

High Performance Battery type Bismuth Vanadate Electrodes for Supercapacitors

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Abstract

An economically viable solution-based approach was employed for fabrication of nanostructured BiVO₄. The evolution of physiochemical and electrochemical features with respect to the synthesis temperature was analysed using structural, morphological and electrochemical analysis. When utilized as a supercapacitor electrode, in 3-electrode setup, the BiVO₄ exhibited highly impressive specific capacity of 1864 Cg⁻¹ at a high current density with battery type behaviour. Also, this attractive material exhibits very lesser charge transfer resistance of 4 ohm, which is highly beneficial for performing charge / discharge at higher current rates. Further, this material retained 84% of its initial capacity after 3000 repeated charge discharge cycles. The behaviour of the same electrode material can be either battery-like or pseudocapacitive, depending on its shape, size, and intercalation ion. Although it can be challenging to draw a precise border, the range of b values between 0.5 and 1.0 denotes a "transition" area between pseudocapacitive and battery-type materials. It is important to note that when the reaction temperature rises from 140°C to 160°C, 180°C, and 200 °C, more electroactive sites emerge, leading to improved

electrochemical performance. The battery type behavior is dominated as the reaction temperature is increased from 140 °C and it is consistent with the voltogram analysis.

Key words: Energy storage; Bismuth vanadate; Hydrothermal; Battery type electrode

1. Introduction

The rudiments in making performance optimized supercapacitors requires careful selection of electrode materials to combat the high-power density and low energy density perplexities [1]. An economically viable solution-based approach was employed for fabrication of nanostructured BiVO₄ to exhibit coherent high efficiency and effectiveness. The new pinnacle in the electrochemical energy storage devices are the battery type materials in alternate to lithium. Amidst them, Bismuth Vanadate (BiVO₄) is a mixed metal oxide semiconductor [2,3]. This compendious work reviews the investigation of multinary oxide vanadate (BiVO₄) a super abundant inorganic material as an electrode material for a super conductor [4,5]. Ternary metal sulphides, oxides, phosphides were reported to perform excellent electro chemical characteristics in literature.[6,7]. Surface area and reactivity of layered transition metal oxides are constantly stimulating and surprising each other [8,9]. d-block elements show a range of oxidation states due to the comparatively small energy difference between the (n-1) d and n s orbitals. When orbitals participate in bond formation at two different energy levels, multiple oxidation states might arise [10]. The novelty of the work lies in the emanation of battery type electrode material which is only little studied. The current investigation *apprehend* the importance of material as a negative electrode [11]. The energy density of the device was greatly increased by creating a hybrid supercapacitor by combining the electrodes of a battery and a supercapacitor in one unit.

The ground-breaking discovery of mesoporous silica in the 1990s has sparked the research on the synthesis, characterization, and use of mesoporous materials in a wide range of applications,

including adsorption/separation, sensors, catalysis, energy storage and conversion and biotechnology. Recently, the research in the development of supercapacitor electrode has been centered on the transition metal compounds, particularly those with mesoporous architectures. This is because nano confined mesoporous architectures can be related to the basics of study about the mass transport kinetics/diffusion process, charge transfer, storage mechanism, and the interface electrochemical reactions[12].Furthermore, the high specific surface area of mesoporous materials allows for huge charge storage and improved rate performance by not only increasing the electrochemical reaction across the electrode/electrolyte interface but also through reduced charge transfer resistance[12][13][14].

Over the past few decades, various kind of mesoporous structured materials including carbon based materials [15][16][17], transition metal based compounds [18] [19], rare earth metal based compounds[20] and conducting polymers with different types of energy storage process have been examined for their suitability as supercapacitor electrodes. However, most of the transition metal-based compounds are studied to develop the positive electrodes of the supercapacitor. The study to improve the electrochemical performance of the supercapacitor negative electrode is feeble. Very few of transition metal-based compounds have been explored as negative electrodes of supercapacitors owing to the nature of fast degradable cyclic performance, low specific capacitance and poor rate capability. It is worth noting that the development of negative electrodes is a vital back up for the performance of positive electrodes in order to commercialize.

The iron, vanadium, and bismuth-based metal oxides exhibit notable performance for supercapacitor negative electrodes due to their wide range of oxidation states, abundance in nature, chemical stability, and affordability [21-23]. Additionally, the binary form of these three materials are receiving a great deal of interest in the supercapacitor applications due to their improved electrical characteristics [24]. Especially, bismuth vanadate nanostructures are recently explored

as a supercapacitor negative electrode because of wide range of operating potential and multiple valance states. Furthermore, the electrochemical performance is found to be superior when the shape and size of morphology of bismuth vanadate materials are scaled down to nano-level of the aforementioned materials.

As a consequence, modifying the shape and size with significant textural properties of a nanostructure is a superior strategy to enhance the electrochemical performance. The suitable synthesis method and appropriate physiochemical conditions are imperative in the preparation of these elegant nanostructures. The hydrothermal method is most suitable and efficient method for the engineering of nanosized materials with the qualities of mesoporous texture.

Herein, the bismuth vanadate nanostructures are synthesized using hydrothermal techniques for various temperatures of hydrothermal conditions. The structural, morphological and textural characteristics of the bismuth vanadate materials have been examined upon various hydrothermal conditions. Furthermore, the electrochemical performance was also studied to identify optimal synthesis conditions for the preparation of bismuth vanadate electrodes for commercial applications.

2. Experimental

Analytical grade Ammonium meta vanadate (NH_4VO_3), bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$) were purchased form Sigma Aldrich, India. Sodium hydroxide (NaOH) solution was purchased from SRL Chemicals, India. All chemicals and reagents are used without further purification process.

Firstly, 1.754 g of Ammonium meta vanadate (NH_4VO_3) is blended with double distilled water (DDW). This solution mixture is termed as solution 1. In a separate beaker, 5.924 g of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$) is mixed with 30 mL of DDW using magnetic stirrer under normal condition and is labelled as solution 2. Now the solution 2 is slowly mixed with solution 1 using stirrer at 75°C . The mixing of solutions leads to light yellow in color. Further a few drops of NaOH was added to adjust the pH between 7- 7.5. The solution was stirred for 1 h and transferred to 100 mL

autoclave and kept in temperature 140 °C for 24h. The material is washed thrice with ethanol and water. The as prepared material was dried at 80 °C for 12 h and calcinated at 500 °C for 1 h to get the final product. The sample prepared using 140°C is termed as 140 BV. Moreover, same method was employed for the preparation of samples with different hydrothermal temperature and termed as 160BV, 180BV and 200BV for the temperatures 160°C, 180°C and 200°C respectively.

2.1 Material characterization

Different types of analytical tools are used to investigate the as-synthesized materials. The crystalline nature and phase of the prepared materials are analyzed between the range 10°C - 80°C using the X-ray diffraction (XRD, BRUKER-D8) attached with Copper K α radiation. Scanning electron microscope (SEM, ZEISS-EVO, Germany) was utilized to understand the morphological features of the samples. Surface area and nitrogen adsorption and desorption measurements were carried out using Quantachrome surface area and pore size analyzer (Quantachrome Instruments V11.05). Before measurements the samples were degassed at 100 °C for 24 Hr. FT-Raman spectrum was obtained using FEKI (STR-500 mm focal length, JAPAN) laser Raman spectrometer.

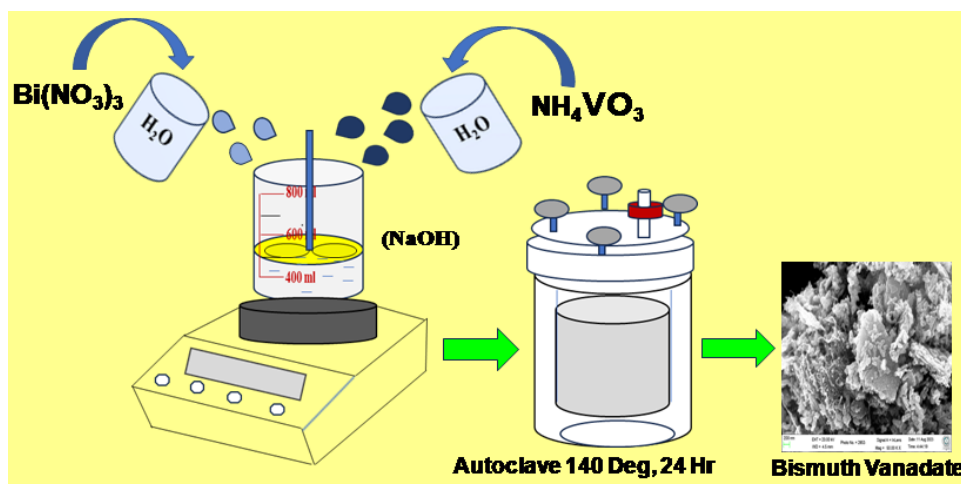
2.1.1 Electrochemical Measurements

Electro chemical Workstation (CH Instruments, 660 C, USA) was employed to investigate electrochemical features of the prepared samples. A three- electrode set up having Ag/AgCl reference electrode, platinum wire counter electrode and as prepared bismuth vanadate as working electrode. The working electrode was prepared as follows: Firstly, 85% active material, 10% Activated carbon and 5% of Polytetrafluoroethylene (PTFE) binder was blended and transferred to a vial containing 10 μ L of ethanol and sonicated for a minute. Secondly, the as prepared slurry was coated to a graphite sheet (1 cm²) current collector. Finally, the as prepared electrodes were dried at 80°C in a hot air oven for 4 hr. All electrochemical investigations were carried out using 2M KOH electrolyte solution.

3. Results and discussions

3.1 Synthesis Protocol

Fig 1. Fabrication Schematic of nanostructured BiVO_4 (Prepared at 140°C)



Synthesis protocol of nanostructured BiVO_4 SC electrode material is presented in Fig 1.

3.2 Structural and morphological investigations

3.2.1 Physicochemical characterizations -Stoichiometric Analysis

Strategies for Controlling Elemental Ratio.

The several strategies can be followed to control the elemental ratio of the prepared materials: precursor selection, controlled synthesis and post synthesis treatment. The stoichiometry ratio of elements (Bi:V) for the preparation of composites (BiVO_4) should be precise. The synthesis conditions like temperature, pressure and pH of the solutions, etc., are highly influence the formation of selected composites. The non-stoichiometry ratio of elements under uncontrolled synthesis conditions may paved the way for formation of selected composites along with the impurity peaks. The post synthesis process such as annealing can also affect the elemental ratio. The optimum temperature can be used for the preparation of selected composites. Therefore, three strategies which are stoichiometry ratio of elements, suitable synthesis conditions and post-synthesis treatment are highly influence the elemental ratio of the composites.

Influence of Elemental Ratio on Electrochemical Activity

The non-stoichiometry ratio of elements may facilitate the formation defect regions (For

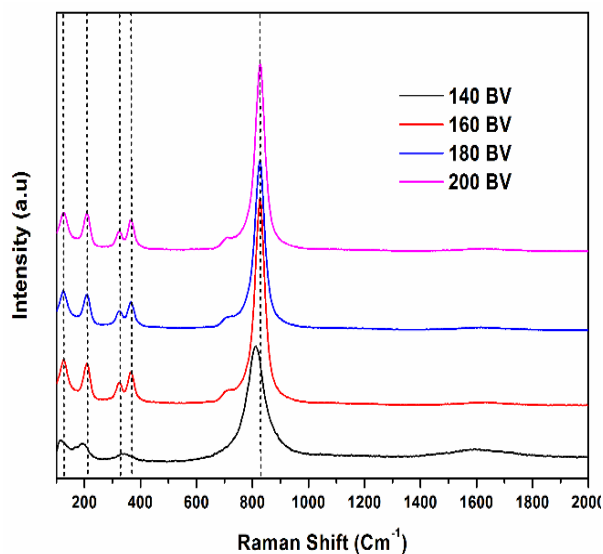
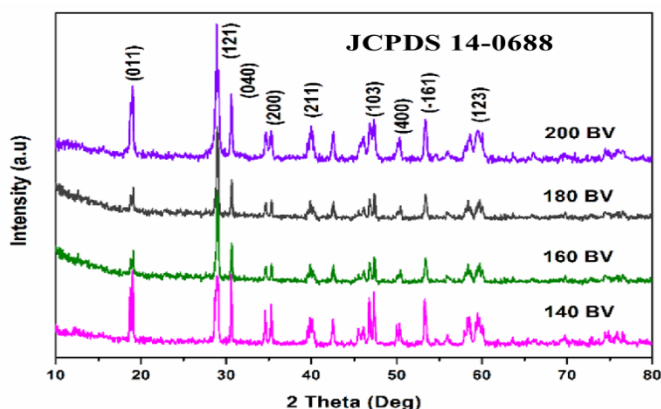
instance, oxygen deficient regions) in the materials which highly influence the electrochemical performance by providing additional active sites. Also, the electronic structure of the composited prepared under non-stoichiometry ratio of elements or unfavorable synthesis conditions is strongly modified due to the interaction of impurity phases affecting the charge transfer kinetics. In addition to that, the chemical strength of the prepared composites could be affected by the non-stoichiometry ratio of elements. The optimal concentration could provide better stability against continuous charge discharge process.

3.2.2 Morphology Analysis

The X-Ray diffraction investigations were performed for better understanding of phase, purity and structural information of the prepared samples. The XRD spectrum of bismuth vanadate samples prepared at different hydrothermal temperatures matched well with the JCPDS card number 14-0688 and exhibits monoclinic phase. Further, the presence of prominent higher intensity peaks indicates the better crystallinity of the samples. It is also noted that the absence of the additional peaks ensured the purity of the as prepared samples.

Raman spectroscopy is the oft-used tool to study the molecular structure, composition, stability and crystalline properties of inorganic as well as organic compounds. Measurement of the parameter, Raman shift, is useful in identifying the different stretching and bending modes of various bonds present in a sample as it is highly characteristic of a particular molecule as a whole. In the present study, the various BiVO_4 samples have been subjected to Raman spectroscopy in order to examine the composition, crystallinity and isomorphism among the samples. The Raman spectra of the samples are shown in Fig. 2 b and it indicates the creation of monoclinic BiVO_4 .

Fig 2. (a) XRD spectrum of samples synthesized at 140°C, 160°C, 180°C and 200°C
(b) FTIR spectrum of samples synthesized at 140°C, 160°C, 180°C and 200°C.



The highest band is at 826 cm^{-1} and the assignments of the peaks are given in Table. 1. Except the as-prepared sample (BV) with only 5 peaks, all other samples displayed 6 prominent peaks of varying Raman intensities. The Raman Shift and pattern of the peaks indicates the isomorphous nature of the samples. The peaks in the range $327\text{-}367 \text{ cm}^{-1}$ and $825\text{-}830 \text{ cm}^{-1}$, attributable to ν_2 bending of VO_4 anion and ν_1 symmetric stretching mode of VO_4 anion, are typical for BiVO_4 molecule [25]. The two peaks appearing in the lower frequency range ($119\text{-}128 \text{ cm}^{-1}$ and $197\text{-}210 \text{ cm}^{-1}$) are due to the lattice modes, i.e., vibration of the unit cells. As far as the intensity is concerned, the peak due to ν_1 symmetric stretching mode of VO_4 anion was obviously the most intense. Similarly, a weak band at $1619 \text{ cm}^{-1} / 1642 \text{ cm}^{-1}$ (all other samples) is probably due to the HOH bending mode of water [26, 28].

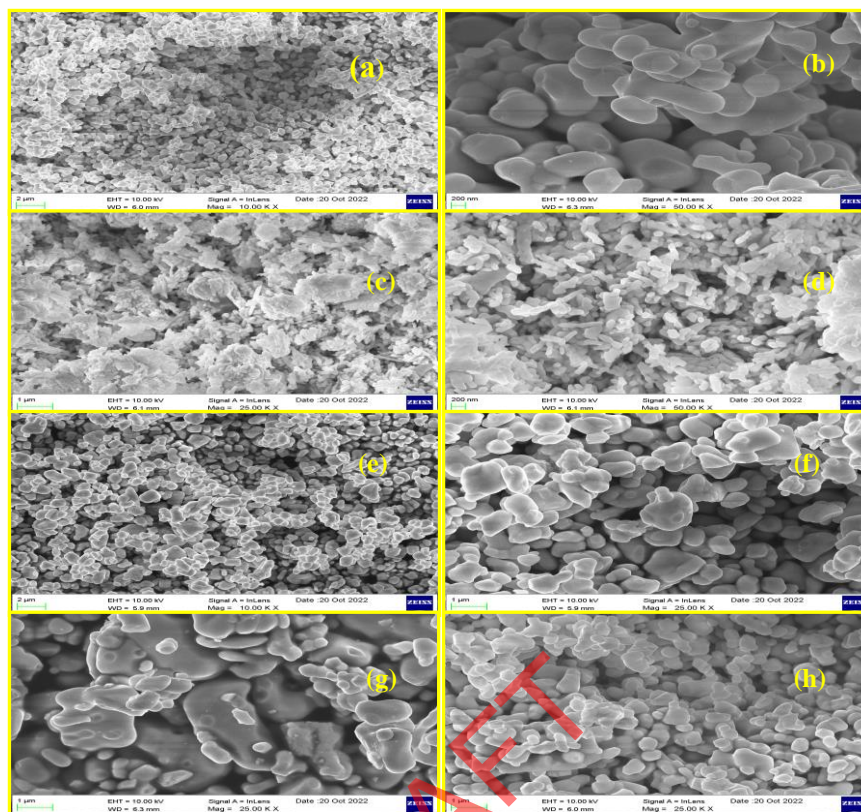
Table 1 Raman shift (cm^{-1}) for the samples

S.NO	Electrode materials	Raman shift (cm^{-1})	Assignment
1	BV140	119, 197 340 81 1642	Lattice modes ν_2 bending of VO_4 anion ν_1 symmetric stretching mode of VO_4 anion Water HOH bending mode
2	BV160	128, 210 331, 367 825 1642	Lattice modes ν_2 bending of VO_4 anion ν_1 symmetric stretching mode of VO_4 anion Water HOH bending mode
3	BV180	124, 210 327, 367 825 1619	Lattice modes ν_2 bending of VO_4 anion ν_1 symmetric stretching mode of VO_4 anion Water HOH bending mode
4	BV200	128, 210 331, 367 830 1642	Lattice modes ν_2 bending of VO_4 anion ν_1 symmetric stretching mode of VO_4 anion Water HOH bending mode

The Figure 3 (a-h) presented the SEM images of the samples prepared at different hydrothermal temperature. The samples prepared at 140°C exhibits spherical ball kind of structure with sizes ranges from 200 to 700 nm.

When the hydrothermal temperature raised form 140°C to 160°C , it is interesting to mention here that the spherical ball kind structure of BiVO_4 changed into the rod form of structure. Further increase of hydrothermal synthesis temperature leads to the collapse of rod like a visible morphology and transformation of rough surfaces for the samples prepared at 180°C and 200°C . From the morphological investigations, it is well understood that the morphological features of the samples predominately depend on the hydrothermal temperature.

Fig 3 SEM images of samples synthesized at 140°C (a, b), 160°C (c, d), 180°C (e, f) and 200°C (g, h) with different magnifications



Electrochemical measurements

Initially, three electrode electrochemical cell is employed to investigate the charge storage performance of the prepared bismuth vanadate nanostructures. The preparation of electroactive materials and electrodes were discussed in the section 2.4. The measurements were carried out in 2 M aqueous potassium hydroxide solution in the potential range between -1.1 and 0 V. Notably, as the electrode can store charge via either by double layer method, redox process, or combination of both, which is vital to identify the charge storage mechanism of the prepared materials. The cyclic voltammetry is an efficient tool to identify the feasible charge storage mechanism of the bismuth vanadate electrodes and thus it is performed at various scan rates. The results of cyclic voltammetry studies are displayed in Figure 4, demonstrating strong Faradaic peaks indicating that the charges are stored through diffusion-controlled process of electrolyte ions. The voltammograms of bismuth vanadate electrodes display two oxidation peaks at an appropriate

potential accounting the transformation from Bi⁰ to Bi³⁺. The reduction of Bi³⁺ into Bi⁰ is also seen by displaying one dominant redox peak during the reverse scan [29][30]. The partial reversibility thus identified during the redox process is due to the partial dissolution of bismuth sites in the bismuth vanadate electrodes [31,32]. Moreover, the electrodes of bismuth vanadate prepared under different hydrothermal conditions retains the shape of voltammograms upon varying the scan rate suggesting the stable charge storage performance.

Moreover, nature of electrochemical performance of the bismuth vanadate electrodes could be identified using the power law, $I = av^b$ of $\log I = \log a + b \log v$ (where, I is current density (mA cm⁻²), v is scan rate (mV s⁻¹), a and b are the constants). The slope of the straight line thus obtained between $\log I$ and $\log v$ (Figure 4 c) details the nature of energy storage mechanism of the bismuth vanadates and it is close to 0.5 indicating the battery-type behavior.

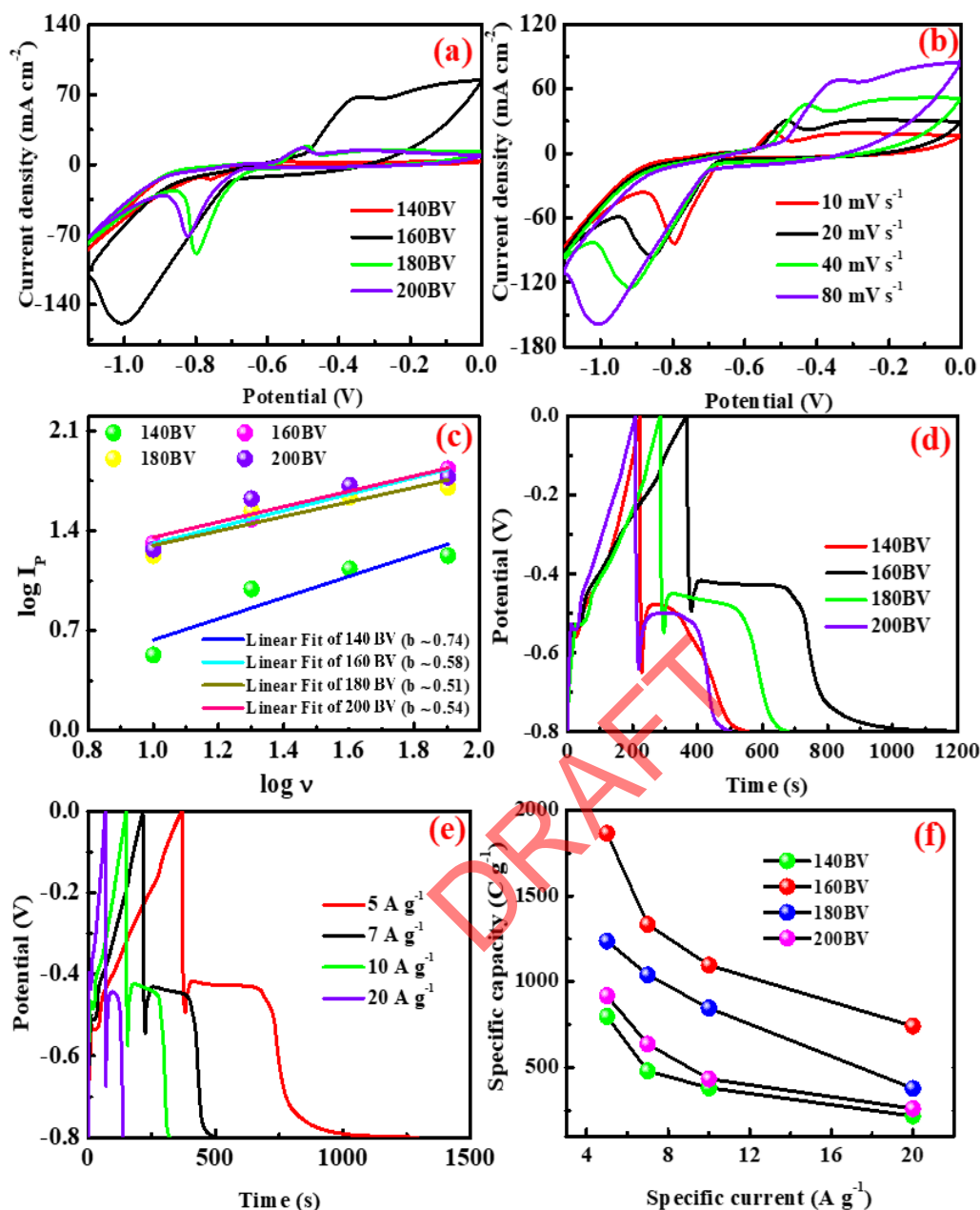
The specific capacity of bismuth vanadate electrodes is calculated using the relation,

$$C_s = \frac{\int I dV}{2 m v} \quad 1$$

Where, $\int I dV$, area under CV curve (A V), m , mass of electroactive material (mg) and v , scan rate (mV s⁻¹). The specific capacities of 684, 1135, 973 and 894 C g⁻¹ are estimated at a scan rate of 10 mV s⁻¹ for the electrodes of bismuth vanadates prepared at 140°C, 160°C, 180°C and 200°C hydrothermal conditions respectively. Among, the bismuth vanadate electrode synthesized under 160°C hydrothermal condition demonstrated superior charge storage performance by yielding high specific capacitance of 1135 C g⁻¹ at a scan rate of 10 mVs⁻¹. Nearly, 65.9% capacity improvement is enhanced when compared to bismuth vanadate prepared at 140°C. Besides, the capacity is found to be degrading for higher hydrothermal conditions of 180°C and 200 °C.

Figure 4. (a) CV curves of bismuth vanadate electrodes at 80 mV s⁻¹, (b) CV curves of 160BV, (c) $\log I$ versus $\log v$ of bismuth vanadate electrodes, (d) GCD curves of bismuth

vanadate electrodes at 5 A g^{-1} , (e) GCD curves of 160 BV and (f) C_s versus specific current of bismuth vanadate electrodes.



Furthermore, the bismuth vanadate electrode was subjected to diagnose the charging and discharging characteristics at a constant specific current within a potential range of -0.8 to 0 V. The non-linearity in the charging and discharging curves observed in the electrodes made of bismuth vanadate (Figure 4 d) may be primarily attributed to ion diffusion in the electrolyte. Also, the discharge curves of the bismuth vanadate electrodes exhibit a sharp kink that accounts for the quasi-conversion reaction (oxidation of unconverted Bi^0) and is in accordance with the findings of

the CV study [33] . It is noteworthy that, the same kind of charge storage mechanism is reported for Ag incorporated NiO [34]. Also, recent work on nickel bismuth oxide and silver molybdate reported by William et al. explained the charge storage performance on basis of quasi conversion reaction process[31,35]. The specific capacity of the bismuth vanadate electrodes synthesized at 140°C, 160°C, 180°C and 200°C hydrothermal conditions were estimated using the equation 2,

$$C_s = \frac{2I \int V dt}{m V} \quad 2$$

Where I, specific current ($A g^{-1}$), $\int V dt$, area under discharge curve (V s), m, mass of electroactive material (mg) and V, potential window (V). The estimated specific capacity for the electrodes of 140BV, 160BV, 180BV and 200BV are 798, 1864, 1237 and 919 $C g^{-1}$ for specific current of 5 $A g^{-1}$ respectively. The bismuth vanadate electrode prepared under 160°C hydrothermal conditions exhibited superior electrochemical performance by demonstrating higher specific capacity of 1864 $C g^{-1}$ and which is attributed to the unique nanosized spherical-like particles. The less time for dumping of charges on the electrode during charging and extraction of charges from the electrode during discharging can be made accountable for the degradation of charge storage performance while increasing the specific current to 20 $A g^{-1}$.

The slope of the straight line thus seen between $\log I_p$ versus $\log v$ for 140BV electrode is found to be 0.74 indicating domination of surface controlled process when compare to battery type behavior. Whereas, the slope value is shifted towards the 0.5 for the bismuth vanadate electrodes prepared under the thermal conditions of 160°C, 180°C and 200 °C. Thus, it is noteworthy to mention that, as the reaction temperature is increased from 140°C to 160°C, 180°C and 200 °C, the electroactive sites are additionally formed resulting in an enhanced electrochemical performance.

Since the energy is stored through the diffusion controlled process, it is identified from the results of CV and GCD techniques that the electrodes of bismuth vanadate could offer certain

degree of impedance for the diffusion of electrolyte ions and it could be obtained using the electrochemical impedance spectroscopy technique [36]. The frequency range of 10 mHz to 100 kHz was used to analyze impedance behaviour at an amplitude of 5 mV. The obtained spectra is fitted to the modified Randle's circuit (inset of Figure 5 a) and it is displayed in Figure 5 a. The fitted spectra show one semi-circle and inclined linear part at high frequency and low frequency region respectively. The electrochemical performance of the bismuth vanadate electrodes is influenced by the charge transfer process while the frequency approaching zero and it is indicated by the semi-circle in Nyquist plot [37]. However, the straight line inclined about 45 degrees at low frequency region of Nyquist plot is due to the diffusion process of electrolyte ions.

Generally, it can be expressed as $Z_F(\omega) = R_{CT} + Z_W(\omega)$; where R_{CT} is charge transfer resistance and $Z_W(\omega)$ represents Warburg impedance ($Z_W(\omega) = \frac{\sigma}{\omega^\alpha}(1 - j)$ or $\log |Z''| = \log \sigma + \alpha \log\left(\frac{1}{\omega}\right)$). Here, the term α , transfer coefficient, indicates the nature of electrochemical performance of the mathematical description of Faradaic impedance prepared electrodes. The value of α can be obtained from the slope of straight line thus obtained between $\log |Z''|$ versus $\log(1/\omega)$. If α is close to 0.5 and 1, the charge storage process is controlled by Faradaic and capacitive behavior respectively.

The intercalative or pseudocapacitive process can be identified if it is between 0.5 and 1. Figure 5 c-e displays the linear plot of $\log |Z''|$ versus $\log(1/\omega)$ of all the electrodes displaying the slope value close 0.5 except the electrode 140BV which is 0.75 (Figure 5 b). This analysis indicates dominance of capacitive behavior in 140 BV electrode and it can be reasoned for low specific capacity than the other electrodes. In addition to that, the Bode Phase angle plot is analyzed to further support the results of $\log |Z''|$ versus $\log(1/\omega)$. Figure 5 f exhibits the Bode phase angle plot of all the samples consisting time constants at middle frequency region and it is indicative of double layer capacitance [38]. Also, the electrodes of 160BV, 180BV and 200BV display the Y intercept at low frequency region close to 45° implying the dominance of

pseudocapacitance nature resulting high electrochemical performance. Whereas, the 140BV electrode intercepts at 70°C suggesting the capacitive behavior. Therefore, the results of $\log |Z''|$ versus $\log (1/\omega)$ and Bode phase angle plot suggest that the electrochemical performance of 140BV electrode is governed by the capacitive behaviour whereas the pseudocapacitance nature governs the charge storage process in 160BV, 180BV and 200BV electrodes and it is consistent with the results obtained in the CV and GCD analysis. Moreover, the charge transfer resistance (R_{CT}) of 140BV, 160BV, 180BV and 200BV was obtained from the diameter of the semi-circle and it is of 7.2, 4, 4.7 and 10 Ω respectively. The solution resistance (R_s) of all the samples can be identified from the X intercept and it is found to be close to the value of 3 Ω . Herein, the bismuth vanadate electrode synthesized under 160 °C hydrothermal condition shows the low charge transfer resistance of 4 Ω over other electrodes accounting the superior electrochemical performance.

Figure 5b-e exhibits the linear plot of $\log |Z''|$ versus $\log (1/\omega)$ for all the electrodes. The 140BV electrode demonstrates the slope of 0.75 accounting the surface-controlled process. Besides, the bismuth vanadate electrode prepared under the hydrothermal conditions of 160°C, 180°C and 200°C shows the slope value close to 0.5 as result of formation of additional active sites. Thus, battery type behavior is dominated as the reaction temperature is increased from 140 °C and it is consistent with the CV analysis.

Table 2: Comparison of electrochemical characteristics of bismuth vanadate with other reported bismuth and vanadate based materials.

S. No.	Electrode materials	Synthesis method	Morphology	Potential window V	Specific capacity C g ⁻¹ @A g ⁻¹	Stability % @ cycles	Ref
1	BiVO ₄	Hydrothermal	Nanorods	0 – 0.4	466.4 @1	80 @ 500	[9]
2	BiVO ₄ /RGO	Hydrothermal	Hierarchical structure	-0.4 – 0.4	274.4@1	87 @ 2000	[10]
3	Bismuth vanadate	Hydrothermal	Dendritic-like	-1.1 – 0.4	403.2@ 5	--	[11]
4	BiVO ₄	Hydrothermal	Rice-pellet-like	-1.2 – 0.6	1203 @ 2	-	[12]
5	Bismuth vanadate	Hydrothermal	Spherical nano particles	-0.8 – 0	1864 @ 5	84 @ 3000	Present work

Furthermore, the electrodes of bismuth vanadate were employed to diagnose the stability upon 3000 continuous charge discharge cycles. The study was carried out using the galvanostatic charge discharge technique at a current density of 10 mA cm⁻². The capacity retention is estimated for each 200 cycles interval to understand the lifespan of the prepared materials. Figure 5g displays the profile of variation of capacity over 3000 continuous charge discharge cycles. Initially, the bismuth vanadate electrode prepared under 160 °C hydrothermal condition shows increased trend of capacity retention and reached maximum of 114% retention for 400 continuous charge discharge cycles and same value is retained upto 800 continuous GCD cycles [39,40]. The capacity is gradually decreased for further increasing the GCD cycles and retained 84% of its initial value even after 3000 charge discharge cycles.

4. Conclusions

High performance BiVO₄ nanostructures are prepared using simple hydrothermal protocol with monoclinic phase crystalline structure. The variation of synthesis hydrothermal temperature greatly influenced the morphological and electrochemical features significantly. The BiVO₄ nanostructure prepared with 160°C exhibits superior specific capacity of 1864 Cg⁻¹ at a higher current in 2M KOH electrolyte solution with a very small charge transfer resistance of 4 ohm. These notable electrochemical features make this prepared material as one among the best electrode material for energy storage applications.

5. Author Credits

J Shoba conceived the study and participated in formulating the ideas for conducting the research and investigation process. **S Maruthamuthu** designed the methodology and performed the experiments. The reproducibility of results and other research outputs was verified by **K Sakthivel**. **Aslam Khan** analysed the data, created figures and drafted the initial manuscript including revision and edits.

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Conflicts of Interest

The authors have no conflicts of interest to disclose.

7. References

- [1] Jayaraman Theerthagiri, Raja Arumugam Senthil, (2020) Recent progress and emerging challenges of transition metal sulfides based composite electrodes for electrochemical supercapacitive energy storage. *Ceramics International* 46 ;14317-14345. <https://doi.org/10.1016/j.ceramint.2020.02.270>
- [2] Bhargav Akkinapally , Nandini Robin Nadar , (2024) Unlocking enhanced electrochemical performance of SnO₂ -Bi₂WO₆ nano flowers for advanced supercapacitor device. *Jr of Alloys and Comp* .970;172677. <https://doi.org/10.1016/j.jallcom.2023.172677>
- [3] Bhargav Akkinapally, I. Neelakanta Reddy, Promising electrode material of Fe₃O₄ nanoparticles decorated on V₂O₅ nanobelts for high-performance symmetric supercapacitors, *Ceramics International* 49 (2023) 6280-6288, <https://doi.org/10.1016/j.ceramint.2022.10.161>
- [4] K. Narthana, G. Durai, P. Kuppusami , J.Theerthagiri , (2021) One-step synthesis of hierarchical structured nickel copper sulfide nanorods with improved electrochemical supercapacitor roperties, *Inter. J. Energy Research*. 45; 9983. <https://doi.org/10.1002/er.6492>

- [5] K Thiagarajan, D Balaji, J Madhavan, J Theerthagiri, (2020) Cost-Effective Synthesis of Efficient CoWO₄/Ni Nanocomposite Electrode Material for Supercapacitor Applications, *Nanomaterials*, 10; 2195. <https://doi.org/10.3390/nano10112195>.
- [6] Jayaraman Theerthagiri, Arun Prasad Murthy, (2021) Recent progress on synthetic strategies and applications of transition metal phosphides in energy storage and conversion. *Ceramics International* 47; 4404-4425. <https://doi.org/10.1016/j.ceramint.2020.10.098>
- [7] Bairi Sri Harisha, Bhargav Akkinapally, Jaesool Shim, (2024) Hybrid NiO@TiO₂ nano-architecture for improved electrochemical performance with simulation corroboration. *Jr of Energy Storage*, 87;111466. <https://doi.org/10.1016/j.est.2024.111466>.
- [8] Subhasree Panda, Theerthagiri Jayaraman, (2022) MXene based emerging materials for super capacitor applications: Recent advances, challenges, and future perspectives. *Coordination Chemistry Reviews* 462 ;214518. <https://doi.org/10.1016/j.ccr.2022.214518>
- [9] Seung Jun Lee, Jayaraman Theerthagiri, (2021) Heteroatom-doped graphene-based materials for sustainable energy applications. A review, *Renewable & Sustainable Energy Reviews* 143;110849. <https://doi.org/10.1016/j.rser.2021.110849>
- [10] Yi Jiang, Ya-Ping Deng, (2020) ,d-Orbital steered active sites through ligand editing on heterometal imidazole frameworks for rechargeable zinc-air battery. *Nature Communications* 11; 5858 <https://doi.org/10.1038/s41467-020-19709-6>
- [11] Parnia Forouzandeh, Vignesh Kumaravel, Suresh C. Pillai, (2020) Electrode Materials for Supercapacitors: A Review of Recent Advances. *Catalysts*, 10; 969. <https://doi.org/10.3390/catal10090969>
- [12] L. Zu, W. Zhang, L. Qu, L. Liu, W. Li, A. Yu, D. Zhao, (2020) Mesoporous Materials for Electrochemical Energy Storage and Conversion, *Adv. Energy Mater.* 10 ; 2002152. <http://dx.doi.org/10.1002/aenm.202002152>
- [13] G. Xiang, Y. Meng, G. Qu, J. Yin, B. Teng, Q. Wei, X. Xu, (2020) Dual-functional NiCo₂S₄ polyhedral architecture with superior electrochemical performance for supercapacitors and lithium-ion batteries. *Sci. Bull.* 65 ;443–451. <http://dx.doi.org/10.1016/j.scib.2020.01.004>
- [14] J. Acharya, T. Hoon, M. Seo, M. Khil, H. Kim, B. Kim, (2020) Oxalic acid assisted rapid synthesis of mesoporous NiCo₂O₄ nanorods as electrode materials with higher energy density and cycle stability for high-performance asymmetric hybrid supercapacitor applications. *J. Colloid Interface Sci.* 564 ;65–76. <https://doi.org/10.1016/j.jcis.2019.12.098>
- [15] S. Joseph, D.M. Kempaiah, M.R. Benzigar, H. Ilbeygi, G. Singh, S. Naidu, D. Park, A. Vinu, (2019) Highly ordered mesoporous carbons with high specific surface area from carbonated soft drink for supercapacitor application. *Microporous Mesoporous Mater.* 280; 337–346. <https://doi.org/10.1016/j.micromeso.2019.02.020>
- [16] A. Apriwandi, E. Taer, R. Farma, R.N. Setiadi, E. Amiruddin, (2021) A facile approach of micro-mesopores structure binder-free coin / monolith solid design activated carbon for electrode supercapacitor. *J. Energy Storage.* 40; 102823. <https://doi.org/10.1016/j.est.2021.102823>

- [17] Y. Mo, J. Du, H. Lv, Y. Zhang, A. Chen, (2021) N-doped mesoporous carbon nanosheets for supercapacitors with high performance. *Diam. Relat. Mater* 111; 108206. <https://doi.org/10.1016/j.diamond.2020.108206>
- [18] X. Dong, Y. Yu, Y. Zhang, Z. Xu, H. Jiang, C. Meng, C. Huang, (2021) Synthesis of cobalt silicate nanosheets with mesoporous structure and high surface area as the promising electrode for high-performing hybrid supercapacitor. *Electrochim. Acta.* 380; 138225. <https://doi.org/10.1016/j.electacta.2021.138225>
- [19] P. Li, M. Zhang, H. Yin, J. Yao, X. Liu, S. Chen, (2021) Hierarchical mesoporous NiCoP hollow nanocubes as efficient and stable electrodes for high-performance hybrid supercapacitor. *Appl. Surf. Sci.* 536; 147751. <https://doi.org/10.1016/j.apsusc.2020.147751>
- [20] P.E. Saranya, S. Selladurai, (2019) Mesoporous 3D network Ce doped NiO nanoflakes as high-performance electrodes for supercapacitor applications. *NewJ.Chem.* 43; 7441–7456. doi:10.1039/C9NJ00097F.
- [21] R. Packiaraj, P. Devendran, S. Asath Bahadur, N. Nallamuthu, (2018) Structural and electrochemical studies of Scheelite type BiVO₄ nanoparticles: synthesis by simple hydrothermal method. *J Mater Sci: Materials in Electronics* 29; 13265–13276. <https://link.springer.com/article/10.1007/s10854-018-9450-0>
- [22] S. Boukhalfa, K. Evanoff, G. Yushin, (2012) Atomic layer deposition of vanadium oxide on carbon nanotubes for high-power supercapacitor electrodes. *Energy Environ. Sci.*; 6872–6879. <https://doi.org/10.1039/C2EE21110F>
- [23] Y. Yan, B. Li, W. Guo, H. Pang, H. Xue, (2016) Vanadium based materials as electrode materials for high performance supercapacitors. *J. Power Sources* 329 ;148–169. <https://doi.org/10.1016/j.jpowsour.2016.08.039>
- [24] J. Wen, S. Sun, B. Zhang, N. Shi, X. Liao, G. Yin, Z. Huang, X. Chen, X. Pu, (2019) Facile synthesis of a Bi₂MoO₆/TiO₂ nanotube arrays composite by the solvothermal method and its application for high-performance supercapacitor. *RSC Adv.*94693–4699. <https://doi.org/10.1039/c8ra08604d>.
- [25] Paul Brack et al., (2015) Aerosol assisted CVD of Bismuth Vanadate thin films and their Photo-electrochemical properties. *Chem. Vap. Deposition.* 20 ;1-5. <https://doi.org/10.1002/cvde.201407142>
- [26] Y. Liang, Toshiki Tsubota, 2011 Highly Improved Quantum Efficiencies for Thin Film BiVO₄ Photoanodes. *J. Phys. Chem. C* 115;17594–17598. <https://doi.org/10.1021/jp203004>
- [27] F. D. Hardcastle, Israel E. Wachs, (1991) Determination of vanadium-oxygen bond distances and bond orders by Raman spectroscopy. *J. Phys. Chem.* 95; 5031.
- [28] R. L. Frost, Dermot A. Henry, (2006) Raman spectroscopy of three polymorphs of BiVO₄: clinobisvanite, dreyerite and pucherite, with comparisons to (VO₄)³⁻-bearing minerals: namibite, pottsite and schumacherite. *J.Raman Spectrosc* 37 ;722. <https://doi.org/10.1002/jrs.1499>
- [29] J.Wen, S. Sun, B. Zhang, N. Shi, X. Liao, G. Yin, Z. Huang, X. Chen, X. Pu, (2019) Facile synthesis of a Bi₂MoO₆/TiO₂ nanotube arrays composite by the solvothermal method and its

application for high-performance supercapacitor. RSC Adv 94693–4699.<https://doi:10.1039/c8ra08604d>.

[30] Vivier, A. Régis, G. Sagon, J.Y. Nedelec, L.T. Yu, C. Cachet-Vivier, (2001) Cyclic voltammetry study of bismuth oxide Bi₂O₃ powder by means of a cavity microelectrode coupled with Raman microspectrometry. *Electrochim. Acta.* 46; 907–914.[https://doi:10.1016/S0013-4686\(00\)00677-0](https://doi:10.1016/S0013-4686(00)00677-0).

[31] J. Johnson William, I. Manohara Babu, G. Muralidharan, (2021) Nickel bismuth oxide as negative electrode for battery-type asymmetric supercapacitor. *Chem. Eng. J.* 422; 130058. <https://doi:10.1016/j.cej.2021.130058>

[32] N.M. Shinde, Q.X. Xia, J.M. Yun, P. V. Shinde, S.M. Shaikh, R.K. Sahoo, S. Mathur, R.S. Mane, K.H. Kim, (2019) Ultra-rapid chemical synthesis of mesoporous Bi₂O₃ micro- sponge-balls for supercapattery applications. *Electrochim. Acta.* 296; 308-316.<https://doi:10.1016/j.electacta.2018.11.044>.

[33] S.X. Wang, C.C. Jin, W.J. Qian, (2014) Bi₂O₃ with activated carbon composite as a super capacitor electrode. *J. Alloys Compd.* 615; 12–17. <https://doi:10.1016/j.jallcom.2014.06.149>

[34] S. Nagamuthu, K.-S. Ryu, (2019) Synthesis of Ag/NiO Honeycomb Structured Nanoarrays as the Electrode Material for High Performance Asymmetric Supercapacitor Devices. *Sci. Rep.* 9; 4864. <https://doi:10.1038/s41598-019-41446-0>

[35] J. Johnson William, B. Saravanakumar, M. Mariyappan, G. Muralidharan, A.J. Britten, M. Mkandawire, (2022) Mesoporous β-Ag₂MoO₄ nanopotatoes as supercapacitor electrodes. *Mater. Adv.* 3; 8288–8297. <https://doi:10.1039/d2ma00708h>.

[36] K.K. Purushothaman, I.M. Babu, B. Saravanakumar, (2017) Hierarchical mesoporous Co_xNi_{1-x}O as advanced electrode material for hybrid supercapacitors. *Int. J. Hydrogen Energy.* 42; 28445–28452. <https://doi:10.1016/j.ijhydene.2017.09.115>.

[37] R. Packiaraj, (2018) Structural and electrochemical studies of Scheelite type - BiVO₄ nanoparticles: synthesis by simple hydrothermal method. *J. Mater. Sci. Mater. Electron.* 29 ; 13265–13276. <https://doi:10.1007/s10854-018-9450-0>.

[38] C. Sengottaiyan, N. Abdul Kalam, R. Jayavel, R.G. Shrestha, T. Subramani, S. Sankar, J.P. Hill, L.K. Shrestha, K. Ariga, (2019) BiVO₄/RGO Hybrid Nanostructure for High Performance Electrochemical Supercapacitor. *J. Solid State Chem.* 269; 409–418. <https://doi:10.1016/j.jssc.2018.10.011>.

[39] L. Deng, J. Liu, Z. Ma, G. Fan, Z.-H. Liu, (2018) Free-standing graphene/bismuth vanadate monolith composite as a binder-free electrode for symmetrical supercapacitors. *RSC Adv.* 824796–24804. <https://doi:10.1039/c8ra04200d>.

[40] C. Murugan, K. Subramani, R. Subash, M. Sathish, A. Pandikumar, (2020) High-Performance High-Voltage Symmetric Supercapattery Based on a Graphitic Carbon Nitride / Bismuth Vanadate Nanocomposite. *Energy & Fuels.* 34; 16858–16869. <https://doi:10.1021/acs.energyfuels.0c03261>.