

Enhancing Electrochemical Performance of V_2O_5 Thin Film by using Ultrasonic Weltering

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Abstract: A vanadium pentoxide (V_2O_5) thin films were deposited cathodically on stainless steel substrate (SS304) using aqueous vanadium tri-chloride (VCl_3) as source of vanadium. Morphological, structural, physical properties were studied using SEM, XRD and contact angle test. Morphological study revealed that there is decrease in diameter and increase in depth of micro-pores which tends to increase in specific area of the film and thus enhancement in electrochemical performance. Eventually due to ultrasonic weltering V_2O_5 thin film became more viable as electrode in supercapacitor. Also retention of micro-pores facilitated effective electrolytic transport. The specific capacitance estimated for film before ultrasonic weltering was 333 F/g and it had been increased to 397 F/g after ultrasonic weltering.

Keywords: V_2O_5 thin film, Micro-pores, Cathodic Electrodeposition, Ultrasonic Weltering, Super-capacitive Performance.

I. Introduction

Substitution of fossil fuels with green and clean energy sources to reduce worst effects of climate change and greenhouse gases (CO_2 and NO_x) is the need of time. Use of renewable energy is the most viable option for sustainable development. Solar energy has tremendous potential as energy source; however its intermittent availability limits its uses. This problem can be overcome by use of effective and efficient energy storage systems [1]. So the researchers motivated to work on development of advanced energy storage gadgets so that energy can be stored as and when it is available and it can be used later as per requirement [2].

Electrochemical capacitors, popularly known as supercapacitors or ultra-capacitors, have acknowledged by scientist at globe as future energy storage device, owing to their potential to deliver high levels of electrical power, portable, cost effective and long cycle lifetimes and thus they are most suitable for high power applications [3-7]. Exploring inherent properties of electrochemically active nano-porous and nano-granular high specific area nano-scale material to enhance the specific capacitance value is one of the areas of research interest [8-11]. Main focus of research in last couple of decades is on to increase both the energy density and power density of supercapacitors. Nevertheless supercapacitors are considered as potential energy storage devices to supplement batteries and fuel cells [12]. Each of these has their own inherent distinctive technological benefits. Batteries and fuel cells have high energy densities, but slow power delivery. Supercapacitors technology is growing day by day with the interest of development of high power energy storage device [12]. Published reports showed that supercapacitor can deliver 10 kW/kg in few second and thus it is most suitable for actuator applications [12]. Nano-engineering which is related to tailoring the properties of material at nano-scale, is used to reform the configuration of supercapacitors [13, 14]. Thus supercapacitor is probably anticipated as future energy storage gadget [3].

Supercapacitors can bridge the gap between batteries and electrostatic capacitors. In present article, emphasize is given on to engineer the nano-porous and nano-granular structure via ultrasonically weltered cathodically deposited V_2O_5 thin film. How ultrasonic weltering is favoring the modification in structural, morphological, physical and electrochemical properties of V_2O_5 thin films were discussed at the length.

II. Experimental Details

The V_2O_5 thin films were deposited on stainless steel (SS304) substrate. Vanadium tri-chloride (VCl_3 ; 99+ Merck Germany) powder was used to prepare aqueous precursor solution. Before the deposition of V_2O_5 thin films, SS304 substrate were cleaned with detergent and then rinsed by double distilled water. It was then dried by passing warm air. For good quality V_2O_5 thin films; 0.2 M VCl_3 in HPLC water, with pH 1 was used. Two samples were prepared. Three electrodes system was used for the deposition of the film. Where working electrode was SS304, counter electrode was carbon rod and Saturated Calomel Electrode (SCE) as reference electrode. In both the cases cathodic electrodeposition was carried out for 15 minutes each. The substrates were

then rinsed in double distilled water and dried in air. The second sample was treated by passage of 30 kHz ultrasonic through the distilled water for 15 minutes.

The morphology and crystal structure of vanadium oxide thin films were investigated by scanning electron microscopy and X-ray diffraction techniques (XRD) respectively. Wettability of the film was checked with contact angle study. The electrochemical properties of V₂O₅ films were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge methods in 0.5 M K₂SO₄ aqueous solution. A three electrodes cell was used; SS304 substrate with V₂O₅ thin films as cathode and platinum electrode as an anode and SCE as reference electrode. Cathodic electrodeposition was carried out at potential of -1.2V at room temperature in potential window of -200 mV to 600 mV.

III. Results And Discussion

3.1 Film Formation Mechanism

The deposition mechanism for V₂O₅ film formation is described as follows. Due to passage of electric current vanadium metal ion (V⁺²) gets freed and deposited on the SS304 substrate. Subsequently film gets reacted with oxygen to form stable V₂O₅ configuration [15]. Eventually after nucleation, uniform and well adhered film is formed within 15 minutes.

3.2 Structural Analysis

Structural analysis of V₂O₅ thin films was carried out by XRD technique. Fig.1 (a, b) depicts XRD pattern of V₂O₅ thin film before and after ultrasonic weltering respectively. XRD pattern exhibits peaks of V₂O₅

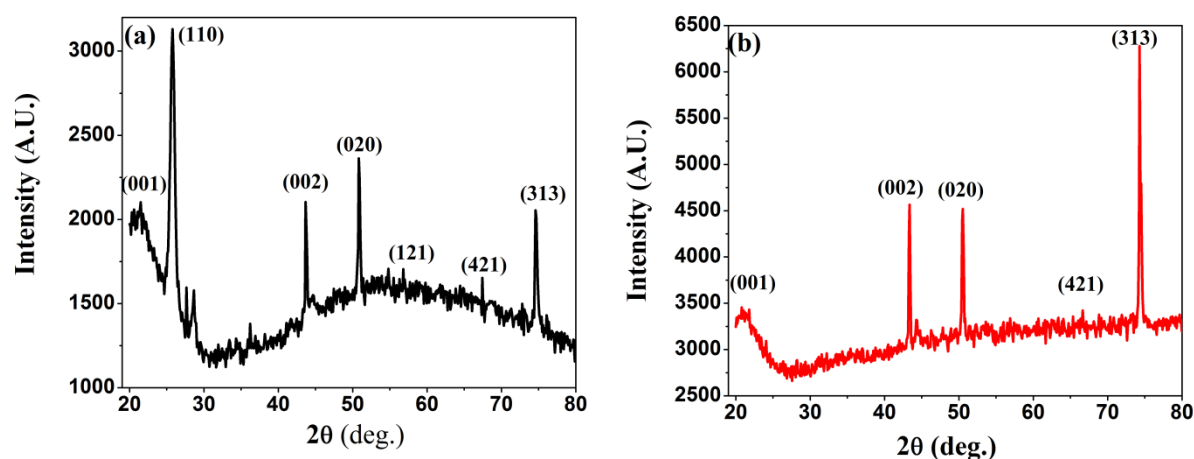


Fig.1 XRD pattern (a) before weltering (b) after weltering

With indices (001), (110), (002), (020), (421) and (313). It is well in correspondence with JCPDS card No 41-1426. As peaks are getting more sharpen and intense after ultrasonic weltering, film becomes more crystalline and there is noteworthy decrease in crystalline size. The peak (110) which was initially showed presence had almost diminished after ultrasonic weltering and this may be due to loss of loosely bonded grains on account of ultrasonic treatment.

3.3 Morphological Analysis

Fig.2 (a, b) shows the SEM image of cathodically deposited V₂O₅ thin film. Film surface shows micro porous spaces among the fine particles distributed almost uniformly on the substrate. Initial smooth morphology became rougher after ultrasonic weltering which is more suitable for super-capacitive application. It also shows increase in density of particles and well connected porous structure, which leads to perpendicular film growth and subsequently increase in specific area of the film. Rougher structure formed on account of ultrasonic treatment is prone to easy electrolyte transport which is useful for charge storage mechanism.

3.4 Contact Angle Measurement

Fig. 3(a, b) shows that water contact angle measurement images of V₂O₅ thin films before and after ultrasonic weltering respectively. Water contact angle before weltering was 51° and it decreased to 46° after weltering. Thus in both the cases nature of the film is hydrophilic however after ultrasonic weltering film has more wettability which helps in more adsorption of electrolytic ions when film is being used as electrode. Hence, hydrous transition metal oxides have been proposed to be promising electrodes materials for supercapacitors because their specific capacitance is usually very high.

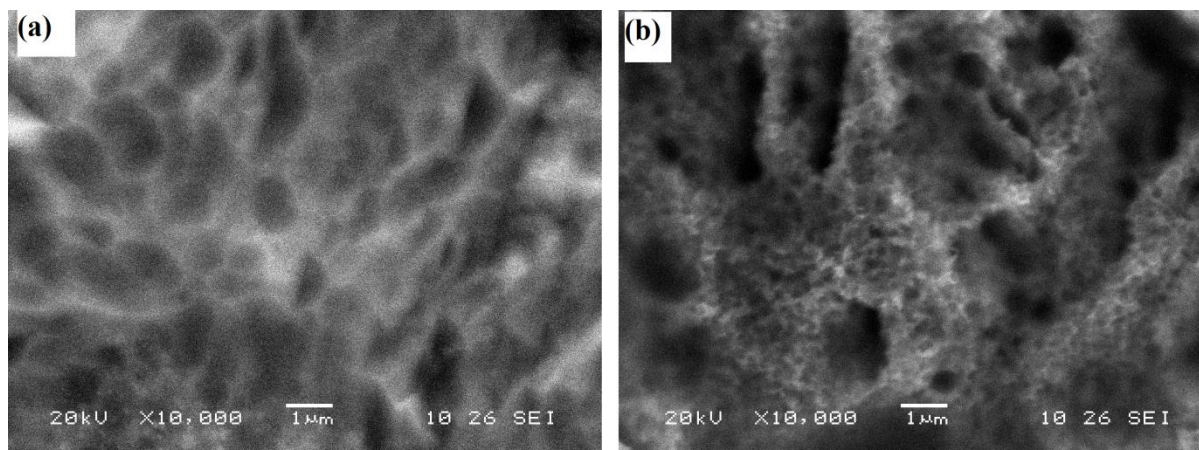


Fig. 2 SEM (a) before wetting (b) after wetting

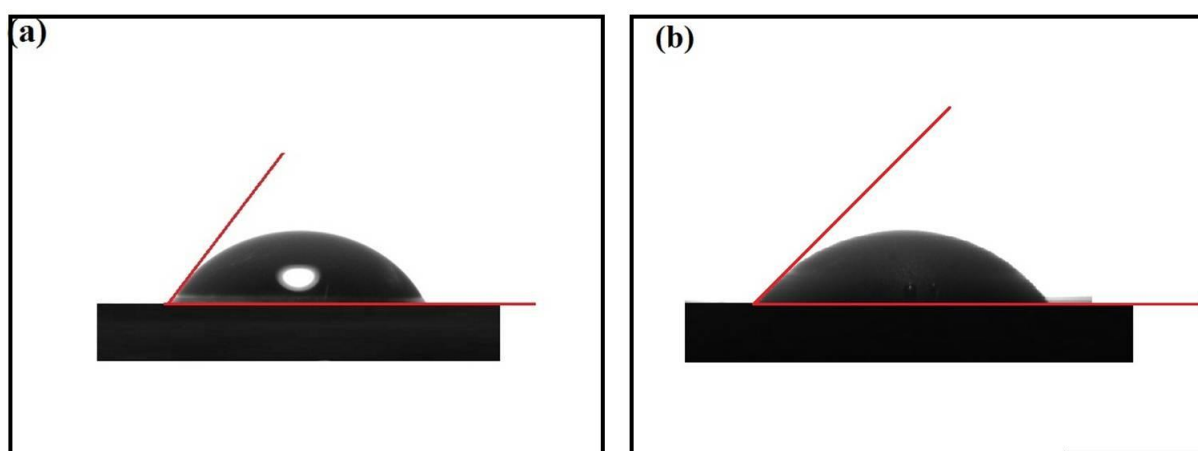


Fig.3 (a) Before Wetting $\theta = 51^\circ$ (b) After Wetting $\theta = 46^\circ$

3.5 Super-capacitive Performance of V_2O_5 Thin Films

Cyclic voltammetry (CV) was used to characterize the capacitive performances of the films as shown in Fig.4 (a, b). Oblong shape of the CV curve before wetting shows fast charge transfer and cations diffusion. Evidently, the symmetry and area of the CV curve and current density and thus the reversibility of the redox characteristics of ultrasonically wettered film was much upgraded over the film before the ultrasonic wettering, it may be possibly due to better crystallinity and rougher surface of the film [16]. Less distinct pair of anodic peak is seen at -0.06 V and 0.5 V and pair of cathodic peak at -0.04 V and 0.44 V which shows the reversibility. Though capacitance in both cases is primarily due to electric double layer (EDLC), weak pseudocapacitance is also observed in case of the film after wetting. This may be due to enhancement in ionic transport which is being taken place due to meso-porosity of the film reformed due to ultrasonic wetting. CV curves of V_2O_5 thin film electrode were recorded at a scan rate of 10 mV/s within the potential from -0.2 to + 0.6 V vs SCE in 0.5M K_2SO_4 electrolyte. The highest specific capacitance calculated was 397 F/g which was initially 333F/g for the film before wetting. This can be attributed, partially, to the high meso-porosity and the well connected, porous structure which is formed on account of ultrasonic wetting. Such structure aids reduction in mass-transfer resistances and ultimately electrolyte penetration and ion diffusion becomes easy [16, 17].The capacitance was calculated using following equation [18]

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

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 active weight (0.023 mg).

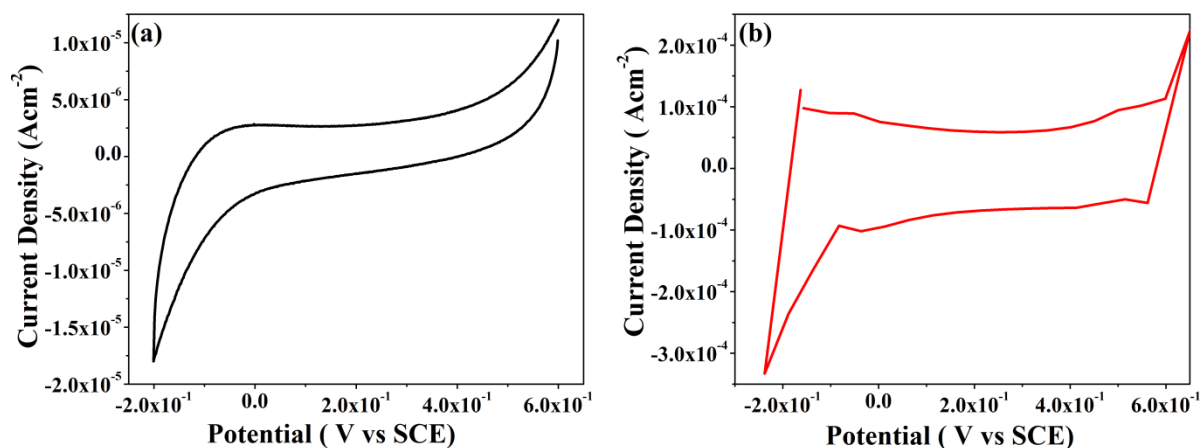


Fig.4 SEM (a) before weltering (b) after weltering

3.6 Charge-Discharge Cycling Performance Measurements

The constant current charge-discharge behavior of V_2O_5 electrode was studied by galvanometric charge-discharge method. Fig. 5 (a, b) represents the charge-discharge behavior of electrode at the current density of 0.1 mA/cm^2 . Symmetric charge discharge curves in both the cases confirm the capacitor behavior of the films. Potential is decreasing almost linearly with discharge time; it shows that capacitance is mainly due to EDLC. Rather longer charging and discharging time and smaller voltage drop reveals enhancement in specific capacitance and decrement in internal resistance for ultrasonically weltered film and it is probably because of formation of rougher surface which offers the less resistance to electrolyte transport [16]. This has well correspondence with the CV curves. The same can be evidenced from morphology, contact angle study and structural details. This proves the practical applicability of the ultrasonic weltering. Performance analysis of V_2O_5 thin film electrodes is summarized in following table 1.

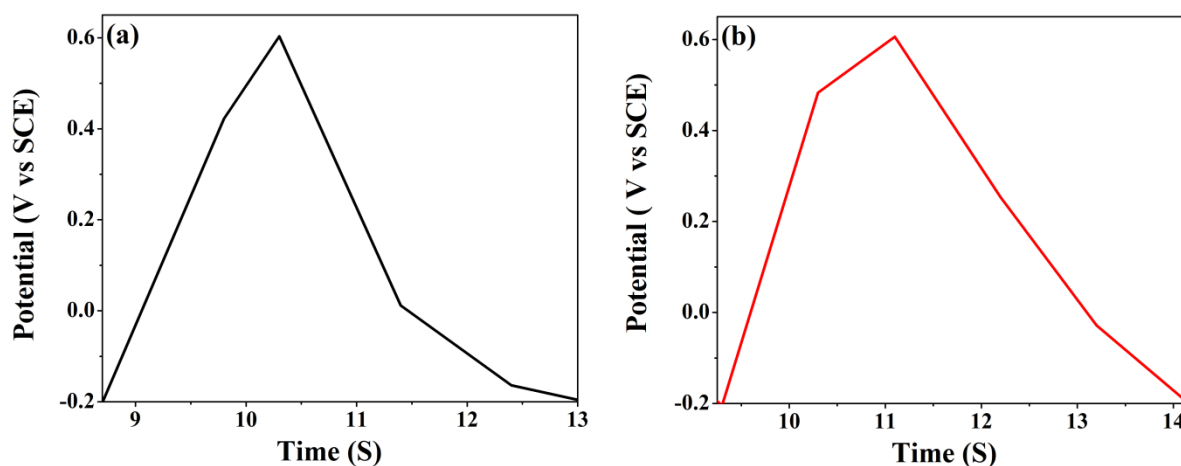


Fig.5 SEM (a) before weltering (b) after weltering

Table 1: Comparison of performance analysis of V_2O_5 thin film.

Sr. No.	Performance parameter	Before Weltering	After Weltering
1	Interfacial Capacitance (F/cm^2)	0.00765	0.00835
2	Specific Capacitance (F/g)	333	397
3	Energy Density (Wh/kg)	2.44	2.97
4	Power Density (kW/kg)	3.11	3.52

IV. Conclusion

In order to improve electrochemical performance of the V_2O_5 electrode, ultrasonically weltered film can stand better to match the practical applications. This is been proved with favorable changes occurred in structural, morphological, physical and electrochemical properties. In short, after ultrasonic weltering, there is increase in crystallinity and evolvement of rougher morphology which leads to easy electrolyte and ion transport. The specific capacitance increases from 333 F/g to 397 F/g on account of ultrasonic weltering; which shows 19% increase in the value. Similarly energy density increases from 2.44 Wh/kg to 2.97 Wh/kg. At the

same time power density has increment from 3.11 kW/kg to 3.52 kW/kg. However the coulombic efficiency in both films is not adequate and no appreciable increment is found in it after ultrasonic weltering. Finally due ultrasonic weltering V₂O₅ thin film is becoming more viable as electrode in supercapacitor.

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