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Polyethylene glycol mediated synthesis of iron vanadate (FeVO₄) nanoparticles with supercapacitive features

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Abstract

Binary transition metal oxides, such as iron vanadate (FeVO₄), possess unleashed potential to be the best electrode material for supercapacitor, owing to their high capacitance, stability and conductivity. This present work reports investigations on the influence of a surfactant, polyethylene glycol (PEG 4000), on the structure, morphology and electrochemical behaviour of FeVO₄ nanoparticles. The P4-FeVO₄ exhibited specific capacitance of 428.0 Fg⁻¹ at a current density of 2.0 Ag⁻¹, and arguably better performance and cyclic stability than FeVO₄ synthesised without PEG 4000. Thus, PEG 4000 significantly influenced the morphological and electrochemical performance of the FeVO₄. Furthermore, the assembled P4-FeVO₄ based symmetric capacitor device had a specific capacitance of 101.0 Fg⁻¹ with an energy density of 14.1 Whkg⁻¹. This improved electrochemical performance of the P4-FeVO₄ based devices is attributed to the physicochemical properties of P4-FeVO₄ nanoparticles, mediated by the PEG 4000.

1. Introduction

Due to the continuous global population growth, the energy demand is reciprocally growing exponentially, creating major crisis. Conventional energy sources, especially fossil fuels, have played a vital role in meeting most of our current energy needs, since the beginning of the last century. However, they have also had a negative footprint on the environment, blamed for significant production of the greenhouse gases leading to climate change and other related pollutions. Further, fossil fuel resources are rapidly getting depleted. Therefore, the need for alternate energy sources, especially renewable, clean and sustainable energy, cannot be overstated. However, the currently advocated alternative energy sources require energy storage technologies, which should also be highly efficient, clean and sustainable for future demand [1].

In most engineering applications, batteries, fuel cells and electrochemical supercapacitors are widely used as energy storage devices [2–4]. Among various electrochemical energy storage devices, supercapacitors (SCs) have attracted notable interest due to their unique attributes, including fast charge-discharge, exceptional stability, slow self-discharge rate, flexible packaging, wide thermal range (−40 °C to 70 °C), low maintenance, low weight and high-power delivery [5, 6]. The SCs are currently used, among others, in hybrid electric vehicles along with batteries and fuel cells [7]. In comparison to batteries, the SCs have significantly higher power density, but lower cycle life and higher production cost. Most studies have attributed the lower cycle life and higher production cost of the SCs on the electrodes of the devices, which need to be made from affordable and high-performing materials [1, 8].

A typical supercapacitor consists of two electrodes (symmetric or asymmetric), an electrolyte (organic, aqueous, polymer or solid-state gel) and a separator. The supercapacitor electrodes are mostly made from (i) carbon materials with high specific surface area (e.g., carbon aerogel, activated carbon, carbon nanotubes and graphene) [9–14]; (ii) metal oxides (e.g., MnO₂, RuO₂, NiO, Co₃O₄, MoO₃, and Fe₂O₃) [15–20]; and,
(iii) conducting polymers (e.g., polypyrrole, polyaniline and polythiophene) [21–23]. Currently, transition metal oxides (TMOs) are also gaining prominence for use as electrodes, due to their high conductivity, substantial specific capacitance and better electrode response time [15]. Among the TMOs, ruthenium and manganese oxides have been widely examined for their potential as electrode materials for capacitors. For instance, hydrous ruthenium oxide offers higher capacitance (>700 F g yourself) than conducting polymers and carbon materials. But the high cost and lack of abundance are among the major demerits of using ruthenium) [1]. Similarly, hollow metal oxides like manganese oxides have the major drawback of allow packing density.

Binary transition metal oxides (BTMOs) possess higher reversible capacity, excellent structural stability and electronic conductivity. They are the right candidate for electrode materials for SCs. BTMOs contain at least one transition metal ion and one or more electrochemically active/inactive ions [24–26]. One class of the BTMOs being used in various applications are the orthovanadates. Some of these orthovanadates synthesised and characterised for the preparation of electrode materials are BiVO₄, CeVO₄, LaVO₄, PrVO₄, GdVO₄, and NdVO₄ [27]. There is also the affordable, but less investigated, FeVO₄, which has relatively more chemical and thermal stability and better redox reaction than most vanadates. Due to these properties, the FeVO₄ are being employed in energy storage, electrochromism and photocatalytic applications [24, 28–34]. However, its optimum performance as supercapacitor electrode material has not yet been unleashed, mostly because the FeVO₄ with optimum structure, morphology and electrochemical features is yet to be synthesised.

From previous studies, we ascertained the influence of surfactant’s on the structural, morphological and electrochemical properties of CuO based capacitor electrode [35]. This current research work focused on using polyethylene glycol (PEG) as a structure-directing agent to synthesise FeVO₄ nanostructures with superior structural, morphological and electrochemical features required for a high-performing supercapacitor device. The PEG was selected because, inter alia, it is a hydrophilic and highly water-soluble synthetic polymer. The solubility of PEG in water is attributed to its hydration with bound water molecules, which increases with polymer molecular weight [36–38]. Specifically, PEG4000 was used to synthesise FeVO₄ nano electrodes.

To assess their performance, we assembled a symmetrical supercapacitor device using P4-FeVO₄ electrode material. The choice of an electrolyte for supercapacitor depends on following factors: wide voltage window; high electrochemical stability; high ionic concentration; low solvated ionic radius, resistivity, viscosity, volatility, and toxicity; affordable cost; and availability at high purity. Liquid (aqueous, organic and ionic) and solid-state electrolytes are commonly used in these studies. When compared to the organic electrolytes, the ionic conductivity, dielectric constant and specific capacitance are high for aqueous electrolytes like H₂SO₄ and KOH [38].

Therefore, this paper reports the influence of PEG 4000 on the reduction of the particles size and enhancement of electrochemical activity on FeVO₄ nanoparticles, as well as the improved capacitance and cycle life in 2M KOH electrolyte of supercapacitor devices made with P4-FeVO₄ electrode material.

### 2. Materials and methods

#### 2.1. Preparation of FeVO₄ nanostructures

The starting materials for the synthesis of FeVO₄ nanostructures were solutions containing 1.32 g of NH₄VO₃ and 2.72 g of FeNO₃, which were prepared using 50 ml of deionised water (DI) for each. Then, a solution containing 0.45 g of PEG 4000, also made with DI water, was added to FeNO₃ solution. The PEG-FeNO₃ solution was blended with the NH₄VO₃ solution. The precipitate was formed after adding a few drops of 2 M NaOH to the solution mixture. The precipitate was separated from the supernatant by centrifugation and dried at 80 °C for 6 h. The procedure was repeated, but without using PEG, to synthesise the bare FeVO₄. Here-in-after bare FeVO₄ are denoted simply as FeVO₄ and those made with PEG 4000 as P4-FeVO₄.

#### 2.2. Material characterizations

The structure, phase and purity of the as-prepared FeVO₄ and P4-FeVO₄ samples were determined using PANalyticalX’pert- PRO x-ray diffractometer equipped with CuKα radiation (λ = 1.5406 Å) from 10° to 80°. In addition, we also performed-IR analyses using NICOLET 6700 spectrometer to identify and verify the surface functional groups in the samples. The morphology of the samples was analysed by Transmission Electron Microscope (JEOL JEM2100, 200 KeV) and Scanning Electron Microscopy (TESCAN VEGA 3 LMU). The Brunauer–Emmett–Teller (BET) procedure was adopted to estimate the surface area of the samples. The nitrogen adsorption—desorption measurements were carried out using Micromeritics ASAP 2020 analyser. The porosity distribution pattern produced from the desorption branch of the isotherm utilising the Barrett–Joyner–Halenda (BJH) method.
2.3. Electrochemical investigations

The electrochemical properties of the FeVO₄ and P₄-FeVO₄ nanoparticles were investigated using a CHI660C electrochemical workstation with a 2 M KOH electrolyte with three electrode configurations. The Ag/AgCl and a platinum wire were used as reference and counter electrodes. The FeVO₄ was used as working electrode, which was prepared by mixing 85 wt% active material, 10 wt% activated carbon and 5 wt% polytetrafluoroethylene binder with few drops of ethanol. This slurry mixture was coated onto a current collector (Ni foam, 1 cm²) and dried at 60 °C for 4 h. The electrochemical processes of the as-prepared electrodes were characterised using cyclic voltammetry (CV). At the same time, the retention of capacity was investigated using galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). All electrochemical features were estimated by using the electrode mass of the active material (0.8 mg) present in the electrode. GCD profiles are used to calculate capacitance from the following equation:

\[ C_s = \frac{I \times \Delta t}{m \times V} (\text{F g}^{-1}) \]  

where \( C_s \), \( I \) (mA), \( \Delta t \) (s), \( V \) (V) and \( m \) (mg) are the specific capacitance, current, discharge time, potential window and mass of the electro active material respectively. A symmetric type supercapacitor device was assembled using P₄-FeVO₄ nanoparticles as electrodes. Polypropylene film (Celgard, 2400) and 2 M KOH were utilised as a separator and electrolyte. The Energy (E) and power (P) densities of the device were estimated using the following relations:

\[ E = \frac{0.5 \times C_s \times (V_{\text{max}}^2 - V_{\text{min}}^2)}{3.6} \text{ (Wh kg}^{-1}) \]  

\[ P = \frac{3600 \times E}{T} \text{ (W kg}^{-1}) \]  

Here \( V_{\text{max}} \) and \( V_{\text{min}} \) are the potential maximum and minimum during charge/discharge, and \( T \) is the discharge time. The Columbic efficiency (\( \eta \)) is determined using the following relation:

\[ \eta = \frac{t_d}{t_c} \]  

where \( t_d \) and \( t_c \) are charging and discharging time.

3. Results and discussion

3.1. Structure and morphology

Confirmation of synthesis of the desired structure was done through analysis of the XRD pattern of FeVO₄ and P₄-FeVO₄ nanoparticles, which are presented in figure 1(a). The diffraction patterns of both FeVO₄ and P₄-FeVO₄ nanoparticles matched with the structure in the crystal database reference JCPDS-38-1372. The matching of the pattern with the database structure in addition to the accompanying lattice parameter data obtained during the XRD confirmed that both synthesised FeVO₄ and P₄-FeVO₄ were triclinic. The lattice parameter values were \( a = 8.0572 \text{ Å, b = 9.347 Å, c = 6.7138 Å and } \alpha = 106.59°, \beta = 101.52° \) and \( \gamma = 96.69° \), which agree with previously reported values [39, 40]. A close inspection of the XRD pattern shows that higher intensity for the P₄-FeVO₄ than the bare FeVO₄ nanoparticles, indicating the better crystallinity of the P₄-FeVO₄ sample than the latter.

The spectra of FTIR analyses to identify the surface functional groups in the FeVO₄ and P₄-FeVO₄ nanoparticles are presented in figure 1(b). The FTIR spectra have absorption bands at 505 cm⁻¹, 678 cm⁻¹, 735 cm⁻¹, 839 cm⁻¹ and 972 cm⁻¹, which corresponds to the stretching vibrations of V=O bonds [41]. The absorption band centred at 1249 cm⁻¹ is related to C–O stretching mode. Further, the absorption band at 1662 cm⁻¹ indicates the presence of a residual amount of water moieties in the sample. FTIR spectra indicate the presence of Vanadium (V) and Iron (Fe) by their respective absorption bands.

The surface morphology of FeVO₄ and P₄-FeVO₄ particles were characterised using TEM, and the obtained TEM images are presented in figure 2. Figures 2(a) and (b) reveal that the bare FeVO₄ are spherical with size ranging from 150–180 nm (figure S1 is available online at stacks.iop.org/MRX/7/064010/mmedia). The P₄-FeVO₄ nanoparticles have the same morphology as bare FeVO₄ but are significantly smaller with sizes ranging from 50 to 100 nm (figures 2(c), (d), and S2). Thus, the use of PEG 4000 led to the fabrication of nanoparticles of FeVO₄ via P₄-FeVO₄, reducing the size of the particles.

The nitrogen adsorption-desorption measurements were performed to gain insight into the pore structure and distribution of the prepared samples. The adsorption-desorption isotherms for FeVO₄ and P₄-FeVO₄ samples are presented in figure 3. These adsorption isotherms display combined characteristics of type III/IV, which are characterised by a vertical increment of nitrogen uptake with loop kind of isotherm and indicates the
presence of pores in the samples [42]. The BET specific surface area (SSA) of FeVO₄ and P₄- FeVO₄ samples are 31.12 m² g⁻¹ and 41.06 m² g⁻¹, respectively. Here it is evident that the SSA of P₄- FeVO₄ has significantly improved due to the use of surfactant during the synthesis process. In addition, the porosity measurements were carried out using the BJH model, and respective distribution curve of the samples are presented in inset of figures 3(a), (b). The pore size distribution maxima observed at 116 nm, 220 nm and 302 nm for FeVO₄ and 17 nm, 19.3, 24.6 nm and 36.6 nm for P₄- FeVO₄. Pore diameters between 2–50 nm are identified as mesopores. Presence of small mesopores in the P₄- FeVO₄ sample is beneficial for energy storage [43].

3.2. Electrochemical features

To gain more insight in the electrochemical richness on the FeVO₄, cyclic voltammetry (CV) investigations were performed on P₄-FeVO₄ nanoparticles, in the potential range of 0 to −0.8 V in a 2 M KOH electrolyte. Presence of well-defined redox peaks in CV (figure 3(a)) curves indicates the influence of the redox reactions on capacitive behaviour of the electrode material. The redox peaks are visible at the potentials ∼−0.3 V and −0.5 V versus Ag/AgCl electrode. Further, the oxidation and reduction peaks shifted with increasing scan rates (figures S3(a) and (b)). It indicates the better reaction kinetics of the electrode material [44]. The peak at −0.5 V represents reduction reaction, and −0.3 V indicates the oxidation reaction [45],

\[
\begin{align*}
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^-
\end{align*}
\]

CV curve of P₄-FeVO₄ nanoparticles shows the higher area under the curve compared to bare FeVO₄ indicating the higher specific capacitance of P₄-FeVO₄. The CV curves of FeVO₄ and P₄-FeVO₄ nanoparticles at

**Figure 1.** (a) XRD spectrum of FeVO₄ and P₄-FeVO₄, (b) FTIR spectrum of FeVO₄ and P₄-FeVO₄.
different scan rates between 5–100 mVs⁻¹ are presented in figure S3. The CV curves are maintaining quasi-rectangular structure up to 100 mVs⁻¹ indicating the better sustainability of the electrodes at higher scan rates.

GCD curves of FeVO₄ and P4-FeVO₄ nanoparticles were measured at a current density of 1 Ag⁻¹ between 0 and −0.8 V and are presented in figure 4(b). The calculated specific capacitance values for P4-FeVO₄ are 428 Fg⁻¹, 271 Fg⁻¹, 158 Fg⁻¹, 90 Fg⁻¹ and 81 Fg⁻¹ at current densities of 2 Ag⁻¹, 4 Ag⁻¹, 6 Ag⁻¹, 8 Ag⁻¹ and 10 Ag⁻¹. The bare FeVO₄ nanoparticles exhibit 247 Fg⁻¹, 200 Fg⁻¹, 121 Fg⁻¹, 75 Fg⁻¹ and 32 Fg⁻¹ at current densities of 2 Ag⁻¹, 4 Ag⁻¹, 6 Ag⁻¹, 8 Ag⁻¹ and 10 Ag⁻¹. It is interesting to note that the P4-FeVO₄ shows higher capacitance compared to bare FeVO₄. It is attributed to the smaller size of the P4-FeVO₄ compared to bare sample and presence of mesopores in the sample. The mesopores provide enhanced diffusion process by facilitating more ion accessing channels. A comparison table (table S1) shows the relative higher capacitance of P4-FeVO₄ electrode to other binary transition metal oxides. Figure 4(c) presents the variation of specific capacitance with different current densities between 2 and 10 Ag⁻¹ for FeVO₄ and P4-FeVO₄ nanoparticles. In addition, GCD curves of FeVO₄ and P4-FeVO₄ nanoparticles at different current densities between 2–10 Ag⁻¹ are presented in figure S4. The specific capacitance of the electrode materials is decreasing with an increase in current densities. At higher current densities, the electrolyte ion doesn’t have enough time to intercalate the active electrode material. It accessed the only surface of active material leading to the poor capacitance.

In contrast, at lower current densities, the ions have ample time to access the whole interior part of the electrode material. It leads to higher capacitance at lower current densities [46]. Figure S5 displayed the enlarged GCD profiles of iR drop (ohmic drop) of FeVO₄ and P4-FeVO₄ nanoparticles and reveals that iR drop of P4-FeVO₄ electrode is lower when compared to the bare FeVO₄ electrode. This tendency of P4-FeVO₄ is due to the smaller size than the bare sample.

The cyclic stability is another critical parameter which determines the sustainability of the electrode material. Figure 4(d) shows the stability curves of FeVO₄ and P4-FeVO₄ electrodes after 1000 repeated charge-discharge cycles at a current density of 10 Ag⁻¹. It demonstrates that P4-FeVO₄ retains more capacitance compared to bare material; it is due to the better-withstanding capacity of electrode material during cycling. Even though P4-FeVO₄ was showing better stability over bare FeVO₄, it’s not sufficient for commercial applications. The P4-FeVO₄ electrode active material was collected after cycling (after 1000 cycles) and SEM images were recorded and presented in figure S6.
The SEM images show the presence of rough surfaces and agglomerated particles, indicating the destruction of sphere morphology due to volumetric stress created by ion intercalation/deintercalation during cycling. The moderate cyclic performance of P4-FeVO4 is attributed to the significant change in the morphology of the active electrode material.

Electrochemical Impedance Spectroscopy (EIS) measurement is a better analytical tool to analyse the resistive characteristics of an electrode. Figure 5 displays the respective Nyquist plot for FeVO4 and P4-FeVO4 electrodes in the frequency range of 0.01 Hz and $1 \times 10^5$ Hz. Inset of figure 4 presents equivalent circuit utilised to fit the EIS data. The charge transfer resistance ($R_{CT}$) and capacitance ($C_{DL}$) produced from the double layer are in a parallel manner to indicate the semicircle present in the high-frequency region. It is interesting to note that the FeVO4 and P4-FeVO4 electrodes do not possess semicircle indicating very less value of $R_{CT}$ [47].

Further, the absence of semicircle in the plot is may attributed to that the presence of a minimal distribution of charge storage and ohmic contact between current collector utilised and active electrode material [48, 49]. Also, the plot is tilted with an angle to the real axis showing the associated resistance with mass capacitance ($C_L$) and its better capacitive nature of the electrode. The transformation of higher frequency region to lower frequency tail is denoted as the Warburg element (W).

3.3. Performance of a P4-FeVO4 based symmetric supercapacitor

Three-electrode set-up was used in a preliminary investigation on the electro active material for its suitability in electrochemical applications. Also, it involves, only one electrode having electro active material. The get complete insight about the prepared sample, we have assembled a symmetric type supercapacitors device.
using P4-FeVO₄ as an active material. Figure 6(a) displays CV curves of this symmetric device at the scan rate from 10 to 50 mV s⁻¹ within the operating cell voltage from 0–1 V. The quasi symmetrical and rectangular-shaped CV curves indicating the better capacitive behaviour of the device. In addition to this, the rectangular
shape of the CV curve is maintained even at higher potential sweep rates confirming the excellent reversibility of this symmetric device.

This discussion is further boosted by the quasi-triangular shape of the GCD profiles at different current densities from 1 $\text{Ag}^{-1}$ to 10 $\text{Ag}^{-1}$, as displayed in figure 6(b). The specific capacitance value of 101 $\text{Fg}^{-1}$ is obtained from GCD measurements at a current density of 1 $\text{Ag}^{-1}$. Figure 6(c) presents the variation of specific capacitance with current density. As observed in the three-electrode system, the increment of current density harms the capacitance due to poor accessibility of electrolyte ions with the active electrode material. This device exhibits Columbic Efficiency (CE) of 73% at a current density of 1 $\text{Ag}^{-1}$. The reduced CE of the device is due to parasitic channels present in the electroactive material and the interfacing between electrode and electrolyte. This includes the measurements parameters and concentration of the electrolyte solution [50].

The cyclic stability is one of the important parameters for a supercapacitors device. The cyclic stability measurements of this device were carried out at 10 $\text{Ag}^{-1}$ up to 1000 repeated charge-discharge cycles (figure 6(d)). This device retains 57% of the initial capacitance after 1000 cycles, owing to the volumetric strain.
created by ion during intercalation and deintercalation process. The EIS measurements were performed on this symmetric device, and respective Nyquist plot is presented in figure 6(e). The $R_{\text{ct}}$ value of 2.7 $\Omega$ was observed from the Nyquist plot.

Estimation of energy density and power density using the two-electrode set-up is more appropriate than using the three-electrode set-up. These values are calculated from the GCD curves measured at different current densities. This device exhibits a maximum energy density of 14.14 Wh Kg$^{-1}$ with a power density of 313 W Kg$^{-1}$ is the specific current density of 1 Ag$^{-1}$. Ragone plot in figure 6(f) displays the variation of energy density with power density.

4. Conclusion

In summary, the use of FeVO$_4$ nanoparticles as electrode enhances the specific capacitance in supercapacitors devices, relatively more than most metal oxides. The material exhibits low charge transfer resistance, which is beneficial for performing charge-discharge at different rates. Synthesising FeVO$_4$ nanoparticles with structure-directing surfactant PEG improves their performance as electrode even further, higher than the bare FeVO$_4$, because the surfactant reduced the size, increases porosity, and improves the electronic properties of the FeVO$_4$. Therefore, this study revealed that the surfactant-assisted synthesis of FeVO$_4$ helps to reduce the particle size and improve the electrochemical performance of the supercapacitor device significantly. The symmetric supercapacitor device fabricated with FeVO$_4$ electrodes exhibits improved electrochemical properties.

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