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ARTICLE

Bronze-type vanadium dioxide holey nanobelts as high performing cathode material for aqueous aluminium-ion batteryYi Cai,^{†a} Sonal Kumar,^{†a} Rodney Chua,^a Vivek Verma,^a Du Yuan,^a Zongkui Kou,^b Hao Ren,^a Hemal Arora^c and Madhavi Srinivasan,^{*a,d}Received 00th January 20xx,
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Aqueous rechargeable aluminium-ion batteries (AIBs) are promising post lithium-ion battery candidates. However, the capacity and cycling stability are limited by the cathode materials, hindering their widespread application. Herein, bronze-type vanadium dioxide (VO₂-B) holey nanobelts have been designed as the cathode material to improve both the capacity and cycling stability for high-performance aqueous AIBs. Benefiting from the unique shear structure and two-dimensional holey nanobelts morphology, the VO₂-B electrode delivers a superior specific capacity of up to 234 mAh g⁻¹ at 150 mA g⁻¹ and exhibits high capacity retention of 77.2% over 1000 cycles at 1 A g⁻¹, which are among the best cathode performances reported for aqueous AIBs. Moreover, a combination of electro-kinetic analysis and ex-situ structural evolution characterizations unveils the reaction storage mechanism underlying the superior performance. Specifically, proton and Al³⁺ ions can reversibly co-intercalate/de-intercalate into/from VO₂-B. The integration of shear structure and unique holey nanobelt may open the route to the design of high-performance cathodes for multi-valence ion batteries.

Introduction

Lithium-ion batteries have been widely investigated and applied in the commercial market due to the continuously evolved energy demand. However, the limited lithium resources and safety issue associated with flammable organic electrolytes still hinder their worldwide commercialization.¹ Among potential multi-valence candidates, aluminium-ion batteries (AIBs) have been considered to be promising due to the high theoretical capacity of metallic Al anode (8040 mAh cm⁻³), ~4 times higher than Li, i.e., 2062 mAh cm⁻³, high abundance and low cost.²⁻⁴ Very recently, aqueous AIBs are initiated to address the issues of ionic liquids (IL) based AIBs including water and oxygen sensitivity and high cost, meanwhile showing a great potential for ambient fabrication and thus being economically viable.⁵⁻⁷

Until now, a variety of host materials, including transition metal oxide,⁸⁻¹⁵ NASICON-type Na₃V₂(PO₄)₃,¹⁶ FeVO₄,¹⁷ and Prussian blue analogues,¹⁸⁻²² have been reported for aluminium-ion storage. Nevertheless, the high charge density of aluminium-ion remains a critical issue to pursuit the ideal cathode. Specifically, the strong internal electrostatic force between Al³⁺ ions and host structure can significantly hinder the diffusion of Al³⁺ and lead to a serious structural instability when

Al³⁺ ions are inserted into the cathode material, resulting in rapid capacity degradation.²³ For instance, Nandi et al. reported that bismuth oxide could deliver a specific capacity of 103 mAh g⁻¹ at a current rate of 1.5 A g⁻¹, but it exhibits a dramatic capacity fading and even diminishes after 50 cycles.²⁴ The same issue occurred in the study of Al³⁺ ion intercalation into MoO₃. Although a very high initial capacity of 680 mAh g⁻¹ is observed, the MoO₃ electrode capacity drops to around 170 mAh g⁻¹ after 20 cycles with a capacity retention of only 25%.²⁵ Therefore, it is highly desirable to explore novel electrochemical redox reactions for aqueous rechargeable AIBs with both high capacity and long-term cycling stability.

Bronze-type vanadium dioxide (VO₂-B) possesses a bilayer shear structure with the tunnel-like framework, which is formed by corners and edges sharing of distorted VO₆ octahedra, appearing to be a promising host material for aqueous rechargeable AIBs.²⁶ This unique shear structure of VO₂-B strengthens the structural stability caused by the increased edge shearing and the consequent resistance to lattice shearing during cycling.^{27, 28} Recent investigations have demonstrated that such large tunnels are beneficial for fast metal ions insertion and extraction, such as Mg²⁺ (0.72 Å), Zn²⁺ (0.74 Å), Li⁺ (0.76 Å) and Na⁺ (1.02 Å).²⁹⁻³³ Considering the relatively lower ionic radius of Al³⁺ (0.53 Å), the potential of VO₂-B as a host material for aqueous rechargeable AIB is promising.

On the other hand, recent studies have shown that the 2D nanostructured electrodes have unique advantages in electrochemical storage owing to their unique structure and surface properties.³⁴⁻³⁶ The 2D nanostructure could provide a large interfacial contact area with the electrolyte, enhancing the electrochemical activity. For instance, Zhu *et al.* demonstrated that the large area ultrathin 2D nanostructure could shorten

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lithium-ion diffusion paths and provide a large exposed surface for more lithium-insertion channels.³⁷ Therefore, fabricating 2D nanostructure seems to be an effective strategy for aqueous AIBs cathode hosts.

In this work, VO₂-B holey nanobelts were synthesized via a facile hydrothermal method and used as a cathode material for an aqueous AIB. The unique shear structures of VO₂-B strengthen structural stability due to the resistance to lattice shearing during cycling. Meanwhile, the 2D holey nanobelts structure can provide short ion diffusion pathways and abundant electrolyte-electrode contact, favouring the improvement of electrode properties. As a result, the VO₂-B holey nanobelts can deliver a remarkable capacity of 234 mAh g⁻¹ at 150 mA g⁻¹ and excellent long-term cycling stability with a capacity retention of 77.2% over 1000 cycles at 1 A g⁻¹. Furthermore, a reversible H⁺ and Al³⁺ ions co-insertion storage mechanism has been elucidated via ex-situ studies on the evolution of structure, elemental composition, and valence states during the charge/discharge process.

Results and discussion

The vanadium dioxide material was synthesized by a facile hydrothermal method. As shown in Fig. 1a, all the XRD peaks are well indexed to the monoclinic structure of VO₂-B (C2/m space group, JCPDS No. 31-1438).³⁸ The crystal structure of the VO₂-B is shown in Fig. 1b. The VO₂-B structure is built up of distorted VO₆ octahedra, which share both edges and corners along the c-direction of the unit cell. The unique bilayer shear structures of VO₂-B possess structure stability due to the increased edge shearing along with the resistance to lattice shearing during cycling. Meanwhile, the tunnel size (4.984 Å × 3.281 Å) of VO₂-B is considerably larger than the ionic radius of Al³⁺ (0.53 Å).³⁹ Such framework with tunnel structure is expected to accommodate Al-ion via diffusion through the crystal structure, facilitating the electrochemical reaction.

Fig. 1 Structural characterizations of the VO₂-B products: a) XRD pattern of the VO₂ material, b) specific crystal structure of the VO₂-B product, c) SEM-EDS mapping of the as-prepared VO₂-B, d) TEM and e, f) HRTEM images of the VO₂-B material, inset in (e), the corresponding fast Fourier transform (FFT) pattern.

The morphology and elemental analysis were further investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), as shown in Fig. 1c. The VO₂-B material is composed of nanobelts with an average length of ~5 μm. SEM-EDS result (Fig. 1c) further confirms the uniform distribution of V and O elements in the VO₂-B product. Transmission electron microscopy (TEM) image depicts its belt morphology with a width of around 100 nm (Fig. 1d). The high-resolution TEM image of an individual nanobelt is shown in Fig. 1e. The lattice spacing is 0.35 nm corresponding to the d spacing of the (110) plane of monoclinic VO₂ (B). The corresponding fast Fourier transform (FFT) pattern (the inset of Fig. 1e) indicates that these nanobelts grew along [110] direction. Moreover, holes with diameters around 3 nm are formed on the VO₂-B nanobelts, as shown in Fig. 1f. This unique nanostructure can provide a good electrolyte-electrode contact.

The formation mechanism of VO₂-B nanobelt is further proposed as a simultaneous hydrothermal synthesis and chemical reduction procedure. Glucose (C₆H₁₂O₆) exhibits five hydroxyl (OH) groups. Therefore, it can act as a reduction agent during the synthesis. Under the hydrothermal condition, V₂O₅ powders were initially dissolved in water and then gradually reduced by glucose and formed VO₂-B. The formed belt structure is mainly due to the strong crystal anisotropy of monoclinic VO₂.^{31, 40}

Nitrogen adsorption-desorption measurement was further performed to characterize the pore characteristics of the VO₂-B nanobelts. Fig. S1a depicts the N₂ adsorption-desorption isotherm curves of the VO₂-B. It exhibits a type IV nitrogen isotherm with a hysteresis loop, which is characteristic of mesoporous materials. The BET surface area of VO₂-B is 33.6 m² g⁻¹. The pore size distribution is further presented in Fig. S1b. The as-prepared VO₂-B has a size distribution with a range of less than 10 nm, indicating the porous structure of the VO₂-B. The holey structure can serve as an electrolyte reservoir and reduce mass transfer limitations of electrolyte infiltration and diffusion.⁴¹

X-ray photoelectron spectroscopy (XPS) measurement was also applied to investigate the surface oxidation state of V in the VO₂-B product (Fig. S2). The high-resolution V2p 3/2 peak is resolved into two peaks at 516.7 and 517.7 eV, corresponding to the tetravalent (V⁴⁺) and pentavalent (V⁵⁺) vanadium oxidation state, respectively.^{42, 43} The presence of V⁵⁺ is attributed to the partial oxidation of the surface, and is consistent with previous reports.⁴⁴ Moreover, previous studies have demonstrated that the mixed-valent vanadium on the surface can increase the electronic conductivity of the vanadium oxides.⁴⁴⁻⁴⁶ Thus, this advantage can further project on the promising performance of the VO₂-B holey nanobelts electrode.

Fig. 2 Electrochemical performances of the VO₂-B electrodes: (a) cycling performances in the Al(OTf)₃ electrolytes with different concentrations at 150 mA g⁻¹, (b) Galvanostatic charge and discharge curves in the 5 m Al(OTf)₃ electrolyte, (c) long-term cycling performance at 1 A g⁻¹ in the 5 m Al(OTf)₃ electrolyte, (d) comparison of the capacities with reported cathode materials for aqueous AIBs, (e) CV curves at various scan rates from 0.1 to 1.0 mV s⁻¹, and (f) linear relationship of log(v) and log(i) at specific peak currents.

The potential of the VO₂-B holey nanobelts cathode was then verified in aqueous AIBs. Previous studies in aqueous batteries indicate that the salt concentration has a profound effect on the physical and chemical properties of electrolyte, which eventually can significantly influence battery performance.⁴⁷⁻⁵⁰ Fig. 2a compares the cycling performance of the VO₂-B electrode in Al(OTf)₃ electrolytes with different concentrations at 150 mA g⁻¹. It can be clearly seen that the VO₂-B electrodes show similar capacities in the initial cycles. However, the electrolyte concentration seems to have a major role in cycling stability. Notably, the VO₂-B electrode cycled in 5 m Al(OTf)₃ exhibits the best cycling stability with a capacity of 110.5 mAh g⁻¹ after 100 cycles. This is mainly attributed to the reduced water-induced side reactions, leading to improved cycling stability of the electrode.¹⁸ Meanwhile, it can be observed that the capacities of the VO₂-B electrode decay in the initial cycles. This is possibly due to the partial dissolution of the vanadium ions in the initial cycles. The 5 m Al(OTf)₃ electrolyte is an acidic environment. Previous studies have demonstrated that there are thermodynamically favorable dissolved species of vanadium-based materials depending on the various pH values and oxidation states, such as HV₂O₅⁻, H₃V₂O₇⁻, or VO²⁺ species.^{14, 51} Therefore, in the initial cycles, some vanadium ions dissolve in the acidic electrolyte, resulting in the capacity decay. Similar phenomena are also observed in other aqueous AIBs.^{14, 52} Notably, the dissolved vanadium species can achieve

equilibrium with the vanadium in the electrode and prevent subsequent dissolution after a few cycles, thus achieving good cycling stability in the following cycles.⁵³

Fig. S3 presents the cyclic voltammetry (CV) curve of the VO₂-B electrodes cycled in 5 m Al(OTf)₃ electrolyte at 0.1 mV s⁻¹. It can be observed that there are three pairs of broad redox peaks located at around 0.24/0.15, 0.09/-0.19, and -0.04/-0.32 V vs. Ag/AgCl, indicating a multistep ion intercalation/de-intercalation process. The typical galvanostatic discharge-charge profiles of the VO₂-B cycled in the 5 m Al(OTf)₃ electrolyte at 150 mA g⁻¹ are further presented in Fig. 2b. During the discharge process, the redox plateaus located at around 0.15, -0.19, and -0.32 V vs. Ag/AgCl correspond to the ion intercalation into the VO₂-B. The initial discharge capacity of the VO₂-B electrode (230.9 mAh g⁻¹) is slightly higher than that of charge capacity (214.6 mAh g⁻¹). This is possibly due to the high charge density of Al-ion, the highly charged Al³⁺ probably generates a strong interaction with the surrounding host lattice.¹⁸ Therefore, some Al-ions could be trapped in the initial cycles. As a comparison, the coulombic efficiency of the VO₂-B electrode is reduced to 102% in the 10th cycle. Moreover, the coulombic efficiency is nearly 100% after 20 cycles. Therefore, the remained Al-ion in the host could stabilize the structure, thus achieving good cycling stability in the following cycles.¹⁸ Additionally, the VO₂-B electrode demonstrates good rate performance (Fig. S4).

As one of the key performance indicators, long-term cycling stability of the VO₂-B is further examined (Fig. 2c). The VO₂-B holey nanobelts maintain a high capacity of 56.6 mAh g⁻¹ after 1000 cycles at a high current rate of 1 A g⁻¹ with a high capacity retention of 77.2%. The excellent structural stability is possibly due to the unique shear structure of VO₂-B that can produce the resistance to lattice shearing during cycling. The discharge capacities increase gradually in the first several cycles due to the activation process. The possible mechanism of the activation process may include two aspects. (1) The electrolyte gradually soaks the VO₂-B material, resulting in electrochemical activation and improved reversible reactions during cycling. (2) The dissolution process could be reduced at high current rates.⁵⁴ The electrochemical performances of the VO₂-B electrode are further compared with current cathode materials reported for aqueous AIBs, as displayed in Fig. 2d. The capacity of VO₂-B holey nanobelts is among the highest reported values of cathode materials for aqueous AIBs, such as KCu[Fe(CN)₆] $\cdot$ xH₂O,²² FeFe(CN)₆,¹⁸ MnO₂,¹² TiO₂,⁵⁵ graphene,⁵⁶ and V₂O₅.⁵⁷ Moreover, the superior capacity retention of VO₂-B holey nanobelts is summarized in Table S1, together with the literature reports. Therefore, the VO₂-B holey nanobelt with high capacity and excellent long-term cycling stability is a promising cathode material for aqueous AIBs.

As a proof of concept, the VO₂-B//Al full cell has been assembled. Fig. S5 presents the galvanostatic discharge/charge curves for aqueous VO₂-B//Al cell at a current density of 100 mA g⁻¹. It can be observed that the discharge capacity remains stable at around 182 mAh g⁻¹, indicating that the electrode reactions are reversible, reflecting the potential of our VO₂-B material in a battery device. The energy density and power density are further compared to those of previously reported aqueous AIBs, as shown in Fig. S6. Our VO₂-B//Al battery exhibits an energy density of 134 Wh kg⁻¹ with a power density of 70 W kg⁻¹, which is among the best reported aqueous AIBs.^{12-15, 19, 21}

Electro-kinetics analysis was performed to understand the storage mechanism in the VO₂-B nanobelts electrode. Fig. 2e presents the CV curves of the VO₂-B electrodes cycled in 5m Al(OTf)₃ electrolytes with scan rates ranging from 0.1 to 1.0 mV s⁻¹. When the scan rates increase, the reduction peaks are shifted to lower potentials, and the oxidation peaks shifted to higher potentials because of the enhanced polarization after increasing the scan rate. The relationship between the redox peak currents (*i*) and scan rates (*v*) can be formulated as below:⁵⁸

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

where *b* value of 0.5 indicates a diffusion-controlled process and *b* value of 1 reveals a surface-controlled capacitive behaviour. The *b*-value can be calculated by plotting the log *i* against log *v*, as shown in Fig. 2f. Notably, the *b*-values for the first and second anodic peaks of the VO₂-B electrode are 0.51 and 0.62, respectively. Although there is some capacitive behaviour, diffusion-controlled faradaic processes occur at the peak potentials due to the sluggish electrochemical kinetics with Al³⁺, which has a strong charge density. The broad peaks

with the incremental scan rate indicate that the surface-controlled processes are dominant at high scan rates.

To gain insight into the storage mechanism of Al-ion in VO₂-B, ex-situ studies were carried out on the cycled VO₂-B electrodes at the discharge-charge states. In an Al-ion aqueous acidic environment, the hydrated Al³⁺ ions ([Al(H₂O)₆]³⁺) are hydrolysed to provide H⁺.¹⁸ Therefore, it is reasonable to hypothesize that the protons may intercalate into the VO₂-B structure along with the Al³⁺ ions. Ex-situ XRD patterns of VO₂-B electrodes at full discharge and charge stages are firstly presented to study changes in the structure (Fig. 3a). Compared to the pristine electrode, little change can be observed on the XRD pattern of VO₂-B after fully discharged, indicating the robust crystal structure of VO₂-B. A zoom-in for the magnified XRD pattern (Fig. 3b) reveals that (110) peak slightly shifts by only ~0.1 degree, suggesting the slight lattice expansion as a result of Al³⁺ or H⁺ intercalation during the discharge process. The corresponding unit cell parameters (*a*, *b*, *c*, β) are presented in Table S2. Notably, the expansion and contraction of the crystal structure occur reversibly during the discharge-charge process, implying a small volumetric variation of the VO₂-B lattice. Such a small change can be understood by the characteristics of the unique shear structure of VO₂-B, which could effectively relieve the volume variation. During the subsequent charging process, the peak shifts back to the original position owing to the removal of Al³⁺ or H⁺ ions, indicating clearly the reversibility of the ion intercalation and de-intercalation in the VO₂-B structure. Therefore, the minor structural change of the VO₂-B electrode results in the excellent cycle performance of the aqueous AIBs.

More details of the local structural evolution of VO₂-B were revealed by the Raman spectra of the electrodes (Fig. 3c). In the pristine VO₂-B electrode, the two bands at 288 cm⁻¹ and 408 cm⁻¹ can be assigned to V₂-O and V-O bending vibration modes, respectively.⁵⁹ The broad band located around 400-600 cm⁻¹ is assignable to V₂-O and V₃-O bridging modes. The bands at 685 cm⁻¹ and 991 cm⁻¹ are due to V₂-O and V=O stretching mode, respectively.⁶⁰ From pristine to fully discharged state, there is a red shift of the V=O bond, shifting from 991 cm⁻¹ to 987 cm⁻¹. A change in bond length can be thus caused by the ion intercalation into the VO₂-B tunnels. Such a change in bond length is recovered after being fully charged, which is consistent with the above XRD result.

To further understand the intercalation chemistry, XPS measurement was conducted on the VO₂-B electrode in the pristine and full discharge states, exploring the change of surface composition and valence states of the VO₂-B electrode during the reaction. Fig. 3d presents the V3s and Al 2p spectra of the VO₂-B electrode. In the pristine electrode, the V 3s peak is observed at 70 eV.⁶¹ Clearly, no signal of Al can be detected in the spectrum of the pristine electrode. After fully discharged, the signal for the Al element (74.4 eV) is obvious. Moreover, the Al 2p peak is at a different binding energy value as compared with that of the previously reported Al(OTf)₃ electrolyte (75.8 eV).¹⁰ This suggests that the Al signals in the XPS analysis are mainly from the intercalated Al species and not from the absorbed electrolyte salt. The elemental mapping experiment

Fig. 3 a) Ex-situ XRD patterns and b) the corresponding magnified XRD patterns of the $\text{VO}_2\text{-B}$ cathode operated at different discharge-charge states, c) ex-situ Raman spectra collected at different discharge-charge states, d) XPS spectra of V 3s and Al 2p of the $\text{VO}_2\text{-B}$ electrode at pristine and fully discharged states, e) SEM-EDS mapping of the fully discharged $\text{VO}_2\text{-B}$ electrode, and f) XPS spectra of O 1s of the $\text{VO}_2\text{-B}$ electrodes.

was also performed on the discharged electrode by SEM-EDS, as shown in Fig. 3e. The fully discharged $\text{VO}_2\text{-B}$ electrode consists of uniformly distributed V, O, and Al elements, further confirming the Al^{3+} ions intercalation into the $\text{VO}_2\text{-B}$ structure. SEM image of the discharged $\text{VO}_2\text{-B}$ electrode in Fig. S7 confirms its maintained nanobelts morphology, indicating that the robust $\text{VO}_2\text{-B}$ structure can well accommodate ions intercalation during cycling.

Moreover, the O 1s peaks for $\text{VO}_2\text{-B}$ (Fig. 3f) can be assigned to the H-O-H bond at ~ 532.6 eV for absorbed, or crystal water, the -OH bond at ~ 531.4 eV for the hydroxide and the V-O bond at ~ 530.1 eV.⁶² The characteristic peaks representing -OH and H-O-H bonds at fully discharged state are pronouncedly stronger relative to the initial state, suggesting protons intercalation into $\text{VO}_2\text{-B}$ along with the Al^{3+} ions.^{62, 63} Meanwhile, the weakened characteristic peaks representing V-O bond indicate structural rearrangements in $\text{VO}_2\text{-B}$ likely caused by the intercalation of Al^{3+} , consistent with the changes in the Al 2p spectrum in Fig. 3d. In addition, after fully discharged, the V 2p_{3/2} peak of $\text{VO}_2\text{-B}$ electrode can be

decoupled into two peaks, corresponding to V^{4+} and V^{3+} , respectively (Fig. S8).^{42, 64} Specifically, with reference to the initial state, the intensity of V^{4+} peak decreases and the V^{3+} peak intensity increases, reflecting the reduction of V^{4+} to V^{3+} along with the intercalation of Al^{3+} and H^+ ions.

Based on the above analysis, we propose a reversible H^+ and Al^{3+} co-intercalation/de-intercalation into/from the $\text{VO}_2\text{-B}$ electrode. Fig. 4 depicts the scheme of proton and Al^{3+} ions co-intercalation into and de-intercalation from the $\text{VO}_2\text{-B}$ during

Fig. 4 Schematic illustration of H^+ and Al^{3+} ions co-intercalation into and deintercalation from the $\text{VO}_2\text{-B}$ during the discharge and charge processes.

the discharge and charge processes. The overall electrochemical reaction can be described as follows:

In short, in an Al-ion aqueous acidic environment, the hydrated Al^{3+} ions undergo a hydrolysis reaction with the formation of H^+ . During the discharge process, the protons and Al^{3+} ions co-intercalate into the tunnel structure between VO_2 -B sheets. Upon subsequent charge processes, the proton and Al^{3+} ions are reversibly deintercalated from VO_2 -B. The unique shear structure of VO_2 -B enables effective relief of the volume variation by proton and Al^{3+} ions intercalation/de-intercalation; and the holey nanobelts morphology offers short ion diffusion pathways and abundant electrolyte/electrode contact, resulting in high capacity and good cycling stability of the VO_2 -B based aqueous AIBs.

Conclusions

In summary, VO_2 -B holey nanobelt was rationally proposed as a high-performing cathode material for aqueous aluminium-ion battery. A remarkably high capacity of 234 mAh g^{-1} was obtained at a current density of 150 mA g^{-1} . Moreover, the VO_2 -B electrode exhibits excellent long-term cycling stability (72.9 mAh g^{-1} after 1000 cycles at 1 A g^{-1} with a capacity retention of 77.2%). The electro-kinetic analysis and ex-situ structural characterization results show that the robust shear structure and holey nanobelts morphology of VO_2 -B are beneficial for highly reversible H^+ and Al^{3+} co-intercalation and de-intercalation during cycling. Our study suggests that the VO_2 -B is a promising cathode material for aqueous aluminium-ion batteries with high capacity and long cycle life.

Experimental

Materials and methods

All the reactants and solvents are of analytical grade and used without any further purification. In a typical synthesis of the material, a mixture of V_2O_5 and glucose with a molar ratio of 1.25:1 was dispersed in 30 mL of deionized water and stirred for 1h. Then, the resultant solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and maintained at 180°C for 24 h. After that, the precipitate was washed with ethanol and water and dried at 80°C for 12 h. The resultant product was labelled as VO_2 -B.

Material characterization

X-ray diffraction (XRD) pattern of the product was obtained by using a Bruker D8 Advance powder diffractometer with $\text{Cu-K}\alpha$ radiation. The crystal structure of the VO_2 -B electrode at different states in ex-situ XRD was fitted by Pawley fitting. The morphologies were observed by scanning electron microscopy (SEM, JSM-7600F, JEOL) and transmission electron microscopy (TEM, JEOL 2100F). Raman spectra were recorded by a Confocal Raman Microscopy (WITec) using a 488 nm excitation wavelength at room temperature. The specific surface area was obtained by a surface area and porosity analyzer (Micromeritics, ASAP 2020). X-ray photoelectron

spectroscopy (Kratos AXIS Supra) was performed to analyze the surface electronic states. The binding energies of the spectra were calibrated using $\text{C1s} = 284.6 \text{ eV}$ as a reference.

Electrochemical measurement

The working electrodes were prepared by mixing VO_2 -B powder with super P carbon and teflonized acetylene black (TAB) in a weight ratio of 6: 2: 2. Then, the mixture was pressed onto the titanium mesh (Good Fellow). Electrochemical measurements were carried out via three electrodes set up cells. Graphite paper and Ag/AgCl (saturated KCl) were employed as the counter and reference electrodes, respectively. The VO_2 -B//Al full cell was fabricated in a typical CR2016 type coin cell under the air atmosphere. VO_2 electrode as a cathode was paired with coated Al foil as an anode. The cathode fabrication was done by making a slurry of VO_2 , super P, and PVDF with a weight ratio of 6:2:2 in N-methyl-2-pyrrolidone solvent. This slurry was stirred overnight and painted on Ti foil, which was further dried in vacuum overnight to get rid of the solvent. Al foil (0.25mm thick, annealed, 99.99% (metals basis) Alfa Aesar, CAS: 7429-90-5) was polished and coated with a mixed AlCl_3 and 1-ethyl-3-methylimidazolium chloride ($[\text{EMIm}]\text{Cl}$) inside of the glovebox. A Whatman filter paper was used as the separator. Cyclic voltammetry (CV) measurements were conducted on Solartron 1256 B. Galvanostatic charge-discharge measurements were carried out using the Neware BTS system with the activation process. All the electrochemical performances were tested under room temperature.

Conflicts of interest

There are no conflicts to declare.

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VO₂-B holey nanobelt was rationally proposed as a high-performing cathode material for aqueous aluminium-ion battery.