Nanostructured NickelDopedVanadiumPentoxideThinFilms with Improved Surface Morphology and Electric Conductivityfor Supercapacitor Applications

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Abstract-There is great concern of surface morphology and electricconductivity of materials to be as righteous electrode for supercapacitor application. Thin film electrodes of nickel (Ni)doped vanadium pentoxide (V_2O_5) at different doping proportions(0 wt.%, 2.5 wt.% and 5 wt.%) were prepared on stainless steel (SS304) substrate using electrodeposition with intention to improve ion diffusion kinetics and electric conductivity.Changes in the nature of these film surfaces have been tracked with X-ray diffractometer (XRD), scanning electron microscope (SEM) and contact angle measurements. The proportion of nickel doping was being quantified by using energy dispersive spectrum (EDS). The electrochemical behavior has been investigated through cyclic voltammetry. The porosity, pore density and subsequently electric conductivity are found to be increased as Ni doping increases. Among threefilms, the film with 5 wt.%of Niexhibited the maximum specific capacitance of412 F/g.It is also seen that the maximum peak current was shown by the capacitor cell for5 wt.%of Ni doped V_2O_5electrode.It infers thatNi doped V_2O_5thin film is viable as electrode in supercapacitor.

Key words: Thin film electrode,doping, electrodeposition, electrochemical behavior, specific capacitance, supercapacitor.

1. INTRODUCTION

Nanostructured vanadium oxides thin films and their composites with other transition oxides have attracted researchers because of their special physicochemical behavior and found pertinent in sensors, resonators, electrodes of supercapacitors and batteries [1-7]. However, their applications are limited due to low discharge voltage, slow diffusion kinetics of ions and low electric conductivity[8]. The research is going on in developing electrode with high specific area, low ohmic resistance and enhancing the specific capacitance with assistance of faradic redox reaction. As of now, carbon/carbon base materials, conducting polymers and transition metal oxides have been used as electrode materials [9-11]. Transition metal oxides have potential as electrode material due to their several oxidation states and reasonably good electric conductivity. Ruthenium oxide (RuO_2), Manganese oxide (MnO_2), Nickel oxide (NiO) and vanadium oxide (V_2O_5) are some of the transition metal oxides studied rigorously to achieve desirable level of specific capacitance, energy density and power density [12-15]. Moreover,doped metal oxides are being used to enhance energy density, charge storage capacity, power density, specific capacitance, ionic transport (electric conductivity) and reversibility. Nevertheless attempts were made to optimize the level of doping to make these materialsmore suitable as electrode. Vanadium pentoxidethin film with nickel as dopant hasproved as viable electrode material [7].

Vanadium oxide possesses oxidation states from V^{+2} to V^{+5} with its several oxide forms like VO, V_2O_3, V_2O_5.Of these oxides, V_2O_5 exhibits good reversibility, prolonged cyclability and chemical stability but it has low electric conductivity due to its semiconducting nature [16, 17].Numerous attempts were made to increase conductivity of $V_2O_5$by doping it with sometransition metal oxides.Amongseveral dopants like nickel,manganese, tantalum, cobalt, copper, iron, etc; nickel was found to be better as itis more compatible in stoichiometry with vanadium,havinggood electric conductivity and pseudo-capacitive behavior [18]. In present attempt, nickel (Ni) doped vanadium pentoxide (V_2O_5) thin filmswere electrodeposited on SS304at three different doping proportions (0 wt. %, 2.5 wt.% and 5 wt.%) to get the better electric conductivity and charge storage material. The effects of Ni doping on the structural, morphological, physical and electrochemical behavior of V_2O_5 film have been investigated and the inferences so obtained are reported.

2. EXPERIMENTAL DETAILS:

Ni doped V_2O_5 films were deposited on SS304 substrateby electrodeposition at constant potential of -1.2V using bath of analytical grade vanadium tri-chloride (VCl_3) and nickel chloride ($NiCl_2$). The pH and molarities of deposition bath were maintained at 2 and 0.1M respectively. Different weight percentage (0%, 2.5%, 5%) of nickel concentration were doped. For example, for 5wt.%, bath was containing 25 ml of VCl_3 and 1.25 ml $NiCl_2$.Electrodeposition was carried out for 15 minutes in each case and films were rinsed under distilled water and dried by passing warm air.Structural, morphological and physical properties were studied using XRD, SEM and contact angle measurement respectively. For investigation of electrochemical properties, Ni doped V_2O_5 films were used as working electrode, platinum spiral wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. Using 0.5M potassium-sulphate (K_2SO_4) aqueous electrolyte, electrochemical measurements were done by using cyclic voltammogram (CV) in potential window of -0.2V to 0.6 V at voltage scan rate of 5 mV/s

3. RESULTS AND DISCUSSION:

3.1 Structural Analysis:

Fig. 1(a-c) shows, XRD of the Ni doped V_2O_5 thin films. The intensities of characteristic peaks are found to be gradually diminishing as concentration of nickel increases from 0 wt.% to 5 wt.%. The characteristic peaks are well in correspondence with JCPDS card No. 41-1426 and 47-1049.Peaks with indices (001), (121), (002) and (313) are corresponding to orthorhombic V_2O_5 structure.The XRD patterns suggest that further increment in nickel concentrationmaylead toamorphousnature of the film [19]. It has been proved that amorphous nature of the film is more suitable for developing high specific area electrode material [11].

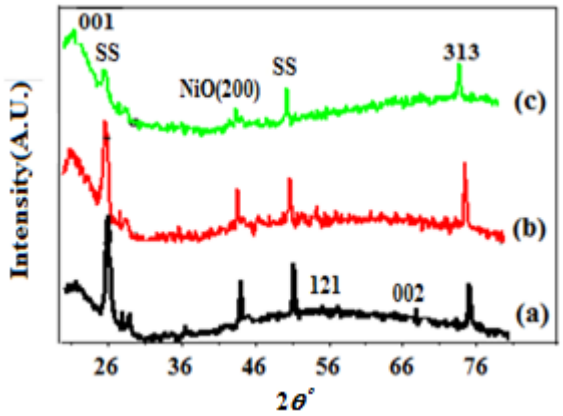

Fig.1: XRD Patterns for films with (a) 0 wt. % (b) 2.5 wt. % and (c) 5 wt. % of Ni doping

3.2 Morphological Analysis:

Fig. 2 (a-c) shows SEM images of Ni doped V_2O_5 thin films for different concentrations of nickel at ×20,000 magnification. These films show the morphological changes with increase in concentration.Essentially all three SEM images show the interconnected pores. It is observed that pore size gradually becoming uniform and smallerhence theporedensity increasing with increase in nickel concentration; which eventually results into enhancement of surface to volume ratio.The film with 5 wt.%of Ni doping shows uniform size tubular structure with high degree of pore density.It may be on account of stoichiometric compatibility of nickelwith vanadium pentoxide that ultimately results into reorganization of crystallites hence the uniform pores size distribution. Such morphology is more pronounced for ionic transport in electrochemical system.Average size of the pores reside in the filmwith 5 wt.% doping of nickel is about 150 nm, which was about 350 nm for pure V_2O_5 film. Inset SEM images portray at ×500 magnification. EDS show increase in nickel wt.% as doping level increases.

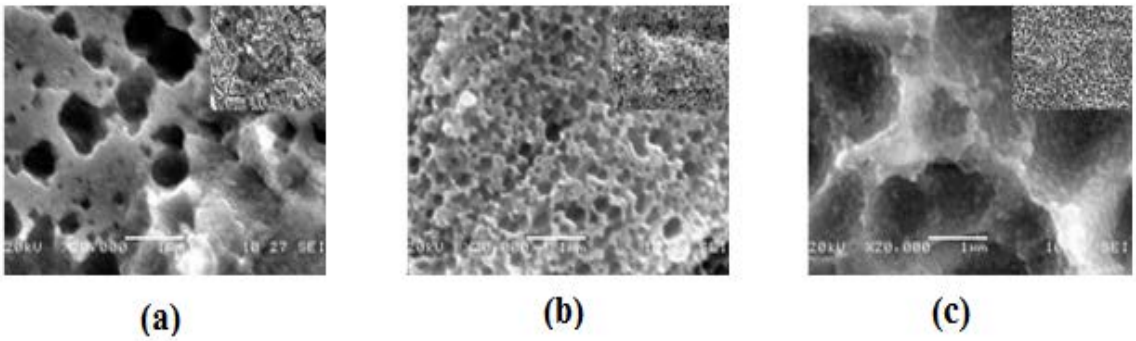

Fig.2:SEM images for films with(a) 0% (b) 2.5 % and (c) 5% Ni doping

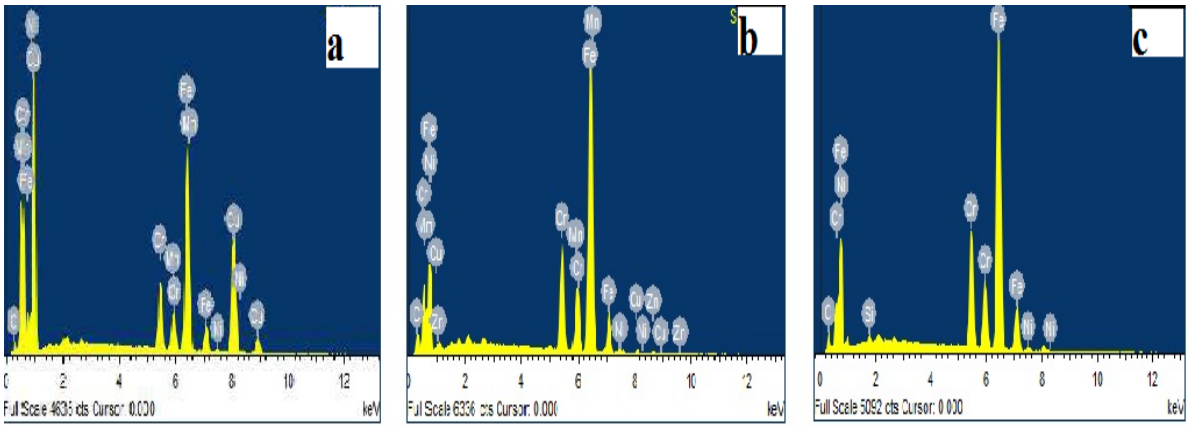

Fig.3: EDSfor films with(a) 0% (b) 2.5 % and (c) 5% Ni doping

Table 1: Nickel weight % observed for different nickel doping levels

Sr. No.	Nickel doping level (wt.%)	Nickel Weight % observed in the film	Nickel Atomic % in the film
1	0.0	0.51	0.32
2	2.5	0.72	0.40
3	5.0	1.10	0.61

Fig. 4 (a-c) depicts the contact angle measurement which reveals physical characteristics of the film surfaces. Contact angles for 0 wt.% , 2.5 wt.% doped and 5 wt.% doped nickel are 75°, 52° and 45° respectively and as water contact angles with film are acute, all three films exhibited hydrophilic nature. Thus one could clearly observe that wettability goes on increasing as nickel wt.% in the film increases. In this way the porosity, hence the effective surface area of the film goes on increasing as nickel wt.% increases. Such type of surface is essential for the electrode material to yield the high specific capacitance. This increase in wettability is in well go withthe results already obtained through XRD and SEM studies.

3.3. Contact Angle Measurement:

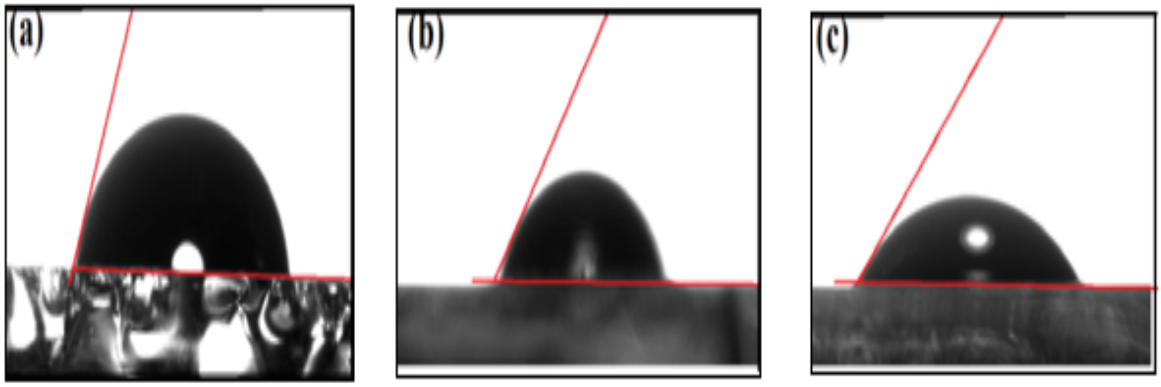

Fig.4: Contact Angles for films with (a) 0% (b) 2.5 % and (c) 5% Ni doping

3.4 Electrochemical Behavior:

3.4.1 Cyclic Voltametry:

Fig.5 (a-c) depicts the cyclicvoltammograms(CVs) of Ni doped V_2O_5 thin films (for 0 wt.%, 2.5 wt.% and 5 wt.% of nickel doping). While recording CVs Ni doped V_2O_5 films were used as working electrode, SCE as reference electrode and platinum spiral wire as counter electrode.Aqueous 0.5 M K_2SO_4 solution was used as electrolyte. CVs show that current density increases with respect to increase in nickel concentration. The escalation of current density for 5 wt.% nickel concentration is primarily because of highpore density formed by substitution of Ni^{+2} ions which facilitate the easy ion transport and finally enhancement in specific capacitance. The same is evidenced from SEM images and contact angle measurements [7, 16].The specific capacitance is calculated using following equation [20].

$$C_s = \frac{I}{m(dv/dt)} \qquad (1)$$

Where 'C_s' is specific capacitance in F/g, 'm' is mass of active film material measured by using weight gain method. 'I' is average current during anodic and cathodic scan and 'dv/dt' is the scan rate. At scan rate of 5 mV/s the highest specific capacitancewas observed for film with 5 wt.% nickel doping and it is 412 F/g . For pure vanadium pentoxide film it was 333 F/g [21].

Fig.6 shows the graph of peak current verses scan rate for different Ni doping wt.%. It is observed that peak current increases with increase in the doping level and it is obvious since nickel is good conductor of electricity. However, for 5 wt.% doping after scan rate of 25 mV/s

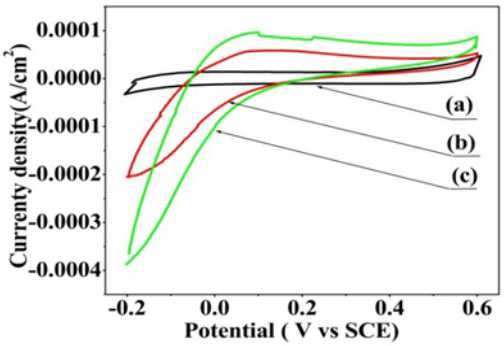

Fig.5: Cyclic voltammograms for films with (a) 0% (b) 2.5% and (c) 5% Ni doping

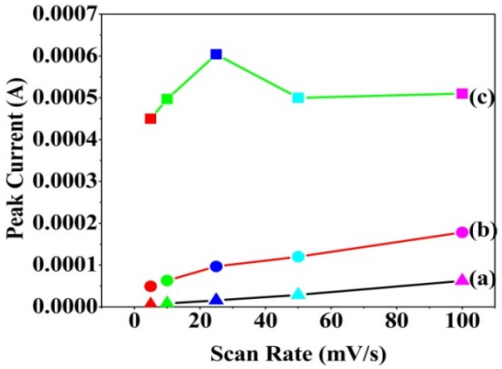

Fig.6: Variation of Peak currents with Scan rates for (a)0 wt.% (b) 2.5 wt.% and (c) 5 wt.% Ni doping

peak current starts decreasing and it may be due to the fact that at high scan rates all the avenues of porous structure may not be utilized. The same can also be confirmed from the CVs which revealthat the increase in current density is on account of doping of nickel. This also can be confirmed from SEM which shows more favorable morphology for ion transport consequently, there is escalation in the conductivity of the electrode material.The values of Specific capacitance and peak currentof the cell with electrodes of different levels of nickel doping are summarized in Table 2.

Table 2: Specific Capacitance, Peak Current

Ni Doping (wt.%)	Scan rate (mV/s)	Specific Capacitance (F/g)	Peak Current (A/cm^{-2})
0.0	5	333	1.70×10^{-05}
2.5	5	369	6.05×10^{-05}
5.0	5	412	9.92×10^{-05}

4. CONCLUSION:

Highly porous Ni doped V_2O_5 thin film with larger pore density was prepared at 5 wt.%of nickel doping and showed maximum specific capacitance 412 F/g. This film exhibited the best ion transport kinetics on accounts of its larger specific area which facilitates easy intercalation and de-intercalation.It seen that electric conductivity increases with increase in nickel doping. The cell with 5 wt.% of Ni doped electrode showedmaximum peak current of 99.2 µA and thus nickel doping made film material more conductive which is very important to escalate specific capacitance of the supercapacitor. Among three different doping levels 5 wt.%of nickel doping exhibited 23% growth in specific capacitance value as compared to the pure

V_2O_5 film. In this way Ni doping partially conquer the limitations of slow diffusion kinetics of ions and low electric conductivity;which finally returnedaswell-intentionedsupercapacitive behavior. Thus Ni doped V_2O_5 thin film electrode is supposed to be better option for supercapacitor application.

References:

[1] Karimov KS, Mahroof-Tahir M, Saleem M, Tariq SaeedChani M, and Khan Niaz1 A, J Semiconductors(2015)36(7):073004-1-073004-5
[2] Joyeeta Nag, Judson D,Ryckman, Michael T,Hertkorn ChoiBoK, Haglund RF (2010)JProc. SPIE 7597Doi:10.1117/12.843866
[3] Dong Shu, CuijuanLv, Fukui Cheng, Chun He, Yang Kun, Junmin Nan, Long Lu (2013) Int. J. Electrochem. Sci.8: 1209 – 1225.
[4] Sang-Ho Cha, (2015) J NanomaterialsID 207525:1-12
[5] Subba Reddy ChV, Kyung-Il Park, Sun-il Mho, In-Hyeong Yeo, Su-Moon Park (2008) Bull.KoreanChem. Soc29(10):2061-2064.
[6] Wang Y, CaoG (2006) Chem. Mater. 18:2787-2804.
[7] Kannam AM, ManthiramA. (2003) Solid State Ionics159:265-271.
[8] Subba ReddyChV, Wei J, Yao ZQ, Rong DZ, Chen W, Mho SI, Kalluru RR(2007) J. Power Sources 166:144-152.
[9] Lee HY, Goodenough JB (1999) J Solid State Chem.148:81-84.
[10] Sarvanakumar B, Purushothaman KK, Murlidharan G(2012) ACS Appl. Mater. Interfaces 4(9):4484-4490.
[11] Kandalkar SG, Gunjkar JL, Lokhande CD(2008) Applied Surface Science254: 5540-5544
[12] Liang YY, Li HH, Zhang XG(2007) J Power Sources 173, 599-605.
[13] Pang SC, Anderson MA, Chapman TW (2000) JElectrochem, Soc147: 444-450
[14] Xing W, Li F, Yan Z, Lu GQ (2004) J Power Sources134: 324-330
[15] Lao ZJ,Konstantinov K, Tournaire Y, Wang GX, Liu HK(2006) ElectrochemCommun162: 1451-1454.
[16] Kumar A, Singh P, Kulkarni N, Kaur D(2008) Thin Solid Films516: 912-918.
[17] Wang Y, Cao G, (2006) Chem. Mater. 18: 2787-2804
[18] Inamdar AI, Kim YS, Pawar SM, Kim JH, (2011) J Power Sources196: 2393-2397
[19] Jaylakshmi K,Vijayakumar S,Muralidharan G,Purushothaman KK, (2013) Material Research Bulletin48: 2578-2582
[20] Zang J, Kong LB,Cai JJ, Li H, Luo YC, Kang L, (2010) MicroporMesopor, Mater132:154-162
[21] Sutar MA,Pawar MS,Rendale MK, Kandalkar SG, (2015) IOSR -JAP 7(6): 41-45