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Li⁺, Na⁺ co-stabilized vanadium oxide nanobelts with a bilayer structure for boosted zinc-ion storage performance⁺

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Addressing the structural instability and torpid kinetic limitation has been a pressing while challenging issue for vanadium oxide cathode materials to realize their outstanding performance in rechargeable aqueous zinc-ion batteries (ZIBs). Herein, vanadium oxide nanobelts with a bilayer structure (LiV₃O₈@NaV₃O₈, LVO@NVO) have been prepared successfully *via* a quick one-pot eutectic oxidation process. When evaluated as a cathode for ZIBs, the LVO@NVO shows an amazing capacity of 476 mA h g⁻¹ at 0.05 A g⁻¹, superior rate properties (236 mA h g⁻¹ @ 5 A g⁻¹), and excellent cycling capability over 2000 cycles with a capacity-retention of 93.4%. Owing to the pre-intercalated Li⁺ and Na⁺ cations and the resulting bilayer structure, higher pseudocapacitance, faster charge-transfer/ion-diffusion kinetics, and a robust architecture have been achieved in the LVO@NVO cathode, which are responsible for the superior zinc-ion storage performance. Furthermore, the energy storage mechanism based on Zn²⁺ and H⁺ co-intercalation/extraction has been proved.

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Introduction

Recent decades have witnessed the development of energy storage and conversion devices (ESCDs) towards the characteristics of remarkable energy density, high reliability and safety.1-3 Nonaqueous systems, represented by lithium-ion batteries, though with high energy density, are facing more safety hazards due to their organic, nocuous and flammable electrolyte.^{4,5} In contrast, rechargeable aqueous batteries are attracting increasing attention as aqueous electrolytes ensure greater security and faster ionic mobility.⁶⁻⁸ In particular, rechargeable aqueous zinc-ion batteries (ZIBs) are identified as one of the future ESCDs given the advantages of metallic Zn anodes with a stable potential (-0.763 V vs. the standard hydrogen electrode) in neutral aqueous electrolytes and a high theoretical specific capacity (819 mA h g⁻¹).^{9,10} However, the lack of highperformance cathode materials is still a bottleneck towards the practical applications of ZIBs.

Up to now, although various cathode materials have been exploited for ZIBs, the low specific capacity, inferior cycling stability, and torpid kinetics are hard to overcome.¹¹⁻¹⁷ Among them, layered vanadium oxides exhibit potential in achieving an outstanding specific capacity (*e.g.*, 589 mA h g⁻¹ for V₂O₅) of more than twice as much as other candidates.¹⁸⁻²⁰ However, the collapse of their structure occurs during Zn²⁺ intercalation/extraction, which leads to poor long-term cycling stability. Typically, preintercalation of metal ions into the layered vanadium oxides can effectively enlarge the interlayer space, as well as form a pillared structure, which guarantees a long-term cycling capability for ZIBs. For example, He *et al.* designed a Na⁺ pre-intercalated vanadium oxide nanowire (Na_{0.33}V₂O₅) for Zn²⁺ storage,²¹ and an enhanced cycling property as long as 1000 cycles at 1 A g⁻¹ was achieved. Other cations, such as Mn²⁺, Cu²⁺, Zn²⁺, and Ca²⁺, were also introduced into the V₂O₅ or V₃O₈ lattices, and improved cycling performance was realized in varying degrees.²²⁻²⁶

On the other hand, heterogeneous material coating has been testified to be rewarding for enhancing the electrochemical performance,²⁷ which can be ascribed to the increased ion-adsorption sites, facilitated electron conductivity, and prevented collapse/dissolution of active materials. For example, the optimal carbon coating promoted the long-term capacity retention of K⁺ pre-intercalated V₂O₅ nanoflowers for ZIBs from 21% to 77% over 2000 cycles at 1 A g⁻¹.²⁸ Similarly, the highly-conductive graphene coating not only reduced the dissolution of the MnO₂ cathode but also improves the capacity.²⁹ Demonstrated by Shang *et al.*, V₂O₅ also can act as a coating material and enable higher Zn²⁺ transport and longer cycling life of the MnO₂ cathode for ZIBs.³⁰ However, most of the current heterogeneous bilayer structures are constructed *via*

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sequential deposition, for which the interfacial contact is imperfect. Unfortunately, one-pot synthesis of a bilayer structure for ZIB cathodes is still rarely reported.

In this work, through a quick one-pot eutectic oxidation process, vanadium oxide nanobelts with a bilayer structure ($LiV_3O_8@NaV_3O_8$ and LVO@NVO) have been successfully prepared. Benefiting from the synergism of the pre-intercalated Li^+ and Na⁺ cations, superior electrochemical performance was achieved in the LVO@NVO. When evaluated as a cathode for ZIBs, the LVO@NVO shows an amazing capacity of 476 mA h g⁻¹ at 0.05 A g⁻¹, excellent rate property (236 mA h g⁻¹ at 5 A g⁻¹), and outstanding cycling performance (a high capacity-retention of 93.4% for more than 2000 cycles). Based on the superior performance, the Zn-ion storage kinetics and mechanism are also systematically investigated.

Experimental

Materials preparation

All chemicals were used directly without purification. The dualphase vanadium oxide materials were prepared through a simple eutectic oxidation process. Typically, 5 g LiNO₃ and 5 g NaNO₃ were mixed and melted at 350 °C in air for about 10 min to obtain a homogeneous mixture. Afterwards, 0.4 g VCl₃ was added to the above-formed eutectics and maintained at 350 °C for 1 min. By cooling down naturally, the resultant powder was washed with DI water to remove residuary nitrate before drying at 60 °C for 12 h to obtain the target product (LVO@NVO). Vanadium oxides with different LVO and NVO ratios were obtained by controlling the feeding mass ratio of LiNO₃ and NaNO₃ (the samples obtained by using LiNO₃ and NaNO₃ with 1 : 3 and 3 : 1 were denoted as LVO@3NVO and 3LVO@NVO, respectively). Similarly, a pure Na⁺ intercalated vanadium oxide material was prepared by only using NaNO₃ (denoted as NVO).

Materials characterization

The morphology and microstructure of the resultant vanadium oxides were observed by using scanning electron microscopy (SEM, Helios G4 CX) and transmission electron microscopy (TEM, Talos F200X). The phase structure of the as-prepared samples was identified through X-ray diffraction (XRD, Bruker D8 ADVANCE). X-ray photoelectron spectroscopy (XPS, PHI VersaProbe III) was applied to study the chemical composition and electronic structure of the vanadium oxides. The specific surface area of the vanadium oxides was measured using the N₂ adsorption/desorption measurement (Micromeritics ASAP 2020). The water content in the samples was estimated through TGA (Mettler Toledo TGA/DSC 3+) under an Ar atmosphere. Fourier transform infrared spectroscopy (FTIR, TENSOR II) and Raman spectroscopy (Renishaw inVia RM200) were further employed to characterize the structural differences of the vanadium oxides.

Electrochemical evaluation

The as-prepared vanadium oxides (70 wt%) were mixed with super P (20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in

N-methylpyrrolidone (NMP). Ti foil was used to load the mixed slurry. Then the electrodes were dried under vacuum (90 °C, 12 h). Afterward, the circular-shape electrodes ($\psi = 12$ mm) were punched, and the loaded mass is about 1.0 mg cm⁻². Coin cells (CR2032) were applied to assemble the ZIBs. Zinc foil, 3.0 M ZnSO₄ aqueous solution, and a fiberglass diaphragm (GF/D) were employed as the anode, electrolyte, and separator, respectively. Cyclic voltammetry (CV) as well as electrochemical impedance spectroscopy (EIS) were performed by using an electrochemical workstation (IVIUM-n-STAT). A Neware battery testing system (BTS 7.5x) was used to evaluate the rate properties and cycling performance.

Results and discussion

The Li⁺, Na⁺ pre-intercalated vanadium oxide bilayer nanobelts were synthesized *via* a one-pot eutectic oxidation process. The V^{3+} in VCl₃ was oxidized to V^{5+} by NO₃⁻ in the nitrate eutectics to form vanadium oxide nanobelts, and the Li⁺/Na⁺ cations in the eutectics intercalated into the interlayer space of vanadium oxide at the same time. Fig. 1a shows the XRD spectrum of the obtained LVO@NVO material. The diffraction peaks at 13.7°, 30.8° , 42.1° , and 44.5° are assigned to the (100), (103), (-301) and (212) planes of LiV₃O₈ (LVO, JCPDS # 72-1193), whereas the diffraction peaks at 12.6°, 23.2°, 25.8°, 28.3°, 30.0°, 39.0°, 40.3°, 50.7° and 52.5° belong to the (001), (300), (002), (110), (011), (003), (311), (303) and (213) facets of NaV₃O₈ (NVO, JCPDS # 28-1171), respectively. The XRD result confirms the formation of a dual-phase product. It's noteworthy that the phase composition of LVO@NVO is transformed from NVO into LVO when regulating the mass ratio of NaNO₃ and LiNO₃ from 3:1 to 1:3(Fig. S1b[†]). However, the resultant phase is entirely different compared with that in LVO@NVO when using pure LiNO₃ (Fig. S1c[†]), implying a pivotal role of the NVO phase in the nucleation and growth of the bilayer nanobelts. The element ratio of Li: Na: V is found to be 0.685: 0.36: 3 through the inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) technique (Table S1, \dagger Na : V = 1.08 : 3 in NVO), suggesting more LVO than NVO in LVO@NVO. Fig. 1b shows the SEM image of the LVO@NVO material. The LVO@NVO material presents the morphology of nanobelts with a few micrometers in length and around 100 nm in width. With an increased ratio of LiNO₃ in the eutectics, the width of the nanobelts increases (Fig. S2[†]). As shown in Fig. 1c, more detailed structural information of LVO@NVO is revealed in the TEM image, in which the LVO@NVO demonstrates a distinct bilayer structure. The selected area electron diffraction (SAED, inset in Fig. 1c) pattern shows a dotted ring feature, indicating the polycrystalline feature of LVO@NVO. The HRTEM and corresponding inverse fast Fourier transformation (FFT) images are shown in Fig. 1d-f, in which an interplanar *d*-spacing of 0.35 nm in Fig. 1e can be attributed to the (022) crystal face of NVO, and 1.19 nm in Fig. 1f belongs to the (001) crystal facet of the LVO phase, respectively. This substantiates that the internal and outer layers in LVO@NVO are assigned to NVO and LVO, respectively. As shown in the energy-dispersive X-ray spectroscopy (EDX) mapping in Fig. 1g and the linear EDX scan results in Fig. 1h, V



Fig. 1 (a) XRD spectra of the LVO@NVO material. (b) SEM, (c) TEM (inset: SAED pattern, (114) and (254) for NVO and (–211) and (–222) for LVO), and (d) HRTEM images of the LVO@NVO nanobelts. (e and f) The inverse FFT image of the selected area in (d). (g) EDX elemental mapping and (h) linear EDX scan of LVO@NVO.

and O elements are homogeneously dispersed throughout the total nanobelt, while the Na element is only dispersed in the internal layer part. This further verifies the bilayer structure of the LVO@NVO nanobelts. Therefore, according to the SEM and TEM analysis, preferential nucleation and growth may occur from the NVO phase in the eutectics, on which an epitaxial growth of the LVO phase leads to the bilayer structure.

In order to identify the surface chemistry of the LVO@NVO material, XPS was applied. The signals of elemental V, O, Na, and Li are evident from the survey (Fig. S3†), which signifies the existence of all the above elements. Fig. 2a shows the high-resolution V 2p spectrum, in which the peaks could be decomposed into two pairs of peaks. The peaks with the binding energies of 524.9 and 517.3 eV are assigned to $V^{5+} 2p_{1/2}$ and $V^{5+} 2p_{3/2}$, and the peaks at 523.7 and 516.4 eV belong to V $2p_{1/2}$ and V $2p_{3/2}$ of V^{4+} , respectively.^{31,32} As shown in Fig. 2b, there are three peaks in the core-level O 1s spectrum. The peaks at 529.9, 530.9, and 533.2 eV are attributed to lattice oxygen (V–O), hydrated oxygen (O–H, from crystalline water), and surface adsorbed oxygen (H–O–H, from free water), respectively.²⁵ The

existence of free water and crystalline water in the LVO@NVO material has been further confirmed by TGA and is approximately 3.1 and 3.8 wt%, respectively (Fig. S4[†]). The highresolution Li 1 s and Na 1 s spectra further verify the existence of Li⁺ and Na⁺ between the [V₃O₈]⁻ layers (Fig. 2c and d).³³ The LVO@NVO was also characterized via FTIR and Raman spectroscopies. As shown in the FTIR spectrum in Fig. S5a,† the peak at 3349 cm⁻¹ corresponds to the O-H bond from free water, and the peaks at 2360 and 1636 cm⁻¹ are attributed to the O-H bond from crystalline water.^{34,35} Besides, the peaks at 500-1050 cm⁻¹ belong to various types of FTIR active vibration from the V₃O₈ backbones, where slight displacements are observed in the spectra between LVO@NVO and NVO.36,37 Fig. S5b† compares the Raman spectra of the LVO@NVO and NVO ranging from 100 to 1050 cm⁻¹, where different degrees of displacements are also observed.^{21,38,39} The difference between LVO@NVO and NVO in the FTIR and Raman spectra may be attributed to additional Li^+ inserted between the $[V_3O_8]^-$ layers in the LVO phase. In addition, the LVO@NVO shows a similar BET surface area to that of NVO (Fig. S6[†]), and the slightly



Fig. 2 Core-level XPS spectra of (a) V 2p, (b) O 1s, (c) Li 1s and (d) Na 1s of the LVO@NVO material.

higher value for NVO may be ascribed to the smaller size of the nanobelts than that of LVO@NVO.

The electrochemical performance of the resultant vanadium oxides was evaluated by assembling as coin-type cells. Fig. 3a shows the first five CV cycles of the LVO@NVO cathode at 0.1 mV s⁻¹. Two couples of redox peaks at 1.04/0.83 and 0.78/ 0.59 V are evident, which are ascribed to the oxidation/ reduction of vanadium and accompanying intercalation/ extraction of cations.40,41 The highly overlapped CV curves in the subsequent cycles indicate superior reversibility and stability of the electrochemical process for the LVO@NVO cathode. Fig. 3b shows the galvanostatic charge/discharge (GCD) curves of the LVO@NVO cathode at 0.05-5 A g⁻¹. The two voltage plateaus observed from the GCD profiles are consistent with the CV curves. It's worth noting that the GCD curves for LVO@NVO possess a highly similar shape when the current density increases from 0.05 (0.04) to 5 A g^{-1} (4.42 mA cm⁻²), which demonstrates a superior rate capability for LVO@NVO. As a comparison, the voltage plateaus of the NVO cathode become less obvious with increasing current densities (Fig. S7[†]), suggesting that the reaction of NVO is gradually suppressed at high current density. Also, excellent rate properties have been achieved for the LVO@NVO cell. As shown in Fig. 3c, the LVO@NVO cathode could exhibit average capacities of 473, 431, 400, 360, 330, 292, and 236 mA h g^{-1} under the current densities of 0.05 (0.04), 0.1 (0.09), 0.2 (0.18), 0.5 (0.44), 1

(0.88), 2 (1.77) and 5 A g^{-1} (4.42 mA cm⁻²), respectively. By returning the current density from 5 (4.42) to 0.2 A g^{-1} (0.18 mA cm^{-2}), a high average capacity of 395 mA h g⁻¹ is recovered, which is close to the initial level. The high rate capability achieved by LVO@NVO is competitive with the vanadium-based cathodes previously reported for ZIBs, *i.e.*, 96 mA h g^{-1} at 2 A g⁻¹ for Na_{0.33}V₂O₅,²¹ 138 mA h g⁻¹ at 5 A g⁻¹ for V⁴⁺-V₂O₅,³¹ 216 mA h g⁻¹ at 10 A g⁻¹ for PANI-V₂O₅,⁴² 193 mA h g⁻¹ at 5 A g⁻¹ for Mn_{0.15}V₂O₅ $\cdot n$ H₂O,²² 154 mA h g⁻¹ at 5 A g⁻¹ for $NaCa_{0.6}V_6O_{16} \cdot 3H_2O_7^{24}$ 217 mA h g⁻¹ at 5 A g⁻¹ for $CuV_2O_6^{,26}$ 102 mA h g⁻¹ at 5 A g⁻¹ for $NaV_6O_{15}^{,32}$ and about 215 mA h g⁻¹ at 5 A g^{-1} for $K_{1,1}V_3O_8$.⁴¹ On the contrary, the NVO cathode only shows a low capacity of 81 mA h g^{-1} at 5 A g^{-1} (4.42 mA cm⁻²), which is nearly three-quarters lower than that of LVO@NVO. Importantly, the rate capacity can be regulated by controlling the composition of eutectics and shows an optimal value with a $LiNO_3$: NaNO₃ ratio of 1:1 (LVO@NVO, Fig. S8[†]). The rate capability of the cathodes is related to the area-specific resistance (ASR) of the electrodes, which is mainly affected by the area and thickness of the electrodes.43,44 In this work, the same area and thickness have been applied for all of the electrodes, indicating that the difference of the rate capability mainly depends on the intrinsic difference of the cathode materials. The Ragone plot in Fig. 3d summarizes the specific power and specific energy of state-of-the-art vanadium-based cathodes for ZIBs.^{22-24,26,40,45} The LVO@NVO ZIB presents a high specific



Fig. 3 (a) CV curves of the LVO@NVO cathode (0.1 mV s⁻¹). (b) GCD profiles of the LVO@NVO cathode (0.05–5 A g⁻¹). (c) Rate capacity (0.05 to $5 \text{ A g}^{-1}/0.04$ to 4.42 A cm^{-1}). (d) The comparison of specific energy and specific power between LVO@NVO and other cathodes for ZIBs from the literature.^{22–24,26,40,45} (e) Cycling properties at 0.2 A g⁻¹ (0.18 A cm⁻¹) after the rate test of the NVO and LVO@NVO cathodes. (f) GCD curves of the LVO@NVO cathodes after the rate test (0.2 A g⁻¹). (g) Long term cycling performance of the LVO@NVO cathode (2 A g⁻¹/1.77 A cm⁻¹).

energy of 398 W h kg⁻¹ at a specific power of 80 W kg⁻¹ and even 186 W h kg⁻¹ at a high specific power of 8000 W kg⁻¹. The specific energy and specific power of our LVO@NVO ZIBs rank at the top tier among the present studies.

The cycling stability of the as-prepared cathodes was also assessed through GCD tests. Fig. 3e exhibits the cycle properties for LVO(a)NVO and NVO cathodes, which were tested at 0.2 Ag^{-1} $(0.18 \text{ mA cm}^{-2})$ after the rate measurement. The LVO@NVO cell could still achieve a high capacity-retention of 89% at a substantial capacity of 352 mA h g^{-1} after 100 cycles. The GCD curve over 100 cycles is similar to the initial cycle (Fig. 3f), indicating excellent cycling stability for LVO@NVO, while the NVO only shows a low capacity-retention of 77% (126 mA h g^{-1}) when operating for 100 cycles. Furthermore, the long-term cycle capability was investigated at 2 A g^{-1} (1.77 mA cm⁻²) as well. As shown in Fig. 3g, the LVO@NVO cathode could deliver a high capacity of 293 mA h g⁻¹ at the beginning (second cycle) and remain at 274 mA h g^{-1} over 2000 cycles (high capacity-retention of 93.5%). The diffraction peaks of LVO@NVO are still distinguishable after cycling, which further confirms the high stability of the LVO@NVO cathode with the long-term cycling test (Fig. S9[†]).

The superior electrochemical performance of the LVO@NVO cathode is closely related to the reaction kinetics. Therefore, it is necessary to better grasp the reaction kinetics. First, CV was applied with a scan rate of 0.1–1 mV s⁻¹ (Fig. 4a). The peak current and scan rate show a linear correlation with each other: $i = a\nu^b$, in which *a* and *b* are two constants. When *b* equals 0.5, it represents a diffusion-controlled behavior, and *b* equals 1 represents the capacitive controlled character.^{8,22,46} Fig. S10a[†] shows the result of $\log(i) \nu s$. $\log(\nu)$ for the LVO@NVO cathode.

The *b* values for peaks A1 and C1 are 0.851 and 0.801, respectively, which indicates a mixed electrochemical mechanism of both diffusion and capacitive characters for LVO@NVO. The capacitive contribution at 0.1–1 mV s⁻¹ for LVO@NVO is calculated as well, which shows a high ratio of up to 82.9% (Fig. S10b and c†). Comparatively, the *b* values of A1 and C1 for NVO (Fig. S11a and b,† 0.780 and 0.794, respectively) are smaller than those for LVO@NVO. Meanwhile, a lower capacitive contribution is observed for the NVO (Fig. S11c,† 56.6–77.5%). This result suggests an enhanced capacitive contribution in LVO@NVO. Moreover, the ion-diffusion coefficients during the anodic/cathodic process are calculated by virtue of the Randles-



Fig. 4 (a) CV curves $(0.1-1.0 \text{ mV s}^{-1})$, and (b) the linear fitting of the peak current vs. square root of the scan rate for the LVO@NVO cathode. (c) Nyquist plots (inset: equivalent circuit, R_s – ohmic resistance, CPE – constant phase element, R_{ct} – charge transfer resistance and Z_w – Warburg impedance). (d) GITT profiles and the ion-diffusion coefficient for the NVO and xLVO@yNVO cathodes.

Sevcik equation (Fig. 4b and S11d†).^{35,47} The ion-diffusion coefficients of the LVO@NVO cathode calculated based on A1 and C1 are 12.43 \times 10⁻¹³ and 5.23 \times 10⁻¹³ cm² s⁻¹, respectively, which are also much higher than those of NVO (3.92 \times 10⁻¹³ cm² s⁻¹ for A1 and 1.39 \times 10⁻¹³ cm² s⁻¹ for C1).

The diffusion kinetics was characterized by EIS and GITT techniques as well. Fig. 4c shows the results of EIS, in which the Nyquist plots include a compressed semicircle and an inclined line, representing charge-transfer resistance (R_{ct}) and Warburg diffusion, respectively.48-50 It is evident that the LVO@NVO exhibits much smaller charge-transfer resistance ($R_{\rm ct} = 336 \Omega$) than that of NVO (504 Ω). Moreover, the calculated diffusion coefficient of ions in the low-frequency region is 1.40×10^{-10} cm² s⁻¹ for LVO@NVO, which is about an order of magnitude higher than that of NVO (2.67×10^{-11} cm² s⁻¹, Fig. S12[†]). The GITT results are depicted in Fig. 4d (a single cycle of the GITT profile and the corresponding linear fitting of LVO@NVO and NVO are plotted in Fig. S13 and S14,† respectively). The overpotential of LVO@NVO (<100 mV) during the charge/discharge process is much smaller than that of NVO (~200 mV), indicating a smaller polarization and faster ion diffusion in LVO@NVO. The corresponding diffusion coefficients calculated for LVO@NVO throughout one cycle are in the 10^{-9} cm² s⁻¹ range, which is almost one order of magnitude higher than those of NVO. Therefore, the decreased charge-transfer

resistance and enhanced diffusion of ions endow LVO@NVO with high electrochemical reactivity and excellent rate capability. Particularly, the diffusion coefficients for LVO@3NVO and 3LVO@NVO are in between those of the NVO and LVO@NVO, which further confirms the critical role of the ratio of LVO and NVO in tuning the electrochemical performance of the title compound.

The excellent electrochemical capability of LVO@NVO could be mainly ascribed to the superiority of the bilayer structure. The LVO outer layer acts as a multifunctional coating layer, which not only provides higher structural stability but also regulates and stores the ion flux with a higher theoretical capacity.²⁷ NVO at the inner layer, on the other hand, functions as the nucleation site for the growth of LVO and facilitates ion diffusivity with a larger interlayer distance. In addition, the phase interfaces afford more sites for the reaction of electrons/ ions and act as channels for fast ion diffusion as well.^{51,52} Therefore, with an optimal LVO and NVO ratio, excellent electrochemical performance is achieved in the LVO@NVO cathode.

To further probe the energy storage mechanism of the LVO@NVO material, *ex situ* XRD technology was applied. Fig. 5a and b show the *ex situ* XRD patterns of LVO@NVO cathodes obtained at scheduled electrochemical reaction states (Fig. 5c). New peaks at 8.3° , 16.8° and 25.4° have emerged during the



Fig. 5 (a and b) *Ex situ* XRD patterns from the LVO@NVO cathodes. (c) The initial charge/discharge curves (0.1 A g^{-1}). (d–f) *Ex situ* SEM images collected at A-, D-, and F-states. (g) EDS elemental mapping of ZSH flakes. (h) V 2p and (i) Zn 2p of the LVO@NVO electrodes at different states.

discharging process (C-state), which are ascribed to zinc sulfate hydroxide hydrate (ZSH, Zn₄SO₄(OH)₆·4H₂O, JPCDS # 44-0673). The formation of the ZSH phase is attributed to the increased pH value of the electrolyte in the region close to the surface of the LVO@NVO cathode as a result of the intercalation of H⁺ into the interlayers of LVO(a)NVO.^{41,53,54} The intensity of peaks for the ZSH phase increases through deep discharging to 0.3 V (Dstate), suggesting the intercalation of more H⁺ and the formation of an additional ZSH phase. Fig. 5d and e show the morphologic changes of the LVO@NVO electrode surface during the discharging process. Compared to that at the initial state (Fig. 5d), a lot of micro-sized flakes grow on the surface of the LVO@NVO cathode at the D-state (Fig. 5e), which corresponds to the ZSH. In the following charging process, the diffraction pattern and the morphology of the electrode surface (Fig. 5f) return to those of the initial state, indicating a reversible co-intercalation/extraction of both H⁺ and Zn²⁺ ions with the deposition/dissolution of ZSH microsheets on the surface of cathodes. The EDX mapping of elemental Zn, O and S further confirms the formation of the ZSH phase at the D-state (Fig. 5g). In addition, the peak at 12.2° ((001) plane of the NVO phase) slightly moves to a higher angle during the discharging stage (Fig. 5b), which may be originated from the intercalated Zn^{2+} . The strong electrostatic attraction caused between the

intercalated Zn^{2+} and $[V_3O_8]^-$ layers makes a local structural distortion.^{23,41,55} The EDX spectrum and elemental mapping of the LVO@NVO material at the D-state also substantiate the intercalation of Zn^{2+} during discharging process (Fig. S15†).

The XPS test was further adopted to characterize the changes of surface chemistry on the LVO@NVO cathode during the electrochemical stage. As shown in Fig. S16a,† the appearance of elemental S at the D-state can be assigned to the ZSH phase, and the element Zn belongs to the ZSH phase and intercalated Zn²⁺. Fig. 5h shows the consequence of the V 2p spectra at the A-, D-, and F-states, which demonstrates the reduction/oxidation of V during the discharging/charging process.⁵⁶ In addition, as shown in Fig. 5i, the Zn 2p spectrum at the D-state could be decomposed into two pairs of peaks, belonging to the intercalated Zn²⁺ and adsorbed Zn²⁺, respectively.^{22,57,58} Only the peaks from the adsorbed Zn²⁺ appeared at the F-state, indicating the extraction of Zn²⁺ during the charging process. In order to further demonstrate the existence of adsorbed Zn²⁺, the fresh cathode was soaked in the electrolyte (3 M ZnSO₄ aqueous solution) for 12 h before being washed with DI water three times and dried in air (60 °C, 12 h). The resultant cathode shows the same peaks as those in the F-state (Fig. S16b[†]), which indicates that the Zn species at the F-state are only adsorbed Zn²⁺ on the surface of the cathode.

Conclusions

In summary, bilayer LVO@NVO nanobelts have been prepared successfully through a quick one-pot eutectic oxidation process. The pre-intercalation of Li⁺ and Na⁺ cations act as stabilizers for the vanadium oxide structure, introducing more ionic transfer channels; meanwhile, the bilayer structure affords higher pseudocapacitance as well as a robust structure. Eventually, a smaller charge-transition resistance, faster ion-diffusion rate, and higher cycling stability are achieved in the LVO@NVO cathode. The LVO@NVO cathode demonstrates an outstanding rate property of 236 mA h g^{-1} (a) 5 A g^{-1} and superior long-term cycling performance over 2000 cycles at 2 A g^{-1} for ZIBs. Moreover, a mechanism of Zn²⁺ and H⁺ co-intercalation/ extraction has been testified for the LVO@NVO. It is believed that the present work would present a fire-new strategy to design and prepare advanced vanadium-based cathode materials for superior ZIBs.

Author contributions

Jinjin Wang: investigation, formal analysis, visualization, and writing – original draft preparation; Xiangyuan Zhao: investigation; Jinzhao Kang: investigation; Xiaomei Wang: investigation; Hong Yu: conceptualization, supervision, and writing – review and editing; Cheng-Feng Du: conceptualization, supervision, and writing – review and editing; Qingyu Yan: supervision.

Conflicts of interest

There are no conflicts to declare.

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