

Multivalent-ion vs Proton Insertion into Battery Electrodes

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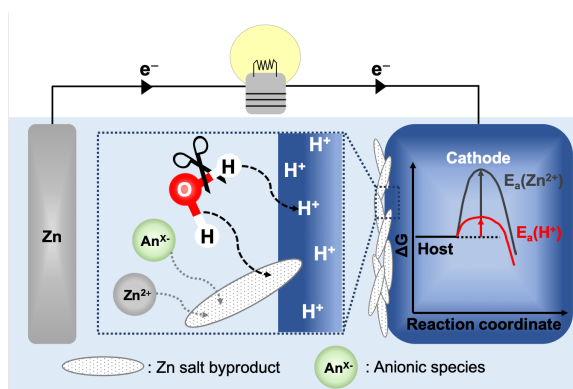
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ABSTRACT

For a sustainable future in the energy storage technology, alternative battery chemistries, such as those based on the insertion chemistry of multivalent (MV) ions (*i.e.*, Mg-, Zn-, Ca-, and Al-ion) have received a significant interest over the years. For their future development, a clear understanding of the underlying chemistry is absolutely critical. This Perspective highlights the propensity of the transition in the charge-carrier ion species from MV ions to protons in a MV-ion system, especially when water is incorporated into the electrolyte either as a solvent or an additive, directly contradicting the commonly held belief that water improves MV-ion mobility. Recent literature demonstrating this phenomenon is introduced, emphasizing the critical need to employ appropriate analytical techniques to unequivocally determine the nature of charge-carrier ions in MV systems.

TOC GRAPHICS



An increasing concern on the global environment and energy sustainability is driving research and development on clean energy storage technologies. Currently, lithium-ion batteries (LIBs)—which operate on the reversible insertion of Li ions into an oxide cathode and a graphite anode—are the most prominent candidate, being commercially used in numerous portable electronic devices and electric vehicles (EVs).¹ It is expected that the number of LIBs used will skyrocket as the EV market grows and the utility industry begins to adopt LIBs. Due to this, there is a growing concern on the availability of Li, which would impact the sustainability and cost of LIBs.² Hence, other insertion-based battery chemistries that utilize cheaper and earth-abundant elements are sought after as “beyond Li-ion” technologies. Among those, multivalent-ion batteries (MIBs) such as Mg-, Zn-, Ca-, and Al-ion batteries have gained significant attention in recent years.³

There are still numerous challenges that must be overcome for MIBs to even be considered as a practical replacement to LIBs. One major problem is the sluggish diffusion kinetics of MV ions in solid-state insertion hosts. Successful demonstrations of reversible Li-ion insertion into various insertion-based solid-state hosts over the years has promoted the perception that similar insertion behavior could be achieved with MV ions. This viewpoint was consolidated partly by the realization of MV-ion insertion, including Mg ions, into exceptional solid-state hosts with a chalcogenide-based framework, such as the Chevrel phase Mo_6T_8 (T: S, Se).⁴ For a given host material, however, the diffusion of MV ions would be much slower than that of Li ions because of the considerably stronger electrostatic interaction between the MV ions and the host, which stems from the higher charge density on MV ions than on Li ions. Therefore, even under the presence of a thermodynamic driving force for the MV-ion insertion, the sluggish diffusion kinetics of MV ions in solid-state hosts translate into a lack of appreciable electrochemical

activity. Even in the Mo_6S_8 cathode, an elevated temperature is required to completely extract the inserted Mg ions after discharging the battery.⁴

Ever since the introduction of the Chevrel phase as a cathode host, much effort has been devoted to investigating oxide-based cathode hosts to improve the energy density of MV-ion batteries.⁵ While such shift in the cathode material chemistry from sulfides to oxides would be beneficial for increasing the operating potential, that would also aggravate the problem of sluggish solid-state diffusion of MV ions in the cathode host due to the stronger electrostatic interaction between the guest MV ions (hard Lewis acids) and the oxidic (hard Lewis-base) host. The work from our group on the attempt to remove magnesium or zinc from their manganese spinel oxides clearly demonstrate that Mg- or Zn-ions cannot be extracted from the oxide host through chemical oxidation—mimicking the electrochemical charging behavior—due to the strong electrostatic repulsion between the divalent working cations and the host cations in close-packed oxides.^{6,7} Out of the blue, however, the so-called rechargeable nonaqueous Zn-ion batteries (ZIBs) with water as an electrolyte additive or even the aqueous analogues, with numerous different oxide cathode hosts of various morphologies demonstrating superior electrochemical performances—some cycling at a rate even higher than 10C—have been reported.⁸ Although immensely puzzling, many of these reports to date have attributed the observed electrochemical performance to the facile nature of Zn-ion diffusion in the solid-state oxide cathode hosts under the presence of water in these ZIBs.

In contrast to the common notion that water improves the MV-ion mobility, however, an increasing number of studies, including our own, have recently reported that the observed promising electrochemical performance in aqueous Zn-ion systems is in fact mostly due to the insertion of protons rather than MV ions into the cathode, making them technically a proton

hybrid battery.^{9,10} Identification of the true charge-carrier ion species lies at the heart of the energy storage systems operating based on insertion chemistry. While the insertion of Li- or Na-ions is expected, respectively, in Li-ion and Na-ion batteries, this is not necessarily the case with MIBs due to the possibility of side-reactions resulting in the introduction of protons into the system. The misidentification of the charge-carrier ions imposes severe consequences on the research and development in the MIB field. In particular, it can severely deter the research efforts when cathode materials identified as a “reversible Zn-ion host” are extended to other MV-ion systems with metals that are, unlike Zn, chemically incompatible with protons (*i.e.*, Mg, Ca, and Al). Moreover, for actual energy storage systems, such as aqueous “Zn-ion” batteries, further improvements and optimization for successful commercialization would strictly depend on acquiring a sound understanding of the underlying chemistry. Hence in this perspective, we aim to establish the importance of assessing the electrochemistry of MV-ion systems by taking both the thermodynamic and kinetic viewpoints into consideration and suggest necessary characterization techniques that should be employed to unequivocally determine the charge-carrier species. To do so, we go through the thermodynamic and kinetic viewpoints by introducing and discussing relevant studies on Zn-ion systems. Then, we introduce studies revealing the role of protons as charge carriers in other MV-ion systems by considering the thermodynamic and kinetic aspects discussed in the Zn-ion systems. Before starting, some physicochemical properties of the ions relevant to MV-ion insertion chemistries are summarized in Table 1. Shannon radius of H^+ is of a particular importance as the negative value establishes a self-consistent trend for all other ionic species in oxide-based solids and indicates the favorable O—H semi-covalent interactions.

Table 1. Some physicochemical properties of the insertion cations commonly encountered in MV-ion insertion electrodes

	Cationic Species					
	H ⁺	H ₃ O ⁺	Mg ²⁺	Zn ²⁺	Ca ²⁺	Al ³⁺
Common coordination number (C.N.)	1,2	Varies	4, 6	4, 6	6, 7, 8	4. 6
Shannon crystal radius (Å)	-0.24 (C.N. 1)	< 1.38 [†]	0.71 (C.N. 4)	0.74 (C.N. 4)	1.14 (C.N. 6)	0.53 (C.N. 4)
Charge density (e Å ⁻³) [‡]	N/A	0.091	1.334	1.178	0.322	4.811
Standard reduction potential, E ⁰ (V)	0.00	0.00	-2.37	-0.76	-2.87	-1.66
Theoretical specific capacity (mA h g ⁻¹)	26536	1409	2205	820	1337	2980

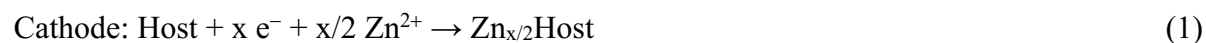
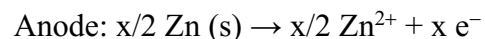
[†] The configuration is not well established. As an approximation, the kinetic radius of H₂O can be assumed (1.38 Å), with the fact that H⁺ coordination reduces the molar volume of H₂O.¹¹

[‡] Obtained from the Shannon crystal radius.

Zn-ion systems. The concept of primary alkaline batteries consisting of a zinc anode, a high-valence manganese oxide cathode (γ -MnO₂), and a basic aqueous electrolyte preceded well before the blooming of the rechargeable aqueous ZIBs research area. In these systems, the active role of protons—supplied by the water solvent—as the charge-carrier ions is well established.¹² The only difference between the primary alkaline batteries and the rechargeable aqueous ZIBs is the use of mild acidic electrolytes instead of a basic electrolyte. By shifting the pH to a lower value, both water oxidation and the reversible Zn-electrode potentials are increased to allow the ZIBs to be recharged while minimizing the problem of water oxidation. Hence, the active role of protons as the charge-carrier ions is also strongly anticipated in the rechargeable aqueous ZIBs with mildly acidic electrolytes. Thus, an unambiguous determination of the true charge-carrier

ions that compensate the electronic charge through bulk insertion requires the core reaction to be examined from the thermodynamic and kinetic perspectives.

At the thermodynamic level, the insertion of Zn ions into a host would only be possible when the reactions defined by Equation (1) give a net negative change in the Gibbs free energy ($\Delta G < 0$):



Otherwise for Zn-ion insertion, the cathode potential has to be shifted below the reduction potential of $\text{Zn}^{2+}/0$, which is practically unachievable. Being a bulk property, a negative change in ΔG should be accompanied by a change in the bulk concentration of the Zn in the host structure. If this is believed to be the source of the observed electrochemical activity, the assessment of bulk Zn-ion concentration within the cathode host should be meticulously probed with bulk-specific characterization techniques. Often, multiple orthogonal analytical techniques should be combined for a conclusive identification of the actual charge-carrier ion in MIBs. Among the bulk-specific techniques, crystallography and X-ray diffraction (XRD) play a central role to provide evidence for the bulk insertion of Zn ions. This is because diffraction-based techniques offer not only compositional information via site occupancy, but also deliver rich data regarding the chemical environment of the inserted Zn ions. These data can be further evaluated for chemical reliability and examined with elemental analysis techniques mentioned below for verification.

Despite this, crystallography is seldom employed to its fullest extent in the context of MV-ion insertion chemistry. This is in part because the electrode materials used in ZIBs studied *in situ* or *ex situ* with XRD are frequently loaded with only minimal amounts of samples (*e.g.*, a few mg),

which are mixed with conductive and binder additives, and broadened peaks that could further reduce the quality of the XRD pattern. Although changes in the lattice spacing of a host could be observed through such measurements, that alone would not be sufficient to indicate the identity of the inserted ion. In such situations, micro-diffraction based on selected area electron diffraction (SAED) can play a pivotal role in the assessment of Zn-ion insertion. For example, using SAED, Lee et al. discovered that discharging the Zn/ α -MnO₂ system in an aqueous electrolyte yields domains of the layered Zn-birnessite that is structurally similar to chalcophanite ZnMn₃O₇·3H₂O, with Zn ions octahedrally coordinated with oxo and aqua ligands (Figure 1a,b).¹³ This important observation is in line with the biphasic voltage-composition profile frequently observed in the first cycle of the Zn/ α -MnO₂ systems, directly indicating that water-shielded Zn-ion diffusion could indeed be a working mechanism in host materials with an open framework structure, though it does not exclude the presence of protons as hydronium ions (please note that more cationic species would be needed to balance for the Mn³⁺ charge in the chalcophanite).

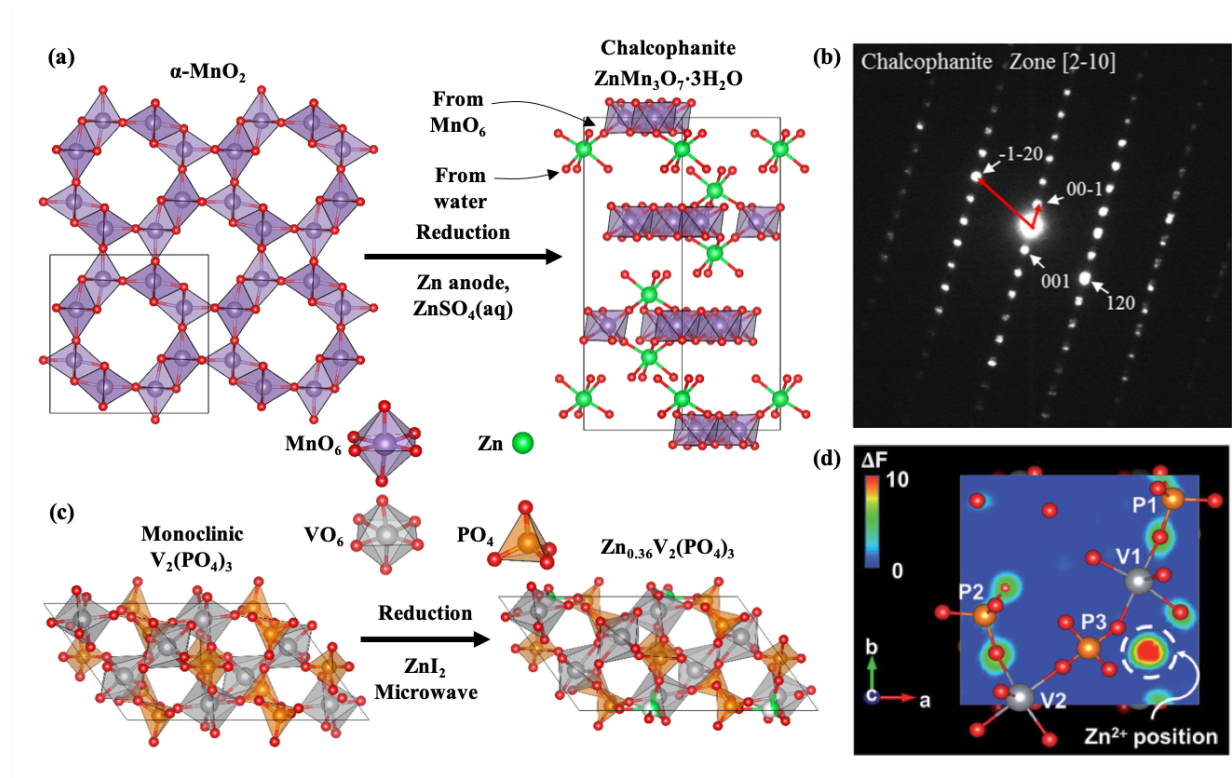


Figure 1. (a) Crystal structures of α - MnO_2 and chalcophanite $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$, respectively, before and after electrochemical discharge in an aqueous ZIB, (b) SAED pattern of the chalcophanite $\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$ along the $[2-10]$ zone axis. Reproduced with permission from ref 13. Copyright 2014 Springer Nature, (c) crystal structures of the monoclinic $\text{V}_2(\text{PO}_4)_3$ (left) and $\text{Zn}_{0.36}\text{V}_2(\text{PO}_4)_3$ (right), and (d) the difference Fourier map cross-section along $[001]$ direction ($z = + 7.62 \text{ \AA}$). Reproduced with permission from ref 14. Copyright 2019 The Royal Society of Chemistry.

For probing the structural aspects of Zn-ion insertion in a cathode host with XRD, generally larger quantities than those commonly employed in electrochemical cells would be needed. Recently, we have developed an expedited MV-ion chemical insertion method based on microwave irradiation to prepare gram-scale quantities of Zn-inserted $\text{V}_2(\text{PO}_4)_3$. Given the covalent nature of the polyanionic host, crystallinity was maintained to a high degree, allowing

us to analyze the host structure for the inserted Zn ions.¹⁴ The results suggested that the Zn ion occupies a tetrahedral site within the $V_2(PO_4)_3$ host and induces a large lattice strain, leading to an extensive cathode dissolution and premature capacity fade in a nonaqueous ZIB (Figure 1c,d). In a strikingly opposite observation, the $Zn/Li_xV_2(PO_4)_3$ system in an aqueous electrolyte is shown to provide acceptable capacity retention and a stable performance of the cathode host, indicating a fundamentally different insertion mechanism compared to the nonaqueous electrolyte.¹⁵ Without a proper proof for Zn-ion insertion, it is highly likely that proton insertion is responsible for the widely different behavior of the $V_2(PO_4)_3$ host in the aqueous system. The strong host-guest interactions observed here could expose the hidden limitations of the true MV-ion based insertion-type energy storage devices. Thus, the solid evidence provided by the crystallographic studies should be employed more often in the characterization of the MV-ion insertion mechanism.

To complement the structural characterizations, there are numerous spectroscopic techniques available to qualitatively or quantitatively determine the presence of an element of interest, such as atomic absorption or emission spectroscopy (AAS or AES), inductively coupled plasma-optical emission spectroscopy (ICP-OES), scanning and/or transmission electron microscope (SEM or TEM or STEM) equipped with energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and electron energy loss spectroscopy (EELS). Among these, XPS or SEM/TEM-EDX are commonly applied but care must be taken. XPS may not be a reliable technique to evaluate the bulk insertion of Zn into a cathode host because its result represents an average picture of only the surface of a cathode sample. Also, when using SEM/TEM-EDX, it is to be noted that a small area of the sample is normally inspected, and the results may not be representative of the total sample. Thus, an indication of insertion reaction

should be double-checked with an independent technique, such as diffraction-based structural characterization (discussed above), to prove that this is not a local observation. Given that the faradaic reaction in Equation (1) exclusively occurs at the cathode host, the determined amount of Zn in a cathode sample from any of the mentioned techniques can be regarded as Zn ions inserted into a cathode host.

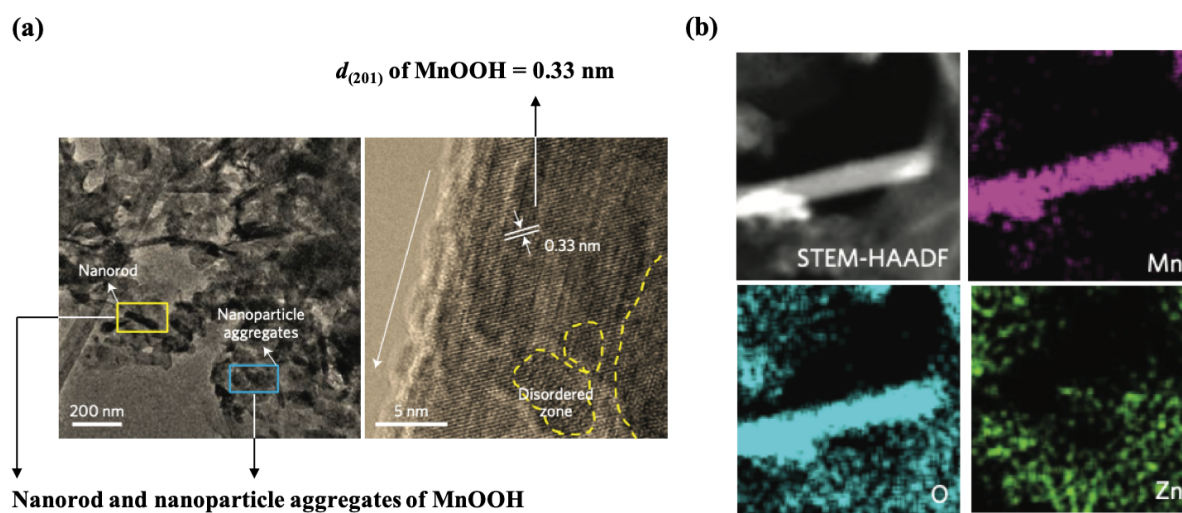


Figure 2. (a) TEM/HRTEM images of α -MnO₂ after discharge to 1.0 V vs. Zn^{2+/0}, respectively, showing the newly formed nanorod/nanoparticle aggregates and the lattice spacing of the (201) plane of monoclinic MnOOH. (b) STEM-High-Angle Annular Dark Field (STEM-HAADF) image of monoclinic MnOOH nanorod and STEM-EDX images, showing Zn from the salt byproduct surrounding the monoclinic MnOOH nanorod. (a) and (b) are reproduced with permission from ref 16. Copyright 2016 Springer Nature.

However, such a conclusion would be invalid if there are any other reactions involving Zn ions that take place at the cathode, as has been demonstrated in various recent studies on aqueous ZIBs. In the investigation of α -MnO₂ as a cathode in an aqueous ZIB with ZnSO₄ electrolyte by Pan et al., a zinc salt byproduct Zn₄SO₄(OH)₆·xH₂O was discovered to precipitate and dissolve on

the cathode, respectively, upon electrochemical discharging and charging through *ex situ* X-ray diffraction (XRD) analyses.¹⁶ TEM and STEM-EDX analyses revealed that the discharge products were monoclinic MnOOH illustrating the insertion of protons rather than Zn ions, and proposed that the flake-like Zn salt byproduct particles precipitated as a result of proton insertion into α -MnO₂ to maintain charge neutrality within the electrolyte (Figure 2a,b). Furthermore, a recent investigation by Oberholzer et al. aimed to provide an explanation for the observed zinc salt byproduct precipitation and dissolution from *in situ* XRD analyses at different states of discharge and charge with oxide cathode hosts (Figure 3a).¹⁷ Their MD simulation results showed that during discharge, the oxide anions at the electrode-electrolyte interface can effectively stabilize the protons in the vicinity via hydrogen bonding for their insertion. This results in an increase in the pH of the electrolyte, which triggers the zinc salt byproduct precipitation. During the charge step, the deinsertion of protons leads to the dissolution of the zinc salt byproduct. Reports of similar byproduct precipitation and dissolution on other oxide cathode hosts with various other aqueous Zn electrolytes, including Zn(CF₃SO₃)₂, ZnCl₂, Zn(ClO₄)₂, and Zn(CH₃COO)₂,^{18–20} suggest that proton insertion is a general phenomenon with mildly acidic aqueous Zn electrolytes.

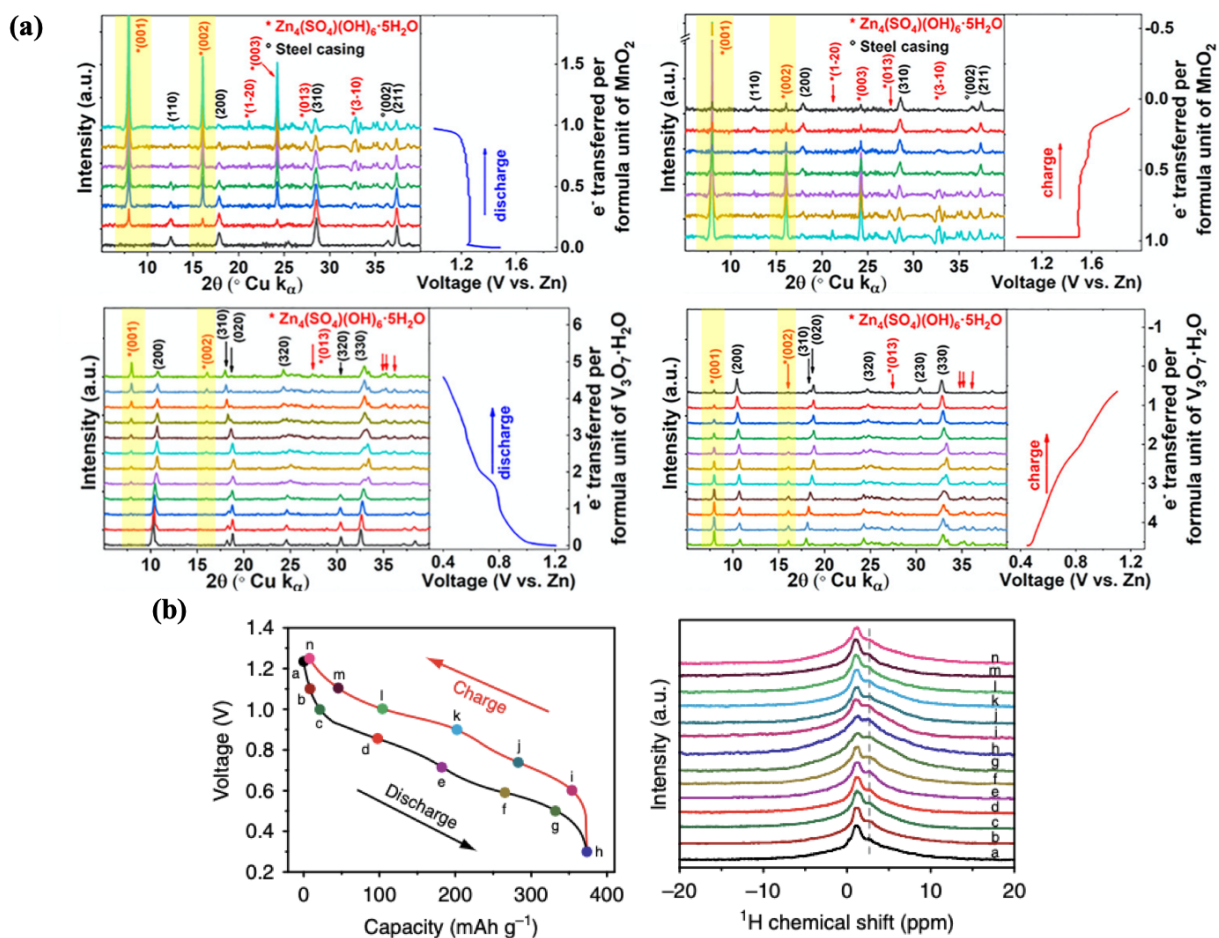


Figure 3. (a) *In situ* XRD patterns of $\alpha\text{-MnO}_2$ and $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$ during electrochemical discharge and charge steps with the yellow bars highlighting the two major peaks of Zn salt byproduct, with their intensity changing according to the state-of-charge. Reproduced with permission from ref 17. Copyright 2019 The American Chemical Society. (b) Second cycle charge-discharge curves of $\text{NaV}_3\text{O}_8\cdot 1.5\text{H}_2\text{O}$ with markers representing the states at which *ex situ* solid-state ^1H -NMR was conducted and the solid-state ^1H -NMR spectra at those states. Reproduced with permission from ref 22. Copyright 2018 Springer Nature.

Because an increase and decrease in the Zn content would be observed, respectively, for a reversible Zn-ion insertion and deinsertion reactions at a cathode (if such reactions were to

occur) and the inherent insensitivity of the above techniques to discriminate the surface from the bulk composition, it is understandable that one may prematurely conclude that Zn ions act as charge-carrier ions at a cathode based on their elemental analysis. Thus, it is imperative to remove the zinc salt byproduct, which would interfere with the elemental analysis. As the zinc salt byproduct is practically insoluble in neutral water, a method such as washing with dilute acid should be employed, given that the acid causes minimal damage to the cathode host (no damage ideally) as demonstrated in recent studies.^{9,10,21} If washing the cathode with a dilute acid causes significant damage, then results from multiple independent characterizations on the cathode must be critically analyzed to ascertain whether Zn ions are the charge-carrier ions.

If the above-mentioned analytical techniques illustrate that Zn ions are not the charge-carrier ions, then none of the above may confirm the insertion of protons. The direct observation of protons in a cathode host is challenging, and may need employing solid-state ¹H-NMR. Despite its associated difficulties, NMR is a powerful technique because of the high sensitivity of a resonance peak chemical shift of hydrogen with respect to its chemical environment such that resolving hydrogen in an OH or in an H₂O site is possible. For example, Wan et al. demonstrated that proton insertion/deinsertion can be directly observed in NaV₃O₈·1.5H₂O cathode.²² Their results indicated that a peak at 2.7 ppm arises due to the insertion of protons, and an increase and a decrease in the peak intensity, respectively, with discharging and charging was observed from *ex situ* characterization of the cathode (Figure 3b). Another peak at 1.5 ppm was determined to arise from the crystalline water and hydroxyl groups in the Zn₄SO₄(OH)₆·xH₂O zinc salt byproduct.

From a kinetics standpoint, examining the cation insertion rate can be quite informative with respect to addressing the nature of the charge carrier in insertion-type energy storage devices.

There are countless examples of experimental and theoretical studies on solid-state diffusion of protons, Li- and Na-ions in host materials used either as electrodes or ion-conducting membranes. On the contrary, such studies are largely lagged for MV-ion diffusion, mainly due to the lack of suitable electrochemical setups and hosts that can reversibly store such charge-dense ions. Despite this, it is widely accepted that the diffusivities associated with the small monovalent cations are orders of magnitude larger than the divalent counterparts in a given host. This information originates partially from the few successful cases of reversible pure MV-ion storage, such as the Chevrel phase, and to some extent from theoretical calculations.

The limited solid-state diffusivity of MV ions would translate to a low rate capability of a specific host. Therefore, a simple rate capability test spanning to high C rates that exhibits excellent performance would provide a clue in that protons might be the charge-carrier ions as Zn-ion diffusion will be too sluggish to compensate for such high electronic current. For instance, the reports of aqueous ZIBs commonly express large C rates, from 1C to rates even greater than 10C, meaning that a considerable fraction of the theoretical capacity can be realized within a few minutes of the (dis)charge. It is to be noted that the state-of-the-art Li-ion batteries, which are operating based on the high diffusivities of Li ions in the solid matrix, are limited to about 1C.²³ Thus, with orders of magnitude lower diffusivity, the solid-state diffusion of Zn ions (or its hydrated forms) seems physically unable to support such high reaction kinetics. On the other hand, the fast diffusion kinetics of protons, especially in the hydrated media is the primary candidate that can explain the observed high C-rate operations.

For quantitative assessments, transient electrochemical measurements, such as galvanostatic intermittent titration technique (GITT) or electrochemical impedance spectroscopy (EIS) can provide valuable information regarding the diffusivities of the charge carriers in the systems

under consideration. Recently in our work, we performed GITT to measure the diffusion coefficient for the charge carrier in the Zn/VPO₄F system, employing an ionic-liquid electrolyte with trace levels of water present in it; the diffusion coefficient obtained was in the order of 10⁻¹² cm² s⁻¹ that is comparable to the reported diffusion coefficient of Li ions in VPO₄F host, and thus matches with the diffusion of the monovalent protons rather than the Zn ions present in the electrolyte.⁹ This was further verified through an elemental analysis after acid washing, indicating a near absence of Zn species in the fully discharged cathode. Therefore, when the derived diffusivities or activation energies for the diffusion fall within the values typically observed for monovalent cation diffusion, a vetting process is necessary to verify the involvement of Zn ions in the cathode redox reactions, especially those at high C rates.

Finally, in the context of the MV-ion insertion reaction kinetics in solid-state hosts with nonaqueous electrolytes, it is frequently observed that the presence of water as an additive (wet electrolyte) leads to an apparent improvement of the MV-ion insertion kinetics. As an underlying reason, it is commonly argued that the coordination of H₂O molecules to the MV-ion within the electrolyte helps to minimize the desolvation energy barrier at the electrode-electrolyte interface.²⁴ On the other hand, the improved performance of such systems in the presence of water can also be explained by a fundamental change in the insertion chemistry, from pure MV-ion insertion in the dry electrolyte to a facile insertion of protons originating from the water in a wet electrolyte. Hence, in addressing the role of water as an electrolyte additive, two issues must be considered.

First, the issue of the desolvation energy of Zn ion must be assessed. According to recent *in situ* studies based on extended X-ray absorption fine structure spectroscopy (EXAFS), Zn ion adopts the octahedral coordination in both water and acetonitrile (ACN), which is commonly

used as the solvent of choice in nonaqueous ZIBs.^{25,26} Furthermore, previous calorimetric studies revealed that the $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ ($\text{Zn}(\text{Otf})_2$, a common ZIB electrolyte salt) solvation is more endothermic in water, compared to ACN (respectively, -79.9 and -54.8 kJ.mol⁻¹).²⁷ Therefore, one may expect that the desolvation of the hexanitride-Zn complex to be chemically more facile than the hexaaquo analogue, opposite to what is commonly believed.

Second is the issue of the Zn-ion adsorption energy barrier at the electrode-electrolyte interface. There have been speculations that the presence of water as the additive can lower the adsorption energy barrier of the Zn ions to the cathode surface.²⁴ Previously, our work has shown that the transfer of the Mg^{2+} ions from the all-phenyl complex (APC) electrolyte to the hexagonal $\text{K}_x\text{W}_3\text{O}_9$ host involves a rate-limiting electro-adsorption step, from combined cyclic voltammetry and EIS techniques (Figure 4).²⁸ The slow electro-adsorption step, which is a capacitive process from the EIS perspective, adds ~ 300 mV overpotential burden to the charge-discharge processes. While this overpotential was observed for the insertion of Mg^{2+} ions from APC electrolyte that contains a complex binuclear Mg^{2+} ions, it was absent from the Zn-ion electrochemical insertion from the $\text{Zn}(\text{Otf})_2/\text{ACN}$ electrolyte into the $\text{K}_x\text{W}_3\text{O}_9$ host. Thus, we anticipate that the extent of such interfacial charge-transfer resistance to be small in the electrolytes that are based on the dissolution of simple salts, such as the one commonly used in ZIBs. As a characterization technique, EIS has the adequate sensitivity to discriminate between the electro-adsorption (capacitive nature) rate-limiting step at the electrode-electrolyte interface and the MV-ion solid-state diffusion/electroplating (Warburg/inductive nature), respectively, at the cathode and the metallic anode. Therefore, the prevalence of desolvation overpotential at the cathode-electrolyte interface as the rate-limiting-step should be first demonstrated with EIS

before the addition of water to a nonaqueous electrolyte could be claimed as a remedy, which can interfere with the MV-ion diffusion through the proton rivals.

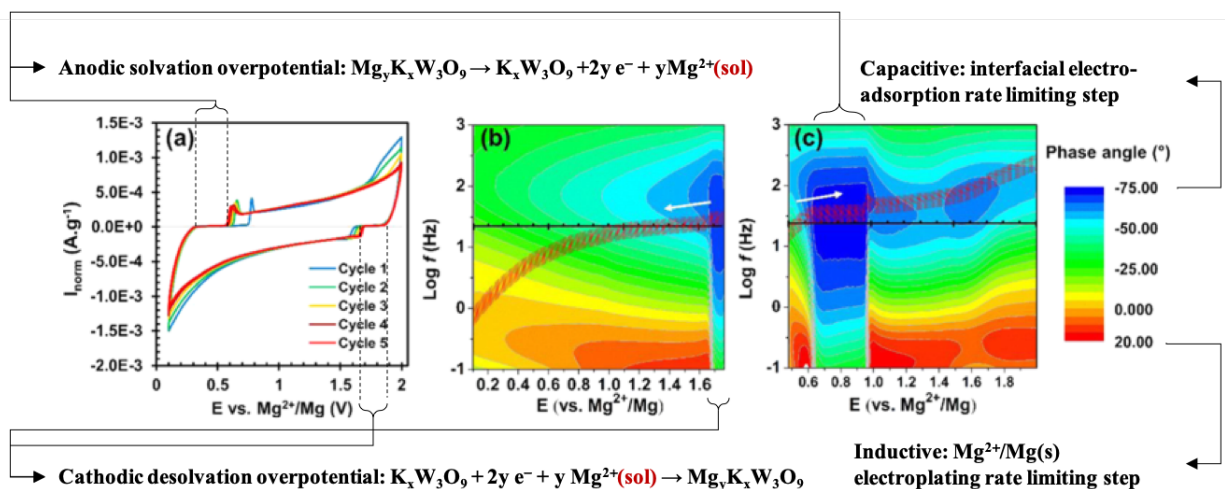


Figure 4. (a) Cyclic voltammetry of Mg-ion insertion/extraction into/from $\text{K}_x\text{W}_3\text{O}_9$, and staircase potentiostatic electrochemical impedance spectroscopy (SPEIS) contour plots obtained from (b) the cathodic and (c) anodic scans of the $\text{Mg}|\text{K}_x\text{W}_3\text{O}_9$ cell with the impedance complex phase angle (ϕ) represented as color-coded contours. The interfacial Mg^{2+} (de)solvation overpotential ranges are indicated with negative ϕ in panels (b) and (c). Reproduced with permission from ref 28. Copyright 2019 The American Chemical Society.

Other MV-ion systems (Mg-, Ca-, and Al-ion). From a viewpoint of energy density, batteries based on other MV metals, such as Mg, Ca, or Al, as the anode are more sought after because of their lower reduction potential compared to that of Zn, leading to higher energy density batteries. Unlike in a Zn-ion or Al-ion battery setup, however, a fair evaluation of oxide cathode hosts in a traditional two-electrode Mg- or Ca- battery setup is difficult due to the lack of suitable nonaqueous electrolytes. Hence, numerous studies on oxide hosts have been limited to electrochemical investigations in a three-electrode system with a reference electrode and a non-insertion type counter electrode like an activated carbon or a Pt electrode.^{3,29}

Alike various publications on aqueous ZIBs, recent studies on oxide hosts in other MV-ion systems have demonstrated that water in the electrolyte acts as the source of protons that insert into those cathode hosts by performing the analytical techniques that consider the thermodynamic and kinetic aspects as discussed earlier. Sa et al. in their investigation of α -V₂O₅ in a Mg-ion system with a wet electrolyte clarified that proton insertion accounts for the majority of the discharge capacity through various characterization techniques, including ¹H-NMR spectroscopy.³⁰ Similarly, Hyung et al. in their investigation of K_{0.31}MnO₂·0.25H₂O (birnessite structure) in an aqueous Ca-ion system determined that a significant amount of the discharge capacity is due to the insertion of hydronium ions by combined analyses of electrochemical and ICP elemental characterizations.³¹ Furthermore, Zhao et al. in their work on α -V₂O₅ in an aqueous Al-ion system elucidated that reversible proton intercalation/deintercalation chemistry is responsible for the observed electrochemical capacities.³² Also, their discovery of a water-soluble product containing aluminum that forms on the surface of the cathode after discharge again highlights the importance of conducting multiple analytical techniques to unambiguously determine the charge-carrier ion species.

Because of the huge charge density of Al ions which stems from their trivalent positive charge, insertion of protons into any cathode hosts would be greatly favored over Al ions, even more so than the divalent ions like Mg, Ca, and Zn ions. In addition, due to the high charge density of Al ions (*i.e.*, strong Lewis acids), they form the [Al(H₂O)₆]³⁺ hexaaquo complexes (weak Brønsted acid, pK_a = 4.97) in the aqueous electrolyte, which would act as the latent source of protons during the electrochemical discharge as suggested by Kim et al. in their recent study on proton insertion into anatase TiO₂.³³ Based on the cyclic voltammetry results, the authors claim that the hexaaquo complexes of Zn and Mn, respectively, in ZnCl₂ and MnCl₂ electrolytes act as the

latent proton donors alike the hexaaquo aluminum complexes, which may explain the generation of protons for insertion in aqueous ZIBs.

As emphasized throughout this perspective, water is an obvious source for proton insertion in MV-ion chemistries. However, even in strictly nonaqueous electrolytes, proton insertion into cathode hosts may be observed due to electrolyte decomposition reactions, as demonstrated by Verrelli et al.³⁴ *Ex situ* synchrotron XRD analyses of α -V₂O₅ cycled in various nonaqueous Mg- and Ca-ion electrolytes at 100 °C revealed that although electrochemical capacities with reversible changes in the crystal structure of α -V₂O₅ were observed, the measured electron charge transfer was not due to Mg- or Ca-ion insertion/extraction to/from the α -V₂O₅ structure. The phase after discharge was determined to be the Häggite phase (H_xV₄O₁₀) from their crystal structure refinement, which indicates that the abundant C-H bonds in the organic solvent of the electrolyte supplied the protons for insertion as it was being oxidized. Such decomposition reactions could also occur on the counter electrode during discharge, liberating protons into the system. Elevating the temperature of the system to improve the solid-state diffusion of MV-ions in a host structure seems logical, but it necessitates in-depth characterizations to unequivocally confirm that the observed capacity is not due to any electrolyte decomposition reaction, which may further lead to proton insertion reactions.

In pursuit of alternative energy storage technologies, considerable effort has been made toward MV-ion chemistry analogous to the state-of-the-art Li-ion chemistry. Despite the research efforts over decades, a noticeable breakthrough in the development of MV-ion batteries is yet to be observed due to two major problems; the lack of suitable electrolytes and more importantly, the sluggish solid-state diffusion kinetics of MV-ions. The latter issue became more pronounced as the focus of cathode research shifted from exceptional chalcogenide hosts, such as the Chevrel

phase, to oxide hosts to improve the energy density. The problem of slow diffusion of MV ions in oxide hosts seemed to have been partly solved by the incorporation of water into the electrolyte either as a solvent or as an additive. However, as revealed in numerous recent literature, the attractive electrochemical rate performance emanates from the change in the charge-carrier ion species from MV ions to protons that originate from water in the electrolyte. Such transition in the charge-carrier ion species to protons has also been observed in special cases of nonaqueous MV-ion systems, with protons being liberated oxidatively from the organic solvents, indicating that after all, the facile MV-ion insertion chemistry with solid-state hosts may not be achievable as many have believed it could be.

The importance of gaining a proper understanding of the underlying chemistry of a battery system cannot be stressed enough. For instance, if a truly stable oxide cathode host for Zn ions is discovered, then its application could be extended to other MV-ion batteries to achieve higher energy density. Also, the proper understanding would guide the future direction in the research. For example, having elucidated that the dominant charge carrier in the rechargeable aqueous Zn batteries is protons, more focus should be placed to effectively mitigate the detrimental effect of the zinc salt byproduct on the long-term cell reliability to bring one step closer to being a practical energy storage system. Thus, we recommend that future investigations of MV-ion systems to be conducted in a comprehensive manner, employing multiple characterization techniques, including: (i) crystallography (XRD, neutron diffraction, and SAED) to probe the increase in atomic-site occupancy due to charge-carrier insertion, (ii) spectroscopy (*e.g.*, ICP-OES, SEM/TEM-EDX, XPS and *etc.*) for elemental analysis while being cautious of any interference from external MV-ion containing species, and (iii) transient electrochemical characterizations (GITT and EIS) to assess whether MV ions act as charge carriers or not. If MV

ions can be ruled out as charge carriers or the amount involved is not sufficient to explain the observed electrochemical capacities, spectroscopic techniques such as proton or deuteron solid-state NMR can be applied to discern whether protons act as charge carriers.

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Selected Quotes

Identification of the true charge carrier ion species lies at the heart of the energy storage systems operating based on the insertion chemistry. While the insertion of Li- or Na-ions is expected, respectively, in Li-ion and Na-ion batteries, this is not necessarily the case with MIBs due to the possibility of side-reactions resulting in the introduction of protons into the system.

The assessment of bulk Zn-ion concentration within the cathode host should be meticulously probed with bulk-specific characterization techniques. Often, multiple orthogonal analytical techniques should be combined for a conclusive identification of the actual charge carrier in MIBs.

The limited solid-state diffusivity of MV ions would translate to a low rate capability of a specific host. Therefore, a simple rate capability test spanning to high C rates that exhibits excellent performance would provide a clue in that protons might be the charge carrier ions as Zn-ion diffusion will be too sluggish to compensate such high electronic current.

As emphasized throughout this perspective, water is an obvious source for proton insertion in MV-ion chemistries. However, even in strictly nonaqueous electrolytes proton insertion into cathode hosts may be observed due to electrolyte decomposition reactions.

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REFERENCES

- (1) Manthiram, A. A Reflection on Lithium-Ion Battery Cathode Chemistry. *Nat. Commun.* **2020**, *11*, 1550.

- (2) Grey, C. P.; Tarascon, J. M. Sustainability and *In Situ* Monitoring in Battery Development. *Nat. Mater.* **2017**, *16*, 45–56.
- (3) Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G. Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chem. Rev.* **2017**, *117*, 4287–4341.
- (4) Levi, E.; Levi, M. D.; Chasid, O.; Aurbach, D. A Review on the Problems of the Solid State Ions Diffusion in Cathodes for Rechargeable Mg Batteries. *J. Electroceram.* **2009**, *22*, 13–19.
- (5) Novák, P.; Imhof, R.; Haas, O. Magnesium Insertion Electrodes for Rechargeable Nonaqueous Batteries — a Competitive Alternative to Lithium? *Electrochim. Acta* **1999**, *45*, 351–367.
- (6) Knight, J. C.; Therese, S.; Manthiram, A. On the Utility of Spinel Oxide Hosts for Magnesium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 22953–22961.
- (7) Knight, J. C.; Therese, S.; Manthiram, A. Chemical Extraction of Zn from ZnMn₂O₄-Based Spinel. *J. Mater. Chem. A* **2015**, *3*, 21077–21082.
- (8) Konarov, A.; Voronina, N.; Jo, J. H.; Bakenov, Z.; Sun, Y.-K.; Myung, S.-T. Present and Future Perspective on Electrode Materials for Rechargeable Zinc-Ion Batteries. *ACS Energy Lett.* **2018**, *3*, 2620–2640.
- (9) Yaghoobnejad Asl, H.; Sharma, S.; Manthiram, A. The Critical Effect of Water Content in the Electrolyte on the Reversible Electrochemical Performance of Zn–VPO₄F Cells. *J. Mater. Chem. A* **2020**, *8*, 8262–8267.

- (10) Park, M. J.; Manthiram, A. Unveiling the Charge Storage Mechanism in Nonaqueous and Aqueous Zn/Na₃V₂(PO₄)₂F₃ Batteries. *ACS Appl. Energy Mater.* **2020**, *3*, 5015–5023.
- (11) Marcus, Y. Volumes of Aqueous Hydrogen and Hydroxide Ions at 0 to 200 °C. *J. Chem. Phys.* **2012**, *137*, 154501.
- (12) Paik, Y.; Bowden, W.; Richards, T.; Sirotina, R.; Grey, C. P. ²H MAS NMR and SPECS Studies of γ -MnO₂ Reduction in Zinc Alkaline Primary Batteries. *J. Electrochem. Soc.* **2004**, *151*, A998–A1011.
- (13) Lee, B.; Yoon, C. S.; Lee, H. R.; Chung, K. Y.; Cho, B. W.; Oh, S. H. Electrochemically-Induced Reversible Transition from the Tunneled to Layered Polymorphs of Manganese Dioxide. *Sci. Rep.* **2014**, *4*, 6066.
- (14) Park, M. J.; Yaghoobnejad Asl, H.; Therese, S.; Manthiram, A. Structural Impact of Zn-Insertion into Monoclinic V₂(PO₄)₃: Implications for Zn-Ion Batteries. *J. Mater. Chem. A* **2019**, *7*, 7159–7167.
- (15) Wang, F.; Hu, E.; Sun, W.; Gao, T.; Ji, X.; Fan, X.; Han, F.; Yang, X.-Q.; Xu, K.; Wang, C. A Rechargeable Aqueous Zn²⁺-Battery with High Power Density and a Long Cycle-Life. *Energy Environ. Sci.* **2018**, *11*, 3168–3175.
- (16) Pan, H.; Shao, Y.; Yan, P.; Cheng, Y.; Han, K. S.; Nie, Z.; Wang, C.; Yang, J.; Li, X.; Bhattacharya, P.; Mueller, K. T.; Liu, J. Reversible Aqueous Zinc/Manganese Oxide Energy Storage from Conversion Reactions. *Nat. Energy* **2016**, *1*, 16039.

- (17) Oberholzer, P.; Tervoort, E.; Bouzid, A.; Pasquarello, A.; Kundu, D. Oxide versus Nonoxide Cathode Materials for Aqueous Zn Batteries: An Insight into the Charge Storage Mechanism and Consequences Thereof. *ACS Appl. Mater. Interfaces* **2019**, *11*, 674–682.
- (18) Zhang, L.; Rodríguez-Pérez, I. A.; Jiang, H.; Zhang, C.; Leonard, D. P.; Guo, Q.; Wang, W.; Han, S.; Wang, L.; Ji, X. ZnCl₂ “Water-in-Salt” Electrolyte Transforms the Performance of Vanadium Oxide as a Zn Battery Cathode. *Adv. Funct. Mater.* **2019**, *29*, 1902653.
- (19) Wei, T.; Li, Q.; Yang, G.; Wang, C. Pseudo-Zn–Air and Zn-Ion Intercalation Dual Mechanisms to Realize High-Areal Capacitance and Long-Life Energy Storage in Aqueous Zn Battery. *Adv. Energy Mater.* **2019**, *9*, 1901480.
- (20) Liu, W.; Dong, L.; Jiang, B.; Huang, Y.; Wang, X.; Xu, C.; Kang, Z.; Mou, J.; Kang, F. Layered Vanadium Oxides with Proton and Zinc Ion Insertion for Zinc Ion Batteries. *Electrochim. Acta* **2019**, *320*, 134565.
- (21) Li, L.; Hoang, T. K. A.; Zhi, J.; Han, M.; Li, S.; Chen, P. Functioning Mechanism of the Secondary Aqueous Zn-β-MnO₂ Battery. *ACS Appl. Mater. Interfaces* **2020**, *12*, 12834–12846.
- (22) Wan, F.; Zhang, L.; Dai, X.; Wang, X.; Niu, Z.; Chen, J. Aqueous Rechargeable Zinc/Sodium Vanadate Batteries with Enhanced Performance from Simultaneous Insertion of Dual Carriers. *Nat. Commun.* **2018**, *9*, 1656.
- (23) Tomaszewska, A.; Chu, Z.; Feng, X.; O’Kane, S.; Liu, X.; Chen, J.; Ji, C.; Endler, E.; Li, R.; Liu, L.; Li, Y.; Zheng, S.; Vetterlein, S.; Gao, M.; Du, J.; Parkes, M.; Ouyang, M.; Marinescu, M.; Offer, G.; Wu, B. Lithium-Ion Battery Fast Charging: A Review. *eTransportation* **2019**, *1*, 100011.

- (24) Kundu, D.; Vajargah, S. H.; Wan, L.; Adams, B.; Prendergast, D.; Nazar, L. F. Aqueous vs. Nonaqueous Zn-Ion Batteries: Consequences of the Desolvation Penalty at the Interface. *Energy Environ. Sci.* **2018**, *11*, 881–892.
- (25) D'Angelo, P.; Barone, V.; Chillemi, G.; Sanna, N.; Meyer-Klaucke, W.; Pavel, N. V. Hydrogen and Higher Shell Contributions in Zn^{2+} , Ni^{2+} , and Co^{2+} Aqueous Solutions: An X-Ray Absorption Fine Structure and Molecular Dynamics Study. *J. Am. Chem. Soc.* **2002**, *124*, 1958–1967.
- (26) D'Angelo, P.; Migliorati, V. Solvation Structure of Zn^{2+} and Cu^{2+} Ions in Acetonitrile: A Combined EXAFS and XANES Study. *J. Phys. Chem. B* **2015**, *119*, 4061–4067.
- (27) Hedwig, G. R.; Parker, A. J. Solvation of Ions. XXIII. Enthalpies of Transfer of Some Divalent Metal Ions from Water to Nonaqueous Solvents. *J. Am. Chem. Soc.* **1974**, *96*, 6589–6593.
- (28) Yaghoobnejad Asl, H.; Manthiram, A. Mass Transfer of Divalent Ions in an Oxide Host: Comparison of Mg^{2+} and Zn^{2+} Diffusion in Hexagonal $\text{K}_x\text{W}_3\text{O}_9$ Bronze. *Chem. Mater.* **2019**, *31*, 2296–2307.
- (29) Arroyo-de Dompablo, M. E.; Ponrouch, A.; Johansson, P.; Palacín, M. R. Achievements, Challenges, and Prospects of Calcium Batteries. *Chem. Rev.* **2019**. <https://doi.org/10.1021/acs.chemrev.9b00339>.
- (30) Sa, N.; Wang, H.; Proffit, D. L.; Lipson, A. L.; Key, B.; Liu, M.; Feng, Z.; Fister, T. T.; Ren, Y.; Sun, C.-J.; Vaughey, J. T.; Fenter, P. A.; Persson, K. A.; Burrell, A. K. Is Alpha- V_2O_5 a Cathode Material for Mg Insertion Batteries? *J. Power Sources* **2016**, *323*, 44–50.

- (31) Hyoungh, J.; Heo, J. W.; Hong, S.-T. Investigation of Electrochemical Calcium-Ion Energy Storage Mechanism in Potassium Birnessite. *J. Power Sources* **2018**, *390*, 127–133.
- (32) Zhao, Q.; Liu, L.; Yin, J.; Zheng, J.; Zhang, D.; Chen, J.; Archer, L. A. Proton Intercalation/De-Intercalation Dynamics in Vanadium Oxides for Aqueous Aluminum Electrochemical Cells. *Angew. Chem., Int. Ed.* **2020**, *59*, 3048–3052.
- (33) Kim, Y.-S.; Harris, K. D.; Limoges, B.; Balland, V. On the Unsuspected Role of Multivalent Metal Ions on the Charge Storage of a Metal Oxide Electrode in Mild Aqueous Electrolytes. *Chem. Sci.* **2019**, *10*, 8752–8763.
- (34) Verrelli, R.; Black, A. P.; Pattanathummasid, C.; Tchitcheкова, D. S.; Ponrouch, A.; Oró-Solé, J.; Frontera, C.; Bardé, F.; Rozier, P.; Palacín, M. R. On the Strange Case of Divalent Ions Intercalation in V_2O_5 . *J. Power Sources* **2018**, *407*, 162–172.