Interfacial adsorption–insertion mechanism induced by phase boundary toward better aqueous Zn-ion battery

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Abstract
Biphasic and multiphasic compounds have been well clarified to achieve extraordinary electrochemical properties as advanced energy storage materials. Yet the role of phase boundaries in improving the performance is remained to be illustrated. Herein, we reported the biphasic vanadate, that is, Na1.2V3O8/K2V6O16·1.5H2O (designated as Na0.5K0.5VO), and detected the novel interfacial adsorption–insertion mechanism induced by phase boundaries. First-principles calculations indicated that large amount of Zn2+ and H+ ions would be absorbed by the phase boundaries and most of them would insert into the host structure, which not only promote the specific capacity, but also effectively reduce diffusion energy barrier toward faster reaction kinetics. Driven by this advanced interfacial adsorption–insertion mechanism, the aqueous Zn/Na0.5K0.5VO is able to perform excellent rate capability as well as long-term cycling performance. A stable capacity of 267 mA h g⁻¹ after 800 cycles at 5 A g⁻¹ can be achieved. The discovery of this mechanism is beneficial to understand the performance enhancement mechanism of biphasic and multiphasic compounds as well as pave pathway for the strategic design of high-performance energy storage materials.

KEYWORDS
aqueous zinc-ion battery, cathode, energy storage mechanism, phase boundary, vanadium-based materials
1 | INTRODUCTION

Aqueous zinc-ion batteries (ZIBs) are considered as promising energy storage system because of the low-cost, environmental benign, resource abundance, high capacity (theoretically 820 mAh g⁻¹), and low redox potential (−0.76 V vs. SHE) of metallic zinc anode as well as the high ionic conductivity of aqueous electrolyte.¹⁻¹⁰ Despite the various cathode may apply, such as manganese-based,¹¹⁻¹⁸ vanadium-based,¹⁹⁻²⁵ cobalt-based,²⁶ and organized materials,²⁷⁻³² most of the reported aqueous ZIBs system are based on the conventional Zn²⁺ intercalation and the performance of the systems is therefore largely limited by the inferior reaction kinetics. The electrochemical reaction kinetics in ZIBs on the cathode side can be generally described as follows:³³ cation first releases from liquid electrolyte to the electrolyte/cathode interface, then passes through the electrolyte/cathode interface and inserts into host structure, and eventually the ions complete solid-state diffusion process within the host framework. The first step is dominated by the electrolyte properties,³⁴ while the last two steps significantly rely on the material properties. Henceforth, extensive efforts have been devoted to exploiting new material structures can either facilitate the ions transport through the electrolyte/cathode interface or ensure high-speed ions diffusion within the host structure.

Recent studies have shown that biphasic materials are conducive to achieve enhanced performance due to the existence of more active sites and synergic effect,³⁵⁻³⁸ therefore introducing the phase boundaries is proposed to improve the electrolyte/cathode interface. Our previous research has shown that biphasic materials present excellent performance for sodium storage³⁹,⁴⁰ however, the intrinsic mechanism of enhanced electrochemical behavior remains unclear. Construction of biphasic cathode materials in aqueous ZIBs is expected to be a feasible way to promote electrochemical performance. An in-depth study into this issue is favored to not only accelerate the understanding and application of biphasic compounds, but also serves as a constructive reference for further strategically design and exploitation of other high-performance biphasic products.

In this work, we introduce a biphasic Na₀.⁵K₀.⁵VO material with abundant phase boundaries composed of potassium vanadium oxide hydrate (KₓVₓO₁₆·1.₅H₂O, KVO) and sodium tri-vanadium octa-oxide (Na₁₂V₆O₃₆, NaVO) as high-performance cathode for aqueous ZIBs. Monophasic and biphasic products were synthesized by sol–gel method. Li/Na/KVO precursors were fabricated by adding various contents of Li₂CO₃/Na₂CO₃/KHCO₃ and then followed by calcination at 450°C for 4 h to obtain the final products. Experimental results manifest that Na₀.⁵K₀.⁵VO have much superior electrochemical performance than the monophasic counterparts. Theoretical calculations indicate that phase boundaries can absorb numerous Zn²⁺ and H⁺ ions during electrochemical reaction and thus facilitate the subsequent intercalation process. This novel interfacial adsorption–insertion mechanism can, on the one hand, enable faster reaction kinetics than bulk intercalation process, on the other hand, give rise to additional diffusion/capacitive-controlled capacity toward enhanced capacity. Different alkaline vanadates of Li/NaVO and Li/KVO products are prepared as well to further elucidate our proposed mechanism and the synthesis procedure can be seen in Figure S1 (SI). Na/KVO products were chosen as the major research object in this study due to the best electrochemical properties they exhibit compared with Li/NaVO and Li/KVO products. Experimental measurements confirm that the formation of biphasic materials is a reliable strategy to enhance electrochemical properties.

2 | RESULTS AND DISCUSSION

The X-ray power diffraction (XRD) technology is applied to determine the phase of the as-prepared hybrid alkali vanadates, as seen in Figure 1(A) and Figure S2 (SI), respectively. These XRD results indicate that biphasic Na₀.⁵K₀.⁵VO are composed of monophasic NaVO and KVO, which is similar to Li₀.⁵Na₀.⁵VO and Li₀.⁵K₀.⁵VO. Transmission electron microscope (TEM) is applied to identify the morphology and size of monophasic NaVO, KVO, and Na₀.⁵K₀.⁵VO products (Figure S3, SI). All three products manifest similar nanorod structure with length of several micrometers and width of several hundreds of nanometers. The schematic illustration of Na₀.⁵K₀.⁵VO structure with phase boundaries can be seen in Figure 1 (B). High-angle annular dark-field scanning TEM and EDS elemental mapping results (Figure 1(C)) reveal that Na₀.⁵K₀.⁵VO displays nanorod structure with evenly existence of Na, K, V, and O, indicating the homogeneous distribution of NaVO and KVO, as demonstrated by the two-phase lattice fringes in Figure 1(D). Furthermore, the selected area electron diffraction pattern in Figure 1 (E) confirms the coexistence of NaVO and KVO in as-prepared Na₀.⁵K₀.⁵VO product. Near edge X-ray absorption fine structure spectra is an effective tool to identify the electronic structure and chemical bonding of materials. The position and shape of V L₃ peaks depend sensitively on both the vanadium valence and the local coordination environment, which is always associated with the crystallinity. Note that the fine shoulders (517.2 eV) in V L-edge are always weak or absent in disordered vanadium-based product. The diminished
Intensity of $t_{2g}$ peaks at O K-edge is attributed to structural distortion. From Figure 1(F), it can be observed that the monophasic NaVO and KVO display more pronounced shoulder and stronger intensity of $t_{2g}$ peaks than Na$_{0.5}$K$_{0.5}$VO, indicating greater structure distortion in Na$_{0.5}$K$_{0.5}$VO due to two phase domains. X-ray photoelectron spectroscopy data (Figure 1(G)) further confirm the signals of Na and K in biphasic Na$_{0.5}$K$_{0.5}$VO, corresponding to XRD patterns and EDS mapping results.

To better characterize the shape and morphology of Li/Na/KVO products, low-magnification SEM images were collected in Figure S4 (SI), where all these products display nanorod shapes.

The electrochemical Zn storage behaviors of Na/KVO materials were measured to compare the performance of monophasic and biphasic systems. It is obvious that the
biphasic Na0.5K0.5VO displays synergistic redox characteristics of monophasic NaVO (0.74/0.87 and 1.01 V) and KVO (0.62, 0.84/0.75, and 0.93/0.96 V) materials as seen from the cyclic voltammetry (CV) profiles in Figure 2(A), and enhanced electrochemical properties are obtained in as-synthesized biphasic Na0.5K0.5VO compared to monophasic NaVO and KVO. Particularly, Na0.5K0.5VO can deliver a remarkable capacity of 393 mA h g⁻¹ at 0.1 A g⁻¹, higher than the total amount of NaVO and KVO, as seen in Figure S5 (SI). The enhancement can be induced by the additional capacitive Zn²⁺ and H⁺ absorption of phase boundaries in biphasic system Na0.5K0.5VO also manifests both superior cycling performance and much better rate capability than the monophasic counterparts, as seen in Figure 2(B–D). The slight increase of capacity in the initial cycles of Na/KVO materials is attributed to the activation process.41–43 Similar phenomenon can be observed in Li/NaVO and Li/KVO products as well (Figure S6, SI). The LED lamp has been successfully lightened up with aqueous Zn/Na0.5K0.5VO coin-cells (Figure S7, SI). In addition, electrochemical measurements reveal that the Na/KVO material with the ratio of Na:K = 5:5 presents the most excellent electrochemical behavior (Figure S8, SI), which could be attributed to the most abundant stoichiometric phase boundaries in Na0.5K0.5VO. Electrochemical measurement of Li/NaVO with different Li:Na ratios were carried out to investigate the relationship to correlate the metal ions ratio and performance, as seen in Figure S9 (SI). Li/NaVO with the ratio of Li:Na = 5:5 demonstrates the best electrochemical performance. Table S1 (SI) summarized and compared the electrochemical behaviors of ions insertion/extraction mechanism-based NaVO and KVO materials in aqueous from references. It is obvious that the as-synthesized Na0.5K0.5VO with interfacial adsorption-insertion mechanism exhibits much better performance than the reported NaVO and KVO materials.

In order to explore the electrochemical kinetics, the pseudocapacitive behavior has been tested via the analysis of CV curves at various scan rates within 0.1–1.2 mV s⁻¹, as seen in Figure 3(A,B) and Figure S10 (SI). Note that the close-to-0.5 b value indicates that the capacity is mainly contributed by the diffusion process, while the close-to-1 b value signifies that the capacitive effect dominates the discharge–charge process. The fitting results indicate that the b value of NaVO and KVO is closer to 0.5, while in the biphasic Na0.5K0.5VO, the b value manifests significant increase and become closer to 1.0. The b values of NaVO and KVO indicate typical battery behavior whose kinetics is dominated by diffusion process, while capacitance behavior of biphasic Na0.5K0.5VO suggests ion absorption reaction which is mainly surface capacitive-controlled.44 In addition, Na0.5K0.5VO indicates higher capacitive contribution ratio than the monophasic NaVO and KVO (Figure 3(B) and Figure S10(C), SI). These results can be attributed to interfacial absorption of Zn²⁺ and H⁺ in phase boundaries of Na0.5K0.5VO. The contribution ratio of capacitive

![Figure 2](image-url)

**Figure 2** (A) Cyclic voltammetry (CV) curves; (B) cycling performance at the current density of 0.5 A g⁻¹ (insert: discharge–charge curves); (C) the rate performance at applied current density of 0.1, 0.3, 0.5, 1, 2, and 5 A g⁻¹; and (D) long-term cycling performance at 5 A g⁻¹ of as-prepared NaVO, KVO, and Na0.5K0.5VO materials, respectively.
The effect of Na$_{0.5}$K$_{0.5}$VO displays increasing trend with the scan rates from 0.1 to 1.2 mV s$^{-1}$, and it could reach 88% at the scan rate of 1.2 mV s$^{-1}$, demonstrating fast electrochemical reaction kinetics. The Galvanostatic Intermittent Titration Technique has been executed to characterize the Zn$^{2+}$ ion diffusion and conductivity properties upon charge–discharge process, as can be observed in Figure 3(E) and Figure S11 (details in the supporting information, SI). It is obvious to see that Na$_{0.5}$K$_{0.5}$VO display higher diffusion coefficient as well as reduced fluctuation, superior to NaVO and KVO, which is attributed to the existence of numerous phase boundaries in Na$_{0.5}$K$_{0.5}$VO. These phase boundaries could absorb plenty of Zn$^{2+}$ and H$^{+}$ ions for subsequent insertion process. The excess Zn$^{2+}$ and H$^{+}$ ions can also provide more diffusion channels and reduced ion diffusion path than monophasic host structure, thus obtaining faster kinetics and accelerating ions diffusion process. Electrochemical impedance spectra data have been measured to further study the reaction kinetics. As seen from Table S2 and Figure S12(A) (SI), Na$_{0.5}$K$_{0.5}$VO presents remarkable transfer resistance of 87.73 Ω, which is much lower than that of NaVO (160.4 Ω) and KVO (129.2 Ω), indicative of enhanced electronic transportation property of biphasic material. In addition, the $R_d$ of Na$_{0.5}$K$_{0.5}$VO gradually decreases after cycles (Table S3 and Figure S12 (B), SI), which indicates increased kinetics upon cycling. Nyquist plots of NaVO, KVO, and Na$_{0.5}$K$_{0.5}$VO materials at different temperatures at fully charged state can be seen in Figure 3(C). Figure 3(D) presents the activation energy comparison curve of NaVO, KVO, and Na$_{0.5}$K$_{0.5}$VO at fully charged state. Impressively, the interface activation energy of Na$_{0.5}$K$_{0.5}$VO is significantly lower than that of NaVO and KVO, indicating that the existence of phase boundaries in Na$_{0.5}$K$_{0.5}$VO is beneficial to facilitate the electrochemical reaction.

In addition, first-principles calculations based on the density functional theory with local density approximation were performed for better understanding of the reaction mechanism, as demonstrated in Figure 4 (computational details can be in the supporting information, SI). The calculation models of Na/KVO products are presented in Figure S13 (SI). To provide more insights into the diffusion properties of Zn$^{2+}$ on the Na$_{0.5}$K$_{0.5}$VO interface, nudged elastic band method was adopted to identify the diffusion barrier. The values of Zn-diffusion energy barriers are relative to the most stable binding site. A possible pathway with high structural symmetry from one low-energy adsorption hollow site to the nearest neighboring hollow site was considered, and Figure 4(A) illustrates a side view of the migration pathway. The simulated results indicate that the energy barrier of Zn$^{2+}$ ion on the Na$_{0.5}$K$_{0.5}$VO interface is 0.47 eV (Figure 4(B)), which is much lower than that of NaVO (0.82 eV) and
KVO (1.52 eV) materials, as seen in Figure S14 (SI). Figure 4(C) shows the total density of states and partial density of states of the interface model and the corresponding blocks. DOS calculations for bulk phases suggest an open bandgap for KVO while it closes when forming the interface structure, indicating a metallic nature of the biphasic system. The metallic character mainly originates from the strong hybridizations between the $d$-orbitals of V atoms from both NaVO and KVO blocks and $p$-orbitals of O atoms from NaVO block in Na$_{0.5}$K$_{0.5}$VO. By calculating the adsorption energies of H$^+$ and Zn$^{2+}$ in NaVO and KVO, we found that only Zn$^{2+}$ embedded into KVO is energetically favorable to form with calculated energy about $-0.23$ eV, while H$^+$ is unlikely to be absorbed by NaVO and KVO. As comparison, the adsorption energies for H$^+$ and Zn$^{2+}$ embedded
into the Na$_{0.5}$K$_{0.5}$VO model are calculated to be $-0.33$ and $-1.01$ eV, respectively, much lower than that of the bulk models. A more negative adsorption energy suggests stronger tendency of thermodynamic favorable adsorption process. This result clarified the significant benefits of phase boundaries in H$^+$ and Zn$^{2+}$ ions adsorption, which can help illustrate the superior performance of Na$_{0.5}$K$_{0.5}$VO. Charge distributions around the interface area (Figure 4(D)) suggest that H$^+$ and Zn$^{2+}$ shall interact with the interfacial O atoms and therefore reduce the energy barriers for adsorption. In addition, the ex situ results in Figure S15 indicate accumulation of much greater amount of zinc hydroxide sulfate in discharged-state Na$_{0.5}$K$_{0.5}$VO compared to the single-phase counterpart, indicating that the phase boundary is conducive to proton participation in electrochemical process$^{19,48-50}$.

As well illustrated above, the interfacial adsorption–insertion mechanism is proposed for Zn/Na$_{0.5}$K$_{0.5}$VO cell. To make it clear, a schematic comparison of reaction mechanism of monophasic NaVO, KVO, and biphasic Na$_{0.5}$K$_{0.5}$VO can be seen in Figures 4(E) and S16 (SI), respectively. The main bottleneck of monophasic products lies in the inferior reaction kinetics, which is greatly dominated by ions migration through the electrolyte/cathode interface and the slow solid-state diffusion process in the host framework. Biphasic Na$_{0.5}$K$_{0.5}$VO manifests much superior performance through combined enhancing behavior of both processes. First, the phase boundaries in Na$_{0.5}$K$_{0.5}$VO could absorb numerous Zn$^{2+}$ and H$^+$, thus giving rise to the specific capacity and contributing to the subsequent movement of cation which pass through the electrolyte/cathode interface and insert into host framework. Second, with the existence of sufficient phase boundaries, biphasic Na$_{0.5}$K$_{0.5}$VO could provide more diffusion channels and shorter diffusion path than monophasic counterparts, which facilitates the solid-state diffusion and leading to brilliant kinetics. Third, Na$_{0.5}$K$_{0.5}$VO has advanced properties of lower diffusion energy barrier and smaller activation energy, which ensures faster and more effective ions migration during electrochemical reaction, thus prompting overall battery performance. Consequently, the as-prepared Na$_{0.5}$K$_{0.5}$VO performs higher capacity and faster reaction kinetics, thus exhibiting superior electrochemical behavior, such as enhanced ion diffusion coefficient, higher pseudocapacitive contribution and better cycling performance.

3 | CONCLUSIONS

In conclusion, we have detected a novel adsorption–insertion mechanism based on aqueous Zn/Na$_{0.5}$K$_{0.5}$VO battery system. As comparison to the inferior kinetic in monophasic counterparts, the existence of numerous phase boundaries in biphasic material possesses the capability of absorbing H$^+$ and Zn$^{2+}$ ions and facilitating the subsequent ions insertion process. The combined enhancement of the processes brings about enhanced capacity as well as faster reaction kinetics, thus leading to brilliant capacity and remarkable long-term cycling stability. The discovery of this novel interfacial adsorption–insertion mechanism in the case of biphasic materials is beneficial to the understanding and application of biphasic materials with excellent performance, thus putting forward the strategical design of high-performance materials in battery system.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**SUPPORTING INFORMATION**

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