Reversible $\text{V}^{3+}/\text{V}^{5+}$ double redox in lithium vanadium oxide cathode for zinc storage

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1. Introduction

Renewable energy resources have gained the global spotlight owing to continuous environmental pollution and energy consumption, which greatly stimulates the development of scalable energy storage systems [1]. Among various storage options, lithium-ion batteries (LIBs) dominate the markets for decades because of their high energy densities [2]. However, the large-scale applications of LIBs are limited by the continuously increasing cost and potential safety hazard [3]. As an alternative, batteries based on low-cost and abundant Mg, Al, and Zn anodes have received increasing attention [4]. Especially, compared with magnesium ion batteries (MIBs) or aluminum ion batteries (AlIBs), zinc ion batteries (ZIBs) show unique advantage due to their applicability to the aqueous electrolytes, which show higher ionic conductivities, better safety, and lower cost [5]. Whereas, the aqueous zinc systems suffer enduring challenges of cathode materials, such as limited capacity, low working voltage, and poor cycle life, which are caused by the cathode dissolution, and the side reactions of $\text{H}_2/\text{O}_2$ evolution [6].

In recent years, a series of materials with various structures were investigated as the cathodes for ZIBs, including manganese oxides [7], chalcogenides [8–10], Prussian blue analogous [11], Na superionic conductor (NASICONs) [12–14], and ZnMn$_2$O$_4$ spinels [15,16]. However, the capacities (<300 mA h g$^{-1}$) and/or the cycling life (<1000 cycles) were not satisfactory. Recently, substantial optimization strategies have been used to address the issues above. The structure water showed a lubricating effect during $\text{Zn}^{2+}$ insertion in bilayer $\text{V}_2\text{O}_5\cdot\text{nH}_2\text{O}$ cathode, which was demonstrated by Mai and Wang et al. [17,18]. By controlling the phase, various structures of manganese oxides ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$-type MnO$_2$) were investigated as hosts for ZIBs in the nearly neutral electrolyte, which showed improved cycling stability compared with traditional alkaline zinc-manganese battery [19–27]. In addition, the cycling life was further improved by using Mn$^{2+}$-addictive electrolyte, which could balance the Mn$^{3+}$ and/or the cycling life (1000 cycles) [28–29]. Furthermore, by stabilizing/enlarging the diffusion channel, the Na$_{0.33}\text{V}_2\text{O}_5$ nanowires, bilayer $\text{Zn}_0.25\text{V}_2\text{O}_5\cdot\text{nH}_2\text{O}$, and Ca$_{0.25}\text{V}_2\text{O}_5\cdot\text{nH}_2\text{O}$ were designed, which showed excellent cycling stability (>1000 cycles) [30–32]. This consideration, designing suitable vanadium-rich cathodes with faster insertion kinetics for Zn$^{2+}$ is promising for constructing high capacity and long-life ZIBs.
The layered LiV₃O₈ shows feasibility for hosting excess guest ions [33]. Firstly, the high oxidation state (V⁵⁺) of vanadium holds the capability for a bi-electronic transfer reaction (V⁵⁺/V⁴⁺/V³⁺), yielding an extremely high theoretical capacity of ~560 mA h g⁻¹ based on the reaction of V⁵⁺ converting to V³⁺. Secondly, there are plenty of vacant sites in the layered structure of LiV₃O₈, which provide sufficient intercalation sites for the guest ions. The literature-reported results show the theoretical capacity of LiV₃O₈ for LIBs is ~280 mA h g⁻¹ according to three Li ions intercalation per formula unit [34]. Compared with Li⁺/Na⁺ intercalation, the divalent Zn²⁺ intercalation provides the possibility to double the electron transitions under the same intercalation quantities, thereby doubling capacities. In addition, the approximate ionic radii of Zn²⁺ (0.74 Å) and Li⁺ (0.76 Å) show the potential for three Zn ions intercalation per formula unit, which further support our hypothesis. The Zn²⁺ storage in LiV₃O₈ particles was reported in previous work by Kim et al. [35]. However, they only investigated the insertion of 1.5 mol Zn²⁺ into LiV₃O₈ with reversible V⁴⁺/V³⁺ redox in the voltage of 0.6–1.2 V, delivering the discharge capacity of 256 mA h g⁻¹, which is far below the assuming theoretical capacity as discussed above (~560 mA h g⁻¹). So, it’s urgent to realize the fully zinc insertion in the LiV₃O₈ (3 mol Zn²⁺ insertion) to achieve higher energy density. More importantly, the storage mechanism and reaction kinetics are expected to be more complex under this situation. As a result, the fully understanding of the storage mechanism, structural evolution of the electrode material, and the changes of reaction kinetics based on this bi-electronic transfer reaction mechanism is interesting and necessary.

Herein, we demonstrated a new stepwise insertion of Zn²⁺ in LiV₃O₈ cathode with reversible V³⁺/V⁵⁺ double redox mechanisms. Six-electron transition in LiV₃O₈ was achieved with only 7.64% volumetric expansion, yielding the highest capacity of 557.5 mA h g⁻¹, and good cycling retention of 85% over 4000 cycles. The use of the V³⁺/V⁵⁺ double redox will open-up new opportunities for designing vanadium-rich cathodes for high-performance Zn ion battery.

2. Results and discussion
2.1. Characterization of LiV₃O₈ nanorods

A facile and scalable liquid stirring followed by solid annealing method was adopted to prepare LiV₃O₈ nanorods (Supplementary Information). The precursor shows a non-crystalline structure as detected by X-ray diffraction (XRD) (Fig. 1a). After annealed at 450 °C for 2 h, the crystalline LiV₃O₈ is formed with characteristic diffraction peaks, which are consistent with monoclinic LiV₃O₈ with P2₁/m space group (JCPDS: 01-072-1193, a = 6.68 Å, b = 3.60 Å, c = 12.03 Å). The LiV₃O₈ is composed of VO₆ octahedrons and edge-sharing VO₅ tetragonal, forming V₉O₂₃ layers structure with lithium ions pillar (inset in Fig. 1b). The Raman spectrum shows nine characteristic peaks in the range of 60–1100 cm⁻¹ (Fig. 1b), which qualitatively reflect the vibrations of V–O bonds along coordinate axes based on the atomic displacements in LiV₃O₈ unit cell [36]. Typically, the low-wavenumber peaks (99, 142, and 195 cm⁻¹) usually derive from the relative motions of the chain translation, which are associated with the layered structure. The peaks, in the medium/high wavenumber region (285, 409, 528, and 696 cm⁻¹), reflect the stretching/bending of V–O, V–O–V, and O–V–O bonds in the internal modes. Specifically, the peak at 995 cm⁻¹ is assigned to the shortest V⁵⁺=O bonds oriented along the c-axis [37]. The field emission scanning electron microscopic (FESEM) image of the precursor shows a uniform wrinkle sheet structure (Fig. 1c). After the thermal treatment, a block with abundant cross-linking is obtained, which consists of nanorods with several micrometers in length, 200–500 nm in width (Fig. 1d). Transmission electron microscopic (TEM) image displays solid nanorods structure with smooth surfaces (Fig. 1e). The high-resolution TEM (HRTEM) image (Fig. 1f, Fig. 5a) shows a spacing of 6.36 Å, corresponding to the d-spacing of the (100) planes of LiV₃O₈ nanorods. The selected area electron diffraction (SAED) pattern demonstrates the single crystalline nature of the LiV₃O₈ nanorods (Fig. S1b).
2.2. Electrochemistry performances of Zn//LiV₃O₈ cells

The electrochemical performances of LiV₃O₈ are investigated by assembling coin cell with Zn foil anode and 3 M Zn(CF₃SO₃)₂ electrolyte. The open-circuit voltages of these systems are in the range of 0.95–1.25 V, and gradually stabilize at about 1.30 V after resting for 3 h. Also, the systems show excellent stability with negligible self-discharge after 432 h (Fig. S2). The initial four cyclic voltammetry (CV) profiles (Fig. 2a) show four pairs of reduction/oxidation peaks, located at 0.46/0.65, 0.59/0.77, 0.76/1.05, and 1.15/1.31 V, respectively, indicating a multistep reaction mechanism. The Zn//LiV₃O₈ battery shows an extremely high capacity of ~450 mA h g⁻¹ at the current density of 0.1 A g⁻¹ in the initial several cycles and stabilizes at 350.2 mA h g⁻¹ after 60 cycles (Fig. S3). Notably, the capacity of LiV₃O₈ nanorods is much higher than the previous result [35], which is attributed to various optimizations: (1) the extended operating voltage range ensures the fully reaction of the cathode; (2) the optimized electrolyte exhibits faster kinetics and better reversibility of Zn deposition/dissolution [16]; (3) the one-dimension nanorods exhibit better adhesion onto a current collector, unique structural stability for ion storage [2]. The galvanostatic charge/discharge profiles at 1.0 A g⁻¹ are shown in Fig. 2b. An initial discharge capacity of 298 mA h g⁻¹ is achieved with the Coulombic efficiency of ~89.2%. In the subsequent 20th - 100th cycles, the battery delivers a capacity of ~345 mA h g⁻¹, with an average operating voltage of ~0.72 V. In addition, the voltage profiles are nearly overlapped, suggesting slight structural changes, which indicates a reversible process. Impressively, an extremely high capacity of 337.1 mA h g⁻¹ is maintained after 100 cycles, with a capacity retention of 94.3% (against the highest capacity of 357.3 mA h g⁻¹) (Fig. 2c). The LiV₃O₈ cathodes also show outstanding rate capability (Fig. 2d). They exhibit a very high capacity of 464.2 mA h g⁻¹ at 0.05 A g⁻¹. Even after the current density increasing to a hundred times (5.0 A g⁻¹), a capacity of 182 mA h g⁻¹ is still achieved. Meanwhile, after cycled at various current rates, the capacity can recover to 394.5 mA h g⁻¹ (85% capacity retention) as the current density abruptly recovers from 5.0 to 0.1 A g⁻¹, indicating high reversibility of the redox reactions and excellent crystal structure stability. Furthermore, the sloping discharge profiles at 0.05 A g⁻¹ can be divided into four stages, thus 1.6–0.87, 0.87–0.70, 0.70–0.55, and 0.55–0.2 V, respectively, indicating a complex reaction mechanism (Fig. 2e). Interestingly, the plateaus below 0.65 V in discharge curves can hardly be distinguished at high rates, which will be discussed in the part of storage mechanism in detail. When cycled at a high rate of 5.0 A g⁻¹, an average capacity of ~200 mA h g⁻¹ is achieved over 4000 cycles, with capacity retention of 85% (Fig. 2f). It’s worth noting that the increased specific capacity of LiV₃O₈ cathode in the initial 400 cycles is attributed to the gradually activating process and electrolyte penetrating in the active material, which is commonly observed in vanadium-based electrode materials [38]. In summary, the LiV₃O₈ cathodes exhibit both impressive high energy density (~400 W h kg⁻¹) and outstanding power density (~4200 W kg⁻¹), which demonstrates a superior electrochemical performance among the previous reported...
works (Fig. 2g) [9,11,14,21,32,39,40].

2.3. Energy storage mechanism and structural evolution

The Zn$^{2+}$ insertion mechanism in LiV$_3$O$_8$ was investigated by ex situ XRD during the third cycle at 0.1 A g$^{-1}$ (Fig. 3a). The diffraction peak at 18.1° is attributed to the poly(tetrafluoroethylene) (PTFE) binder, which does not change upon cycling. The reversible shifts, appearance, and disappearance of the diffraction peaks are attributed to the active material phases transformation during discharge/charge process. The characteristic diffraction peaks at 13.92°, 23.28°, and 28.36° reflect to the (100), (003), and (−111) lattice planes, respectively. According to the discharge curve and ex situ XRD patterns, the Zn insertion process can be divided into four regions, as marked by the red (Step I), blue (Step II), green (Step III), and purple (Step IV) colored boxes (Fig. 3a). In the first discharge region (1.60–0.87 V), the diffraction peak of (100) plane reveals a slightly shift to the higher angle with the intercalation of ~0.5 Zn$^{2+}$ per formula (Fig. 3c), and the corresponding discharge potential curve shows a gradual slope, which reveals that a solid-solution behavior predominates in this single-phase domain (Zn$_x$LiV$_3$O$_8$, 0 < $x$ < 0.5) [35]. In the subsequent discharge process (0.87–0.55 V), the (100) diffraction peak shifts from 13.92° to 14.41°, indicating the reduction of the respective (100) distance, which is closely related to strong electrostatic interaction between the (V$_3$O$_8$)-layers framework and the intercalated Zn$^{2+}$. A splitting diffraction peak of the (100) is accompanied with the shift, and the corresponding discharge potential curve shows two
Fig. 4. X-ray photoelectron spectroscopic analysis of the electrodes. (a) Zn 2p region of the XPS spectra, Zn 2p component (2p3/2: 1022.1 eV). (b–d) V 2p region of the XPS spectra, (I) initial state, II (discharge to 0.2 V), III (recharge to 1.6 V).

consecutive discharge platforms, indicating that a successive two-phase transformation process may occur in this region (Zn0.5LiV3O8, 0.5 < x < 2). In the last discharge process (Region IV, from 0.55 to 0.20 V), there are two diffractions at 14.66° (denoted as (100)*) and 28.61° (denoted as (−111)*) splitting from their original positions and gradually increase in intensity, indicating a phase transition between the initial α-LiZn0.5V3O8 (x < 2) and the newly formed phase of β-LiZn0.5V3O8 (2 ≤ y ≤ 3). Interestingly, this phase transition would not generate at high discharge current densities (≥ 0.5 A g−1) with the intercalation of Zn2+ content below 2.0 Zn2+ per formula. The reverse evolutions show some differences in the following charge process. In the initial charge region (step V), the diffraction of (100) lattice plane shifts to lower position along with the disappearance of the diffraction of (100)* lattice plane, indicating a solid-solution behavior accompanying the β-LiZn0.5V3O8 phase transform to α-LiZn0.5V3O8 caused by the de-intercalation of Zn2+. In the following process, two solid-solution regimes (step VI and step VIII) separated by a two-phase process (step VII) are observed, and the diffraction of (100) lattice plane return to the origin position, indicating a highly reversible process of Zn storage in LiV3O8 host. These unique discharge/charge reaction mechanisms are related to the Zn2+-content during the intercalation/de-intercalation process.

To get further insights into the Zn storage mechanism, density functional theory (DFT) simulations are performed to investigate the structural evolutions of LiV3O8 during the Zn2+-intercalation process. The initial lattice parameters calculated by DFT shows a similar result to the data obtained from XRD, and corresponding detail information is listed in Table S1. The structure/phase evolutions and Zn2+-insertion sites in LiV3O8 with different energies are predicted by DFT simulations based on the lowest energy solution (Figs. S4a–b, Table S2). In the initial stage of Zn intercalation, there is a 5.90% increase in unit cell volume from LiV3O8 to Zn1LiV3O8 (Fig. 3d–f), which is attributed to the single-phase reaction (from LiV3O8 to Zn0.5LiV3O8) and the two-phase reaction (from Zn0.5LiV3O8 to Zn1LiV3O8) during this process. With the increase of Zn2+ content, the unit cell volume shows 0.33% decrease from Zn1LiV3O8 to Zn1.5LiV3O8 (Fig. 3g), which relates to the closer (V3O8)-layers caused by the Zn-ion bonding. At the intermediate stage (Zn2LiV3O8, 1.5 < x < 2, Fig. 3h), the unit cell volume expansion is up to 16.73%, caused by the excessive zinc ion embedding. Accordingly, there is an increment of lattice parameter by 2.07 Å and 0.14 Å in a-axis and b-axis, respectively. At the final stage (β-Zn3LiV3O8, 2 ≤ y ≤ 3, Fig. 3i), the volume expansion (7.64%) is effectively suppressed by this phase transformation. Overall, the structure/phase evolutions during the Zn2+ intercalation process are interesting, which include two solid-solution reactions (from α-LiV3O8 to α-Zn0.5LiV3O8; β-Zn0.5LiV3O8 to β-ZnLiV3O8) separated by a two-phase process (Zn0.5LiV3O8 to Zn2LiV3O8) and a phase transformation (from α-Zn2LiV3O8 (x < 2) to β-Zn3LiV3O8 (2 ≤ y ≤ 3)).

X-ray photoelectron spectroscopic (XPS) analysis was further used to provide proof of Zn2+ intercalation and the valence state change of vanadium. The initial (I) and recharged stated (III) electrodes show weak signal of Zn 2p component, while the intensity of core level spectra (Zn 2p3/2: 1022.1 eV; Zn 2p1/2: 1045.2 eV) increases to a very strong level at fully discharged stated (II), indicating a highly reversible insertion/desorption of Zn2+ in LiV3O8 host during discharge/charge process (Fig. 4a). For the initial electrode, three peaks located at 517.1 eV, 524.3 eV, and 530.3 eV are observed, corresponding to the binding energies of V5+ (2p1/2), V5+ (2p3/2), and O 1s, respectively. The signals of V5+ (2p1/2) and V5+ (2p3/2) are nearly replaced by the V3+ (2p1/2: 515.2 eV; 2p3/2: 522.5 eV) signals at the discharged state, which indicates that all V5+ are converted to V3+ at the fully discharged state. To the contrary, the signals of V3+ (2p3/2) and V5+ (2p1/2) are back to the initial positions at the charged state, indicating a reversible V3+/V5+ transformation.
during Zn\(^{2+}\) insertion/desertion process.

### 2.4. Changes in reaction kinetics

To study the reaction kinetics of Zn\(^{2+}\)-(de)intercalation process, the galvanostatic intermittent titration technique (GITT) measurements are applied (Fig. 5a-b). As shown in Fig. 5a, a very high capacity of 557.5 mA h g\(^{-1}\) at the current density of 10 mA g\(^{-1}\) is achieved at fully discharge state, indicating a reversible V\(^{3+}/V^{5+}\) double redox in LiV\(_3\)O\(_8\) with the insertion of zinc ions. There are four plateau regions in the discharge curve and the Zn\(^{2+}\) diffusion coefficients (D\(_{2n2}\)) change with the discharge depth (Fig. 5c). In the first discharge plateau, the D\(_{2n2}\) is about \(10^{-11} \cdot 10^{-10}\) cm\(^2\) s\(^{-1}\), whereas, there are 2–3 orders of magnitude decreases of D\(_{2n2}\) in the second discharge plateau (\(\approx 10^{-14} \cdot 10^{-10}\) cm\(^2\) s\(^{-1}\)), which is attributed to both ionic diffusion and the ions-transportation through the interphase boundary. Interestingly, the D\(_{2n2}\) of cathode materials increases to the magnitude of \(10^{-12}\) cm\(^2\) s\(^{-1}\) in the following regions, indicating a high D\(_{2n2}\) in this two-phase region. It’s worth noting that there is a sharp decrease of D\(_{2n2}\) (\(\approx 10^{-13}\) cm\(^2\) s\(^{-1}\)) at the phase of Zn\(_{x}\)LiV\(_3\)O\(_8\) (\(y \approx 2\)), which should be attributed to the phase transformation between \(\alpha\)-Zn\(_{x}\)LiV\(_3\)O\(_8\) to \(\beta\)-Zn\(_{x}\)LiV\(_3\)O\(_8\). In the final region, the D\(_{2n2}\) comes back to the magnitude of \(10^{-12}\) cm\(^2\) s\(^{-1}\), which reflects the ionic diffusion coefficient in \(\beta\)-Zn\(_{x}\)LiV\(_3\)O\(_8\) (\(2 \leq y \leq 3\)) phase. Similarly, the D\(_{2n2}\) of the cathode varies with the Zn\(^{2+}\) concentration and the phase regions during the subsequent charge process. And the D\(_{2n2}\) is in the magnitude of \(10^{-12} \cdot 10^{-10}\) cm\(^2\) s\(^{-1}\) during the whole charging process.

The multiple-scan CV curves at the scan rates from 0.2 to 1.0 mV s\(^{-1}\) show similar shapes, and the redox peaks display gradually widening trend (Fig. 5d). The redox peaks at 0.46/0.65 fade away at high scan rates (\(>0.5\) mV s\(^{-1}\)), which is consistent with the charge/discharge curves that the special plateaus disappear at high rates. When increasing the scan rates from 1.0 to 10.0 mV s\(^{-1}\) (Fig. 5sa), there is only one pair of reduction/oxidation peaks remained, with opposite shifting in peak potentials, and large polarization currents are generated at extremely high sweep rates (from 10.0 to 100.0 mV s\(^{-1}\), Fig. 5sb). It is assumed that the peak currents (i) in CV curves follow an empirical power-law regularity with the scan rate (v) as below [41]:
reflects the Warburg impedance, which is related to the solid-state diffusion component. There are 140 EIS plots during the whole discharge/charge processes, and the resistance contour plots vary with the potential change (Fig. S8). In the initial discharge process (from 1.6 V to 0.85 V, green color), the impedance shows slight increase with a straight Warburg line along nearly 45°, indicating fast solid-state diffusion in this solid-solution reaction region (Fig. 6a). In the subsequent discharge process (from 0.85 V to 0.55 V, light yellow color), the impedance shows larger increase, with the straight Warburg line less than 45°, caused by the two-phase reaction mechanism. In the last stage (from 0.55 V to 0.20 V, light red color), a new semicircle appeared with large increase in impedance, which can be explained by the formation of a new phase. On the contrary, the resistances decrease during charge process, and the impedances show nearly opposite tendency to discharge as expected (Fig. 6b). The Nyquist impedance collected at selected potentials are shown in Fig. 6c, which typically represent the impedances of solid solution reaction region (discharge 1.5 V, charge 1.5 V) and two-phase reaction region (discharge 0.7 V, charge 0.9 V). Intriguingly, two semicircles are observed at the phase transformation reaction region (discharge 0.4 V, charge 0.45 V), and better fit is obtained when considering the two-step charge transfer modes (Fig. 6d). In a word, the resistance associated with the Zn2+ diffusion process and the phase transformation of the cathode closely, and SPEIS measurement would be an effective method to understand this process.

3. Conclusions

In conclusion, a reversible V3+/V5+ double redox with the stepwise insertion of Zn2+ in LiV3O8 cathode was illustrated. Benefiting from this multielectron transition mechanism, the cathode delivered the highest capacity of 557.5 mA h g⁻¹, and high capacity retention of 85% over 4000 cycles, which is superior to most reported aqueous energy storage devices. Furthermore, the reaction kinetics analyses and the structural evolution characterization indicated that, although the phase transformation between α-Zn2LiV3O8 (x < 2) and β-Zn2LiV3O8 (2 ≤ y ≤ 3) lead to increased resistance and reduced kinetics of the system, it can effectively suppress the volume expansion (7.64%) of LiV3O8 host. Moreover, this study also shows that using V3+/V5+ double-redox will open-up new opportunities for designing vanadium-rich cathodes for low-cost, high-performance, and environmentally friendly energy storage system.

Declaration of competing interest

The authors declare no competing interests.

CRediT authorship contribution statement

Pan He: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Mengyu Yan: Formal analysis, Writing - review & editing. Xiaobin Liao: Formal analysis, Writing - review & editing. Yanzhu Luo: Conceptualization, Writing - review & editing. Liqiang Mai: Conceptualization, Writing - review & editing. Ce-Wen Nan: Writing - review & editing.

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