Water-Activated VOPO$_4$ for Magnesium Ion Batteries

Xiao Ji, Ji Chen, Fei Wang, Wei Sun, Yunjun Ruan, Ling Miao, Jianjun Jiang, and Chunsheng Wang

ABSTRACT: Rechargeable Mg batteries, using high capacity and dendrite-free Mg metal anodes, are promising energy storage devices for large scale smart grid due to low cost and high safety. However, the performance of Mg batteries is still plagued by the slow reaction kinetics of their cathode materials. Recent discoveries demonstrate that water in cathode can significantly enhance the Mg-ion diffusion in cathode by an unknown mechanism. Here, we propose the water-activated layered-structure VOPO$_4$ as a novel cathode material and examine the impact of water in electrode or organic electrolyte on the thermodynamics and kinetics of Mg-ion intercalation/deintercalation in cathodes. Electrochemical measurements verify that water in both VOPO$_4$ lattice and organic electrolyte can largely activate VOPO$_4$ cathode. Thermodynamic analysis demonstrates that the water in the electrolyte will equilibrate with the structural water in VOPO$_4$ lattice, and the water activity in the electrolyte alerts the mechanism and kinetics for electrochemical Mg-ion intercalation in VOPO$_4$. Theoretical calculations and experimental results demonstrate that water reduces both the solid-state diffusion barrier in the VOPO$_4$ electrode and the desolvation penalty at the interface. To achieve fast reaction kinetics, the water activity in the electrolyte should be larger than $10^{-7}$. The proposed activation mechanism provides guidance for screening and designing novel chemistry for high performance multivalent-ion batteries.

KEYWORDS: Water cointercalation, layered VOPO$_4$, desolvation penalty, magnesium battery, first-principles calculation, water equilibrium

The increasing demand of clean energy in modern society drives the search for reliable, sustainable electrochemical energy storage. Among the various energy storage technologies, rechargeable lithium-ion batteries are currently the most attractive candidate. However, increased concerns about the safety and cost of lithium-ion batteries are triggering the society to explore low cost and high energy "beyond Li-ion" technologies, such as Li-air, Li-S, sodium-ion, and multivalent-ion (MV-ion) batteries.

Among these "beyond Li-ion" technologies, the magnesium battery has drawn much attention due to high energy density, low cost, and high safety. Although extensive efforts have been devoted to enhancing the performance of Mg-ion batteries, only limited advance in performance of cathode materials has been achieved because of sluggish reaction kinetics or even deactivation of the host caused by the strong electrostatic interactions between Mg$^{2+}$ ions and the anions in the host structure. Only few compounds, including Mo$_6$S$_8$, Prussian blue (such as V$_2$O$_5$, MnO$_2$, layered TiS$_2$, Li$_x$V$_2$(PO$_4$)$_3$), sulfur spinel compounds, and Prussian blue analogues, have been reported for Mg battery cathode materials. However, these cathodes either suffer from low energy density (such as Mo$_6$S$_8$, Prussian blue) or poor rate performance and cycle life (such as V$_2$O$_5$, MnO$_2$, layered TiS$_2$, Li$_x$V$_2$(PO$_4$)$_3$).

Recently, it was reported that the introduction of H$_2$O into the organic electrolyte can significantly improve the electrochemical performance of the multivalent-ion cathodes, and it is believed that the water in electrolytes can be inserted into cathode lattice by cointercalation of Mg with coordinated water molecules and that the intercalated crystal water in MnO$_2$ can change the MnO$_2$ phase from spinel to a layered Birnessite structure, enlarging the layered structure, thus accelerating the MV-ion mobility. In addition, the strong-dipole water molecules presumably "shield" the charges of divalent Mg-ion and reduce the electrostatic interaction between the concentrated charges, which also enhance the Mg-ion diffusivity. Theoretical calculation demonstrated that H$_2$O in wet electrolytes can shuttle with the Mg-ion...
during Mg-ion insertion/extraction in Xerogel V2O5, yielding higher voltages and fast reaction rate. Although the H2O in the electrolyte and/or in the lattice of the layered structured host significantly changed the thermodynamics and kinetics of Mg-ion intercalation, the precise mechanism is still under debate. The systematic investigation of the role of water in the electrolyte and the host lattice will provide guidance for design of high-performance Mg-ion batteries.

In this work, we used layered VOPO4 as a model cathode to systematically investigate the mechanism for water activation of an MV-ion cathode. The H2O in the electrolyte and/or in the lattice of the layered structured host significantly changed the thermodynamics and kinetics of Mg-ion intercalation, the precise mechanism is still under debate. The systematic investigation of the role of water in the electrolyte and the host lattice will provide guidance for design of high-performance Mg-ion batteries.

In this work, we used layered VOPO4 as a model cathode to systematically investigate the mechanism for water activation of an MV-ion cathode. The H2O in the electrolyte exchanges and equilibrates with H2O in VOPO4 lattice, which alert the VOPO4 structure and reaction pathway. The thermodynamic phase diagrams of Mg–VOPO4–H2O at different Mg and H2O contents were calculated. The solid-state diffusion barrier for Mg2+ intercalation into VOPO4·nH2O electrode and the desolvation energy penalty at the electrode–electrolyte interface were also investigated to provide insight into the kinetics for Mg-ion insertion/extraction in VOPO4·nH2O cathodes. The electrochemical performance of the anhydrous VOPO4 and VOPO4·2H2O in the organic electrolytes with different H2O content verified the theoretical calculation, revealing the mechanism for water activation of VOPO4. The theoretical analysis on thermodynamics and kinetics of VOPO4·nH2O cathodes sheds light on the electrochemical performance of VOPO4·nH2O under different electrolytic conditions at an atomic scale.

**Results and Discussion.** The layered VOPO4·2H2O was synthesized using a hydrothermal method, and H2O-free VOPO4 was obtained by further dehydration of synthesized VOPO4·2H2O (Materials Synthesis, Supporting Information). Figure 1a demonstrates the X-ray diffraction (XRD) patterns of the layered VOPO4 and VOPO4·2H2O. All the peaks of VOPO4·2H2O and VOPO4 can be indexed to tetragonal VOPO4·2H2O (JCPDS No. 84-0111) and VOPO4 (JCPDS No. 27-0947), which belong to the P4/nmm space group. The peak of (001) plane of VOPO4·2H2O is located at 2θ = 11.93°, indicating an interlayer distance of d = 7.41 Å, which is significantly larger than that of anhydrous VOPO4 (d = 4.17 Å). Therefore, the intercalation of water into VOPO4 can be readily viewed using XRD. The scanning electron microscopy (SEM) image (inset of Figure 1a) shows the layered architecture of VOPO4·2H2O cathodes. The electrochemical performances of the anhydrous VOPO4 and VOPO4·2H2O in the organic electrolytes were measured in a three-electrode cell using 0.1 M Mg(ClO4)2 and wet (0.1 M Mg(ClO4)2·6H2O-PC) electrolyte at a constant current density of 5 mA/g in a three-electrode cell with Ag/AgCl and active carbon as reference and counter electrode, respectively. The potential also converted to Mg/Mg2+ reference for convenience. (d) OCVs, hysteresis, and specific capacities of the tenth cycle for VOPO4 and VOPO4·2H2O in dry and wet electrolytes. The hysteresis is calculated by subtracting the mid voltage of charge by that of discharge.

**Figure 1.** Material characterization and electrochemical performance of VOPO4 cathode. (a) XRD pattern of layered VOPO4 and VOPO4·2H2O cathode (inset: the SEM image of VOPO4·2H2O). (b) Thermogravimetric analysis of VOPO4 and VOPO4·2H2O powder measured between room temperature and 200 °C with a heating rate of 5 °C per min. (c) Typical voltage profiles of VOPO4 and VOPO4·2H2O in dry (0.1 M Mg(ClO4)2·PC) and wet (0.1 M Mg(ClO4)2·6H2O-PC) electrolyte at a constant current density of 5 mA/g in a three-electrode cell with Ag/AgCl and active carbon as reference and counter electrode, respectively. The potential also converted to Mg/Mg2+ reference for convenience.
open circuit voltage (OCV), and voltage hysteresis are listed in Table 1. Only negligible capacity can be accessed from VOPO₄

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Table 1. Capacities (mAh/g), Hysteresis (V), and OCVs (V) for the Four Scenarios of VOPO₄ and VOPO₄·2H₂O in Wet and Dry Electrolytes

in the dry electrolyte (8.0 mAh/g). VOPO₄·2H₂O in the wet electrolyte provides maximum capacity of 89 mAh/g in the first cycle, which is comparable to that of layered V₂O₅·nH₂O.34 However, just introducing water to either a VOPO₄ electrode or a Mg(ClO₄)₂·PC electrolyte could improve the capacity only slightly. The introduced water in electrode or electrolyte renders the increased capacity of VOPO₄·xH₂O confirming that water can activate the VOPO₄ cathodes.

The OCVs, voltage hysteresis, and specific capacity of VOPO₄ after ten cycles with and without water in the electrode or electrolyte are summarized in Figure 1d. Thermodynamically, the OCVs are increased due to the presence of water in electrode and/or electrolyte, and the VOPO₄·2H₂O in the wet electrolyte exhibits the highest OCV. Kinetically, the voltage hysteresis was obtained by subtracting the mid voltage of charge from that of discharge to reflect the kinetics of the electrochemical process. Introducing water in both VOPO₄ electrode and electrolyte significantly reduces the voltage hysteresis from 1.15 to 0.49 V, indicating the obvious promotion of the kinetics. These results manifest that the presence of water has remarkable influence on the thermodynamics and kinetics of the electrochemical process.

Figure 1c shows that the water in either VOPO₄ interlayer or electrolyte increase the capacity, but VOPO₄·2H₂O in wet electrolyte has the highest capacity, also suggesting that H₂O exchange between interlayer of VOPO₄ and in the electrolyte. The exchange of H₂O in VOPO₄ and electrolyte during charge/discharge was characterized using XRD since the (001) peak position in XRD is highly sensitive to the H₂O and Mg²⁺ charge/discharge was characterized using XRD since the (001) peak after complete Mg extraction from Mg₀.5VOPO₄ indicates that the intercalation of Mg²⁺ ions into VOPO₄ (Process I) in a wet electrolyte. Water intercalates with Mg until xₘg ≈ 0.5 but then remains unchanged as more Mg-ions are inserted. The intercalation of water with MV-ions has also been found in the VOPO₄ and V₂O₅ for zinc-ion batteries.35,36 The relative energy difference among VOPO₄·xH₂O (n = 0, 1, and 2) is small, indicating the stability of these three phases are close in wet electrolyte.

More generally, the stability of all Mg_VOPO₄·nH₂O phases were further evaluated as a function of α_H₂O and Mg chemical potential (µ_Mg) by minimizing the grand-potential, as shown in Figure 2c. In this phase diagram, a high µ_Mg refers to highly magnesiated while decreasing the µ_Mg corresponds to the demagnesiation process. The increase in α_H₂O represents more water in the electrolyte, and a water activity of 10⁻⁴ corresponds to ~10 ppm by weight of water under the ideal solution approximation in solvents. Each colored region stands for the stable phase under the state of charge and electrolytic condition. The boundaries represent the coexistence of two phases, while the three-phase coexistence is marked with triple points. According to Figure 2c, when Mg intercalation occurs from an electrolyte with water activity above 10⁻², Process I works. For an electrolyte with water activity in the range between 10⁻⁵ to 10⁻², VOPO₄ → Mg₀.5VOPO₄ → VOPO₄·2H₂O (Process II) would be the electrochemical process. For an electrolyte with water activity below 10⁻⁵, VOPO₄ → Mg₀.5VOPO₄ → MgVOPO₄ (Process III) would be the main reaction route.

Accordingly, the average equilibrium voltage of the electrochemical processes under different electrolytic conditions were evaluated, as illustrated in Figure 2d. The red curve indicates the high-voltage two-phase transformation plateau (0 ≤ x ≤ 0.5), and the blue curve represents the low-voltage two-phase transformation plateau (0.5 ≤ x ≤ 1.0). The plateaus also correspond to the redox couple of V⁵⁺/V⁴⁺ and V⁴⁺/V³⁺, respectively. The slopes indicate the intercalation voltage change, while Mg and H₂O cotercation takes place. The V⁵⁺/V⁴⁺ voltage plateau decreases as water activity decreases from 3.10 to 2.95 V as the water activity decreases from 1 to 10⁻² and then maintain the voltage. The V⁴⁺/V³⁺ voltage plateau stays at 2.19 V until the water activity becomes lower than 10⁻². In the range of water activity from 10⁻² to 10⁻³, H₂O exits from the structure with Mg-ions, decreasing the voltage to 1.79 V. It is apparent that the voltage increases with the increase of the water activity. This increase can be explained by realizing higher activity of water in electrolyte can supply more water to the electrode, which can stabilize the Mg_VOPO₄ structures. However, it should be noted that adding water to the electrolyte narrows the electrolytic potential window. At a low water concentration in the electrolyte, the low voltage plateau of Mg_VOPO₄·nH₂O is
lower than the water decomposition voltage; thus, only one electron can be stored per formula VOPO$_4$·2H$_2$O, i.e., $x = 0.5$ Mg, reducing the capacity.

Therefore, the change in the XRD pattern after charge and discharge can be explained by the aforementioned analysis. The reduction in the interlayer distance in Figure 2a during Mg$^{2+}$ ion intercalation into the interlayer of VOPO$_4$·2H$_2$O is attributed to the strong electrostatic interaction between Mg$^{2+}$ ions and O atoms in water and on the VOPO$_4$ layer, which decreases the interlayer distance of VOPO$_4$·2H$_2$O (Figure 2e).

Upon Mg-ion deintercalation (charging), water molecules in the VOPO$_4$·2H$_2$O exit with Mg$^{2+}$ forming VOPO$_4$·nH$_2$O ($n < 2$), which makes the slight shift of (001) peak of VOPO$_4$·2H$_2$O (Figure 2a). The water content in VOPO$_4$·nH$_2$O also changes.
the phase transformation pathway during Mg-ion intercalation, thus changing the reaction kinetics and capacity.

To fully understand the effects of water in VOPO$_4$·$n$H$_2$O and in electrolytes on capacity, the reaction kinetics of VOPO$_4$·$n$H$_2$O with different H$_2$O content in dry and wet electrolytes were also investigated. First, the kinetics of Mg$^{2+}$ diffusion in the electrode was assessed. Based on the phase diagram in Figure 2c, the initial states in dry and wet electrolytes are VOPO$_4$ and VOPO$_4$·H$_2$O, respectively. Hence, these two phases were employed to investigate the kinetic characteristics. Figure 3a illustrates the diffusion pathway in VOPO$_4$ and VOPO$_4$·H$_2$O. In VOPO$_4$·H$_2$O structure, the O atoms of structure water before diffusion are represented by red balls, while the O atoms of structural water after diffusion are represented by pink balls. It is obvious that structural water molecules rotate to accommodate the host structure and Mg$^{2+}$ ions and codiffuse with Mg$^{2+}$ ions. The corresponding energy barriers are plotted in Figure 3b. The diffusion barriers of Mg$^{2+}$ in VOPO$_4$ and VOPO$_4$·H$_2$O are 1.56 and 0.48 eV, and according to the Arrhenius equation, the room temperature diffusion coefficient of Mg$^{2+}$ ions in VOPO$_4$·H$_2$O is $1.2 \times 10^{18}$ times higher than that of VOPO$_4$. The high diffusion barrier in VOPO$_4$ can even block the intercalation of Mg$^{2+}$. The energy barrier for Mg$^{2+}$ diffusion in VOPO$_4$·H$_2$O is comparable to that of Mg$^{2+}$ diffusion in spinel metal sulfides and V$_2$O$_5$, which are considered to be promising candidates for Mg-ion batteries. The presence of intercalated water significantly lubricates the diffusion of Mg$^{2+}$ ion in the electrode bulk.

Figure 3. Kinetics of VOPO$_4$ as Mg-ion battery cathode. (a) Illustration of Mg$^{2+}$ diffusion in VOPO$_4$ and VOPO$_4$·H$_2$O and its corresponding (b) diffusion energy barriers. The red balls represent O atoms of water before diffusion, while the pink balls stand for the O atoms of water after diffusion. (c) Electrostatic potential of VOPO$_4$ and VOPO$_4$·H$_2$O. The black arrow and dashed circle indicate the influence of layer expansion and water dipole effect on electrostatic potential, respectively. (d) Formation energies for [Mg(PC)$_6$]$^{2+}$ and [Mg(PC)$_6$(H$_2$O)$_n$]$^{2+}$ ($n \leq 6$). (e) Chemical reaction for [Mg(PC)$_6$]$^{2+}$ desolvation in different electrolytes. The desolvation energies are also shown next to each complex. (f) GITT profiles for VOPO$_4$·2H$_2$O in wet and dry electrolytes.
The role of water in improving the diffusion process in electrodes was further studied by evaluating the electrostatic potentials along the diffusion path of VOPO$_4$ and VOPO$_4$·$n$H$_2$O (Figure 3c). The electrostatic potentials show a strong correlation with the energy barriers in Figure 3b. The oscillations of electrostatic potential of VOPO$_4$ are found larger those that of VOPO$_4$·$n$H$_2$O, which indicates a larger change of electrostatic interaction between Mg$^{2+}$ ions and the VOPO$_4$ layer during diffusion. The overview of electrostatic potential difference (black arrow) results mainly from the different interlayer distances. The small local oscillation in the black dashed line is contributing from the water dipole effect. Therefore, according to the electrostatic potential plot, the electrostatic interaction decrease results mainly from the expanding of the interlayer distance by structural water.

In addition to the diffusion barriers in the electrode, the desolvation energy of Mg$^{2+}$ ions at the interface between electrode and electrolyte is considered to be another main factor for the kinetics because Mg$^{2+}$ ions have to desolvate before intercalation. The formation free energies are calculated to measure the desolvation penalty of Mg$^{2+}$ ions in dry and wet electrolytes. According to the formation energies shown in Figure 3d, the most energetically favorable solvate configuration is [Mg(PC)$_6$]$^{2+}$ in dry electrolytes. When water exists in the electrolyte, Mg$^{2+}$ ions prefer to solvate with water rather than PC molecules, forming [Mg(H$_2$O)$_6$]$^{2+}$ with formation energy of $\sim 0.94$ eV. During the electrochemical process, the large desolvation energy (2.27 eV) for [Mg(PC)$_6$]$^{2+}$ makes it difficult for Mg$^{2+}$ ions to desolvate and intercalate (Figure 3e). However, as we mentioned above, water molecules can intercalate with Mg$^{2+}$ through only partial desolvation, and the dihexacyanamide ion is especially easy to intercalate into the near-surface. Mg$^{2+}$ ions solvate six water molecules in liquid electrolyte, but only four water molecules coordinated with Mg$^{2+}$ in the VOPO$_4$ electrode which apparently makes it easy for Mg$^{2+}$ intercalation.

The reaction kinetics of VOPO$_4$·$n$H$_2$O in dry and wet electrolytes at different Mg-ion intercalation levels were also measured using the galvanostatic intermittent titration technique (GITT). As shown in Figure 3f, the overpotential for VOPO$_4$·$n$H$_2$O in dry electrolyte is much larger than that in wet electrolyte. As theoretically predicted, the large overpotential of VOPO$_4$·$n$H$_2$O in dry electrolyte is attributed to both the large desolvation energy of [Mg(PC)$_6$]$^{2+}$ and the extremely lower diffusivity of Mg-ion in VOPO$_4$ since the H$_2$O in VOPO$_4$·$n$H$_2$O will transport into dry electrolyte to reach equilibrium.

According to the theoretical analysis, materials characterization, and electrochemical behavior of VOPO$_4$·$n$H$_2$O in dry and wet electrolytes, the water activation mechanisms for VOPO$_4$ as Mg-ion battery cathode materials were proposed (Figure 4). During the electrochemical process, the desolvation energy penalty at the interface and diffusion barrier in the electrode act as two gates for Mg$^{2+}$ intercalation. For VOPO$_4$ in dry electrolyte, the Mg-ion intercalation into VOPO$_4$ will first form Mg$_{0.5}$VOPO$_4$ and then MgVOPO$_4$, with extreme low reaction kinetics due to the very large desolvation energy (2.27 eV) of [Mg(PC)$_6$]$^{2+}$ and the high diffusion barriers of 1.56 eV of Mg$^{2+}$ in VOPO$_4$. Although VOPO$_4$·$n$H$_2$O in wet electrolyte also shows similar two-stage reaction from Mg$_{0.5}$VOPO$_4$·$n$H$_2$O and then MgVOPO$_4$·$n$H$_2$O, the reaction kinetics is very fast because the water molecules can intercalate with Mg$^{2+}$ through only partial desolvation, and the diffusion coefficient of VOPO$_4$·$n$H$_2$O is $1.2 \times 10^{18}$ times higher than that of VOPO$_4$. As for VOPO$_4$ in wet electrolytes, thermodynamically, the water cointercalates with Mg$^{2+}$ ions, thereby expanding the interlayer distance, stabilizing the VOPO$_4$·$n$H$_2$O phases, and increasing the equilibrium voltage. However, the presence of water narrows electrolyte decomposition window, limiting the capacity to the value corresponding to one electron per chemical formula. Kinetically, the diffusion barrier in the electrode and desolvation penalty in the interface are largely reduced after water cointercalation into VOPO$_4$·$n$H$_2$O. The presence of structural water in the electrode and electrolyte in the electrolyte open both of the two gates, releasing the capacity of Mg$^{2+}$ ions. For VOPO$_4$·$n$H$_2$O in dry electrolyte, the structural water in the electrode expands the interlayer distance providing the possibility for fast diffusion in the electrode. However, only a small amount of [Mg(PC)$_6$]$^{2+}$ can desolvate and intercalate into the near-surface. Mg$^{2+}$ ion diffusion into the bulk remains sluggish due to the small interlayer distance. The VOPO$_4$·$n$H$_2$O in the wet electrolyte shows decent cycle stability and high Coulombic efficiency (Figure S6, Supporting Information). The stable performance indicates the capacity can be activated and maintained in the
layered VOPO₄ by the addition of water. Screening additives in electrolyte, which are not only stable with both Mg anode and high voltage layered cathode but also play the similar role as water, can be an effective way to further increase the performance of layered cathode Mg batteries.

In summary, combining electrochemical experiments and DFT calculations, we demonstrate that the capacity of VOPO₄ can be largely activated and maintained by introducing water both in VOPO₄ structure and in the electrolytes. Water activity in the electrolyte should be larger than 10⁻² to equilibrate with structural water in VOPO₄ to ensure the reversible cointercalation/decointercalation of water-solvated Mg²⁺ ions. The presence of water promotes the voltage but limits the charge transfer of one electron per chemical formula. Water not only lubricates the solid-state diode but also reduces the penalty of interfacial charge transfer process, releasing the capacity limited by kinetics. The development of novel multivalent-ion batteries should systematically focus on the thermodynamics and kinetics.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b02854.

Computational details, experimental details, structure, grand phase diagram, different charge distribution, cyclic voltammetry profiles, and cycle stability (PDF)

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X.J. and J.C. synthesized the electrodes, characterized the sample, tested the electrochemical performances, analyzed the results, and wrote the manuscript. F.W. and W.S. synthesized the VOPO₄ powder and performed the SEM and TGA tests. X.J., Y.R., L.M., and J.J. designed and conducted the computational works. All authors discussed the results. C.W. supervised the study.

Notes
The authors declare no competing financial interest.

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