ldots\ldots\beta)$$

Where W is mass of the V_2O_5 electrode dipped in the electrolyte.

The electrical parameter, specific energy (E) was calculated using following equation;

$$E = 0.8\frac{I_d T_d}{W} \ldots\ldots\ldots\ldots(4)$$

Where I_d and T_d are the discharge current and discharge times, respectively.

The W was the mass of V_2O_5 film electrode.

The electrical parameter, specific power (P) was calculated using following equation;

$$P = 0.8\frac{I_d}{W} \ldots\ldots\ldots\ldots(5)$$

Where, I_d was the discharge current.

The W was the mass of V_2O_5 film electrode.

III. RESULTS AND DISCUSSION

3.1 Effect of Different Electrolytes

The electrochemical capacitor performance of V_2O_5 thin film was conducted in different electrolytes viz. KCl, NaOH, KOH, and K_2SO_4. Fig.1 illustrates the CV curves of V_2O_5 electrode in different electrolytes. The performance in K_2SO_4 electrolyte was the best one. The specific capacitance in KCl, NaOH, KOH electrolytes was relatively less. Also stability of the film obtained in KCl, NaOH, and KOH was poor. In KCl electrolyte the film observed to be detaching from the substrate in couple of minutes. Thus specific capacitance and also stability observed to be best in K_2SO_4 electrolyte.

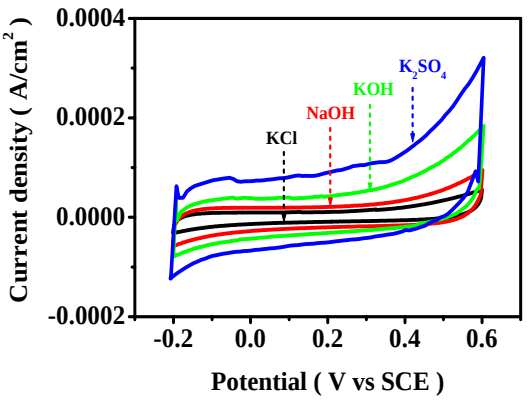

Fig.1The CV Curves of V_2O_5 Electrode in 0.5 M Electrolytes a) KCl b) NaOH c) KOH d) K_2SO_4 at Scanning Rate of 10 mV/s.

3.2 Effect of K_2SO_4 Electrolyte Concentration

The effect of concentration of K_2SO_4 electrolyte was studied by keeping the scan rate and potential scanning range constant. The concentration of the K_2SO_4 electrolyte was varied from 0.25M to 0.75M. Fig.2 illustrates the CV curves of V_2O_5 electrode at scan rate 10 mV/s within the potential window of -0.2V to 0.6V vs. SCE in K_2SO_4 electrolyte of different concentrations. It is seen from the fig.2 that the current under curve increased as the concentration of K_2SO_4 electrolyte increased from 0.25 to 0.5M. The continuous increase in the area under the CV was observed up to the 0.5M K_2SO_4 concentration, at 0.75 M concentration the decrease in the area under the curve was observed. The maximum specific capacitance was obtained at 0.5 M concentration of K_2SO_4 electrolyte.

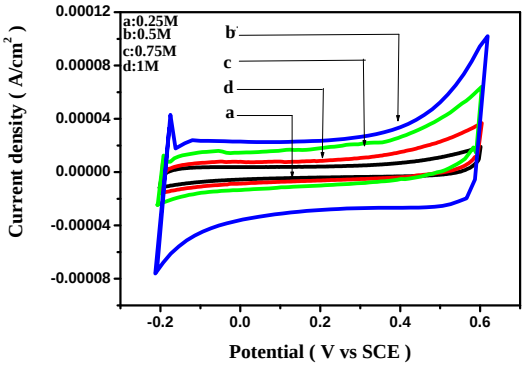

Fig.2 The CV curves of V_2O_5 electrode at different concentrations of K_2SO_4 electrolyte on SS substrate

3.3 Specific Capacitance

The cyclic voltammetry (CV) measured at scan rate of 10 mV/s for the V_2O_5 thin film on SS substrate is shown in Fig.3the appropriate potential window is defined as -0.2 to 0.6 V (vs.SCE). The CV curves exhibit capacitor behavior showing nearly rectangular shape. As Fig.3illustrates the shape of the CV curves, revealing good electrochemical reversibility for the V_2O_5 material. Generally, it is suggested that the electrochemical capacitive mechanism of the V_2O_5 arises from a combination of the electrical double-layer formation and the faradic redox reactions that take place on the surface of the film, and the higher electrical double-layer capacitance is endorsed to its higher specific surface area which can progress the utilization rate of material during the electrochemical process.

The specific capacitance of V_2O_5 electrode on SS substrate in K_2SO_4 electrolyte of 0.5 M at scan rate of 10 mV/s obtained was 310 F/g.

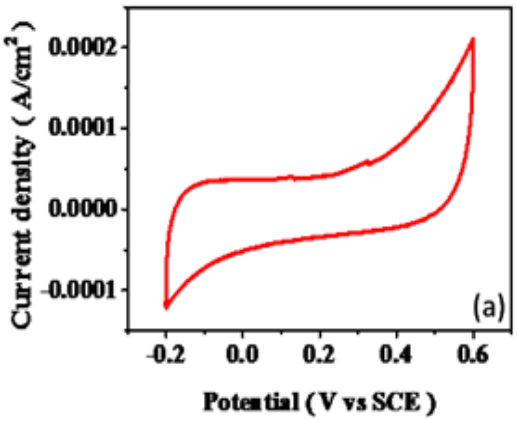

Fig. 3 The CV Curves of As-Deposited V_2O_5 Thin Film Electrode on SS at 10 mV/s Scanning Rate and 0.5 M Concentration of K_2SO_4 .

3.4 Charge/Discharge

The charge/discharge behavior of V_2O_5 electrode was studied by galvanometric charge/discharge technique at a constant current of 2 mA/cm^2 between -0.2V and 0.6 V.

Fig.4 illustrates the typical charge/discharge curve of V_2O_5 electrode. From figure, the asymmetric behavior of voltage-time curve was seen.

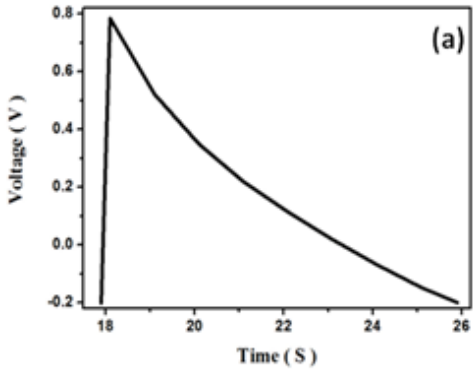

Fig. 4 The Charge/Discharge Curve of V_2O_5 Electrode in 0.5 M K_2SO_4 Electrolyte at 2mA/cm^2

3.5 Specific Energy (E)

The electrical parameter, specific energy (E) was calculated using equation4.

Where I_d and T_d are the discharge current and discharge times, respectively. The W was the mass of V_2O_5 film electrode. The specific energy of V_2O_5 electrode on SS substrate observed 21.34 Wh/kg

3.6 Specific Power (P)

The electrical parameter, specific power (P) was calculated using equation5.

Where, I_d was the discharge current. The W was the mass of V_2O_5 film electrode. The specific power of V_2O_5 electrode on SS substrate observed 13.34 kW/kg.

IV. CONCLUSION

The electrochemical capacitor performance of V_2O_5 thin film was observed in different electrolytes viz. KCl, NaOH, KOH, and K_2SO_4.The performance in K_2SO_4 electrolyte was the best one. The specific capacitance in KCl, NaOH, KOH electrolytes was relatively less. Also stability of the film obtained in KCl, NaOH, and KOH was poor. In KCl electrolyte the film observed to be detaching from the substrate in couple of minutes. Thus specific capacitance and also stability observed to be best in K_2SO_4 electrolyte. The electrochemical study revealed that the SILAR deposited V_2O_5 electrode had specific capacitance of 310 F/g in 0.5M K_2SO_4 solution at a scan rate 10mV/s within the potential range -0.2 to 0.6V versus SCE. Specific energy of 21.34 Wh/kg and specific power of 13.34 kW/kg and cycle stability of 91.25% was observed.

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