

Hydrothermal Synthesis of Flower-like Fe-doped VO₂(B) with Enhanced Lithium Ion Storage Performance

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Flower-like Fe_xVO₂(B) samples (x=0-0.045mol%) have been successfully fabricated via a hydrothermal method followed with annealing in argon atmosphere at 350°C for 1 h. The physical properties of the prepared samples were analyzed by XRD, XPS, FESEM, and EDS analyses. The electrochemical properties of the prepared samples were characterized by cyclic voltammetry(CV), electrochemical impedance spectroscopy (EIS), and charge-discharge tests. The results demonstrated that Fe doping could enhance the electrochemical reaction reversibility, decrease charge transfer resistance, and increase the specific capacity of VO₂(B). In particular, the Fe_{0.03}VO₂(B) sample showed the best lithium storage performance with initial discharge capacity of 306 mAh g⁻¹ at the current density of 0.1 C in the voltage range from 1.5 to 4.0 V, much higher than that (195 mAh g⁻¹) of the pure VO₂(B).

Keywords: lithium-ion batteries; electrochemical performance; VO₂(B); Fe doping; hydrothermal method

1. INTRODUCTION

The ever-increasing demand for electric vehicles (EV) and renewable energy sources (wind, water, and solar energy) is pushing the development of high performance energy storage and conversion devices. Lithium-ion batteries (LIBs) are currently considered as one of the most popular energy storage devices due to the advantages of their high-energy density, high-rate capability, relatively low self-discharge rate, and high energy density[1-6]. However, it still a great challenge for LIBs to meet the requirements for applications in the fields of EV and large-scale stationary (“grid”) energy storage. Among various potential cathode materials for the next-generation LIBs, vanadium oxides (V₂O₅, V₆O₁₃, VO₂, V₂O₃, etc.) have attracted more and more attentions because of their

distinct advantages of high specific capacity, abundant sources, and low cost [7-17]. In particular, VO₂ (B) stand out for LIBs due to its large theoretical capacity (320 mAh g⁻¹) [18] and unique bilayer structure with abundant tunnels for fast Li⁺ intercalation/deintercalations[19-21]. Unfortunately, the practical application of VO₂ (B) as cathode material of LIBs has been hampered due to its slow electrochemical kinetics, low electronic and ionic conductivity, and poor structural stability[22]. One of the ways to surmount these drawbacks is to carry out transition elements doping, such as Cu²⁺, Al³⁺ and Ti⁴⁺[23,24].

Herein, we report a Fe-doped VO₂(B) material with flower-like morphology prepared by using a facile hydrothermal method. The effect of Fe doping on the microstructure and electrochemical performance of VO₂(B) are investigated in detail. The results demonstrate that Fe doping could significantly enhance the lithium storage performance of VO₂(B).

2. MATERIALS AND METHODS

2.1. Synthesis of Fe doping VO₂(B)

Fe-doped VO₂(B) were synthesized by a facile hydrothermal method. All chemical reagents were analytical grade and used without further purification. In a typical synthesis procedure, 1.25 g oxalic acid dihydrate (C₂H₂O₄·2H₂O) and 0.4g Vanadium pentoxide (V₂O₅) were dissolved in 20 mL of deionized water. The mixed solution was kept under constant stirring at 80°C in a water bath until a blue colored VO₂C₂O₄ solution formed, and then a suitable amount of Fe(NO₃)₃·9H₂O, 20ml of the VO₂C₂O₄ solution and 3 ml of 30% H₂O₂ were added into a 100 ml Inner lining of reaction kettle pre-filled with 30 ml of deionized water. After stirring for 10 minutes, the autoclave was sealed and maintained at 160°C for 24 h in an oven, followed by natural cooling to room temperature. After the hydrothermal reaction, the resultant precipitate was collected by filtration, washed with deionized water several times, and then freeze dried to get the precursor. Finally, the obtained precursor was annealed in nitrogen atmosphere at 350°C for 1 h to obtain the Fe-doped VO₂(B). The molar ratios of Fe to V were increased gradually from 0% to 4.5% and the corresponding samples were labeled as pure VO₂(B), Fe_{0.015}VO₂(B), Fe_{0.03}VO₂(B), and Fe_{0.045}VO₂(B).

2.2. Characterization

All the samples were characterized by using a Philips X'pert Pro diffractometer with a Cu K α radiation source ($\lambda = 0.154$ nm) at the scanning rate of 6 °/min. Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 field emission scanning electron microscopy. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB 250Xi spectrometer using a Al K α (1486.6eV) X-ray source. All spectra were calibrated to the binding energy of the C 1s peak at 284.8 eV. The base pressure was around 10⁻⁸ Pa.

2.3. Electrochemical measurements

The electrochemical performances of the Fe-VO₂(B) samples were investigated in two electrode coin-type cells (CR2025) that were assembled in a glove box. Filled with ultrahigh-purity argon. Fe-VO₂(B), acetylene black, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 7:2:1 were mixed and then dispersed in N-methyl-2-pyrrolidone (NMP) solvent to make a slurry, which was then coated uniformly on Al foil and dried in a vacuum oven at 90°C for 12 h to obtain the cathodes. 1 mol/L LiPF₆ dissolved in a mixture of dimethyl carbonate (DMC), ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte (DMC/EC/DEC=2:2:1 in volume). Lithium metal was employed as the counter and reference electrodes, and Celgard 2400 was used as the separator. Galvanostatic charge/discharge measurements were performed using a multichannel battery testing system (NEWARE CT3008W). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were tested using a CHI760D electrochemical workstation.

3. RESULTS AND DISCUSSION

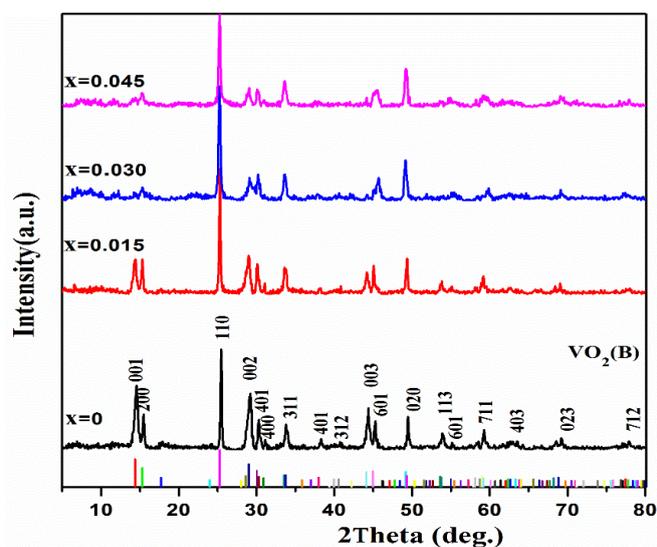


Figure 1. XRD patterns of the series of Fe-VO₂(B) samples.

Figure 1 shows the XRD patterns of the pure VO₂(B) and Fe-doped VO₂(B) samples. The peaks from all the samples show a single monoclinic VO₂ phase (JCPDS Card No.81-2392) and no impurity phase is detected [25], suggesting that Fe doping has no effect on the phase structure of VO₂(B). However, with the increase of Fe content, the (001) diffraction peak decreases gradually. Table 1 compares the lattice parameters of the pure VO₂(B) and Fe-doped VO₂(B) samples. The lattice parameters were determined by using the MDI Jade software (Jade 6 XRD Pattern Processing Software). Obviously, the interlayer distance (*c*) increases with the increase of Fe doping content, which can be due to the larger ionic radius of Fe³⁺ (0.65 Å) than that of V⁴⁺ (0.58 Å) [26,27].

Table 1. Comparison of the lattice parameters and cell volume for the series of Fe-VO₂(B) samples.

Specimen	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
VO ₂ (B)	12.0396	3.6737	6.4199	271.79
Fe _{0.015} VO ₂	12.0684	3.6833	6.4321	274.17
Fe _{0.030} VO ₂	12.0010	3.7042	6.4593	274.51
Fe _{0.045} VO ₂	12.0649	3.6968	6.4613	275.22

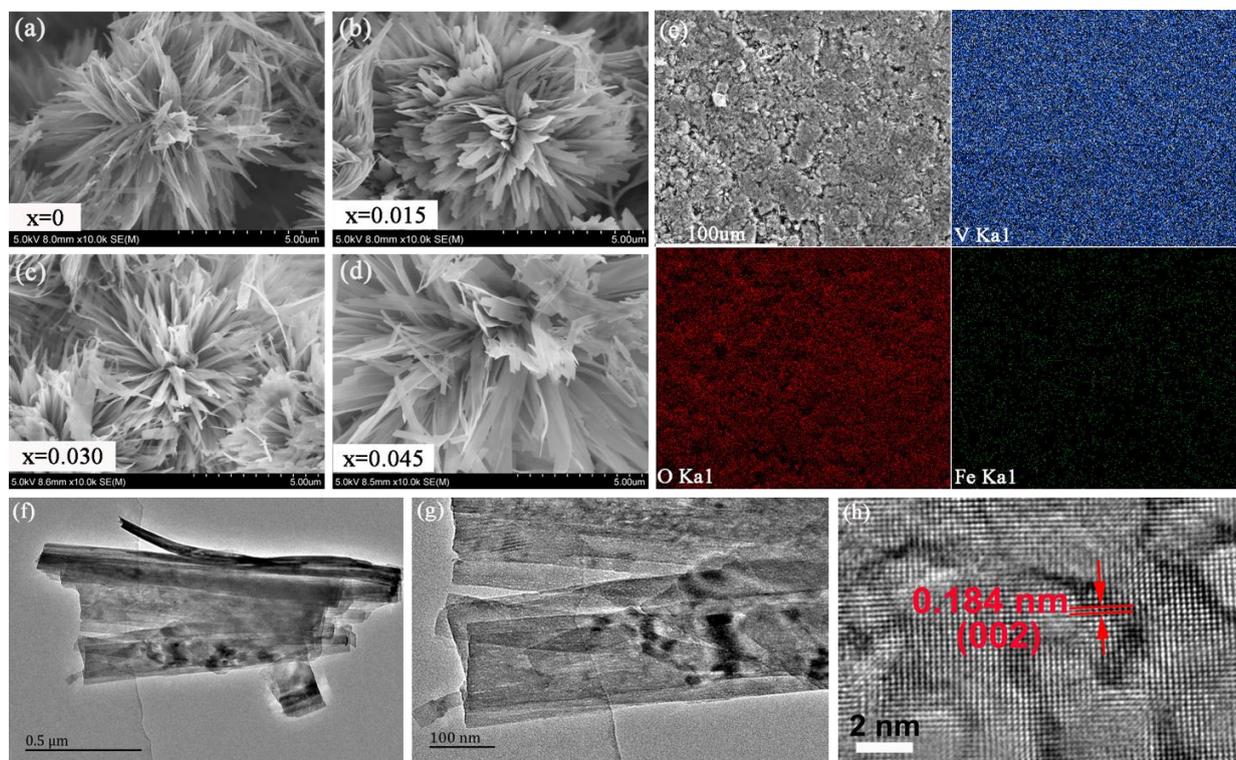
**Figure 2.** (a-d) FESEM images of the series of Fe-VO₂(B) samples; (e) element mapping images of V, O, and Fe of Fe_{0.030}VO₂(B); (f-g) TEM images of Fe_{0.030}VO₂(B); (h) HRTEM image of Fe_{0.030}VO₂(B).

Fig. 2 (a-d) presents the FESEM images of the series of Fe-doped VO₂(B) samples. It can be clearly seen that all the four samples exhibit hierarchical flower-like microspheres morphologies, which are composed of end-connected nanosheets. There are plenty of structural voids between the primary building blocks, which is beneficial for electrode/electrolyte contact and enhances the kinetics performance. Meanwhile this special structure was also beneficial to the transport of Li⁺. By a detail observation, one can find that the lateral size of the nanosheets increases with the increase of Fe doping content. The Sheet width of VO₂(B) is about 150nm observed from the TEM image (Fig. 2g), which is in accordance with the FESEM image. The high resolution TEM (HRTEM) image shown in Fig. 2h bring out the clear lattice fringes of the Fe_{0.030}VO₂(B) with lattice interplanar spacing of 0.184 nm, which corresponding to the (002) crystal plane of VO₂(B) and is in good agreement with the XRD results. Table 2 gives molar ratio of Fe to V in the series of Fe-VO₂(B) samples estimated from EDS

analysis.

Table 2. The molar ratio of iron to vanadium in the series of Fe-VO₂(B) samples.

Specimen	mass ratio	mol ratio
VO ₂ (B)	0	0
Fe _{0.015} VO ₂	0.012	0.013
Fe _{0.030} VO ₂	0.030	0.038
Fe _{0.045} VO ₂	0.047	0.052

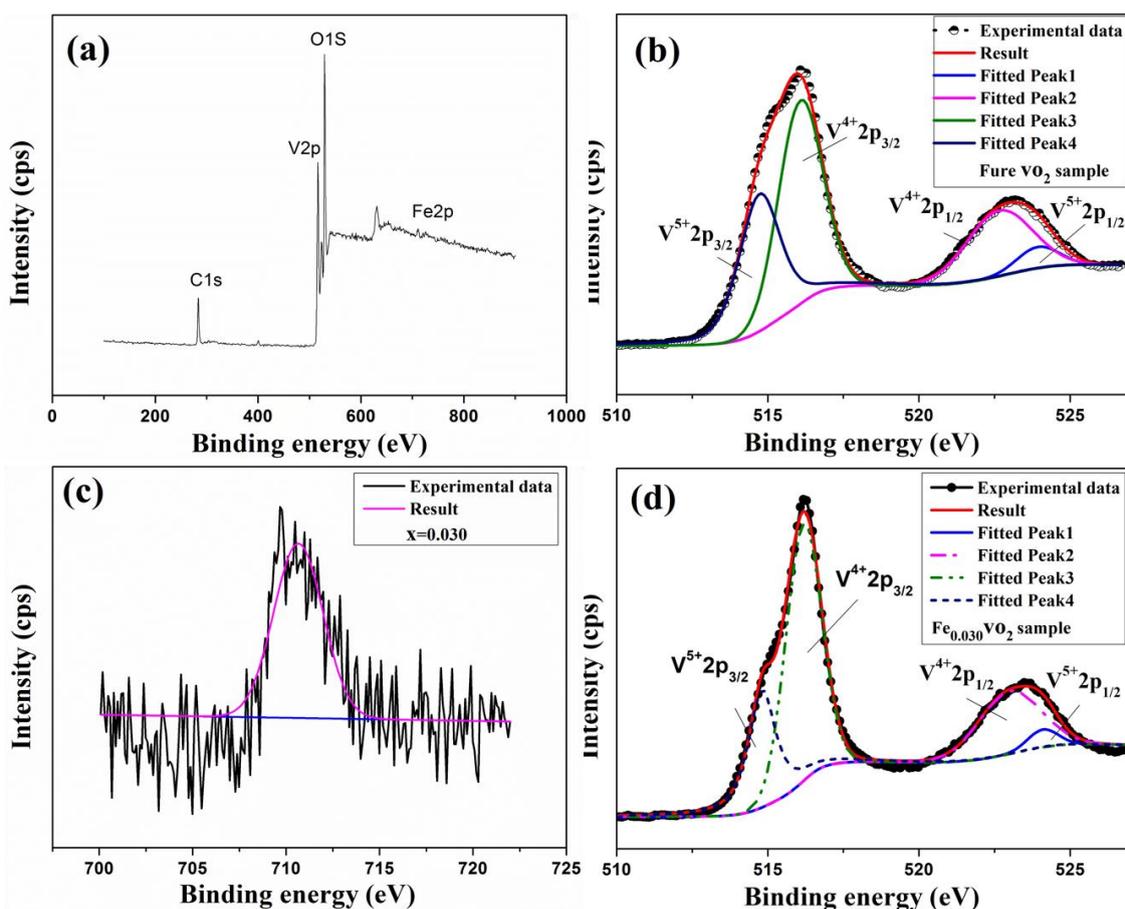


Figure 3. (a) XPS survey spectrum of the Fe_{0.030}VO₂(B) sample; (b) high-resolution spectrum of V 2p core-level spectrum for pure VO₂(B) sample; (c) high-resolution spectrum of Fe 2p core-level spectrum for Fe_{0.030}VO₂(B) sample; (d) high-resolution spectrum of V 2p core-level spectrum for Fe_{0.030}VO₂(B) sample.

XPS were carried out on the pure VO₂(B) and Fe-doped VO₂(B) samples to investigate chemical information such as the oxidation state, and the results are shown in Fig. 3. The binding energy appeared at 514.68, 516.03, 522.69 and 523.95eV in the sample of pure VO₂(B) could be assigned to V⁵⁺ 2p_{3/2}, V⁴⁺ 2p_{3/2}, V⁵⁺ 2p_{1/2} and V⁴⁺ 2p_{1/2} peaks, respectively[28-32]. Meanwhile, these four binding energy values also existed in the Fe_{0.030}VO₂(B) sample. It indicates that the iron atoms are successfully doped into the VO₂(B). Meanwhile, Energy dispersive X-ray spectroscopic element

mapping analysis (Fig. 2 (e-h)) indicates that Fe, V and O uniformly distributed in the microparticles. It is confirmed that the Fe^{3+} is uniformly doped in $\text{VO}_2(\text{B})$ (Fig.2 (e-h)).

However, the $\text{V}^{5+} 2p_{3/2}$ concentration in the Fe-doped $\text{VO}_2(\text{B})$ sample is much lower than that in the pure $\text{VO}_2(\text{B})$ sample. Therefore, Fe doping contributes to the formation of low valence state vanadium in $\text{VO}_2(\text{B})$. Maybe it's because Fe^{3+} replace the site of V^{5+} . For the Fe-doped $\text{VO}_2(\text{B})$ sample, Fe element is displayed with sharp photoelectron peaks at binding energies of 710.56 eV (Fig.3c). This agrees well with the reported data of $\text{Fe}^{3+} 2p_{3/2}$ in $\text{VO}_2(\text{B})$ [33] indicating that the Fe atoms in Fe-doped $\text{VO}_2(\text{B})$ sample primarily exist in the form of Fe^{3+} ions.

Table 3. Comparison of the lithium storage performance of the Fe doping $\text{VO}_2(\text{B})$ to reported cathode materials.

Samples	Current density (mA g^{-1})	Capacity retention (mA h g^{-1})	Ref.
Fe-doped $\text{VO}_2(\text{B})$	32.4	198 after 100 cycles	This work
Al-doped $\text{VO}_2(\text{B})$	32.4	202 after 50 cycles	[23]
Cu-doped $\text{VO}_2(\text{B})$	42	234 after 51 cycles	[24]
Ti-doped $\text{VO}_2(\text{B})$	42	217 after 51 cycles	[24]

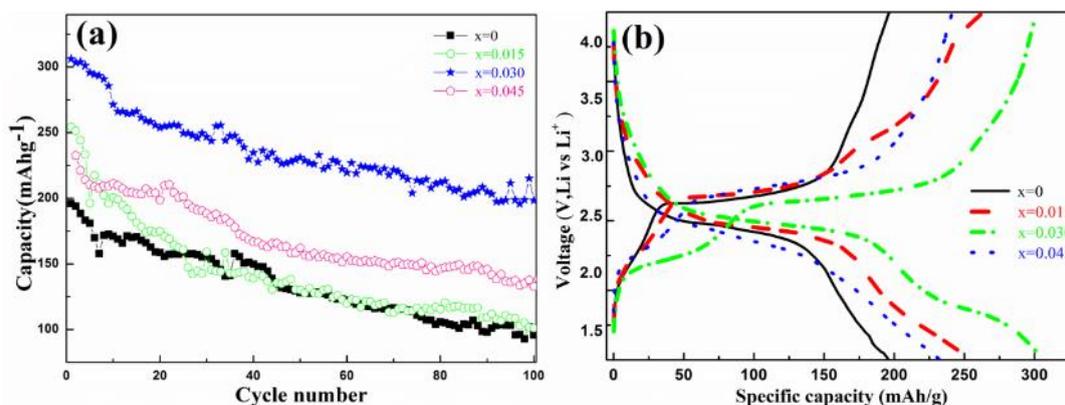


Figure 4. (a) Cycling performance of the pure $\text{VO}_2(\text{B})$ and Fe-doped $\text{VO}_2(x=0.015, 0.030, 0.045)$ samples at 0.1C discharge-charge rate; (b) Initial charge-discharge profiles of the samples at 0.1C in the voltage range of 1.5-4.0V.

Fig. 4a gives the cycling performance of the pure $\text{VO}_2(\text{B})$ and Fe-doped $\text{VO}_2(x=0.015, 0.030, 0.045)$ samples under a current density of 0.1C (32.4 mA g^{-1}). It can be seen from Figure 4 that the $\text{Fe}_{0.03}\text{VO}_2(\text{B})$ sample shows the highest lithium storage activity. For example, the initial discharge capacities of the $\text{Fe}_{0.03}\text{VO}_2(\text{B})$ sample is 306 mA h g^{-1} , which is much higher than that (195 mA h g^{-1}) of the pure $\text{VO}_2(\text{B})$. After 100 cycles, the specific capacity of the $\text{Fe}_{0.03}\text{VO}_2(\text{B})$ sample stabilized at 198 mA h g^{-1} , while the specific capacity of pure $\text{VO}_2(\text{B})$ is only 95 mA h g^{-1} . The cycling stability are much superior to the previous reported cathode vanadium oxide materials (as listed in Table 3).

Fig. 4b showed the first charge-discharge curves of the pure VO₂(B) and Fe-doped VO₂ samples at the current density of 0.1 C. All of them show a distinct charge platform at about 2.7 V and a distinct discharge platform at about 2.5V, which are agreement with that of the reference [7, 34, 35]. The results suggested that appropriate Fe³⁺ doping could significantly improve the lithium storage performance of VO₂(B). This performance enhancement can be due to the expansion of interlayer space resulting from Fe³⁺ doping as illustrating in Table 1[36].

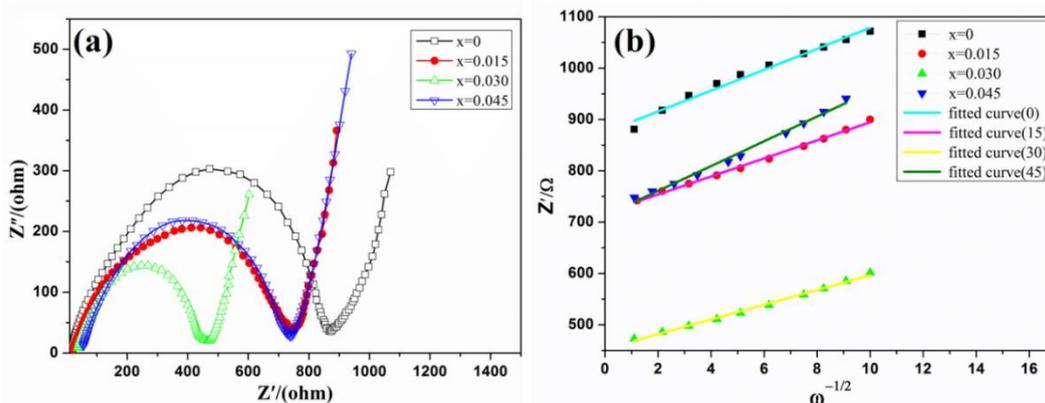


Figure 5. (a) Nyquist plots of the pure VO₂(B) and Fe_xVO₂ (x=0.015, 0.030, 0.045) electrodes; (b) The relationship between Z' and $\omega^{-1/2}$ at low frequencies.

Table 4. R_s and R_{ct} values of pristine VO₂ (B) and Fe³⁺ doped VO₂(B) products.

Specimen	R_s (Ω)	R_{ct} (Ω)
VO ₂	11	889.7
Fe _{0.015} VO ₂	17.37	736.5
Fe _{0.030} VO ₂	33.34	414.9
Fe _{0.045} VO ₂	49.63	692.9

To further explore the influence of Fe³⁺ doping on electrochemical property, EIS spectra are measured at the 1th fully discharged state and the Nyquist plots are shown in Figure 6. In the equivalent circuit diagram, R_s is the electrolyte resistance; R_{ct} is the charge-transfer resistance, which can be calculated by the diameter of the semicircle; W is the Warburg impedance related to the diffusion process of lithium-ions into the bulk of the electrode materials; CPE is employed to consider the porosity and tortuosity characteristics of the electrode. Table 4 gives the simulated R_s and R_{ct} values of the four electrodes. It can be seen that the pure VO₂(B) electrode shows a R_{ct} value of 889.7 Ω . After Fe³⁺ doping, the R_{ct} value decreases and in particular the Fe-doped VO₂(x=0.030) electrode exhibit the smallest R_{ct} value of 414.9 Ω , which is only about half of that for the pure VO₂(B). This result indicates that the Fe³⁺ doping makes the electrochemical reaction in VO₂(B) proceeds more easily.

The Li⁺ diffusion coefficients (D) in the Fe-doped VO₂ samples are also estimated according to the following equation[37]:

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma_w^2} \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the anode, n is the number of electrons per molecule during cycling, F is Faraday constant, C is the concentration of lithium ion, σ_w is the Warburg factor which can be obtained from the following equation[38]:

$$Z' = R_s + R_{ct} + \sigma_w \omega^{-1/2} \quad (2)$$

where R_s is the resistance of the electrolyte and electrode material, R_{ct} is the charge transfer resistance and ω is the angular frequency in the low frequency region. The relationship plot between Z' and $\omega^{-1/2}$ at low frequency region is shown in Fig. 6b. According to Eqs. (1) and (2), the Li^+ diffusion coefficient of the Fe-doped $\text{VO}_2(\text{B})$ samples ($x=0, 0.015, 0.030, 0.045$) is $8.04 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, $1.07 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, $1.61 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ and $5.65 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, respectively. With the increasing of doping concentration, the lithium diffusion coefficient firstly increases and then decreases and the sample of $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ has the maximum D_{Li} . It indicates that a proper amount of Fe^{3+} doping is beneficial to the diffusion of lithium ions.

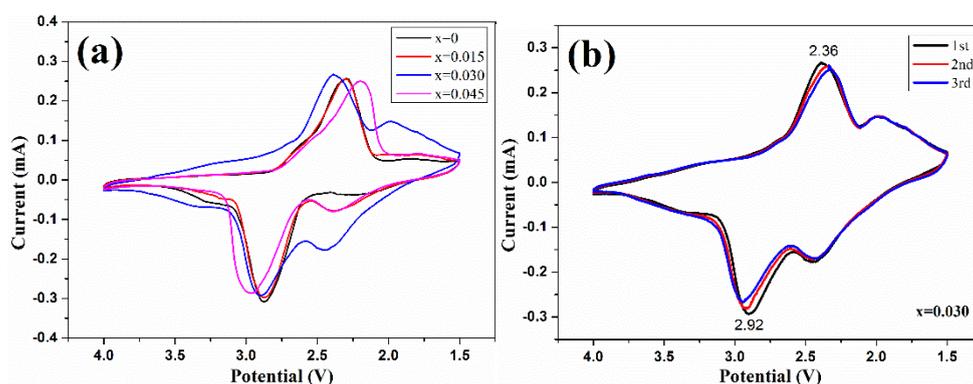


Figure 6. (a) Comparison of the first CV cycles of the pure $\text{VO}_2(\text{B})$ and Fe-doped $\text{VO}_2(\text{B})$ samples at a sweep rate of 0.1 mV s^{-1} ; (b) CV curves of the $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ electrode at a scan rate of 0.1 mV s^{-1} .

Furthermore, the first cycle CV curves of the pure $\text{VO}_2(\text{B})$ and Fe-doped $\text{VO}_2(\text{B})$ samples are investigated at a sweep rate of 0.1 mV s^{-1} in the potential range from 1.5 to 4.0 V (Fig. 7a). The four samples exhibit similar CV features: in the first scan, an obvious reduction peak centered at 2.4 V can be observed in the discharge process, and meanwhile, corresponding oxidation peak at 2.9 V can be observed in the charging process. The redox peak potentials were in accordance with the literature [39].

Owing to the potential difference reflects the polarization degree of the electrode and the encapsulated area of the cathodic scan reflects battery capacity[40]. By comparison, we have found that the $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ sample exhibits the largest curve area, least polarization, and highest redox currents among the four samples. The results indicate that the $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ present the highest electrochemical reaction activity and the best electrochemical reaction reversibility. Fig. 7b presents the CV curves of the $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ electrode for the first three CV cycles at a sweep rate of 0.1 mV s^{-1} from 1.5 to 4.0 V. Its cyclic voltammetry (CV) peak positions and intact areas retain almost invariant in the first three cycles, indicating excellent electrochemical reversibility and superior cycling stability of the $\text{Fe}_{0.030}\text{VO}_2(\text{B})$ electrode.

4. CONCLUSIONS

In summary, Fe-doped VO₂(B) samples have been synthesized by a hydrothermal process following with annealing at 350 °C for 1 h in nitrogen. The as-prepared samples exhibit hierarchical flower-like microsphere morphologies, which are composed of end-connected nanosheets. Fe doping expand interlayer distance and increase the V⁴⁺/ V⁵⁺ ratio of VO₂(B). The Fe-doped VO₂(B) samples exhibit higher reversible capacity, lower electrochemical reaction resistance, and higher electrochemical reversibility as compared to the pure VO₂(B). In particular, the Fe_{0.03}VO₂(B) sample showed the best lithium storage performance with initial discharge capacity of 306 mAh g⁻¹ when recorded at the current density of 0.1C in the voltage range of 1.5 to 4.0 V, much higher than that (195 mAh g⁻¹) of the pure VO₂(B). According to the results, the improve lithium storage performance may attributed to the increased interlay distance of VO₂(B), which facilitates lithium ion fast migration in VO₂(B) during charge/discharge process. Moreover, the substitution of Fe³⁺ to V⁴⁺ in VO₂(B) can form Fe–O–V bonds, which could stabilize the VO₆ octahedras, and therefore improve the cycling performance.

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