

W 掺杂改性的 V_2O_5 纳米片球作为高性能水系锌离子电池正极材料

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摘 要: 水系锌离子电池由于其优异的安全性、地壳丰度、成本低廉及绿色环保等优势被认为是一种有前景的储能设备, 但设计出一种高比容量、长循环寿命及优异倍率性能的水系锌离子电池正极材料依然面临诸多挑战。本文提出了一种重金属钨掺杂改性的 V_2O_5 纳米片球水系锌离子电池正极材料。钨掺杂提高了 V_2O_5 的晶面间距和离子迁移速率, 且 W—O 键的形成明显改善 V_2O_5 在循环过程中因结构破坏, 较低的本征电导率等问题导致的容量衰减情况。W 掺杂的 V_2O_5 在 0.1 A/g 电流密度下循环 100 圈后比容量为 195 mA·h/g, 在 1 A/g 大电流密度下循环 1 000 圈后比容量为 243 mA·h/g。此工作为今后设计出高性能水系锌离子电池正极材料提供了一种简易、高效、可行的方案。

关键词: 正极材料; 锌离子电池; 钨掺杂五氧化二钒

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W Doped V_2O_5 Nanosheets as Cathode Material for High-Performance Aqueous Zinc Ion Battery

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Abstract: Aqueous zinc-ion batteries (ZIBs) are considered to be prospective candidates in energy storage devices because of their excellent safety, crustal abundance, low cost and environmental benignity. Whereas, the design of a satisfied cathode material with a large specific capacity, superior rate performance and long-cycle life is still a significant challenge for ZIBs. Herein, a new strategy is proposed to use W doped V_2O_5 as cathode material for aqueous ZIBs. The W doping can effectively enlarge the lattice spacing and ion migration efficiency of V_2O_5 , and the formation of W—O bond can obviously alleviate the capacity decay problem caused by structural damage and low intrinsic conductivity in the cycling process. As a result, the V_2O_5 -W cathode exhibits an excellent capacity of 195.0 mA·h/g after 100 cycles at 0.1 A/g, and an impressive rate capability of 243.0 mA·h/g at the high current density of 1 A/g after 1 000 cycles. This work provides a simple, efficient and feasible strategy for designing high-performance cathode materials in ZIBs.

Keywords: cathode material; zinc ion battery; tungsten doped vanadium pentoxide

1 Introduction

In recent years, exploring eco-friendly, efficient and renewable energy is becoming an inevitable choice for human beings due to the increasing energy crisis and

environmental pollution. Meanwhile, the intermittent problems of the renewable energy like wind and solar power stimulate the requirement of high energy storage equipment such as lithium ion batteries (LIBs) and so on^[1-4]. Also, the limited lithium resources result in a great

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cost issue and restrict the further development of LIBs^[7–9]. In contrast, aqueous zinc ion batteries (ZIBs) have some advantages of safety, low cost and eco-friendly, which are expected to be a promising potential replacement of LIBs^[10–12]. Nevertheless, the electrochemical properties of the cathode materials in ZIBs still cannot satisfy the demand due to their intrinsic conductivity and slow kinetics of Zn^{2+} ions. In this regard, a series of cathode materials studied mainly include MnO_2 ^[13–18], prussian blue analogues^[19–22], polyanion skeleton cathode material^[23], and platelike sulfides (MoS_2 ^[24] and VS_2 ^[25]). For MnO_2 , there exists a problem for the structure collapse that severely affects the cycling performance, accompanying with a series of irreversible side reactions leading to the severe capacity loss and the Coulombic efficiency reduction. Prussian blue analogues possess a three-dimensional open framework with large ion transfer channels, yet generally delivering a relatively low specific capacity. For instance, the specific capacity of $\text{NiFe}(\text{CN})_6$ is just 76.2 mA·h/g at 0.1 A/g, and the specific capacities of $\text{CuFe}(\text{CN})_6$ and $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ are only 53.0 mA·h/g and 66.5 mA·h/g at 0.06 A/g, respectively^[19,26]. Also, the metal oxides, polyanionic materials and layered sulfides also suffer from the structural damage and irreversible by-product formation during the cycling process. In this case, V_2O_5 has attracted attentions because vanadium has multiple valence states that lead to the redox reaction with a multiple electron transfer and a high theoretical capacity. V_2O_5 has a typical lamellar crystal structure, in which V and O atoms form VO_5 square pyramid with the layer spacing of approximately 0.44 nm, which is much larger than that of Zn^{2+} (i.e., 0.075 nm) and thereafter is conducive to the intercalation/de-intercalation of Zn^{2+} ^[27–28]. However, V_2O_5 has a serious structural damage and a low intrinsic conductivity in the cycling process with a low voltage platform (i.e., 0.8 V) and a poor cycle stability (i.e., <1 000 cycles)^[29–30]. The lamellar structure of V_2O_5 can be stabilized via pre-intercalation of transition metal ion (such as $\text{Li}_x\text{V}_2\text{O}_5$ ^[31], $\text{Na}_{0.33}\text{V}_2\text{O}_5$ ^[32], $\text{Ca}_{0.25}\text{V}_2\text{O}_5$ ^[33], $\text{Ag}_{0.33}\text{V}_2\text{O}_5$ ^[34]). The pre-inserted metal ions can act as a pillar to stabilize and enlarge the layered construction to provide the more active sites. Inspired by the previous work, we synthesized W-doped V_2O_5 as a cathode material for ZIBs at an optimal W doping amount. At the optimal W doping amount, the radius of V_2O_5 nano-sheet microspheres with an expanded layered spacing is approximately 2 μm . The V_2O_5 -W cathode exhibits a superior reversible capacity (195.0 mA·h/g after 100 cycles at 0.1 A/g), a rate capability, and a cycling stability (243.0 mA·h/g after 1 000 cycles at 1 A/g).

2 Experimental

2.1 Materials and preparation procedure

V_2O_5 was synthesized by simple solvothermal

process and subsequent heat treatment with NH_4VO_3 , WCl_6 , isopropyl alcohol as raw materials. Firstly, NH_4VO_3 of 0.6 g was added into isopropyl alcohol of 60 ml and stirred for 2 h. Then, different amounts of WCl_6 (the molar ratio of W to V is 2:100, 4:100 and 6:100) were added, and transferred to 80 mL autoclave and kept at 200 °C for 24 h. The obtained powders were washed with deionized water and ethanol, and dried in a vacuum drying oven at 60 °C for 12 h. Pure V_2O_5 was also prepared by a similar process without adding WCl_6 as a precursor. Finally, the obtained precursor powder was annealed for 2 h at 350 °C in air, and the as-derived samples were labeled as V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6, respectively.

2.2 Characterizations

The morphology, structure and composition of the derived samples were determined by a model RINT-2000 X-ray diffractometer (XRD, Ultima IV, Rigaku) with Cu K_α radiation, a model JSM-7500F field emission scanning electron microscope (FESEM, JSM-7500F, JEOL), a model JSM-F200 high-resolution transmission electron microscopy (HRTEM, JEM-F200, JEOL), and a model AXIS-ULTRA DLD-600 W X-ray photoelectron spectroscope (XPS, Escalab 250Xi, Thermo Scientific), respectively. The battery test system (LAND CT2001A, China) was used for charge-discharge test with the voltage window of 0.2–1.6 V. The cyclic voltammetry (CV) curve and alternating current (AC) impedance of the battery were measured by a model CHI 614C/D/E electrochemical workstation (Chenhua, China). The CR2025 coin cells assembled in air were used to evaluate the electrochemical performance of the cathode materials. The active materials, acetylene black and poly tetrafluoroethylene in a mass ratio of 7:2:1 were mixed in N-methyl-2-pyrrolidinone and coated on Ti foils. The mass loading of the active material is 2.0 mg/cm². The zinc foil is used as the reference electrode and counter electrode, and 3 mmol/L $\text{Zn}(\text{CH}_3\text{F}_3\text{SO}_3)_2$ in distilled water is used as an electrolyte. The electrochemical impedance spectroscopy (EIS) tests were operated on a model CHI660C electrochemical workstation (Chenhua, China) at 0.01 Hz–100 kHz.

3 Results and discussion

Fig. 1(a) shows the crystal structure of V_2O_5 . W acts as a pillar between V_2O_5 layers to expand the layer spacing. The existing form of doping W in V_2O_5 is in V_2O_5 interlayers and effectively enlarges the lattice spacing. The lattice spacing is 0.48 nm, corresponding to (001) plane after W doping relative to bare V_2O_5 (i.e., 0.425 nm). Fig. 1(b) shows the XRD patterns of pure phase V_2O_5 and V_2O_5 with different W doping amounts. Clearly, W doping does not change the crystal phase of V_2O_5 , in which the characteristic peaks at 15.5°, 20.6°, 25.7° and 31.9° are corresponding to orthorhombic V_2O_5 (JCPDS 41–1426) without any impurity peaks. The

narrow and sharp peaks indicate a good crystallinity. Fig. 1(c) shows the XPS spectrum of V_2O_5 -W4. In Fig. 1(c), the sample contains V, O, and W elements. Fig. 1(d) shows the high-resolution V 2p XPS spectrum of V_2O_5 -W4, in which two peaks at 517.4 and 525.3 eV are related to V 2p_{3/2} and V 2p_{1/2} corresponding to V⁵⁺ ions^[35–36]. The O 1s peak can be matched with three peaks at 530.6, 531.3 eV, and 532.7 eV corresponding to W—O, C=O, and C—O bonds, respectively^[37–38].

The high-resolution W 4f XPS spectrum can be fitted with two peaks at 37.8 eV and 35.4 eV, corresponding to W 4f_{5/2} and W 4f_{7/2}^[39–41]. Fig. 1(g) shows the corresponding energy dispersive spectrum. In Fig. 1g, the element W exists. And the molar ratios of W in V_2O_5 for the three samples can be calculated to be $\text{V}_2\text{W}_{0.019}\text{O}_5$, $\text{V}_2\text{W}_{0.032}\text{O}_5$ and $\text{V}_2\text{W}_{0.047}\text{O}_5$, corresponding to V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 (see ICP measurement in Fig. 1(h)).

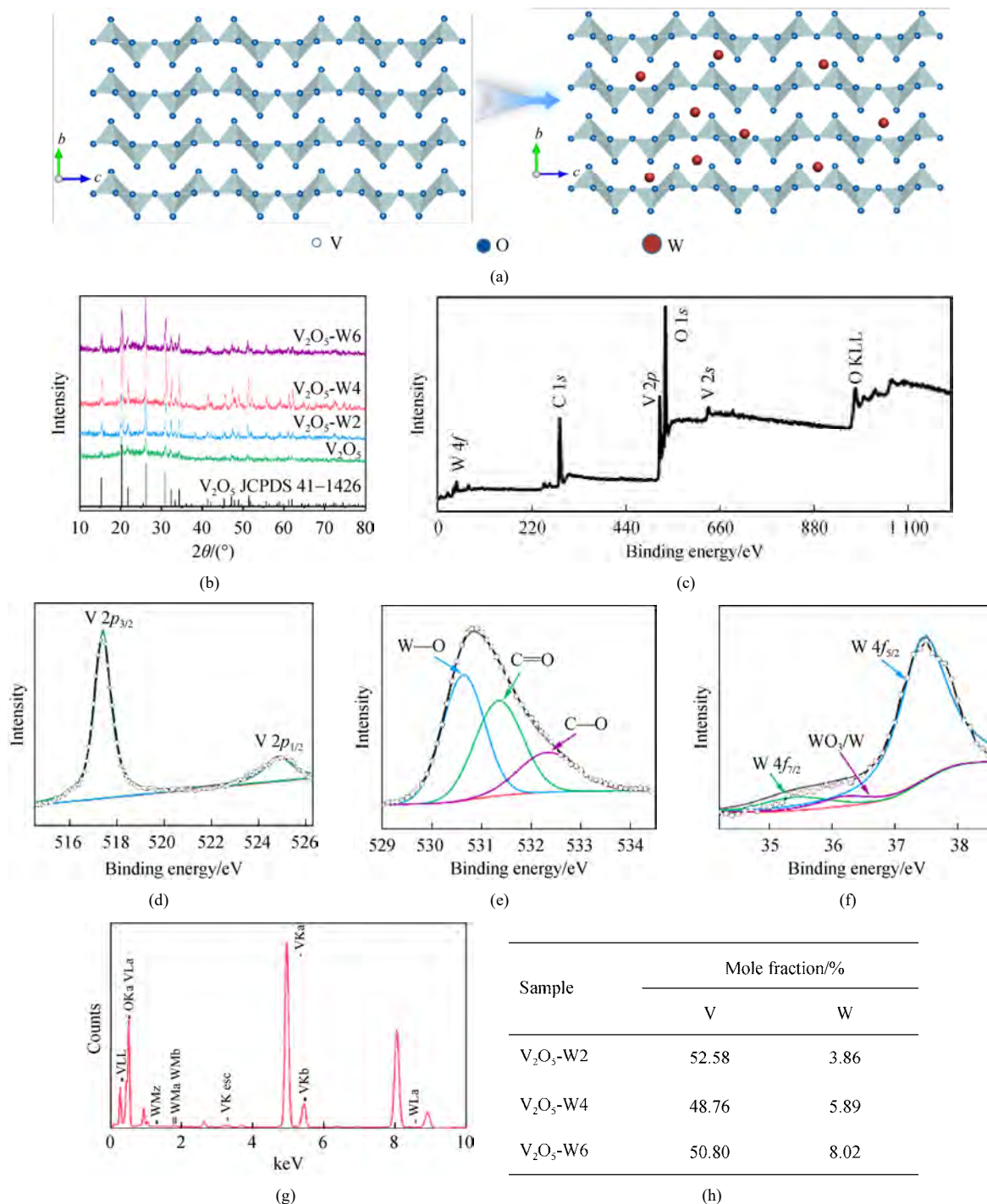


Fig. 1 (a) Crystal structure of V_2O_5 and V_2O_5 -W; (b) XRD patterns of the V_2O_5 , V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 samples; (c) Whole XPS spectrum of V_2O_5 -W4; (d–f) High-resolution XPS spectra of V 2p, O 1s and W 4f of V_2O_5 -W4; (g) EDX spectrum of V_2O_5 -W4; (h) ICP of the V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 samples

Fig. 2(a) shows the SEM image of pure phase V_2O_5 synthesized. Clearly, pure phase V_2O_5 has a typical microsphere morphology with a radius of approximately $0.5\ \mu\text{m}$. Fig. 2(b) shows the SEM image of $\text{V}_2\text{O}_5\text{-W2}$. The doping of W can transform the V_2O_5 microspheres to nanosheets. Fig. 2(c) shows the SEM image of $\text{V}_2\text{O}_5\text{-W4}$. The V_2O_5 nanosheets turn to be nanosheet assembled microspheres with the radius of approximately $2\ \mu\text{m}$, accompanying with the increase of doping amount of W in V_2O_5 . Fig. 2(d) shows the SEM image of $\text{V}_2\text{O}_5\text{-W6}$. At this doping amount, the construction of nanosheet microsphere can still maintain, Fig. 2(e) shows the TEM image of $\text{V}_2\text{O}_5\text{-W4}$, in which the nanosheet microsphere with a hollow architecture appears. This particular construction can effectively overcome the volume expansion and enhance the migration rate of Zn^{2+} , thus improving the cyclic stability of V_2O_5 . Fig. 2(f) and Fig. 2(g) show the high-resolution TEM images of $\text{V}_2\text{O}_5\text{-W4}$. The lattice spacings of 0.48 and 0.58 nm correspond to

(001) and (200) planes of V_2O_5 , which are greater than those of bare V_2O_5 ^[41]. The enlarged spacing of (001) planes can favor the diffusion of Zn^{2+} ions. Fig. 2(h) show the EDS mappings of V, O and W elements, implying the even distributions of V, O and W elements.

Fig. 3(a) and Fig. 3(d) show the charge-discharge curves of pure phase V_2O_5 and V_2O_5 with different W doping amounts at $0.1\ \text{A/g}$. The stability of the first three cycles of pure phase V_2O_5 is better than that of the other three materials with different W doping amounts. Fig. 3(b) – Fig. 3(d) show the charge-discharge curves of $\text{V}_2\text{O}_5\text{-W2}$, $\text{V}_2\text{O}_5\text{-W4}$ and $\text{V}_2\text{O}_5\text{-W6}$ electrodes. The charge-discharge curves of the first cycle are slightly different from those of the subsequent cycles, indicating that there is an obvious activation process in the first cycle^[42]. Moreover, the reduction of reversible capacity for the W doped V_2O_5 in the initial cycles, which might be caused by the W occupying part of the active site of V_2O_5 .

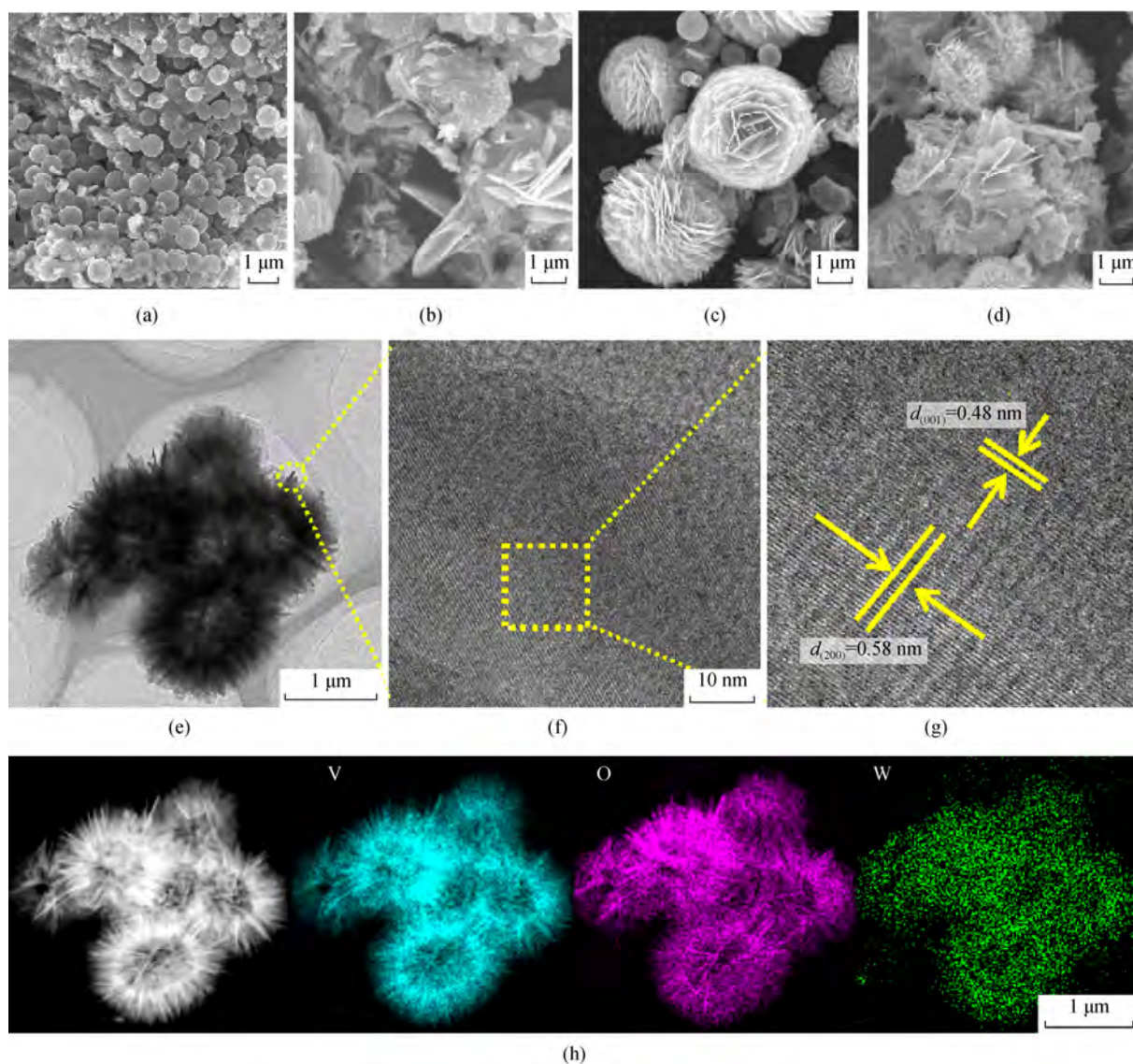


Fig. 2 (a–d) SEM images of the V_2O_5 , $\text{V}_2\text{O}_5\text{-W2}$, $\text{V}_2\text{O}_5\text{-W4}$ and $\text{V}_2\text{O}_5\text{-W6}$ samples. (e) TEM, (f, g) HRTEM, (g) partial enlarged view of (f), (h) elemental mappings of $\text{V}_2\text{O}_5\text{-W4}$

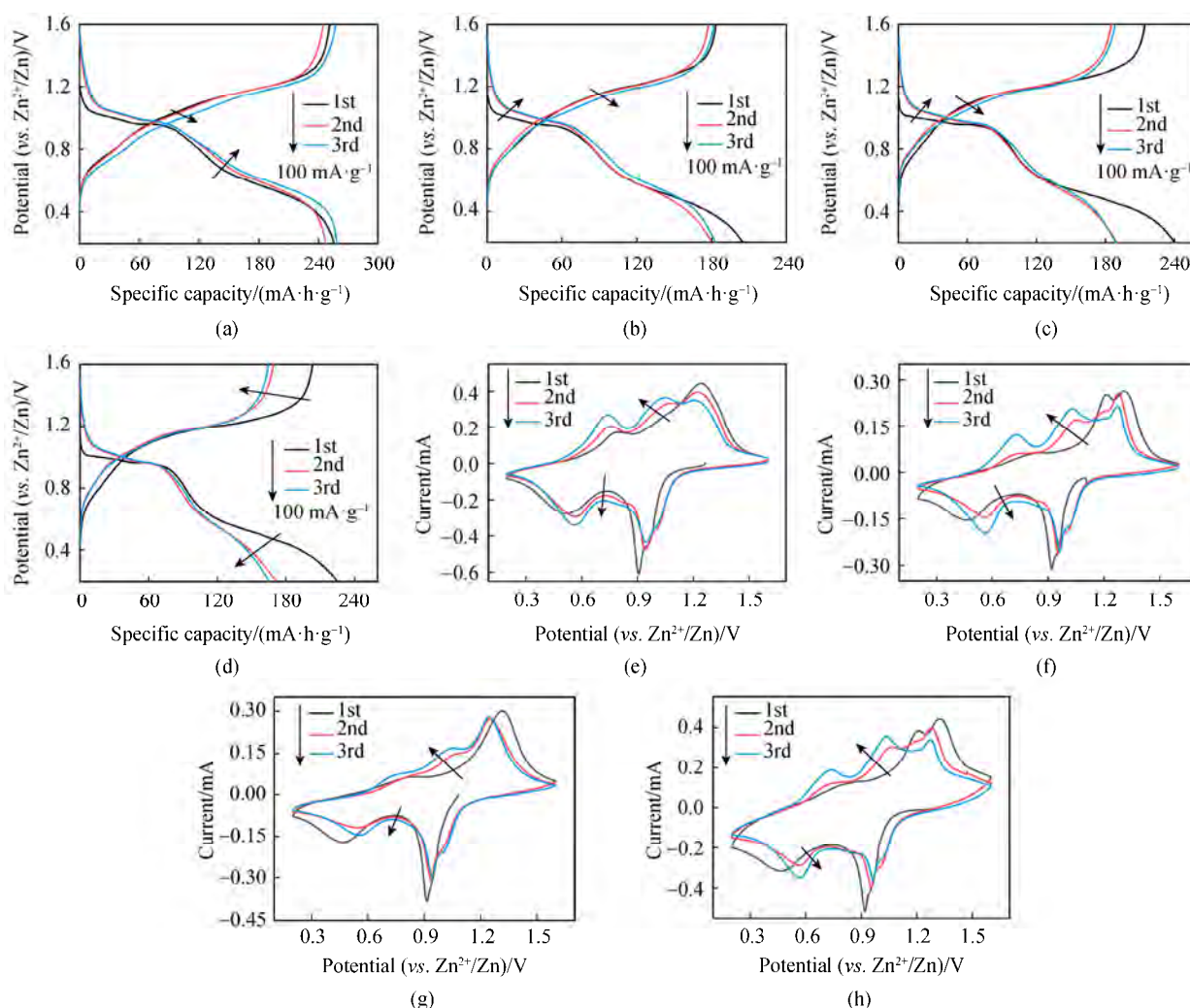


Fig. 3 Charge-discharge profiles for (a) V_2O_5 , (b) V_2O_5 -W2, (c) V_2O_5 -W4 and (d) V_2O_5 -W4 electrodes. in the potential window of 0.2–1.6 V at $0.2 \text{ mV} \cdot \text{s}^{-1}$ for (e) V_2O_5 , (f) V_2O_5 -W2, (g) V_2O_5 -W4 and (h) V_2O_5 -W6 electrodes

Fig. 4(b)–Fig. 4(d) show the cycling and rate performances of pure phase V_2O_5 and V_2O_5 with different W doping amounts under different current densities. Fig. 4(b) shows that the discharge capacity of V_2O_5 -W4 cathode is $194 \text{ mA} \cdot \text{h/g}$ after 100 cycles at 0.1 A/g , which is greater than that of other three V_2O_5 samples with different W doping amounts. In Fig. 4(c), V_2O_5 -W4 cathode delivers a capacity of $243 \text{ mA} \cdot \text{h/g}$ after 1000 cycles at 1 A/g . Fig. 4(d) depicts the rate capability of pure phase V_2O_5 and V_2O_5 with different W doping amounts. All the samples are activated for 10 cycles at 0.1 A/g . The average reversible capacities of V_2O_5 -W4 cathode at 0.5 A/g , 1 A/g , 2 A/g and 5 A/g current densities are $327 \text{ mA} \cdot \text{h/g}$, $330 \text{ mA} \cdot \text{h/g}$, $316 \text{ mA} \cdot \text{h/g}$ and $280 \text{ mA} \cdot \text{h/g}$, respectively. When the current density returns to 0.1 A/g , the average reversible capacity is still as high as $364 \text{ mA} \cdot \text{h/g}$. The excellent rate performance and cyclic stability indicate that the W-doping into V_2O_5 can effectively improve the electrochemical performance of V_2O_5 . To explore the reaction kinetics of W-doped V_2O_5 electrode, the alternating current (AC) impedance was tested within 100 cycles at 0.1 A/g . The inset in

Fig. 4(e)–Fig. 4(h) shows the equivalent circuit diagrams of AC impedance results, in which R_s is the electrolyte resistance, R_{sf} is related to ohmic resistance, R_{ct} is related to the charge transfer resistance at the interface, and W is the Warburg coefficient related to the diffusion of Zn^{2+} . Clearly, within 100 cycles, the R_{ct} of the pure phase V_2O_5 electrode becomes larger. Before the cycling test, the R_{ct} is 79.9Ω . And the R_{ct} increases to 351.4Ω after 100 cycles. Although the R_{ct} of V_2O_5 -W2 and V_2O_5 -W6 cathodes decreases in the initial cycles, the increase of R_{ct} is also detected in the subsequent cycles. However, the V_2O_5 -W4 electrode demonstrates the smallest charge transfer resistance change during 100 cycles. This result indicates that the novel design of W-doped V_2O_5 nanosheet microsphere with an appropriate W doping amount accelerates the rapid transfer of electrons. We can use the following equation to calculate the diffusion coefficient of zinc ions:

$$D = 0.5 \left(\frac{RT}{An^2 F^2 \sigma_\omega C} \right)^2 \quad (1)$$

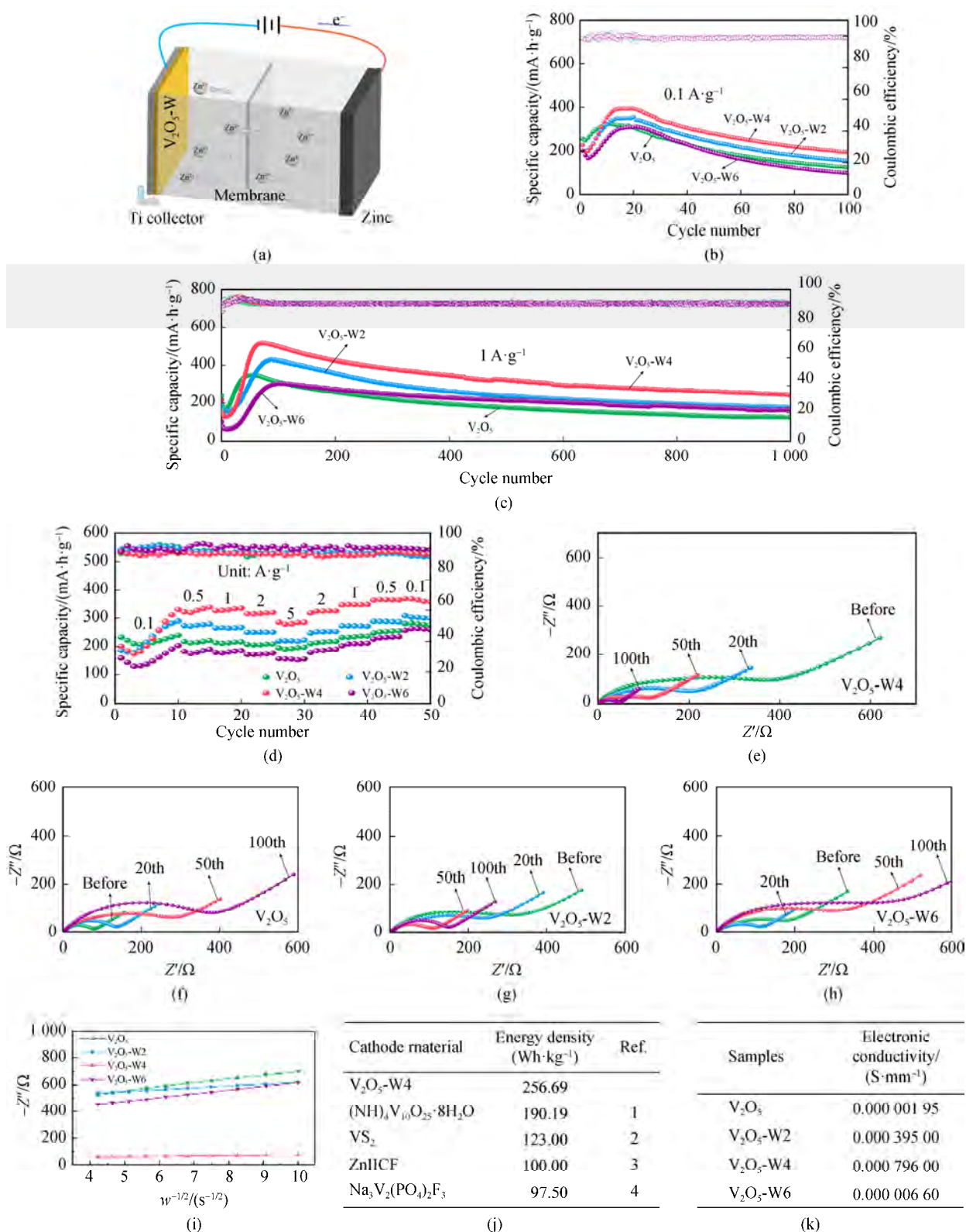


Fig. 4 (a) Battery structure diagram; (b) Cycling performance of the V₂O₅, V₂O₅-W2, V₂O₅-W4 and V₂O₅-W6 electrodes at the current density of 0.1 A/g; (c) Cycling performance of the V₂O₅, V₂O₅-W2, V₂O₅-W4 and V₂O₅-W6 electrodes at the current density of 1 A/g; (d) Rate performance of the V₂O₅, V₂O₅-W2, V₂O₅-W4 and V₂O₅-W6 electrodes; (e–h) Nyquist plots of the V₂O₅, V₂O₅-W2, V₂O₅-W4 and V₂O₅-W6 electrodes at the current density of 0.2 A/g after 100 cycles; (i) Diagram of Z' and $\omega^{-1/2}$ in the low-frequency region of the different samples; (j) Comparison of energy density of V₂O₅-W4//Zn with recently reported cathode materials in ZIBs; (k) Comparison of electronic conductivity of the V₂O₅, V₂O₅-W2, V₂O₅-W4 and V₂O₅-W6 powder

where R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the Kelvin temperature (298 K), A is the surface area of the electrode, n is the number of electrons transferred per mole of active material involved in the electrode reaction, and F is the Faraday constant, C is the molar concentration of zinc ions, and σ is the slope after straight-line fitting in the low-frequency region. The diffusion coefficients (D) of zinc ions for V_2O_5 , V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 samples were calculated to be $3.46\times 10^{-13} \text{ cm}^2\cdot\text{s}^{-1}$, $1.48\times 10^{-12} \text{ cm}^2\cdot\text{s}^{-1}$, $7.33\times 10^{-11} \text{ cm}^2\cdot\text{s}^{-1}$ and $3.77\times 10^{-13} \text{ cm}^2\cdot\text{s}^{-1}$. Moreover, the energy density of V_2O_5 -W4 electrode is $256.69 \text{ Wh}\cdot\text{kg}^{-1}$, which is higher than that of previous results^[48–51]. Also,

the electronic conductivities of V_2O_5 , V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 were calculated to be 1.95×10^{-6} , 3.75×10^{-5} , 7.96×10^{-5} , $6.6\times 10^{-6} \text{ S}\cdot\text{mm}^{-1}$, respectively.

Fig. 5(a) shows the cyclic voltammetry (CV) curves of V_2O_5 -W4 cathode measured at scan rates from 0.1 mV/s to 1.0 mV/s. To further probe the kinetics reaction of V_2O_5 -4, the capacitive contribution was calculated using the equation $I = av^b$ ^[44], where a and b are adjustable parameters. When b is less than 0.5, the diffusion control accounts for the major capacity contribution, while b is close to 1, it means that the pseudo-capacitance control accounts for the major capacity contribution^[19, 45]. The b value was obtained by

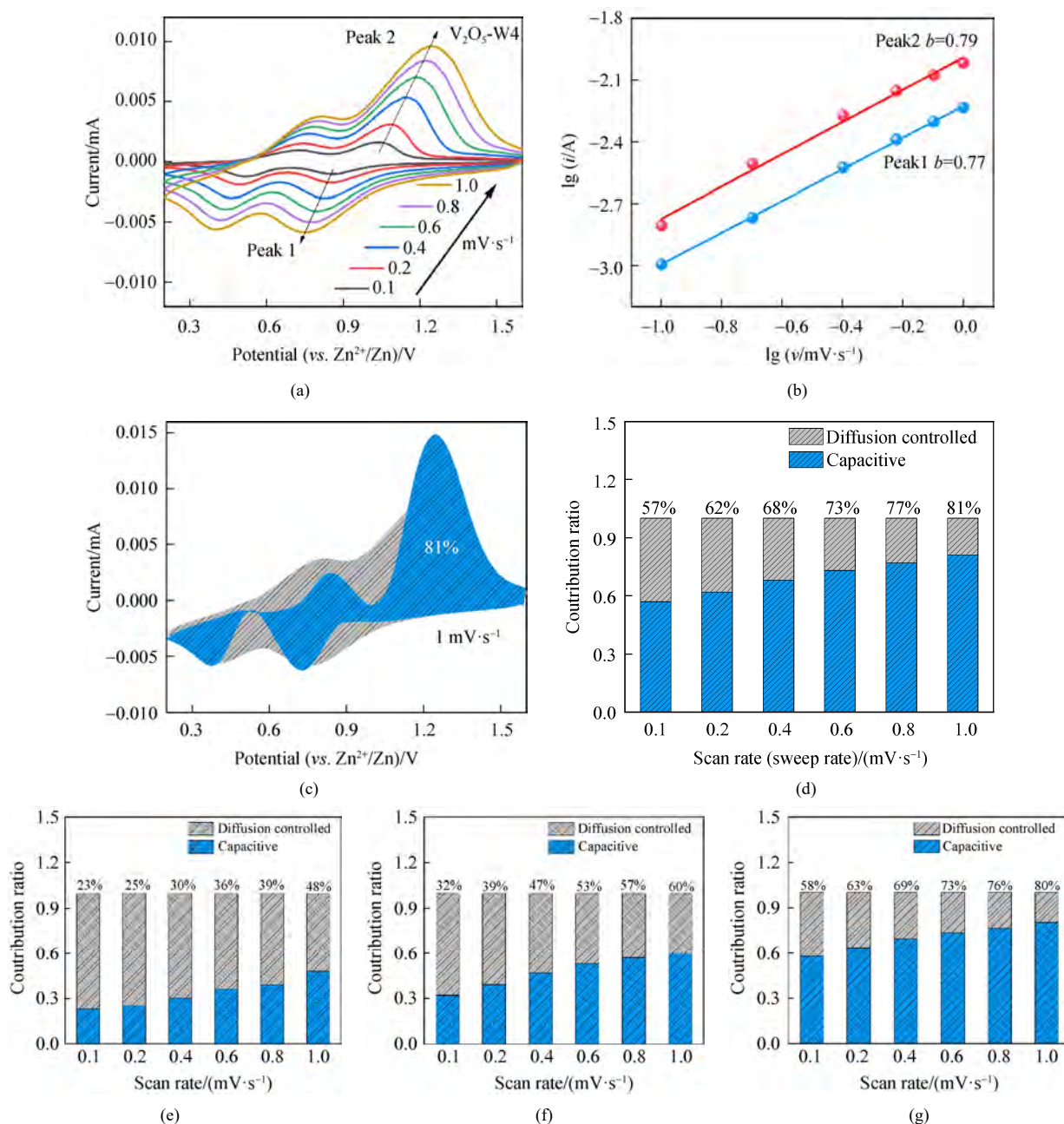


Fig. 5 (a) CV curves at various scan rates of the V_2O_5 -W4 electrodes; (b) corresponding $\lg i$ vs $\lg v$ plots at specific peak; (c) currents capacitive contribution to the capacity at the scan rate of 1 mV/s; (d–g) corresponding percent of pseudo-capacitive contribution of the V_2O_5 , V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 electrodes

fitting the peak current and scanning rate. Fig. 5(b), b values both are larger than 0.5, indicating the coexistence of diffusion control and pseudo-capacitance control processes. Fig. 5(c) shows the capacitive contribution occupying 81% of the whole capacity. In addition, the capacitive contribution rate also becomes larger as the scan rate increases (see Fig. 5(d)). The capacitive contribution of the other three electrodes is lower than that of the V_2O_5 -W4 cathode, indicating the faster charge transfer kinetics of V_2O_5 -W4 cathode.

The galvanostatic intermittent titration technique (GITT) is applied to estimate the ion diffusion coefficients in V_2O_5 , V_2O_5 -W2, V_2O_5 -W4 and V_2O_5 -W6 cathodes. The calculation method is based on the following equation^[45–46]:

$$D = \frac{4}{\pi \tau} \left(\frac{m_B V_m}{M_B A} \right) \left(\frac{\Delta E_s}{\Delta E_r} \right)^2 (\tau \ll L^2 / D) \quad (2)$$

Where τ is the current pulse time (sec), m_B is the active mass in sample (g), V_m and M_B are the molar volume and molar mass of B (cm^3/mol , g/mol), and S is the active surface area of the HCM electrodes (cm^2). ΔE_s and ΔE_r can be obtained from the GITT curves, L is effective thickness of the electrode.

The system experiences a pulse of 20 mA for 40 min

after a rest of 2 h. In Fig. 6(a) and Fig. 6(b), the ion diffusion coefficient of V_2O_5 -W4 (i.e., $5.08 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$) is greater than that of V_2O_5 (i.e., $2.80 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$), V_2O_5 -W2 (i.e., $3.89 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$) and V_2O_5 -W6 (i.e., $3.60 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$) electrodes, further confirming that V_2O_5 -W4 cathode delivers faster reaction kinetics. Fig. 6(c)–Fig. 6(e) show the XRD patterns of the V_2O_5 -W4 during the initial two cycles. Clearly, the characteristic peaks of V_2O_5 well maintain in the whole process. A diffraction peak at 33.62° can be assigned to $\text{Zn}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ emerged after the first full discharge process^[45]. However, this diffraction peak becomes weak and even disappears during the charge process. Noted that V_2O_5 -W4 undergoes a structural evolution and transforms to a layered $\text{Zn}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ due to the co-insertion of Zn^{2+} and H^+ , and this is a reversible change during discharge/charge process. A diffraction peak at 21.72° corresponding to the (110) lattice planes shifts to lower angles during the discharging process, indicating that the interlayer spacing of V_2O_5 -W4 nanosheet sphere increases due to the insertion of Zn^{2+} and H^+ ions (see Fig. 6(e)). However, during the charging process, it shifts inversely as the interlayer spacing decreases due to the extraction of Zn^{2+} ions.

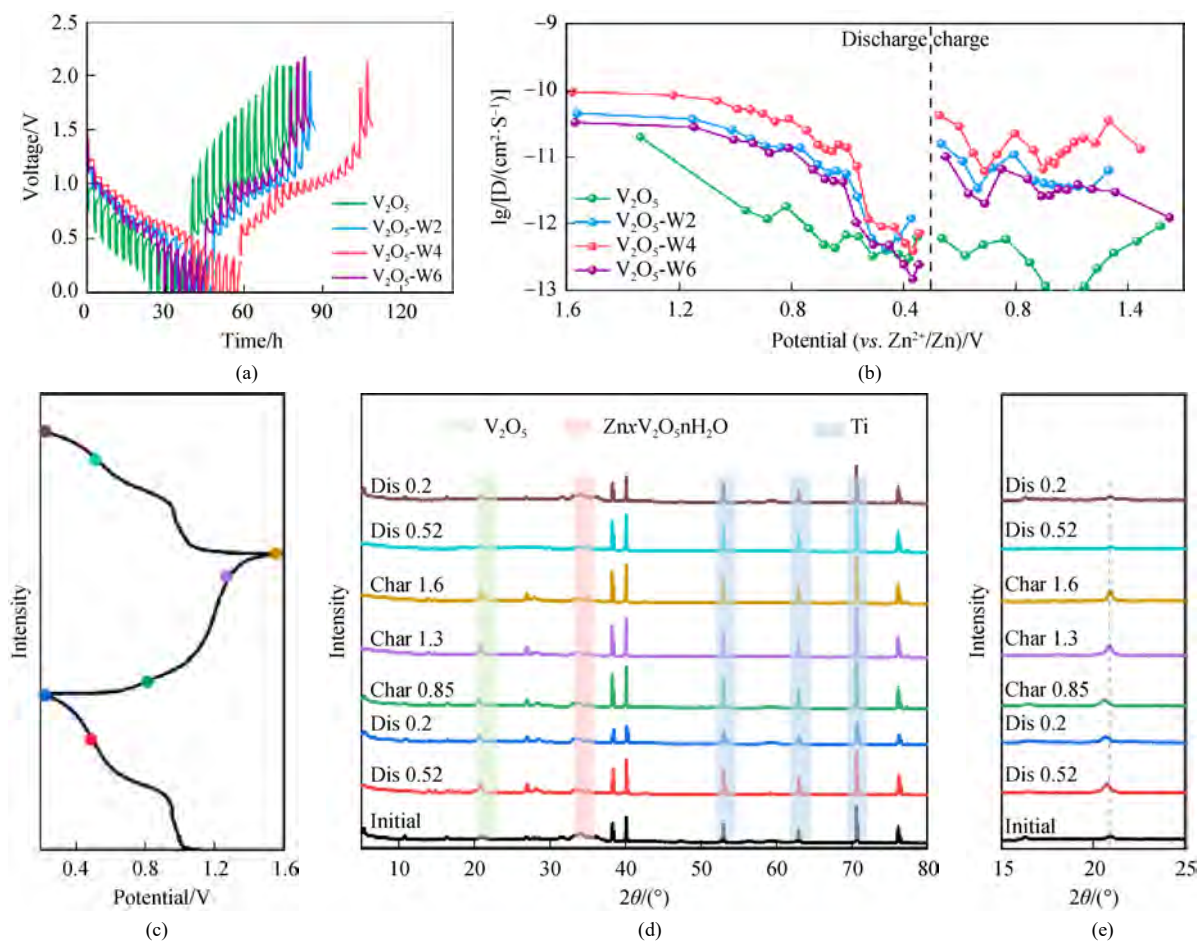


Fig. 6 (a) Galvanostatic charge and discharge profiles of GITT measurement in a potential range of 0.2–1.6 V; (b) Calculated zinc diffusion coefficient of the fore electrodes; (c) Voltage curve; (d) *Ex-situ* XRD patterns of V_2O_5 -W4; (e) Partial enlarged view of (d)

4 Conclusion

W doped V_2O_5 with a nanosheet microsphere morphology was prepared. The construction of nanosheet microsphere of W doped V_2O_5 could provide abundant active sites. In addition, W doping into V_2O_5 improved the conductivity of V_2O_5 and increased the lattice spacing of V_2O_5 , which could favor the intercalation and diffusion of Zn^{2+} . V_2O_5 -W4 cathode had the most competitive performance, delivering a reversible capacity of $195\text{ mA}\cdot\text{h/g}$ at 0.1 A/g , and a capacity of $243\text{ mA}\cdot\text{h/g}$ specific capacity at 1 A/g after 1 000 cycles. The excellent performance of W-doped V_2O_5 could provide an effective strategy for the development of high-performance zinc ion batteries.

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