Influence of the electrochemical properties of vanadium oxides on specific capacitance by molybdenum doping

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Abstract. Molybdenum (Mo)-doped vanadium dioxide (VO₂(B)) nanobelts were successfully synthesized using commercial vanadium pentoxide (V₂O₅) as the starting material and ammonium molybdate as the dopant by a simple hydrothermal route. Then, Mo-doped VO₂(B) nanobelts were transformed to Mo-doped V₂O₅ nanobelts by calcination at 400°C under an air atmosphere. The samples were characterized by X-ray powder diffraction, energy-dispersive X-ray spectrometer, elemental mapping, X-ray photoelectron spectroscopy, X-ray fluorescence and transmission electron microscopy techniques. The results showed that Mo-doped VO₂(B) and V₂O₅ solid solution with high purity were obtained. The electrochemical properties of Mo-doped VO₂(B) and V₂O₅ nanobelts as supercapacitor electrodes were measured using cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD). The specific capacitance of VO₂(B) nanobelts slightly declines with Mo doping, however, the specific capacitance of V₂O₅ nanobelts greatly improves with Mo doping. Mo-doped V₂O₅ nanobelts exhibit the specific capacitance as high as 526 F g^{−1} at the current density of 1 A g^{−1}. Both CV and GCD curves show that they have good rate capability and retain 464, 380, 324 and 273 F g^{−1} even at a high-current density of 2, 5, 10 and 20 A g^{−1}, respectively. It turns out that Mo-doped V₂O₅ nanobelts are ideal materials for supercapacitor electrodes in the present work.

Keywords. Mo-doped VO₂(B) nanobelts; Mo-doped V₂O₅ nanobelts; chemical synthesis; electrochemical properties; specific capacitance.

1. Introduction

Because of the advantages of high-power density, superior rate capability, excellent cycling life and environmentally friendly, supercapacitors (SCs) have grown into novel efficient energy storage devices, which have drawn great attention. SCs have tremendous potential in application in the fields of energy sources, communication, aerospace industry, electronic devices, etc. [1–7]. In order to expand the depth and scope of their application, the energy density is supposed to be improved. In particular, the exceptional electrode material is the key factor. According to the differences in storage mechanisms, SCs can be classified into two types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs). EDLCs physically store charges by reversible ion adsorption at the electrode–electrolyte interface, while PCs mainly chemically store the charges by redox reactions. Typically, electrode materials for EDLCs are composed of high surface area carbon-based materials, while electrode materials for PCs are composed of conductive polymers and transition metal oxides/hydroxides/sulphides [1,8]. Electrochemical capacitors (ECs) based on transition metal oxides/hydroxides/sulphides exhibit much higher specific capacitance than conventional carbon materials and better electrochemical stability than conducting polymers

[9,10]. Thus, it is urgent to discover inexpensive electrode materials made from transition metal oxides/hydroxides/sulphides with excellent performance, which becomes the focus in the research of SCs.

In the previous reports, some kinds of transition metal oxides/hydroxides/sulphides were already studied, including RuO₂, NiO, CuO, MnO₂, Co₃O₄, etc., however, their relatively high price or low conductivity hampered further application [8,11–14]. Under these circumstances, vanadium oxides (VO_x) have drawn increasingly greater interest due to their advantages including low cost, stable chemical and physical properties, high specific capacity and energy density, etc. [6,15–29]. The multiple valence states (V⁵⁺, V⁴⁺, V³⁺ and V²⁺) of vanadium can make it possible to form different kinds of oxides. Meanwhile, the unique layered structure favours the diffusion of metal ions or organic groups. Thus, VO_x have been considered as promising electrode materials, on which plenty of research has been carried out to improve their electrochemical performance.

On the one hand, as the morphology and crystal structure play a significant role in influencing the capacitive properties of electrode materials, VO_x with novel structures have been prepared and studied [16,30,31]. The contact area between the electrode materials and electrolyte can be promoted *via* adjusting the morphology of electrode

materials. As members of the family of VO_x , vanadium dioxide $\text{VO}_2(\text{B})$ and vanadium pentoxide (V_2O_5) are considered to be great candidates for efficient electrode materials which have potential in development and application. In recent years, nano-structured $\text{VO}_2(\text{B})$ and V_2O_5 with different morphologies [16,19,30–36] including hollow spheres, microspheres, thin films, nanofibres, nanowires, nanoribbons, nanotubes, nanorods, nanoporous structures, nanosheets constructing 3D architectures, layer-by-layer structures, interconnected V_2O_5 nanoporous networks, etc. have been synthesized by different approaches and their activity has been tested for SC applications. On the other hand, to improve the structure stability of electrode materials during the insertion and extraction of the metal ions in the electrolyte, materials with multi-composition based on VO_x were prepared and studied, including VO_x /carbon-based materials and doped VO_x . The former VO_x /carbon-based materials have been extensively studied in recent years [17,37–39]. However, doped VO_x materials used in the improvement of the electrochemical properties of VO_x have been comparatively less reported. Jeyalakshmi *et al* [40] reported Ni-doped $\beta\text{-V}_2\text{O}_5$ thin films with 5 wt% of Ni exhibiting the specific capacitance of 417 F g^{-1} at a scan rate of 5 mV s^{-1} . Our group reported W-doped VO_2 showing the specific capacitance of 253 F g^{-1} at the current density of 1 A g^{-1} [20]. Except these, there has been no literature reports about doped VO_x materials used to improve their specific capacitance, to the best of our knowledge [41]. Therefore, to promote the specific capacitance of VO_x electrodes with additives is meaningful and challenging for materials researchers.

Herein, we first prepared Mo-doped $\text{VO}_2(\text{B})$ and V_2O_5 nanomaterials to improve their specific capacitance of VO_x . It was found that 2% Mo-doped V_2O_5 nanomaterials exhibited the best specific capacitance as high as 526 F g^{-1} at the current density of 1 A g^{-1} .

2. Experimental

2.1 Materials

Commercial V_2O_5 , hydrogen peroxide (H_2O_2 , 30 wt%), ammonium molybdate and ethanol (EtOH) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without any further purification.

2.2 Synthesis of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials

Synthesis of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials was carried out according to our previous report [42] with slight modification. In a typical procedure, 0.455 g of commercial V_2O_5 powder was dispersed into 28 ml of deionized water in a 100 ml beaker with magnetic stirring at room temperature for 10 min. Then, 2 ml of H_2O_2 (30 wt%) and 5 ml of EtOH were successively added to the above mixture. After vigorously stirring for 30 min at room temperature, an amount of ammonium molybdate $[n(\text{Mo})/n(\text{V}+\text{Mo}) \times 100\% = 0, 1.0,$

2.0, 4.0, 8.0%; the corresponding content is 0, 0.083, 0.173, 0.348, 0.698 g] was added into the above solution. After another 0.5 h of stirring, the mixture was transferred into a 50 ml Teflon lined stainless steel autoclave, sealed and maintained at 180°C for 48 h. After the reaction, the products were filtered off, washed with H_2O and EtOH several times to remove any possible residue, and dried in a vacuum at 75°C for 12 h.

2.3 Synthesis of Mo-doped V_2O_5 nanomaterials

To obtain Mo-doped V_2O_5 nanomaterials, 0.2 g of the above Mo-doped $\text{VO}_2(\text{B})$ nanomaterials were placed in a crucible and heated using a muffle furnace at a 5°C min^{-1} heating rate under an air atmosphere at 400°C for 4 h, and then cooled to room temperature naturally.

2.4 Materials characterization

The phase and composition of the products were identified by X-ray powder diffraction (XRD, Panalytical X'Pert powder diffractometer at 40 kV and 40 mA with Ni-filtered $\text{Cu K}\alpha$ radiation). The chemical composition of the as-obtained samples was revealed by the use of an energy-dispersive X-ray spectrometer (EDS) and elemental mapping attached to a scanning electron microscope (SEM, QUANTA450). X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of the products and confirm the oxidation state of vanadium performed on an ESCALAB250Xi, Thermo Fisher Scientific. The compositions of the doped materials were tested by X-ray fluorescence (XRF, XRF-1800, Shimadzu, Japan). The morphology and dimensions of the products were observed by transmission electron microscopy (TEM, FEI Tecnai F30, FEI). The samples were dispersed in absolute EtOH with ultrasonication before TEM characterization.

2.5 Electrochemical characterization

Electrochemical tests were performed using a three-electrode cell, in which Ni-grid and saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. The working electrodes were composed of 80 wt% of active material (Mo-doped VO_x), 10 wt% of carbon black and 10 wt% of polyvinylidene difluoride (PVDF). *N*-Methyl-2-pyrrolidone (NMP) was used as a solvent. The mixed slurries were coated onto Ni foils and heated at 80°C overnight to remove the organic solvent. Then, these foils were pressed onto Ni-grids at a pressure of 10 MPa. Cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) were used to obtain the electrochemical characteristics. The electrolyte was $1 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_4$ aqueous solution in the electrochemical tests of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials. CV data were collected between -0.7 and 1.0 V and GCD tests were performed in the potential range of -0.7 to 1.0 V at a current density of 1 A g^{-1} . The electrolyte was 1 mol l^{-1}

Figure 1. XRD patterns of Mo-doped VO_x with different Mo-doped fractions: (a) Mo-doped $\text{VO}_2(\text{B})$ nanobelts; (b, c) Mo-doped V_2O_5 nanobelts.

LiNO_3 solution in the electrochemical tests of Mo-doped V_2O_5 nanomaterials. CV data were collected between -0.5 and 0.6 V at different scan rates (2 – 100 mV s^{-1}) and GCD tests were performed in the potential range of -0.5 to 0.6 V at a current density of 0.2 – 20 A g^{-1} .

The average specific capacitance obtained from CV was calculated according to equation (1):

$$C_v = \frac{S}{2m\nu \cdot \Delta V} \quad (1)$$

where C_v (F g^{-1}) is the specific capacitance, S is the area under the CV curve, m (g) is the mass of active material within the electrode, ν (mV s^{-1}) is the scan rate and ΔV (V) represents the potential drop during the discharge process. The specific capacitance (C_p , F g^{-1}) of the active material in the electrode determined using the charge–discharge curves can be calculated using equation (2):

$$C_p = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (2)$$

where I (A) is the discharge current and Δt (s) is the discharge time. The energy density E (W h kg^{-1}) of the active material in the electrode can be calculated using equation (3):

$$E = \frac{1}{2} C \cdot (\Delta V)^2. \quad (3)$$

The power density P (W kg^{-1}) can be calculated from the energy density E and the discharge time Δt according to equation (4):

$$P = \frac{E}{\Delta t}. \quad (4)$$

3. Results and discussion

3.1 Characterization of Mo-doped VO_x nanomaterials

The crystal structure and phase purity of the prepared samples were characterized by XRD, as shown in figure 1. Figure 1a depicts the XRD patterns of the as-prepared $\text{VO}_2(\text{B})$ with different Mo-doped fractions obtained by the direct hydrothermal route. It could be found that Mo doping had influence on the crystal structure and phase purity of $\text{VO}_2(\text{B})$. Without Mo doping, well crystalline $\text{VO}_2(\text{B})$ (JCPDS no. 65-7960) [43] was obtained and no other VO_x were detected. With the increase of the concentration of Mo-doped fractions, the crystallization of $\text{VO}_2(\text{B})$ decreased compared with the XRD patterns of undoped $\text{VO}_2(\text{B})$ as shown in figure 1a. Meanwhile, it could be observed that some peaks of doped $\text{VO}_2(\text{B})$ shifted slightly towards lower 2θ value. Typically, the peak located at 27.88° shifted towards small reflection angle with increasing Mo-doped fractions, suggesting that the adjacent interplanar distance (d -value) slightly increased. It's well known that the ionic radius of the Mo atom is larger than that of the V atom, so the slight increase in the d -value is attributed to Mo atoms substituting V atoms in the VO_2 lattice, resulting in the peak shift towards low 2θ angle. When the concentration of Mo-doped fractions reached 8%, although the phase $\text{VO}_2(\text{B})$ still remained, the peak at 14.4° and the peak at 44.1° disappeared. The reason could be that the growth of $\text{VO}_2(\text{B})$ had been stunted due to the high concentration of dopants in the system [44]. After the calcination at 400°C under the air atmosphere, Mo-doped $\text{VO}_2(\text{B})$ was converted to Mo-doped V_2O_5 (JCPDS no. 41-1426) [45], as shown in figure 1b. It could also be observed that some peaks of doped V_2O_5 shifted slightly towards lower 2θ value, which was consistent with the result of Mo-doped $\text{VO}_2(\text{B})$.

Figure 2. EDS spectra of 2% Mo-doped VO₂(B) nanobelts and 2% Mo-doped V₂O₅ nanobelts.

Further information about the composition of the as-obtained Mo-doped VO_x was characterized by EDS, elemental mapping and XPS and we chose the samples with the concentration of 2% Mo. Figure 2 shows the EDS spectra of Mo-doped VO₂(B) and Mo-doped V₂O₅. Both of them revealed that the samples consisted of V, O and Mo elements. It is noted that C was from the conducting resin which was used to paste and fix the sample during the test. Figure 3 depicts elemental mapping images of Mo-doped VO₂(B) and Mo-doped V₂O₅, and also reveals that these two samples consisted of V, O and Mo elements. Furthermore, these elements have homogeneous distribution in the field of vision, which corresponded to the XRD observation.

Important information about the surface molecular and electronic structure of the as-obtained sample, as well as the chemical element valence, was provided by XPS. The binding energies obtained from the XPS analysis were corrected for specimen charging by referencing C_{1s} to 284.81 eV [46]. Figure 4 shows the XPS spectra of the as-obtained Mo-doped VO₂(B) and Mo-doped V₂O₅. The survey spectra (figure 4a and d) indicated that there were only three elements V, O and Mo in the spectra of these two samples, in agreement

with the observation of EDS and elemental mapping. As for Mo-doped VO₂(B), binding energy at 530.3 eV (figure 4b) was assigned to the O_{1s} peak. The core-level spectrum of V_{2p} peak (figure 4b) split off into two peaks, including V_{2p_{1/2}} with a binding energy of 524.3 eV and V_{2p_{3/2}} with a binding energy of 516.9 eV, which were the characteristics of vanadium in the +4 oxidation state [47,48], in agreement with XRD observation. The above results were very consistent with the model of Mo-doped VO₂(B) in the previous reports [47–50]. The value for the V_{2p_{3/2}} peak was slightly higher than that for pure VO₂ powder [47,48], but was in agreement with the reports of W-doped VO₂ [44,51], suggesting that the binding energy of V_{2p_{3/2}} increased slightly after Mo doping. As for Mo-doped V₂O₅, the binding energy of the O_{1s} peak was located at 530.5 eV (figure 4e). The V_{2p} peak (figure 4e) consisted of V_{2p_{1/2}} with a binding energy of 525.1 eV and V_{2p_{3/2}} with a binding energy of 517.5 eV, corresponding to vanadium in the +5 oxidation state [47,48]. This result is well in agreement with XRD observation. Figure 4c and f, respectively, describe the core-level spectra of Mo_{3d} peak of these two samples, which split off into two peaks Mo_{3d_{3/2}} and Mo_{3d_{5/2}}. The binding energies of Mo_{3d_{3/2}} and Mo_{3d_{5/2}} peaks were centred at 235.7 and 232.5 eV in Mo-doped VO₂(B) (figure 4c) and 235.9 and 232.7 eV in Mo-doped V₂O₅ (figure 4c). According to the standard binding energy, the existing form of molybdenum in both samples was Mo⁶⁺ [48]. Therefore, based on the analyses of XRD, EDS, elemental mapping and XPS, Mo-doped VO₂(B) and Mo-doped V₂O₅ solid solutions with high purity were successfully synthesized.

Table 1 typically lists the composition of 2% Mo-doped VO₂(B) and 2% Mo-doped V₂O₅ characterized by XRF. The weight contents of O, V and W elements were 38.07, 59.73 and 2.20 wt% of Mo-doped VO₂(B) and 43.51, 54.57 and 1.92 wt% of Mo-doped V₂O₅, respectively, revealing that their atomic ratio was 1.9926:0.9808:0.0192 ($n(\text{Mo})/n(\text{V} + \text{Mo}) \times 100\% = 1.92\%$) and 2.4948:0.9816:0.0184 ($n(\text{Mo})/n(\text{V} + \text{Mo}) \times 100\% = 1.84\%$). These results revealed that the real contents of Mo in final products were slightly lower than its corresponding nominal contents. The reason was that the dopants and VO_x had different speeds of co-precipitation or the dopants impede the growth of VO_x [46]. To be convenient for readers, we used the data of the Mo atomic percent in feed in this study.

The typical TEM images of the samples are shown in figure 5. Without any additives, it could be observed from figure 5a and b that the Mo-doped VO₂(B) displayed the belt-like morphology, thus VO₂(B) nanomaterials were synthesized in agreement with the previous report [42]. The average diameter was in the range of 50–100 nm and the length was up to 1 μm. With 2% Mo dopant, as shown in figure 5c and d, the morphology of Mo-doped VO₂(B) was little influenced by the Mo doping. After the heat treatment at 400°C, the morphology of Mo-doped V₂O₅ was similar to Mo-doped VO₂(B). It could be observed from figure 5e and f that Mo-doped V₂O₅ displayed a belt-like morphology. However, the edge and surface of Mo-doped V₂O₅ nanomaterials became broken and girdle

Figure 3. SEM images and their corresponding elemental mapping images of (a–d) 2% Mo-doped VO₂(B) nanobelts and (e–h) 2% Mo-doped V₂O₅ nanobelts.

Figure 4. XPS spectra of 2% Mo-doped (a–c) VO₂(B) and (d–f) V₂O₅ nanobelts: (a, d) survey spectrum; (b, e) O 1s and V 2p peaks; (c, f) Mo 3d peak.

Table 1. The composition of the doped VO_x by the XRF test.

Sample	O, wt%	V, wt%	Mo, wt%	O:V:Mo, atomic ratio
Mo-doped VO ₂ (B)	38.07	59.73	2.20	1.9926:0.9808:0.0192
Mo-doped V ₂ O ₅	43.51	54.57	1.92	2.4948:0.9816:0.0184

roughness to some extent, which was owing to the growth, transformation or aggregation by surface and boundary diffusion during the calcination process. The above characteristic

of the as-obtained V₂O₅ nanomaterials suggested that they had high capacitance to be used as SC electrodes [31]. Furthermore, the microstructure of the VO_x nanobelts was

Figure 5. TEM images of the samples: (a, b) VO₂(B); (c, d) 2% Mo-doped VO₂(B); (e, f) 2% Mo-doped V₂O₅ nanomaterials.

studied by high-resolution transmission electron microscopy (HRTEM). As shown in figure 6a, the HRTEM image of Mo-doped VO₂(B) revealed that the distance between the neighbouring planes was about 0.311 nm. This value was

consistent with that of the (002) plane of VO₂(B), which was in agreement with the d_{002} spacing in the XRD patterns (figure 1a). The HRTEM image (figure 6b) of Mo-doped V₂O₅ revealed that the distance between the neighbouring planes

Figure 6. HRTEM images of the samples: (a) 2% Mo-doped $\text{VO}_2(\text{B})$ nanomaterials and (b) 2% Mo-doped V_2O_5 nanomaterials.

was about 0.439 nm. This value was consistent with that of the (001) plane of V_2O_5 , which was in agreement with the d_{001} spacing in the XRD patterns (figure 1b).

3.2 Electrochemical properties of Mo-doped VO_x nanomaterials

To exhibit the merits of the as-obtained Mo-doped VO_x nanomaterials, their electrochemical properties for SC electrodes were studied by the CV and GCD methods in a three-electrode cell. Figure 7a shows the CV curves of Mo-doped $\text{VO}_2(\text{B})$ obtained with different concentrations of Mo fractions (0, 1, 2, 4 and 8%). All curves had similar shapes and exhibited two pairs of redox peaks, indicating that all samples had pseudocapacitive behaviour. From the analyses of CV curves, the specific capacitances of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials prepared with the concentrations of Mo-doped fractions (0, 1, 2, 4 and 8%) were, respectively, 227, 191, 200, 158 and 126 F g^{-1} , indicating that Mo-doping is not beneficial for $\text{VO}_2(\text{B})$ nanomaterials to improve their electrochemical performance and the values of pseudocapacitance were also obtained by GCD. Figure 7b shows their corresponding variations of potential vs. time for discharge curves recorded by the GCD test with a high-current density of 1 A g^{-1} . It could be clearly observed that as the concentration of Mo-doped fractions increased, the specific capacitance of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials displayed a downwards trend in general. The specific capacitances of Mo-doped $\text{VO}_2(\text{B})$ nanomaterials prepared with the concentrations of Mo-doped fractions (0, 1, 2, 4 and 8%) are, respectively, 221, 190, 194, 155 and 121 F g^{-1} , corresponding to CV observations. The specific capacitance of Mo-doped $\text{VO}_2(\text{B})$, synthesized when the concentration of Mo-doped fractions was 2%, was slightly higher than that of 1% doping. These results indicated that although Mo doping could not improve the energy storage capability

of $\text{VO}_2(\text{B})$ nanomaterials, a moderate amount of Mo doping may bring about some unique changes in the structure of $\text{VO}_2(\text{B})$ nanomaterials, thus influencing their properties, which deserve further study. Owing to this reason, we transformed Mo-doped $\text{VO}_2(\text{B})$ to Mo-doped V_2O_5 , and it was found that Mo-doped V_2O_5 could improve the specific capacitance of V_2O_5 . Figure 7c shows the CV curves of Mo-doped V_2O_5 nanomaterials obtained with different concentrations of Mo fractions (0, 1, 2, 4 and 8%). All curves had similar shapes and exhibited two pairs of redox peaks, indicating that all samples had pseudocapacitive behaviour. The specific capacitances of Mo-doped V_2O_5 nanomaterials prepared with concentrations of Mo fractions (0, 1, 2, 4 and 8%) from the CV curves were, respectively, 450, 435, 521, 442 and 283 F g^{-1} . Figure 7d depicts their corresponding variations of potential vs. time for discharge curves recorded by the GCD test with a high-current density of 1 A g^{-1} . The relatively symmetrical potential–time curves could be observed. Each curve had two distinct potential plateaus which was well consistent with the redox peaks in the CV curves depicted in figure 7c. This indicated that high value was mainly caused by faradic pseudocapacitance which was much higher than the double layer capacitance. Steep in high potential illustrated that capacitive behaviour was influenced by an electrical double layer structure accompanied by redox reaction, which arise from the electrochemical adsorption and released at the interface of the electrode and electrolyte [16,31]. From figure 7d, it could be clearly observed that V_2O_5 synthesized when the concentration of Mo-doped fractions was 2% displayed the highest specific capacitance. The specific capacitance of Mo-doped V_2O_5 nanomaterials prepared with concentrations of Mo fractions (0, 1, 2, 4 and 8%) were, respectively, 453, 432, 526, 443 and 278 F g^{-1} , in agreement with the results of CV. These results indicated that a moderate amount of Mo doping could improve energy storage capability of V_2O_5 nanomaterials. The reason may be that Mo doping transformed the

Figure 7. (a, c) CV curves at the scan rate of 10 mV s^{-1} and (b, d) potential vs. time for charge and discharge profiles at the current density of 1 A g^{-1} of Mo-doped VO_x nanobelts with different Mo-doped fractions: (a, b) Mo-doped $\text{VO}_2(\text{B})$ nanobelts; (c, d) Mo-doped V_2O_5 nanobelts.

structure of V_2O_5 nanomaterials to an ‘open-type’, which increased utilization of the surface of V_2O_5 nanomaterials and accelerated the transfer of electrolyte ions. To disclose the reason for Mo-doped V_2O_5 exhibiting the best electrochemical behaviour, electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 100 kHz – 0.01 Hz , as shown in figure 8. The semicircle in the high-frequency region of the Nyquist plots represents the interfacial charge transfer resistance, which is mainly dependent on the conductivity of the electrode–electrolyte interface, the pore structure and the thickness of the active material [28]. The semicircle of Mo-doped V_2O_5 is smaller than that of pure V_2O_5 , denoting an excellent interfacial charge-transfer behaviour. The equivalent series resistance including the electrolyte resistance, the intrinsic resistance of the active material, and the contact resistance between the active material and the current collector can be calculated from the intersection of the curve in the high-frequency region. These two samples show low equivalent series resistance, suggesting a good ion response in the high-frequency ranges and good connection between the active material and current collector [52].

According to the above analyses, 2% Mo-doped V_2O_5 nanomaterials had the best electrochemical properties, thus, in the following we focused on this sample. Figure 9 displays the CV curves of Mo-doped V_2O_5 nanomaterials recorded at different scan rates from 2 to 100 mV s^{-1} within a potential window of -0.5 to 0.6 V in $1 \text{ mol l}^{-1} \text{ LiNO}_3$ electrolyte. When the scan rate was under 20 mV s^{-1} , each CV curve showed two pairs of redox peaks (two anodic peaks at positive current density and two cathodic peaks at negative current density), which indicated superior faradaic reactions at the electrode surface and the electrochemical redox reaction based on the Li ion intercalation and extraction was associated with the equation as follows [53]:

The changes of crystal phases occurred along with the whole process were generally designated as α ($0 < x < 0.1$), ε ($0.35 < x < 0.5$) and δ ($0.9 < x < 1$) [34,53]. When the scan rate was over 20 mV s^{-1} , two pairs of redox peaks gradually

Figure 8. The comparable Nyquist plots of pure V_2O_5 and Mo-doped V_2O_5 nanomaterials obtained over the frequency range of 100 kHz to 0.01 Hz.

overlapped with one pair of redox peaks. The response current of electrodes increased with the increase of the scan rate, which demonstrated excellent kinetics and reversibility of electrodes [16,31]. Furthermore, the oxidation peaks shifted positively and reduction peaks shifted negatively with the increasing of scan rates, which was attributed to the polarization effect of electrodes [16,31]. As depicted in figure 9, the redox peaks still existed even at 100 mV s^{-1} which indicated that Mo-doped V_2O_5 nanomaterials had good rate capability [19].

To quantify the rate capability of Mo-doped V_2O_5 nanomaterials, a GCD test was carried out. Figure 10 presents discharge curves performed at various current densities. The specific capacitances of the Mo-doped V_2O_5 nanomaterials calculated from the discharge time were 526, 464, 380, 324 and 273 F g^{-1} at current densities of 1, 2, 5, 10 and 20 A g^{-1} , respectively. With the increase of the current, the specific capacity declined. The gradual reduction of the

Figure 9. CV curves of Mo-doped V_2O_5 nanobelts at different scan rates.

Figure 10. (a) Galvanostatic discharge curves at different current densities of Mo-doped V_2O_5 nanobelts and (b) Ragone plot of Mo-doped V_2O_5 nanobelts.

Table 2. Comparison of specific capacitance of the as-obtained Mo-doped V_2O_5 nanomaterials with V_2O_5 materials reported in the previous literature studies.

Types of V_2O_5 materials	Electrolyte	Potential, V	Current, A g ⁻¹	Capacitance, F g ⁻¹	References
V_2O_5 powders	2 M KCl	-0.2 to 0.7	5 mV s ^{-1a}	262	[55]
V_2O_5 nanobelts, nanoparticles and microspheres	1 M LiNO ₃	-0.4 to 0.8	1	140, 276, 308	[31]
V_2O_5 nanoflowers, nanoballs, nanowires and nanorods	1 M Na ₂ SO ₄	0–1	1	119, 161, 177, 235	[16]
Porous V_2O_5 nanotubes	2 M LiNO ₃	-0.2 to 0.8	1	363	[56]
V_2O_5 nanowires	1 M Na ₂ SO ₄	-0.4 to 0.6	1	146	[57]
Hollow spherical V_2O_5	5 M LiNO ₃	-0.2 to 0.8	5 mV s ^{-1a}	479	[34]
Nano porous V_2O_5	2 M KCl	-0.2 to 0.8	5 mV s ^{-1a}	214	[58]
V_2O_5 tubular nanofibres	2 M KCl	-0.2 to 0.7	5 mV s ^{-1a}	210	[59]
Electrospun V_2O_5 nanofibres	2 M KCl	0–0.9	0.1	176	[35]
Interconnected V_2O_5 nanoporous networks	0.5 M K ₂ SO ₄	0.2–0.8	0.1	304	[32]
3D structures of V_2O_5 nanosheets	1 M Na ₂ SO ₄	-1 to 1	0.5	451	[30]
3D V_2O_5 networks	1 M Na ₂ SO ₄	0–1	0.25	335	[60]
β - V_2O_5 thin films	1 M LiClO ₄ in PC	-0.8 to 1.2	5 mV s ^{-1a}	346	[61]
Ni-doped β - V_2O_5 thin films	1 M LiClO ₄ in PC	-0.8 to 1.2	5 mV s ^{-1a}	417	[40]
Mo-doped V_2O_5 nanobelts	1 M LiNO ₃	-0.5 to 0.6	1	526	This work

^aThe specific capacitance was obtained by the CV curve. M = mol l⁻¹; PC = propylene carbonate.

capacitance may be due to the incremental voltage drop and the insufficient active materials involved in the redox reactions at a higher current density [21,54]. Besides, the process of charge–discharge may lead to a low utilization rate of active materials at high-current density [1]. The attenuation of specific capacitance reduced slowly from the low-current density (1 A g^{-1}) to the high-current density (20 A g^{-1}). The 88.2, 72.2, 61.6 and 51.9% of the capacitance values at 2, 5, 10 and 20 A g^{-1} could remain compared with the value at 1 A g^{-1} . These results indicated that Mo-doped V_2O_5 nanomaterials had good rate capability in agreement with CV observations. In this contribution, we focused on the improvement of specific capacitance of VO_x . Thus, it was necessary to compare the specific capacitance of Mo-doped V_2O_5 nanomaterials with other V_2O_5 materials of previous reports. Table 2 summarizes the values of specific capacitance of present Mo-doped V_2O_5 nanomaterials and other V_2O_5 materials reported in the previous literature. As can be seen, the specific capacitances of V_2O_5 nanomaterials are much higher than the previous values of V_2O_5 materials in the aqueous electrolyte. Furthermore, Mo-doped V_2O_5 nanomaterials (526 F g^{-1}) had higher specific capacitance than Ni-doped $\beta\text{-V}_2\text{O}_5$ thin films (417 F g^{-1}) as reported by Jeyalakshmi *et al* [40]. Figure 8b shows the Ragone plot of the as-prepared Mo-doped V_2O_5 nanomaterials. According to equations (3) and (4), the calculated E values at current densities of 1, 2, 5, 10 and 20 A g^{-1} were 318, 281, 230, 196 and 165 W h kg^{-1} , respectively, and the corresponding P values were 1980, 3960, 9900, 19,800 and $39,600 \text{ W kg}^{-1}$, respectively, which exhibited outstanding electrochemical performance of Mo-doped V_2O_5 nanomaterials. Therefore, nano-structured Mo-doped V_2O_5 prepared in this study using a simple chemical route exhibited an excellent capacity and was considered to be one of the most promising candidates for SC electrodes in the future.

4. Conclusion

In summary, Mo-doped $\text{VO}_2(\text{B})$ and Mo-doped V_2O_5 nanomaterials were successfully synthesized using commercial V_2O_5 as the starting material and ammonium molybdate as the dopant. The samples were characterized by XRD, EDS, elemental mapping, XPS, XRF and TEM techniques. The results showed that Mo-doped $\text{VO}_2(\text{B})$ and V_2O_5 solid solutions with high purity were obtained. The electrochemical properties of Mo-doped $\text{VO}_2(\text{B})$ and V_2O_5 nanomaterials as SC electrodes were measured using CV and GCD. Specific capacitance of $\text{VO}_2(\text{B})$ nanomaterials slightly declined by Mo doping, however, specific capacitance of V_2O_5 nanomaterials greatly improved by Mo doping. Mo-doped V_2O_5 nanomaterials exhibited specific capacitance as high as 526 F g^{-1} at the current density of 1 A g^{-1} , and they had good rate capability. Mo-doped V_2O_5 nanomaterials retained specific capacitances of 464, 380, 324 and 273 F g^{-1} even at high-current densities of 2, 5, 10 and 20 A g^{-1} , respectively. The significance of this

work was that it provided more insights into the influence of Mo doping on the electrochemical properties of VO_x .

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