Synthesis, Characterization and Electrochemical Properties of SILAR Deposited V_2O_5 Thin Film

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Abstract: *Vanadium oxide (V_2O_5) was prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) method. The structure, morphology and surface wet ability were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and contact angle measurement, respectively. The electrochemical capacitor performances were examined by using cyclic voltammetry and galvanostatic charge-discharge method. The specific capacitance of 168 F/g has been obtained in 1M K_2SO_4 solution at a scan rate 25 mV/s within the potential range -0.2 to 0.6V versus SCE. The supercapacitor exhibited a good cycling performance*

Keywords: *V_2O_5, Thin films, cyclic voltammetry, Supercapacitor, Charge-discharge*

1. INTRODUCTION

Supercapacitors, also known as electrochemical capacitors, Gold capacitors and Ultra capacitors have been attracting much attention in recent years due to their significant potential. These potentials make them good candidates for power sources in hybrid electric vehicles,[1] camera-flash equipment, cellular phones and navigational devices [2]. Supercapacitors can fill the energy and power gaps between the conventional electric double-layer capacitors and second batteries. Carbon materials [3-4], transition metal oxides [5-7] or hydroxides [8-9] and conducting polymers [10-11] are the widely used electrode materials for supercapacitors.

Supercapacitors have widely been investigated as the nextgeneration electric double-layer capacitors (EDLCs). EDLCs, which are based on high-surface area carbon materials, mainly utilize the capacitance that purely arises from the nonfaradaic charge separation at the electrode/electrolyte interface. Electrochemical supercapacitors utilize the charge-transfer pseudo-capacitance stemming from the reversible faradic reaction that occurs at the electrode surface. Electrochemical capacitors with pseudo-capacitance, such as V_2O_5, IrO_2 and NiO, have been focused in recent years because their energy density is larger than EDLCs [12-14].

V_2O_5 has been widely examined as an electrode material for electrochemical capacitors that use organic electrolytes [15-16]. Since V_2O_5 has a modest electronic conductivity, composites with metal fibres or carbonaceous materials have been prepared in an attempt to improve electrode performance [17-19]. By contrast, these are very few reports of the pseudo-capacitive behaviour of this oxide. Lee prepared amorphous V_2O_5 by quenching V_2O_5 powders heated at 950^0C and studied in aqueous KCl electrolyte the specific capacitance was 350 F/g [20]. Reddy et al [21] prepared nano-porous V_2O_5 by a sol–gel method and obtained a maximum specific capacitance of 214 F/g at a scan rate of 5mV/s in KCl electrolyte. Recently, there are a few reports on amorphous V_2O_5 used as the cathode material of supercapacitor in organic electrolyte [22, 23], and also few reports on amorphous V_2O_5 used as the electrode material of symmetric supercapacitor in aqueous electrolyte [24, 25].

V_2O_5 thin films have been prepared by using several techniques, such as radio-frequency sputtering [26], dc-magnetron sputtering [27], flash evaporation [28], sole-gel technique [29], plasma enhanced chemical vapor deposition [30] and pulsed laser deposition [31-33].

In this work, V_2O_5 thin film was prepared from vanadium chloride (VCl_3-$6H_2O$) precursor by successive ionic layer adsorption and reaction (SILAR) method on FTO substrate. The structural and

surface morphology was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The capacitive properties of the V_2O_5 thin film were investigated by cyclic voltammetry and galvanostic charge–discharge methods.

2. EXPERIMENTAL

The V_2O_5 thin films are deposited on fluorine doped tin oxide (FTO) coated on glass substrate. Analytical reagent grade (AR) chemicals (VCl$_3$; 99+ Merck Germany) were used for preparation of precursor solution. Before the deposition of V_2O_5 thin films, FTO glass were cleaned with detergent and distilled water and then washed by double distilled water and further ultrasonicated for 10 min. 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 was as follows : 0.2 M VCl$_3$ in HPLC H_2O , pH 1 was adjusted by HNO$_3$ drops, precursor solution temperature were maintained constant at 65 ^{0}C.

Vanadium oxide films were deposited from the cationic precursor of 0.2 M VCl$_3$ in H_2O and addition of HNO$_3$ to make pH ~ 1 and the 0.1 % H_2O_2 as anionic precursor. Double distilled water is alternately placed in between the beakers containing cationic and anionic precursor solutions. Cleaned FTO glass substrate was immersed into the cationic solution of VCl$_3$ for 40s, where vanadium ions are 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 FTO glass substrate to form vanadium oxide film.

The morphology and crystal structure of vanadium oxide thin films were investigated by scanning electron microscopy and X-ray diffraction techniques. respectively. The electrochemical capacitive properties of V_2O_5 film were investigated by cyclic voltammetry (CV) and galvonostatic charge-discharge methods in 1 M K_2SO_4 aqueous solution. A three electrode cell was employed; V_2O_5 thin films as working electrode and platinum electrode as a counter electrode. All electrochemical experiments were carried out at room temperature and all potential values given below refer to a saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1. Film Formation Mechanism

The deposition mechanism for V_2O_5 film formation by SILAR is described as follows. The first deposition bath was made up of solution of VCl$_3$ in H_2O some amount of HNO$_3$ was added and pH was adjusted to 1. After immersion of substrate in the first bath vanadium cations get adsorbed on the substrate surface. Which was then rinsed in double distilled water to remove loosely bounded vanadium cations from the substrate. When this substrate is immersed in anionic solution (H_2O + H_2O_2) , oxygen anions react with pre-adsorbed vanadium cations and formation of vanadium oxide thin layer takes place. Again substrate is rinsed in double distilled water to remove unreacted oxygen anions. These four steps complete one deposition cycle of SILAR. After repeating such appropriate cycles, multilayer film formation of appropriate thickness takes place on the substrate. Whole process may involve chemical reaction as follows

$$2VCl_3 + H_2O + 4HNO_3 \xrightarrow{\Delta} V_2O_5 + 4NO_2 + 6HCL$$
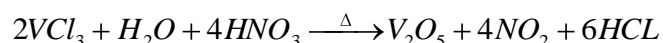
3.2. Structural and Morphological Analysis

Structural analysis of V_2O_5 thin films was carried out by X-ray diffraction technique. Fig. 1 shows typical XRD pattern of V_2O_5 thin film on FTO substrate. XRD pattern exhibits four peaks of V_2O_5 as (2 3 3), (4 4 0), (0 4 6), (7 6 1) were observed. There is a good agreement with the JCPDS file (card no. 45-1074). One peak of FTO substrate located at $2\Theta = 21.37^0$ the the sharpness of the peaks indicate a good crystallites. The V_2O_5 film was polycrystalline.

Fig.2 shows the SEM image of the SILAR deposited V_2O_5 oxide thin film. The substrate is well covered with fine elongated particles having different sizes. Surface also covered with small agglomerates of different sizes. It is difficult to find approximately size of particles. Some micro porous space between the fine particles can also be seen. The porosity of films can enhance the redox

process resulting in high packing density of the active material. Such type of morphology leads to high surface area and porous volume, which provide the structural foundation for the high specific capacitance.
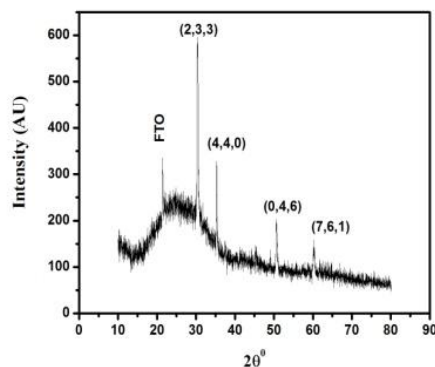

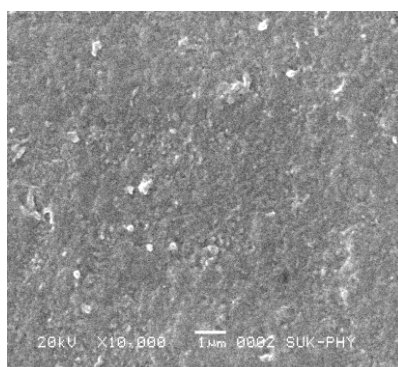**Fig1.** *XRD pattern of V_2O_5 thin films*

Fig2. *SEM image of V2O5 with the magnification of 10,000 X*

3.3. Contact Angle Measurement

Fig. 3 shows that water contact angle measurement images of V_2O_5 thin films onto FTO substrate. The observed water contact angles for film FTO was 70^0. It reveals the hydrophilic ($\Theta < 90^0$) behavior of V_2O_5 thin film onto the FTO substrate. Decrease in water contact angle for V_2O_5 thin film on FTO was attributed to the increase in surface wettability due to increased porous nature of V_2O_5 on FTO. The hydrophilic nature of V_2O_5 thin films deposited onto FTO suggested that the films having potential application as an electrode material for supercapacitors.
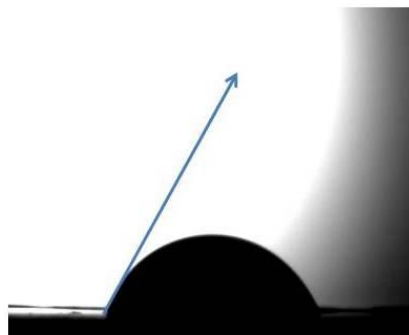

Fig3. *Contact angle measurement*

3.4. Supercapacitive Performance of V_2O_5 Thin Films

The SILAR deposited V_2O_5 thin film electrode is used in electrochemical capacitors and their performance was tested using cyclic voltammetry (CV). Fig.4 shows the cyclic voltammetry (CV) curve of V_2O_5 electrode at a scan rate of 25 mV/s within the potential from -0.2 to + 0.6 V vs SCE in 1M K_2SO_4 electrolyte. From shape of CV it is confirm that capacitance arises from redox transition and EDLC within the electrode/electrolyte and electrolyte/electrode interface, respectively.

The capacitance was calculated from

$$C = \frac{I}{dV / dt}$$

Where 'I' is the average current, dV/dt is the scanning rate. The specific capacitance of the electrode was obtained by dividing the capacitance to weight (0.0014g) dipped in the electrolyte. The specific capacitance of the composites oxide electrode was found to be 168 F/g in 1 M K_2SO_4 electrolyte.
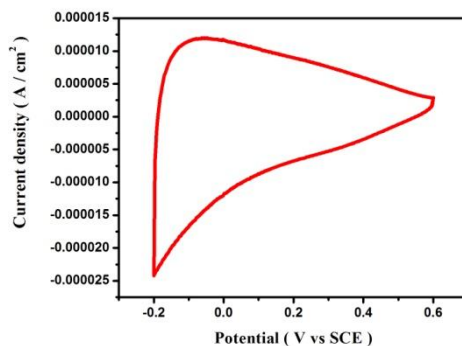

Fig4. *CV curve of V2O5 electrode at 1M of K2SO4 electrolyte. The scanning rate was 25mV/s.*

3.5. Charge-Discharge Cycling Performance Measurements

The charge-discharge behavior of V_2O_5 electrode was studied by galvanometric charge-discharge method. Fig. 5 shows the charge–discharge behavior of electrode at the current density of 2 mA/cm². The shape of the discharge curve does not show the capacitance characteristics of pure double layer capacitor. During discharging curves, linear variations of the time dependence of the potential (-0.2 to 0.6 V) indicate electric double-layer capacitance, which rooted in the charge separation across the interface between the electrode and the electrolyte.
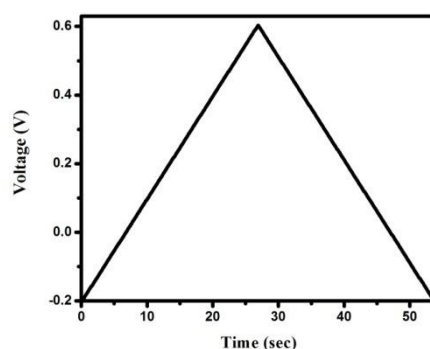

Fig5. *Charge-discharge curve of the V2O5 electrode in 1M K_2SO_4 electrolyte. The charging current was 2 mA/cm2.*

4. CONCLUSIONS

In summary, V_2O_5 thin films prepared by SILAR method onto FTO substrate The XRD measurements confirmed that the V_2O_5 was deposited in the form of polycrystalline. The SEM analysis showed that the substrate is well covered with different sizes fine elongated particles. The electrochemical study revealed that the SILAR deposited V_2O_5 electrode had a specific capacitance of 168 F/g at the scan rate 25 mV/s. Charge-discharge curves confirmed that the capacitance consisted from EDLC and pseududocapacitance. The SILAR method is low cost and promisingly used for the fabrication of nanostructured material for electrochemical supercapacitor

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