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Sol-gel Synthesis and Supercapacitive Characterization of Bismuth Vanadate

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In this work, supercapacitive characterizations of the bismuth vanadate ($BiVO_4$) nanoparticles is studied. $BiVO_4$ is synthesized by the sol-gel method. The single phase of $BiVO_4$ powder obeys monoclinic crystal structure as confirmed from X-ray diffraction. The electrodes of $BiVO_4$ powder were prepared by doctor blade method. Electrochemical characterizations are carried by using cyclic voltammetry gives the maximum specific capacitance 494.1 F/gm at 5 mV/s scan rate. The maximum energy density, power density and efficiency for the optimized electrode is 435 Wh/kg, 1.69 kW/kg and 88.67 %, respectively. According to the electrochemical impedance spectroscopy curve of the optimized sample, the internal resistance of the $BiVO_4$ electrode was 0.12 Ω.

Keywords: Supercapacitor, Sol-gel synthesis, Bismuth vanadate, Cyclic voltammetry, Doctor blade.

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1. INTRODUCTION

The electrochemical supercapacitor (ES) exhibits charge storage mechanism due to its much more advantages such as high power, long life cycles, flexible operating temperature, environmental friendliness and safety [1]. These advantages of electrochemical supercapacitor (ES) play an important role in applications such as electric vehicles, electric hybrid vehicles, digital communication devices, digital cameras, mobile phones. In near future, ES will be considered as a key technology because of its popularity for energy storage systems. Recently, electrochemical supercapacitor (ES) contains both electric double layer supercapacitor (EDLS) and pseudo-supercapacitor has become the subject of interest for electro chemical analysis. Supercapacitors operating in parallel with the rechargeable batteries are being used in electrical storage devices. This can be made possible by using suitable electrode in the supercapacitor. The major materials that have been studied for the supercapacitor electrodes are carbon [2], transition metal oxides including RuO_2 [3], NiO [4], Fe_2O_3 [5, 6], Mn_3O_4 [7], Co_3O_4 [8], TiO_2 [9]. According to recent literature, the $BiVO_4$ is an easily available, low-cost, eco-friendly material exhibit pseudocapacitive behavior [10]. $BiVO_4$ powder was synthesized by various methods such as hydrothermal [11], sol-gel [12], etc. Among these, sol-gel synthesis is a low-cost chemical growth method in all of above discussed techniques.

Hence, in the present investigation $BiVO_4$ powder is synthesized by sol-gel method and was deposited on the stainless steel substrates by doctor blade method. The prepared electrodes were thermally treated to attain the desired conditions. The thermally treated electrodes were characterized to analyze specific capacitance, specific energy, specific power and efficiency.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

In this work, bismuth nitrate [$Bi(NO_3)_3.5H_2O$] was used as the source of bismuth and ammonium metavanadate [NH_4VO_3] was used as the source of vanadium [12] in the synthesis. The experimental procedure for preparing bismuth vanadate ($BiVO_4$) powder by the sol-gel method is schematically shown in flow chart (Fig. 1).

Bismuth nitrate [$Bi(NO_3)_3.5H_2O$] and ammonium metavanadate [NH_4VO_3] were used as the starting precursors with molar ratios 1:1. Solution A: 0.06 M bismuth nitrate [$Bi(NO_3)_3.5H_2O$] dissolved in 25 ml of 4 M nitric acid (HNO_3) and solution B: 0.06 M ammonium metavanadate [NH_4VO_3] dissolved in 25 ml of 4 M ammonium hydroxide (NH_4OH) were mixed together well by stirring for 30 min. Resultant solution is found yellow in color. In that solution, 50 ml of ethanol (C_2H_5OH) was added and heated at 70 °C with stirring for 1 h. Sol get changed to the yellow gel after addition of 25 ml of de-ionized water and 2.5 ml of 1 M acetic acid (CH_3COOH). Finally, the yellow gel was dried in oven at 100 °C for 48 h and further calcined at 400 °C for 2 h [12].

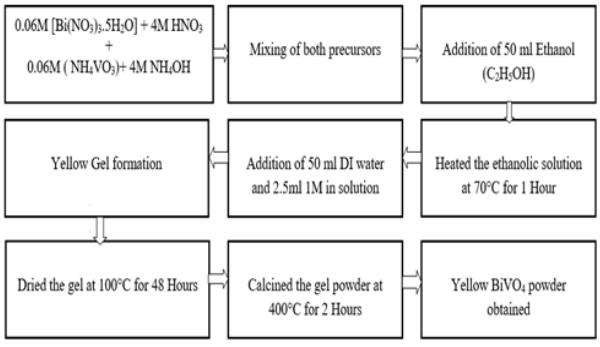

Fig. 1 – Experimental flow-chart

3. ELECTRODE PREPARATION

Stainless steel (SS) strips (304 grades) of dimension 1 cm×5 cm were used as conducting substrate material. The SS strips were mirror polished using polish paper (grade 400) to get the rough finish. To allow the proper

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deposition of the electrode material by adsorption, strips were ultrasonicated for 20 min to make them free from the dirt, oil, strains, etc. First of all, mixture of one gm of bismuth vanadate prepared in the synthesis, carbon black as a conducting powder and polyvinyl diflouride (PVDF) in 8:1:1 respective ratios was prepared. Few drops of NMP was used as a solvent to prepare the slurry. PVDF used in the electrode preparation acts as a binder. Then prepared slurry using above mixture was spread onto the SS substrates using doctor blade method [13]. The prepared samples were kept in the furnace at 100 °C for 8 h.

4. CHARACTERIZATIONS

X-ray diffraction analysis (XRD) was made to determine structural characterization of synthesized powder sample using diffractometer in the range of diffraction angle (2θ) 10°-90°. Weight of the deposited sample was measured by microbalance (Tapson-100TS, USA) with least count 10^{-5} gm [14]. Electrochemical characterization of the deposited electrodes were carried out using electrochemical analyzer (CHI6112D, USA) with standard three electrodes cell in which $BiVO_4$ electrode was a working electrode, platinum electrode was a counter electrode and saturated Ag/AgCl was a reference electrode. In electrochemical characterization, Na_2SO_4 was used as an electrolyte.

5. RESULTS AND DISCUSSION

5.1 Structural Elucidation

Fig. 2 shows XRD pattern of $BiVO_4$ obtained from sol-gel synthesis. XRD pattern of the prepared electrode exhibits the peaks at (2θ) 15.1°, 18.6°, 19.0°, 28.6°, 30.5°, 34.5°, 39.6°, 42.3°, 46.7°, 50.3°, 53.4° respectively. The observed '*d*' values properly match with standard '*d*' values taken from the JCPDS data card No. 83-1697 for $BiVO_4$. The XRD pattern clearly indicates the formation of monoclinic single-phase crystal structure. The particle size was determined from XRD pattern using the Scherer's relation as follows:

$$D = K\lambda/(\beta\cos\theta), \qquad (1)$$

where D is the grain size, K is the shape factor (0.9), β is the full width half maxima and θ is the angle of diffraction. The comparison of standard and observed '*d*' values tabulated in Table 1.

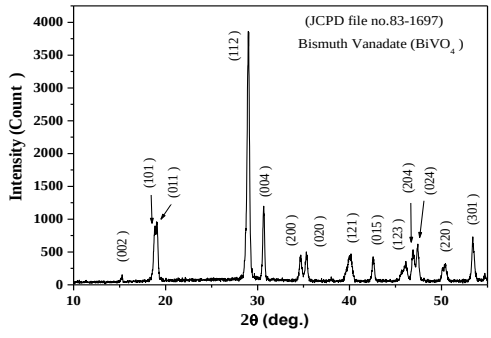

Fig. 2 – XRD pattern of $BiVO_4$

5.2 Cyclic Voltammetric Study

Prepared sample electrode was subjected to the cyclic voltammetry (CV) analysis at different scan rates from 2 to 100 mVS^{-1} in 1 M Na_2SO_4 electrolyte is shown in Fig. 2. Obtained curves clearly indicate the mix-pseudo capacitive behavior of the sample. The CV curves shows peaks at the respective anodic and cathodic sweeps indicating reversible nature of the electrodes. It was observed that the area under CV curve and hence the current integral goes on increasing with the increasing scan rate, but the increase in area is not in the expected proportion to the scan rate, hence the SC value goes on decreasing with increase in the potential scan rate indicating reversible nature of the electrode.

Table 1 – Comparison of observed and standard '*d*' values

2θ°	*d* (Å) (standard)	*d* (Å) (observed)	(*h k l*)
15.1°	5.84	5.68	(0 0 2)
18.6°	4.74	4.74	(1 0 1)
19.0°	4.66	4.66	(0 1 1)
28.6°	3.09	3.08	(1 1 2)
30.5°	2.92	2.92	(0 0 4)
34.5°	2.59	2.59	(2 0 0)
35.5°	2.54	2.54	(0 2 0)
40.1°	2.23	2.24	(1 2 1)
42.6°	2.12	2.13	(0 1 5)
46.1°	1.96	1.97	(1 2 3)
46.8°	1.94	1.93	(2 0 4)
47.4°	1.91	1.91	(0 2 4)
50.4°	1.81	1.81	(2 2 0)
53.4°	1.71	1.71	(3 0 1)

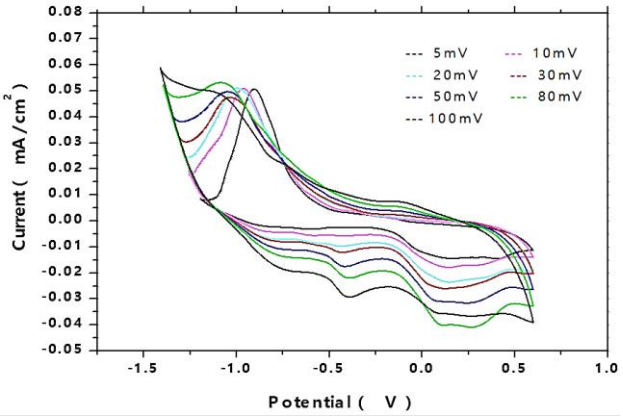

Fig. 3 – CV curves at different scan rates

Specific capacitance (SC) of the prepared electrode from the CV curves was calculated using following formula:

$$\mathrm{SC} = \frac{C}{W} = \frac{\int_{V1}^{V2} Idv}{W\frac{dv}{dt}}, \qquad (2)$$

where V_1 and V_2 are the potential limits, the quantity in the integration indicates the current integral with potential, V is the potential window, and $\frac{dv}{dt}$ is the potential scan rate.The variations in calculated values of SC are given in the Table 2.

5.3 Charge Discharge Curve

Fig. 3 shows charge-discharge study within the potential window – 1.4 to 0.6 V in 1 M Na_2SO_4 for different current densities 2, 4 and 6 mA. Here, prepared electrode shows that with increase in current density charge-discharge time decreases. The non-symmetrical discharging behavior was observed at all current densities. Discharging curve exhibits abrupt change in potential due to change in resistance of the electrode and a capacitive component related to the potential change at 6 mA. At this current density electrode shows nearly symmetric behavior [15].

The specific energy (SE), specific power (SP) and efficiency (η %) were calculated by using the formulae:

$$\text{Specific Energy (SE)} = \frac{VXI(d)\,Xt(d)}{W}, \quad (2)$$

$$\text{Specific Power (SP)} = \frac{VXI(d)}{W}, \quad (3)$$

Table 2 – Specific capacitance at different scan rates

Scan rate (mVS^{-1})	Specific capacitance (Fgm^{-1})
5	494.1
10	325.1
20	202.1
30	144.5
50	104.9
100	66.4

Table 3 – SE, SP and Columbic efficiency at different current densities

Current density, mA/cm^2	Specific energy (SE), Wh/kg	Specific power (SP), kW/kg	Efficiency η (%)
0.2	435.30	0.53	88.67
0.4	255.60	1.08	64.54
0.6	104.20	1.69	82.21

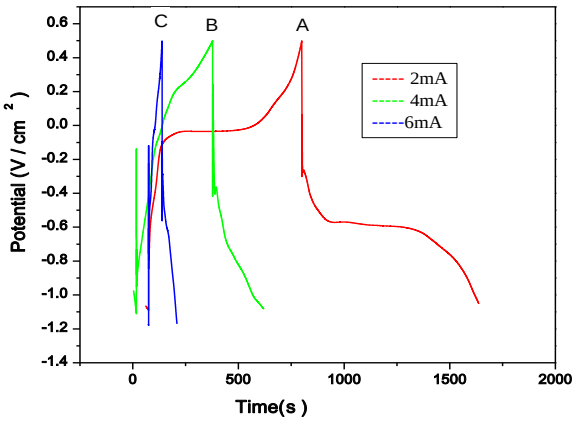

Fig. 4 – Charge-discharge curve of $BiVO_4$

$$\text{Efficiency } (\eta\,\%) = \frac{t(d)}{t(c)}\,X\,100. \quad (4)$$

The calculated specific energy, specific power and efficiency at different current densities are given in Table 3.

5.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were used to search an internal resistance of the electrode [16]. Fig. 4 shows the EIS curve between real and imaginary impedance values in the frequency range 1 mHz to 1 MHz. The observed internal resistance of the $BiVO_4$ electrode was 0.12 Ohm. The result indicates very small resistance is available possess good electrochemical performance of the $BiVO_4$ samples to be used as the supercapacitor.

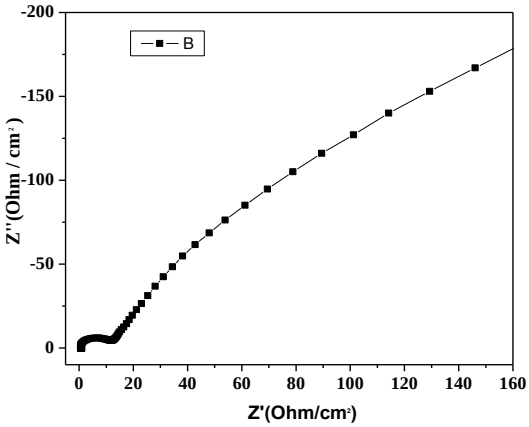

Fig. 5 – EIS curve of $BiVO_4$

6. CONCLUSIONS

The $BiVO_4$ synthesis is possible by using sol-gel method. The single phase of $BiVO_4$ powder has been obtained with monoclinic crystal structure. The electrodes of $BiVO_4$ exhibits good electrochemical performance with the maximum specific capacitance of 494.1 F/gm at 5 mV/s scan rate in 1 M Na_2SO_4 electrolyte. The maximum energy density, power density and efficiency for the optimized electrode is 435 Wh/kg, 1.69 kW/kg and 88.67 %, respectively. Also, the same electrode possess very small internal resistance of 0.12 Ω. These results conclude that the $BiVO_4$ is one of the well suited electrode materials for the electrochemical supercapacitor application.

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