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Boosting Zn-Ion Storage Performance of Bronze-Type VO₂ via Ni-Mediated Electronic Structure Engineering

Yi Cai,¹ Rodney Chua,¹ Zongkui Kou,² Hao Ren,¹ Du Yuan,³ Shaozhuan Huang,⁴ Sonal Kumar,¹ Vivek Verma,¹ Penphitcha Amonpattaratkit,⁵ Madhavi Srinivasan^{*, 1, 6}

¹ School of Materials Science and Engineering, Nanyang Technological University, 11 Faculty Ave, 639977, Singapore

² Department of Materials Science and Engineering, National University of Singapore, Engineering Drive 1, 117574, Singapore

³ Energy Research Institute, 50 Nanyang Drive, X-Frontiers Block, Level 5, Singapore 637553, Singapore

⁴ Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, South Central University for Nationalities, Wuhan, 430074, China

⁵ Synchrotron Light Research Institute (Public Organization), Muang, Nakhon Ratchasima, 30000, Thailand

⁶ Energy Research Institute at Nanyang Technological University, Research Techno Plaza, 50 Nanyang Drive, 637553, Singapore

Email address: madhavi@ntu.edu.sg

Abstract

Aqueous rechargeable zinc-ion batteries are emerging as attractive alternatives for post-lithium-ion batteries. However, their electrochemical performances are restricted by the narrow working window of materials in aqueous electrolytes. Herein, Ni-mediated VO₂-B nanobelt ((Ni)VO₂) has been designed to optimize the intrinsic electronic structure of VO₂-B, and thus achieve much more enhanced zinc-ion storage. Specifically, the Zn/(Ni)VO₂ battery yields good rate capability (182.0 mAh g⁻¹ at 5 A g⁻¹) with superior cycling stability (130.6 mAh g⁻¹ at 10 A g⁻¹ after 2000 cycles). Experimental and theoretical methods reveal that the introduction of Ni²⁺ in the VO₂ tunnel structure can effectively provide high surface reactivity and improve the intrinsic electronic configurations, thus resulting in good kinetics. Furthermore, H⁺ and Zn²⁺ co-intercalation processes are determined via in-situ X-ray diffraction and supported by ex-situ characterizations. Additionally, quasi-solid-state Zn/(Ni)VO₂ soft-packaged batteries are assembled and provide flexibility in battery design for practical applications. The results provide insight into the interrelationships between the intrinsic electronic structure of the cathode and overall electrochemical performance.

Keywords: Zn-ion battery; Aqueous; VO₂-B; Electronic structure; Rate capability

Introduction

In the past decades, the rapid development of lithium-ion batteries has significantly changed human life through an electronics revolution. However, the shortage of lithium resource and the safety issue occurred by flammable organic electrolyte encourage a world-wide upsurge of research on finding the alternative systems.¹ Therefore, aqueous rechargeable batteries have been recently proposed as promising alternatives owing to their high intrinsic safety. Among them, aqueous zinc-ion batteries (ZIBs) have attracted much more attention owing to their unique advantages of high theoretical capacity (820 mAh g⁻¹ or 5854 mAh cm⁻³) and relatively low redox potential (-0.76 V vs. standard hydrogen electrode) of metallic zinc and low cost with high natural abundance.²⁻⁷ However, the strong electrostatic interactions between the host lattice and Zn²⁺ can cause sluggish reaction kinetics, thus leading to poor rate performance and deficient cycling stability.⁸⁻¹⁰ Therefore, exploring suitable cathode hosts that can enable fast and reversible Zn²⁺ storage is highly desirable.

Currently, cathode materials (vanadium-based) are emerging as candidates for aqueous ZIBs, attributing to the low cost, abundant resources, and large charge storage provided by various oxidation states.^{7, 11-16} Recent research shows that tunnel structure may remain a robust, stable structure and is beneficial for the efficient zinc-ion diffusion, as compared to that of layered structure.^{7, 9, 17} In this regard, bronze-phased VO₂ (VO₂-B) possesses a tunnel-like framework with unique shear structure, which can not only accommodate Zn²⁺ (0.74 Å) charge carriers in the vast tunnel (4.984 Å × 3.281 Å) but also provide large resistance to lattice shearing against ion (de)intercalation.^{18, 19} Hence, VO₂-B is highly desirable for enabling fast ion diffusion in the tunnel cavity and meanwhile providing good structural stability.

Apart from the structural stability of the cathode host, the Zn-ion and electron transportation ability also have significant influences on the electrochemical performances of the ZIBs, especially in the rate capability. Compositing the VO₂-B electrode with reduced

graphene oxide (RGO) has been demonstrated to improve the mobility of electrons and enhance its performance in aqueous ZIBs.¹² Alternatively, another approach is proposed by the introduction of substitutional dopants into the VO₂-B material, which enables engineering the electronic structure. When the dopant replaces the cationic metal in the oxide matrix, the host properties can be dramatically affected, resulting in the improvement of electron transportation.^{20, 21} For instance, Gu *et al.* reported that the VO₂-B electronic structure could be tuned *via* W doping, resulting in improved lithium-ion storage.²² Therefore, the deliberate incorporation of dopant atom into the VO₂-B lattice is an efficient way to tailor its electronic properties, and thus superior reaction kinetics is enabled. Among the dopants, Ni²⁺ has a similar ion radius (0.055 nm) as compared to that of V⁴⁺ (0.058 nm). Therefore, it can easily substitute into the VO₂-B host, which could enhance the electronic conductivity and enable the superior electrochemical performance of the host electrode materials.

Herein, we proposed a novel Ni-mediated VO₂-B ((Ni)VO₂) material and employed as a cathode in aqueous ZIBs. The introduction of Ni in the VO₂ lattice has been demonstrated to be effective for boosting the Zn²⁺ storage through experimental measurements and theoretical simulations. Specifically, it improves the intrinsic electronic conductivity by changing the local electronic structure, and it also favors ion intercalation near the interface of electrolyte/electrode, thus resulting in good kinetics. The (Ni)VO₂ cathode demonstrates enhanced cycling and rate performance relative to the VO₂, delivering cycling stability (130.6 mAh g⁻¹ at 10 A g⁻¹ after 2000 cycles) and excellent rate performance. The underlying mechanism is revealed utilizing in-situ X-ray diffraction (XRD), ex-situ XRD, scanning/transmission electron microscopy (SEM/TEM), X-ray absorption near edge structure (XANES) spectroscopy, TEM/energy dispersive spectroscopy (TEM-EDS) and Raman spectroscopy. Additionally, quasi-solid-state Zn/(Ni)VO₂ soft-packaged batteries are further demonstrated to be promising energy storage devices for practical applications.

Experimental methods

Preparation of (Ni)VO₂ cathode material. V₂O₅ and glucose (1.25:1 wt%) were first mixed with 40 mL H₂O, then 0.20, 0.40 mmol of nickel acetate tetrahydrate was added, and stirred, respectively. Next, the mixed solution was put into an autoclave (50 mL) and maintained at 180 °C for 24 h. Then, the final product was obtained by washing it with deionized water and ethanol several times and drying at 60 °C overnight. The resultant products were labeled as (Ni)VO₂ and (Ni)VO₂-2, respectively. For comparison, the VO₂ was synthesized without the introduction of nickel acetate tetrahydrate to the reaction system.

Material characterization. X-ray powder diffractometer (Bruker D8 Advance; Cu-K α radiation, $\lambda = 1.5418 \text{ \AA}$) was employed to study the phase of the sample. The home-made coin cell covered with Kapton tape was used for in-situ XRD measurement. Morphologies of the samples are studied using a scanning electron microscope (JSM-7600F, JEOL) and transmission electron microscope (JEOL 2100F). The elemental amount in the material was tested by Inductively coupled plasma-optical emission spectrometry (Agilent 720). Raman spectrum measurement was achieved using a Confocal Raman Microscope (WITec, 633 nm). The electronic states of the samples at the surface were probed using X-ray photoelectron spectroscopy (Kratos AXIS Supra). V and Ni K-edge spectra were recorded in fluorescence mode via a 4-element silicon-drift detector (Beamline 8, Synchrotron Light Research Institute, Thailand).²³ The collected data were processed and analyzed with ATHENA software (Demeter Suite).²³

Electrochemical testing. The as-prepared product, Super P and polyvinylidene fluoride (7: 2: 1 wt%) were mixed in N-Methyl-2-pyrrolidone, then cast onto stainless steel meshes and dried at 110 °C overnight under vacuum condition. Coin cells (CR2016) were assembled in an ambient condition for electrochemical measurements. The electrolyte is

composed of 3 M zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$) solution. Meanwhile, the separator used was glass fiber (GF/F, Whatman), and the anode employed was zinc foil. Quasi-solid-state full cells were prepared in the form of $(\text{Ni})\text{VO}_2/\text{gel electrolyte}/\text{Zn}$. To prepare the gel electrolyte, 1.2 g acrylamide (AAM) was first dissolved into 6.8 mL $\text{Zn}(\text{OTf})_2$ solution and then mixed with 6 mg N, N'-methylenebis(acrylamide) and 1.2 mg potassium persulfate. A battery testing system (Neware) was used to evaluate the electrochemical performance. Cyclic voltammetry measurements and electrochemical impedance spectroscopy were conducted using Solartron 1256 B.

Computational details. Density functional theory calculations were carried out using the plane-wave technique performed in the Cambridge Sequential Total Energy Package.²⁴ The projector-augmented plane wave pseudopotentials were used to simulate the ion-electron interaction. The generalized gradient approximation expressed by Perdew-Wang 91 (PW91) functional and plane-wave cutoff energy of 500 eV were applied.²⁵ The electronic structure calculations for all surfaces were done with Fermi-level smearing of 0.05 eV.²⁵ $3 \times 3 \times 1$ k-points were used to sample the Brillouin zone. The convergence of energy and forces were set to 1×10^{-5} eV and 0.02 eV/Å, respectively.²⁴ Furthermore, we constructed the Ni mediated VO_2 model by replacing a V atom with a Ni atom and used as an example to qualitatively illuminate the effect of Ni cations on the electronic structure of VO_2 .

Results and Discussion

By varying the molar ratio of Ni/V in the precursor solution, the pure VO_2 and doped with different amounts could be synthesized by hydrothermal reaction. Scanning electron microscopy (SEM) image in Figure 1a reveals that the synthesized material consists of uniform nanobelts ($\sim 5 \mu\text{m}$ length, $\sim 100 \text{ nm}$ width). O, V and Ni elements are uniformly distributed in the $(\text{Ni})\text{VO}_2$ nanobelts (Figure 1b) by High-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) analysis. The high-resolution TEM

(HRTEM) image of the (Ni)VO₂ presents well-resolved lattice spacing of 0.346 nm, which can be assigned to the (110) crystal plane of the monoclinic VO₂ structure (JCPDS No. 65-7960) (Figure 1c). Inductively coupled plasma-optical emission spectrometry was further conducted to determine the actual elemental composition. As a result, the chemical formula of (Ni)VO₂ sample is Ni_{0.011}V_{0.989}O₂. The pure VO₂ shows a similar belt morphology (Figure S1).

X-ray powder diffraction (XRD) patterns indicate that the (Ni)VO₂ product shares the same crystalline phase relative to that of the VO₂ sample (Figure 1d). All the diffraction peaks of (Ni)VO₂ can be indexed to the monoclinic VO₂-B with a space group *C2/m* (JCPDS: 65-7960).²⁶ With the increasing amount of Ni doping, the diffraction peaks of a new phase gradually appeared, as shown in Figure S2. It can be indexed to tetragonal VO₂-R.¹² This phase transformation is probably due to the dopant-induced lattice distortion. The monoclinic VO₂-B host lattice is partially transformed into tetragonal VO₂-R with the increasing amount of Ni doping.

Figure 1. Structural characterizations of the (Ni)VO₂ and VO₂ products. a) SEM image, b) HAADF-STEM and EDS mapping, and c) HRTEM image of (Ni)VO₂ material. d) XRD patterns. XANES results of e) Ni and f) V K-edge in the (Ni)VO₂ material and other standards, g) formal oxidation state of V in the (Ni)VO₂ material determined by edge energies and h) XPS spectra analysis of the V 2p spectra.

To gain further understanding of the electronic structure of the as-prepared (Ni)VO₂ material, XANES spectroscopy measurement was carried out. Figure 1e presents the XANES spectrum at the Ni K-edge for the (Ni)VO₂ with the reference compounds Ni(OH)₂ and Ni foil. It can be observed that the energy position of the Ni edge in the (Ni)VO₂ is the same as compared to that of the standard Ni(OH)₂, indicating that Ni species introduced in the (Ni)VO₂

resembles Ni^{2+} . The corresponding V K-edge XANES spectrum is illustrated in Figure 1f. The strong absorption peak at ~ 5480.6 eV corresponds to the dipole allowed V $1s$ to $4p$ transitions.²⁷ The pre-edge peak located at ~ 5469.5 eV is assigned to the dipole-forbidden transition from the V $1s$ core level to the $3d$ states.²⁷ As shown in Figure 1f, the energy position of the (Ni)VO₂ sample is close to that of the V⁴⁺ standard, indicating a dominant oxidation state of 4+. Moreover, there is a pre-edge peak intensity increase feature of the (Ni)VO₂ sample. In general, the intensity of the pre-edge peak is sensitive to the geometrical structure around the absorbing atom (V).²⁷ The peak intensity increases with the deviation from regular octahedral VO₆ units, where the symmetry of the ligand is decreased.^{27, 28} Therefore, the introduction of the low-valence cation (Ni) induces the minor formation of V⁵⁺ ions nearby the dopants in VO₂ owing to the charge compensating effect, which is equivalent to the oxidation. The oxidation state of V in (Ni)VO₂ sample was further calculated by the linear fitting relationship with standards, as shown in Figure 1g, the valence states of V is ~ 4.2 . The oxidation states of the (Ni)VO₂ and VO₂ samples on the surface were further compared. As shown in Figure 1h, the V 2p energy position of the (Ni)VO₂ slightly shifts to higher energy relative to the VO₂, indicating that the vanadium ions were oxidized with the introduction of Ni, which is consistent with the XANES results.

In order to probe the role of the Ni-mediated structure in the reaction storage, the electrochemical performance of the (Ni)VO₂ cathode was tested for aqueous ZIBs. Figure 2a presents the first three cyclic voltammetry (CV) profiles of the (Ni)VO₂ at 0.1 mV s^{-1} . The curves are almost overlapping, indicating a highly reversible electrochemical behavior. There are three pairs of redox peaks: 1.01/0.74, 0.65/0.53, and 0.52/0.41 V, corresponding to the multistep ion intercalation/deintercalation of (Ni)VO₂ structure.

Figure 2b depicts the typical charge-discharge curves of the (Ni)VO₂ electrode. The (Ni)VO₂ electrode delivers a high initial discharge capacity of 312.2 mAh g^{-1} at 50 mA g^{-1} . The

cycling stability of the (Ni)VO₂ and VO₂ electrodes were further compared (Figure 2c). The VO₂ electrode shows an initial capacity of 271.9 mAh g⁻¹ at 0.2 A g⁻¹, which quickly decays to 191.4 mAh g⁻¹ (a capacity loss of 29.6% after 50 cycles). In comparison, (Ni)VO₂ shows a higher specific capacity (246.1 mAh g⁻¹ after 50 cycles), demonstrating its better-retained capacity.

The rate capabilities of the (Ni)VO₂ and VO₂ electrodes were further evaluated (Figure 2d). Notably, the (Ni)VO₂ electrode exhibits much better rate capability than those of the VO₂ at each respective current density: 295.9 mAh g⁻¹ (100 mA g⁻¹), 241.0 mAh g⁻¹ (1 A g⁻¹), and 206.9 mAh g⁻¹ (3 A g⁻¹), especially at high current density (182 mAh g⁻¹ at 5 A g⁻¹). Furthermore, its capacity can recover to 264.7 mAh g⁻¹ when the current density returns to 100 mA g⁻¹, reflecting good rate reversibility. The improved rate capability of (Ni)VO₂ may be ascribed to the higher electrical conductivity than that of the VO₂. However, the rate performance of (Ni)VO₂-2 electrode decreases significantly with the increasing content of Ni due to the partial phase transformation (Figure S3). The result indicates that the moderate introduction of Ni can enhance the performance of VO₂ in aqueous ZIBs. Figure 2e further shows the Nyquist plots of the (Ni)VO₂ and VO₂ electrodes. Clearly, the charge transfer resistance (R_{ct}) of the (Ni)VO₂ electrode is much smaller as compared to that of the VO₂ sample, indicating better transportation across the electrode/electrolyte interface.

Figure 2. Electrochemical performances of the Zn/(Ni)VO₂ and Zn/VO₂ batteries. (a) Cyclic voltammetry curves at 0.1 mV s⁻¹, b) charge-discharge profiles at 50 mA g⁻¹, c) cycling performances of the (Ni)VO₂ and VO₂, d) rate performances comparison, e) EIS spectra of the cycled (Ni)VO₂ and VO₂, f) Ragone plots of the (Ni)VO₂ material and the reported cathodes (aqueous-based), and g) long-term cycling performance.

In Figure 2f, Ragone plots of the (Ni)VO₂ material and the cathodes reported for aqueous ZIBs, are compared. The (Ni)VO₂ electrode delivers an energy density of 188 Wh kg⁻¹ at a power density of ≈65 W kg⁻¹, and 145 Wh kg⁻¹ with a high power density of ≈43 kW kg⁻¹, representing superior advantageous in aqueous ZIBs, as compared to those of Zn₃V₂O₇(OH)₂·2H₂O,²⁹ VO₂,³⁰ Cu₃(HHTP)₂ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene),³¹ γ-MnO₂,³² and Na_{0.33}V₂O₅.³³ Moreover, the (Ni)VO₂ nanobelts

maintain a high capacity of 130.6 mAh g⁻¹ at 10 A g⁻¹ after 2000 cycles (Figure 2g), indicating the excellent cycling capability of (Ni)VO₂ electrode during ultrafast Zn²⁺ storage process. Additionally, the post-mortem TEM image of the cycled (Ni)VO₂ electrode shows the maintained nanobelts morphology (Figure S4a), demonstrating the good structural stability of the (Ni)VO₂. The lattice fringe spacing in the HRTEM image (Figure S4b) is around 0.56 nm, well indexing to the (-201) plane of the VO₂ structure. Therefore, the (Ni)VO₂ electrode can be a potential cathode candidate for practical aqueous ZIBs.

Figure 3. Electro-kinetics analysis of the storage process in the (Ni)VO₂ and VO₂ materials. (a) CV curves of the (Ni)VO₂ electrodes, b, c) the plots of log(v) vs. log(i) of the (Ni)VO₂ and VO₂ electrodes, respectively, d) diffusion and capacitive contribution of the (Ni)VO₂ sample at 0.7 mV s⁻¹, and e) diffusion and capacitive contribution ratios.

To further understand the storage process in the (Ni)VO₂ electrode, the electro-kinetics analysis was carried out. Figures 3a and S5 depict the CV curves of (Ni)VO₂ and VO₂ electrodes, respectively. The broadened redox peaks indicate that the charge storage mechanisms consist of the diffusion and capacitive-controlled redox process. The scan rate and peak current are related to the equation below:¹⁶

$$i = av^b \quad (1)$$

when b value equals to 0.5 and 1.0, it reveals the diffusion-limited process and surface-controlled capacitive behavior, respectively. The calculated b-values of the (Ni)VO₂ and VO₂ electrodes are presented in Figure 3b and c, respectively. For the (Ni)VO₂ electrode, the values of b are 0.62 and 0.84, larger than those of the VO₂ (0.51 and 0.79), indicating the improved capacitive behavior in the (Ni)VO₂ electrode.

The capacitive contribution is quantitatively evaluated using the equation below:³⁴

$$i(V) = k_1v + k_2v^{1/2} \quad (2)$$

where k_1v corresponds to surface capacitive current, and $k_2v^{1/2}$ corresponds to diffusion-limited current. The corresponding calculated capacitive and diffusion-controlled redox contributions of the (Ni)VO₂ and VO₂ electrodes are displayed in Figure 3 d and e, respectively. Clearly, the capacity from capacitive contribution increases, which is in good agreement with the b-value analysis. These results indicate that the introduction of Ni in the VO₂ lattice induces higher surface reactivity.

Figure 4. The calculated VO_2 and $(\text{Ni})\text{VO}_2$ structures and electronic properties. Crystal structures of the (a) VO_2 and (b) $(\text{Ni})\text{VO}_2$. V atoms are shown in pink, Ni atom in blue, and the O atoms in brown. (c) Illustration of the electron density difference on $(\text{Ni})\text{VO}_2$. (d) Density of states of the VO_2 and $(\text{Ni})\text{VO}_2$. Partial density of states for (e) V, Ni, and (f) O calculated for the VO_2 and $(\text{Ni})\text{VO}_2$. The vertical dash line represents the Fermi level set at zero energy.

Density functional theory (DFT) calculation was further performed to theoretically probe the influences of Ni ions on the $(\text{Ni})\text{VO}_2$ electronic properties. In Figure 4a, the crystallographic structure of VO_2 is monoclinic (space group: $C2/m$). VO_2 possesses a shear-type structure in which VO_6 octahedra are connected in a corner- and edge-sharing manner. Figure 4b presents the Ni-mediated VO_2 structure after optimization, where Ni substitutes a vertex V site. The electron density difference on the $(\text{Ni})\text{VO}_2$ is further illustrated in Figures 4c. The introduction of Ni ions can induce the electronic reorganization of the $(\text{Ni})\text{VO}_2$. The

electron density difference of initial VO_2 as a reference is presented in Figure S6. By comparison, it can find that the introduction of Ni into VO_2 can significantly attract the electrons to adjacent O sites, leading to the increased valence states of V cations, in agreement with the analyses of XPS results. Moreover, the electron accumulation on Ni sites suggests an electron flow from V to Ni, therefore contributing to enhanced electronic conductivity. To further reveal the electronic origin of the calculated properties of the $(\text{Ni})\text{VO}_2$ and VO_2 , the total density of states (DOS) was calculated, as shown in Figure 4d. It is observed that the bandgap of VO_2 becomes smaller with the introduction of Ni due to the shift of the valance band, reflecting an improvement in the electronic conductivity of the $(\text{Ni})\text{VO}_2$. Figures 4e and f present the partial densities of states (PDOS) of V, Ni atom and O atom for the VO_2 and $(\text{Ni})\text{VO}_2$, respectively. Notably, under Ni mediation, the energy levels close to the Fermi level present a new energy level. Thus the bandgap is much reduced, indicating a much-enhanced conductivity. A previous study has demonstrated that the surface reactivity of electrode materials can be optimized by the enhanced electronic conductivity.³⁵ Therefore, as confirmed by our DFT calculations, the introduction of Ni can substantially improve the surface electronic conductivity and therefore promote the surface reactivity.³⁶ The DFT calculation results are consistent with the experimental electrochemical responses, highlighting the Ni-mediated in VO_2 to promote the rate capability by improving the electronic conductivity.

Figure 5. a) In-situ XRD patterns of the (Ni)VO₂ cathode, b) ex-situ Raman spectra, c, and d) ex-situ XANES data of the Ni and V K-edges of the (Ni)VO₂ at the various charge and discharge states, respectively.

Despite the aforementioned promising properties, the underlying storage mechanism of the VO₂-B cathodes in the aqueous ZIBs remains controversial and still under debate. So far, three different reaction mechanisms for VO₂-B material have been reported, which includes: (1) A single-phase evolution reaction with Zn²⁺ intercalation/deintercalation mechanism. In this regard, the VO₂ electrode undergoes a highly reversible single-phase reaction with the formation of Zn_xVO₂.³⁷⁻³⁹ (2) A phase transformation with Zn²⁺ insertion/extraction mechanism.⁴⁰ Dai *et al.* reported that partial VO₂-B could be transformed into the VO₂-R with the Zn-ion insertion during the discharge process and recovered gradually to VO₂-B in the subsequent charge process;¹² and (3) proton insertion mechanism. Li *et al.* demonstrated that

only protons insert into VO_2 cathode accompanied by the reversible deposition of $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot 5\text{H}_2\text{O}$.³⁰ The different reported mechanisms may be due to the differences in the particle size and electrolyte of the Zn/VO_2 batteries. Therefore, it is essential to elaborate and clarify the charge storage mechanism of the $(\text{Ni})\text{VO}_2$ cathode. The $(\text{Ni})\text{VO}_2$ electrode structural evolution was firstly investigated by in-situ XRD measurement. Figure S7 presents the XRD patterns measured during cycling and those after being piled sequentially. A 2D contour map of XRD patterns is displayed in Figure 5a. Note that the unaffected peaks at 33.7° and 43.3° are ascribed to the substrate and Zn anode. Clearly, the XRD patterns evolution of the first two cycles is basically the same, indicating its good reversibility. For the pristine $(\text{Ni})\text{VO}_2$, there are two strong peaks at 45.1° and 49.0° that can be indexed to the (-601) and (020) planes of $\text{VO}_2\text{-B}$ (JCPDS NO: 65-7960), respectively (Figure S7). When discharging to 0.3 V, the peaks shift to a lower angle, suggesting the lattice expansion as a result of Zn^{2+} insertion (Zn_xVO_2) during the discharge process. In the subsequent charge process, the peaks shift back due to the extraction of Zn^{2+} , further revealing the good ions storage reversibility in the $(\text{Ni})\text{VO}_2$ nanobelts. More interestingly, a new peak located at around 33.0° simultaneously appears during the discharging process (Figure 5a). Meanwhile, the peak intensity increases and reaches the maximum after fully discharged. The corresponding ex-situ XRD pattern was further provided to verify the new phase. As shown in Figure S8, except the new peak at around 33.0° , a set of diffraction peaks at 6.5° , 13.0° and 19.6° also emerges, matching well with the pattern of $\text{Zn}_x(\text{CF}_3\text{SO}_3)_y(\text{OH})_{2x-y} \cdot n\text{H}_2\text{O}$ ($\text{Zn}_x(\text{OTf})_y(\text{OH})_{2x-y} \cdot n\text{H}_2\text{O}$).⁴¹ During the subsequent charging process, these peaks become weakened gradually and completely disappear (Figures 5a and S5). The reversible precipitation/dissolution of the $\text{Zn}_x(\text{OTf})_y(\text{OH})_{2x-y} \cdot n\text{H}_2\text{O}$ phenomenon is similar to the mechanism of zinc/zinc vanadate batteries, which possess the H^+ and Zn^{2+} co-insertion/extraction process.⁴¹ Therefore, it is highly possible that proton and zinc ions can co-intercalate into the $(\text{Ni})\text{VO}_2$ structure. The H^+ insertion may dominate in the initial

discharge process. During the initial discharge process, a large number of H^+ insert into the VO_2 structure. With the H^+ insertion proceeds, the OH^- concentration in the electrolyte is high enough to form $Zn_x(OTf)_y(OH)_{2x-y} \cdot nH_2O$. The increased amount of $Zn_x(OTf)_y(OH)_{2x-y} \cdot nH_2O$ indicates that H^+ insertion is ongoing along with Zn^{2+} insertion in the late discharge process. Furthermore, the previous theoretical calculation study simulated the preferential transport pathways of H^+ and Zn^{2+} .⁴² It reveals that the H^+ insertion dominates in the initial discharge process, followed by Zn^{2+} insertion in the late discharge process, which is consistent with our experimental results.

Raman spectroscopy measurement was conducted at selected states during the first cycle to investigate the molecular vibrations (Figure 5b). For the pristine $(Ni)VO_2$ electrode, there are four peaks located at 289, 408, 691, and 992 cm^{-1} , which coincides with the vibrations of VO_2 monoclinic crystalline.^{43, 44} Notably, when the cell was discharged to 0.5 V, peaks located at around 300-500 and 867 cm^{-1} are observed, which may be corresponded to the vibrations of Zn_xVO_2 or $Zn_x(OTf)_y(OH)_{2x-y} \cdot nH_2O$.^{16, 45} As expected, these peaks intensity weakens during the charging process. Ex-situ TEM images and EDS patterns at fully discharged states of $(Ni)VO_2$ electrode are presented in Figure S9, the lattice spacing of the (110) plane expands to 3.53 Å, with an increase of 2% compared to the pristine state (Figure 1c). The expanded lattice plane further demonstrates the Zn^{2+} insertion and coincides well with the TEM-EDS analysis (Figure S10).

The valence evolution of $(Ni)VO_2$ was further investigated by using the XANES technique. The XANES spectra of the Ni and V K-edge at the pristine, fully discharged, and charged states are provided (Figure 5c, d). During the whole charge-discharge processes, the position of the Ni edge in the $(Ni)VO_2$ keeps the same, indicating that the Ni dopant remains Ni^{2+} during the redox reaction (Figure 5c). Different from the Ni K-edge XANES spectra, Figure 5d shows that as potential decreased to 0.3 V, the V K-edge position slightly shifts

toward lower energy, indicative of the reduction of $V^{4+/5+}$ to $V^{3+/4+}$. Meanwhile, the reduced pre-edge peak intensity relative to the pristine state further confirms the increment of ligands symmetry and less distorted octahedron VO_6 units. Similarly, upon the charging process, the V K-edge position shifts back with increased pre-edge peak intensity, presenting the good reversibility of the electrochemical redox reaction of the $(Ni)VO_2$ framework.

Accordingly, reversible H^+ and Zn^{2+} co-intercalation processes are demonstrated. The electrochemical reactions of the aqueous rechargeable $Zn/(Ni)VO_2$ batteries can be formulated as follows:

In the cathode

In the anode

Figure 6. a) Illustration of the quasi-solid-state Zn/(Ni)VO₂ soft-packaged battery, b) cycling performance at 0.1 A g⁻¹, and c) cycling capability at 1 A g⁻¹.

In view of the impressive Zn²⁺ storage capability, the practicability of (Ni)VO₂ was exemplified by fabricating a quasi-solid-state zinc battery. The soft-packaged full cells were assembled in the form of (Ni)VO₂/gel electrolyte/Zn (Figure 6a). Polyacrylamide (PAM)/Zn(OTf)₂ transparent gel was used as both the electrolyte and the separator. As shown in Figure 6b, the soft-packaged battery exhibits a capacity of 248 mAh g⁻¹ at 0.1 A g⁻¹ in the second cycle. Owing to the activation reaction in the initial cycles, the gradual increase of discharge capacity can be observed. Moreover, the soft-packaged battery exhibits promising rate capability (127 mAh g⁻¹ at 1 A g⁻¹ after 1000 cycles; Figure 6c). This further suggests that the Zn/(Ni)VO₂ full cell could be a potential candidate for safe power sources in practical applications.

Conclusions

In summary, Ni-mediated electronic structure engineering of VO₂ nanobelt was proposed for raising Zn-ion storage properties towards aqueous zinc-ion batteries. The introduction of Ni in the VO₂ lattice is effective in optimizing its intrinsic electronic configurations, providing high surface reactivity, and improving Zn²⁺ reaction kinetics. Accordingly, the Zn/(Ni)VO₂ battery displays a high energy density of 188 Wh kg⁻¹ at a power density of ≈65 W kg⁻¹ and 145 Wh kg⁻¹ with a high-power density of ≈43 kW kg⁻¹, and good stability with a remaining capacity of 130.6 mAh g⁻¹ after 2000 cycles at 10 A g⁻¹. Meanwhile, the storage mechanism of the (Ni)VO₂ cathode has been proposed to be a Zn²⁺ and H⁺ co-intercalation/deintercalation reaction. Additionally, quasi-solid-state Zn/(Ni)VO₂ soft-packaged batteries were demonstrated to be promising energy storage devices for practical applications. Our encouraging result provides insight into how the intrinsic properties of material affect the overall electrochemical performance.

Conflict of interest

The authors declare no conflict of interest.

Supporting Information

SEM, ex-situ TEM, and HRTEM images of the pristine and cycled VO₂; CV curves of the VO₂ electrodes; in-situ and ex-situ XRD patterns, ex-situ TEM and HRTEM images, TEM-EDS mapping of the cycled (Ni)VO₂ cathodes; lattice parameters of the VO₂ and (Ni)VO₂.

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