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Effect of pyrolysis temperature on structural, morphological and electrochemical properties of vanadium oxide thin films

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ABSTRACT

Thin films of vanadium oxides (V_2O_5) were deposited on stainless steel substrates (SS) by using new improved automatic spray pyrolysis technique (SPT). Deposition was carried out via aqueous route at different pyrolytic temperatures varied from 473 K–773 K by the interval of 50 K. Structural, morphological and electrochemical properties of the deposited films were studied using X-ray diffractometer (XRD), Scanning electron microscopy (SEM), Cyclic voltammetry (CV), Charge-discharge test (CD) and impedance spectroscopy. Deposited samples show rough, mud like and dense morphology with agglomeration of nano grains. Deposit exhibits orthorhombic crystal structure. Sample deposited at 673 K shows highest values of specific capacitance 428.25 F/g at 5 mV/s scan rate, specific energy 18.73 Wh/kg, specific power 18 kW/kg, and columbic efficiency 74.42% in 1 M aqueous KCl. Electrochemical impedance spectroscopy reveals capacitive behavior for the samples. Sample shows 1.37 Ω combined internal resistance when scanned in the frequency range 1 mHz–1 MHz.

1. Introduction

During last two decades, considerable part of the industries have been involved in preparation of thin films and their applications such as protection, decoration, fabrication of sensors [1], optical switching devices [2] and electrochemical supercapacitors etc. [3–5]. Lot of study has been going on physical and electrochemical properties of thin films such as cyclic voltammetry, charge-discharge and impedance because of their wide range of applications in: industry, hybrid electric vehicles, laser, cellular phones, digital camera, etc. [6]. Electrochemical supercapacitor is viewed as novel kind of energy storage system in addition to batteries. Supercapacitor is mainly used to pick up the efficiency from power system of hybrid electric vehicles and other applications which supply large amount of current within shorter time [7]. Supercapacitor electrodes were prepared using number of materials and different deposition techniques [8,9]. Out of them transition metal oxides (TMOs) are more capable in the sense of low electrochemical series resistance (ESR), various oxidation states, long cycle life, porous nature etc. TMOs show different capacitive properties during electrochemical oxidation or reduction processes [10]. Most extensively studied transition metal oxides for ECs are hydrous ruthenium oxide [11], iridium oxide [12], vanadium oxide [13,14], chromium oxide [15] etc.

Among different transition metal oxides, cheap and abundantly available vanadium oxide is one of the promising electrode materials because of its large potential window, multi valences, high redox activity, 3D architecture and large stability [16]. Day and Sullivan reported V_2O_5 firstly as a cathode material for intercalation [17] because of its high specific energy and power density [18], reversible top tactic reaction with lithium [19] and good electrochemical activity and stability. Vanadium oxide (V_2O_5) is recognized as promising material for high specific capacitance and suitable layered crystal structures for ion intercalation [20,21]. Amorphous vanadium oxide exhibited around 300 F/g in KCl solution, as reported by Lee et al. [22,23], while V_2O_5 nanofibers prepared by electrospun method shows 190 F/g. The performance of the V_2O_5 nanofibers can be better using $LiClO_4$ electrolyte (250 F/g), those results were only archived at a low voltage scan rate of 5 mV/s. $H_2V_3O_8$ synthesized by a hydrothermal process showed good specific capacitance of 121 F/g but with a non-ideal CV [24].

However, some reports are available on the thin films of V_2O_5 deposited by using sol-gel [25], vacuum evaporation [26], sputtering [27], electron-beam evaporation [28], and spray pyrolysis [29] etc. Spray pyrolysis technique (SPT) offers good quality and adherence of the material on large surface area of the substrates by controlling preparative parameters like solution spray rate, different pyrolysis temperatures, substrate to nozzle distance, air flow

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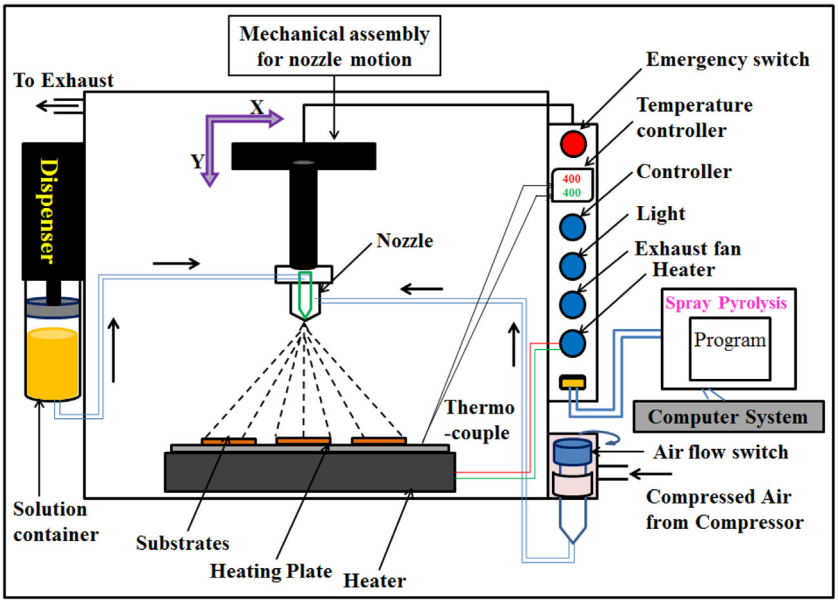

Fig. 1. Schematic view of automatic spray pyrolysis equipment.

Table 1
Spray deposition parameter.

Sr. No.	Parameters	Values
1	Nozzle to Substrate distance	30 cm
2	Spray Rate	10 ml/min
3	Air Flow Rate	10 l/min
4	Nozzle Movement in X and Y direction	70 mm and 90 mm
5	Substrate Temperature	473 K–773 K

rate etc. It also facilitates precise control over droplets. It offers several advantages over conventional deposition techniques for the control of stoichiometry and film structure. Spray process consists of atomization of the precursor solution and transportation towards the hot substrate by means of a gas stream. Within the hot zone above the substrate, the precursor undergoes thermal decomposition in the presence of oxygen resulting into formation of oxide thin film on the substrates [30]. The pyrolysis temperature impacting the surface modification as it is the pyrolysis decomposition process. The surface morphology, adherence and material phase of the film depend on the pyrolysis temperature [31]. Therefore present work focuses on the study of change in physical properties of the deposited samples with different pyrolysis temperature and effect of that physical change on electrochemical properties of the samples, to get the enhanced capacitive performance.

2. Experimental

2.1. Sample preparations

All the chemicals used for the preparation of V_2O_5 thin films are of analytical grade and used without further purification. Samples were prepared by using 0.05 M ammonium metavanadate (S. d. fine, chem.) as a precursor. Ammonium metavanadate was dissolved in 40 ml of double distilled water under vigorous stirring of mixture. Continuous stirring results yellowish solution which was further used for deposition of V_2O_5 samples. Sample deposition was carried on pre-heated stainless steel (SS, no-304) substrates at different pyrolysis temperatures varied from 473 K to 773 K by the interval of 50 K. Spray pyrolysis deposition parameters are tabulated in Table 1, schematic view of an automatic spray pyrolysis apparatus is shown in Fig. 1. The electrodes prepared at different pyrolysis temperatures 473, 523, 573, 623, 673, 723 and 773 K are nomenclatures as T_1, T_2, T_3, T_4, T_5, T_6 and T_7 respectively. Prepared samples were further used for different characterizations.

2.2. Characterization

Structural characterization of the deposited samples were carried out using X-ray diffractometer (Rigaku D/max2550Vb + 18 kw with CuKα 1 = 1.54056 Å), in the range of diffraction angle (2θ) between 10–90° by the step width of 0.2° and morphological evaluation is using by scanning electron microscope (ZEISS Model). Weight of the deposited material was measured by weight difference method using high accuracy (1×10^{-5} g) microbalance (Tapson's, Model-100S). The cyclic voltammetry, Charge-discharge and impedance measurements were carried out using computer controlled potentiostat (H CH 600D Spl. Electrochemical workstation) with standard three electrodes cell. Electrochemical supercapacitive measurements were made for 1 cm^2 surface area of the deposited thin films, for variable scan rate in the range of 0.055 V to −1.35 V potential window in 1 M KCl. Platinum wire was used as a counter electrode and saturated Ag/AgCl (in saturated KCl solution) electrode served as reference electrode. CV curves were used to calculate the specific capacitance (SC) using the relations 1 and 2. Charge-discharge behavior of samples was studied using galvanostatic charge-discharge for different current densities. Multi frequency impedance measurement was carried out in the frequency range 1 mHz–1 MHz using AC signal operating at different potentials. Impedance data was fitted with standard data to search an equivalent circuit using Zsimpwin software.

3. Results and discussion

3.1. Structural analysis

To determine the crystal structure, orientation of the planes and crystallite size, XRD analysis of the deposited samples were carried out. Fig. 2 shows the XRD patterns of the samples deposited on the SS substrates at different temperatures varied from 473 to 773 K (T_1–T_7 respectively) by the interval of 50 K. All XRD patterns exhibit crystalline nature of the material with an orthorhombic crystal structure. The XRD patterns show number of diffraction