Phase Transformation of VO$_2$/rGO Composites as High-Voltage Cathodes in Zinc-Ion Batteries

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Aqueous zinc-ion batteries (ZIBs) are becoming widely concerned candidates as stationary and safe energy storage technology. Vanadium oxides display promising role as cathodes for ZIBs owing to their inherent merits in structures and multiple valence states. However, their unsatisfactory electrical conductivity and narrow voltage window hinder the practical application. Moreover, the charge storage mechanism at the high voltage is unclear. Herein, we synthesized VO$_2$/rGO composites with high electrical conductivity and demonstrated an electrochemically induced phase transition from tunneled VO$_2$/rGO to Zn$_x$(OH)$_2$V$_2$O$_7$·2H$_2$O/rGO with a laminated structure and an enhanced interlayer spacing during the first charge to 1.6 V, which shows preferable Zn$^{2+}$ storage capacity. Concretely, the electrochemical window of as-assembled ZIB expands to 1.6 V with a specific capacity of 329.9 mAhg$^{-1}$ at 0.1 A g$^{-1}$, exhibiting wider window compared with the ZIBs based vanadium oxide reported previously. Simultaneously, a long stable lifetime of 84% capacity retention over 1,000 cycles can be recorded. Our work opens a new idea of design strategy to develop high-voltage ZIBs.

So far, multiple cathode materials have been synthesized in the laboratory scale after tireless efforts from many academics, such as manganese oxides, vanadium oxides and Prussian blue analogues, exhibiting acceptable reversible Zn$^{2+}$ insertion/extraction behaviors.$^{[14–17]}$ Among them, vanadium oxides are one of the most competitive materials in various battery systems on account of multiple oxidation states (from V$^{2+}$ to V$^{5+}$) and varied crystalline structures, which allows for more electrons transfer, such as V$_2$O$_5$·nH$_2$O.$^{[18]}$ VO$_2$.$^{[19]}$ VO$_2$·nH$_2$O.$^{[20]}$ H$_2$V$_2$O$_6$ nanowires$^{[21]}$ and NaV$_2$O$_5$·1.5H$_2$O.$^{[22]}$ Moreover, previous studies have proven that some vanadium compounds undergo irreversible phase transitions during charge/discharge process.$^{[23,24]}$ Luo et al. investigated the structural evolution of V$_2$O$_5$ and the results show a transformation from phase V$_2$O$_5$ to phase V$_2$O$_3$·nH$_2$O.

The VO$_2$ with a tunnel structure (0.82 nm$^2$, 0.34 nm$^2$ and 0.5 nm$^2$ along the b-, a- and c-axis, respectively) is another promising cathode material because it offers an attractive theoretical capacity, which has been calculated as 646 mAh g$^{-1}$. Notwithstanding, the current problems suffered by VO$_2$ cathodes are their limited electrical conductivity, reduced Zn$^{2+}$ diffusion dynamics, as well as the unclear phase transformation during charge/discharge processes especially with a large voltage window. Carbon-based materials possess high electrical conductivity and stable physicochemical properties.$^{[27,28]}$ To solve the limitation including poor structural stability and conductivity, it has been demonstrated that integrating the cathodes with the carbon-based materials, which possess the high electrical conductivity, such as CNTs and graphene, is an efficient strategy.$^{[29–32]}$

Herein, we used a convenient and effective strategy for the synthesis of vanadium-based oxides on the surface of graphene oxide with superior conductivity (VO$_2$/rGO). As demonstrated by the ex-situ experimental analysis, the irreversible phase change occurred in VO$_2$/rGO composite structures after the first charging process at 1.6 V (Scheme 1), and the in-situ formed...
phase (T-VO\textsubscript{2}/rGO) offers better capacity of Zn ion storage and diffusion, making it a competitive cathode candidate for next-generation large-scale ZIBs.

**Results and Discussion**

The VO\textsubscript{2}/rGO composite was produced through two processes. Firstly, the precursor was prepared by a hydrothermal process with graphene oxide (GO) and NH\textsubscript{4}VO\textsubscript{3}; Next, target products were obtained by an annealing process. In addition, two control materials, i.e., the ones without GO or NH\textsubscript{4}VO\textsubscript{3}, were prepared.

The phases and structures of as-prepared products were detected by XRD. The peaks of samples without GO can be indexed to the standard V\textsubscript{2}O\textsubscript{5} phase (JCPDS-41-1426), as shown in Figure 1(a), and rGO exhibits two characteristic signatures at around 25° and 43°, which are recognized as the (002) and (100) planes of graphitic carbon, respectively.\textsuperscript{[33]} Interestingly, XRD results of the composite nicely match with the monoclinic VO\textsubscript{2} (JCPDS-31-1438), which could be caused by the reduction from the rGO.\textsuperscript{[26]} The morphology of VO\textsubscript{2}/rGO composites was observed using SEM and TEM. As illustrated in Figure 1(b and c), VO\textsubscript{2}/rGO composite possesses a porous network, and spiny VO\textsubscript{2} structures are on the surface of rGO. As a comparison, SEM images of the V\textsubscript{2}O\textsubscript{5} and rGO were also recorded, as shown in Figure S1. TEM and HR-TEM images in Figure 1(d and e) further certify the successful combination of VO\textsubscript{2} and rGO. Furthermore, Figure 1(f) shows the TEM-EDS elemental mappings, indicating that the VO\textsubscript{2}/rGO composite contains only C, O and V elements. Based on the Branauer-Emmett-Teller (BET) method, BET surface areas of VO\textsubscript{2}/rGO composite is 72.4 m\textsuperscript{2} g\textsuperscript{-1} and the pore diameter is concentrated at 5 nm, which could provide large electrochemically active surface areas for charge storage (Figure S2).

![Scheme 1. Fabrication and phase transition process of VO\textsubscript{2}/rGO composite.](image)

![Figure 1. a) XRD patterns. b, c) SEM, d) TEM, e) HRTEM images and f) TEM-EDS elemental mappings of VO\textsubscript{2}/rGO.](image)
Figure 2. a) XPS survey spectra. b) V 1p, c) O 1s and d) C 1s XPS spectra of VO$_2$/rGO. e) FT-IR spectrum and f) TGA curve of VO$_2$/rGO.
Figure 3. a) CV curves at 0.1 mV s\(^{-1}\), b) GCD curves at 0.1 Ag\(^{-1}\) of VO\(_2\)/rGO of the first three cycles. c) CV curves at 0.1 mV s\(^{-1}\), b) GCD curves at 0.1 Ag\(^{-1}\), e) long cycling performance at 5 Ag\(^{-1}\) of VO\(_2\)/rGO with different working windows.

Figure 4. a) Rate performances. b) Nyquist plots. c) CV curves at different scan rates of VO\(_2\)/rGO. d) Log(i) vs. log(v) plots of redox peaks. e) Normalized ratios of the capacitive contribution at different scan rates. f) Diffusion and capacitance contribution at 0.3 mV s\(^{-1}\). g) Cycling performances at 5 Ag\(^{-1}\) of VO\(_2\)/rGO and V\(_2\)O\(_5\). h) Ragone plots of VO\(_2\)/rGO and other reported ZIBs cathode materials.
batteries were evaluated by the kinetic behavior analysis. The CV curves of T-VO$_2$/rGO, V$_2$O$_5$, and rGO cathodes at different scan rates are shown in Figures 4(c) and S6. The CV curves of T-VO$_2$/rGO suggest a multi-step Zn$^{2+}$ intercalation/deintercalation with two pairs of redox peaks. According to Equations (S1) and (S2), b values calculated for the Peak 1, 2, 3 and 4 are found to be 0.51, 0.89, 0.72 and 0.55, respectively, and the range of 0.5–1.0 indicates the electrode simultaneously possesses both capacitive and diffusion processes [37,38]. Figure 4(e) summarizes the capacitive ratios of T-VO$_2$/rGO cathodes at 0.1–0.5 mV s$^{-1}$ according to Equation (S3), which gradually increases from 40.1% to 68.6%, suggesting an increased dominance of the capacitance-controlled process as the scan rate increases. The shaded region in Figure 4(f) represents the capacitive contribution at 0.3 mVs$^{-1}$.

The markedly improved structure stability of T-VO$_2$/rGO can also be verified by long cycling tests at 5 A g$^{-1}$, and the capacity of T-VO$_2$/rGO retains 84% after 1,000 cycles. Meanwhile, the Coulombic efficiency is maintained at nearly 100%. Whilst the V$_2$O$_5$ cathode shows the capacity retention of 51% after cycling, which indicates rGO plays a key role in stabilizing structure. The T-VO$_2$/rGO shows a maximum energy/power density of 323.3 Wh kg$^{-1}$/9,796.3 W kg$^{-1}$. The superior electrochemical performances of the T-VO$_2$/rGO electrode are quite competitive, as shown in Figure 4g and Table S1, which is better than those of other reported V-based materials for ZIBs [32,39–51].

The ex-situ XRD was applied to study different phase compositions of VO$_2$/rGO electrode under various charge storage states. As discussed above in Figure 5, the characteristic peaks at 14.4° and 15.4° for VO$_2$·H$_2$O (JCPDS-18-1445) almost disappear completely after the initial charging process to 1.6 V and be never seen again subsequently, which implies the complete variation of phase compositions of VO$_2$·H$_2$O. At full charging state up to 1.6 V, three new weak peaks located at 12.3°, 34.2° and 36.5° appear and are assigned to the Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O (JCPDS-50-0570), indicating the VO$_2$ of VO$_2$/rGO electrode transformed into Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O after the first charging, which may ascribe insertion/extraction of hydrated Zn ion [24,25]. Different from the tunnel-type structure of VO$_2$, Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O possesses layered structure and a sufficient interlayer spacing (0.72 nm) to provide enlarged spaces for Zn$^{2+}$ storage and diffusion (Scheme 1) [35]. When discharged to 0.2 V, the Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O signal decreases significantly because of the intercalation of Zn$^{2+}$. As recharging in the second cycle, the Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O peaks emerged again, which further proves the irreversible reaction from VO$_2$/rGO to the product of Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O/rGO (T-VO$_2$/rGO) with a wide voltage window and specific capacity.

Conclusion

In summary, the VO$_2$/rGO composite cathode by a hydrothermal process followed with high temperature treatment for aqueous ZIBs. This compound structure with rGO promotes the high conductivity and stability simultaneously. Moreover, we verify that the irreversible phase variation from VO$_2$/rGO composite to Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O/rGO (T-VO$_2$/rGO) with layered structure and a large interlayer spacing at the first charging process. Benefitting from the converted structure, the Zn$_2$(OH)$_3$V$_2$O$_7$·2H$_2$O/rGO electrode enables a wide potential window (0.2–1.6 V), a superior specific capacity of 329.9 mAh g$^{-1}$, an excellent cycling stability (capacity retention of 84% after 1,000 cycles), a high specific energy/power density of 323.3 Wh kg$^{-1}$/9,796.3 W kg$^{-1}$, showing promising application as high-voltage vanadium-based cathodes for ZIBs.

Experimental Section

Experimental Section was provided in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: high-voltage · phase transition · vanadium oxides · VO$_2$/rGO composite · zinc-ion batteries
The VO$_2$/rGO cathode for ZIBs: The VO$_2$/rGO compound structure with rGO promotes the fast electron/ion transport and stability simultaneously. It is found that the irreversible phase transition from VO$_2$/rGO composite to Zn$_3$(OH)$_2$V$_2$O$_7$·2H$_2$O/rGO (T-VO$_2$/rGO) with layered structure and a large interlayer spacing at the first charging process.