Recent Advances in Aqueous Batteries with Nonmetal Cations as Charge Carriers

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During the past decades, aqueous rechargeable batteries have been receiving much attention on account of the merits of cost efficiency, high safety, and environmental benignity. Compared to metal-ions (such as Li⁺, Na⁺, K⁺, Mg²⁺, Zn²⁺, Al³⁺ etc.) as charge carriers in aqueous ion batteries, nonmetal charge carriers not only form covalent–ionic bonds in framework, but also act as reversible redox centers. Moreover, nonmetal charge carriers have advantages of low costs and high volumetric energy densities. Recently, huge efforts have been contributed to performance improvements in aqueous nonmetal cation batteries via a variety of methods. Herein, the recently reported cathode, anode materials, and newly proposed electrochemical reaction mechanisms for rechargeable aqueous nonmetal cation batteries are reviewed.

1. Introduction

Aqueous-ion batteries (AIBs) are promising candidates for grid storage systems as their advantages of low-cost, environmentally friendliness, and high-level safety. Compared to the organic electrolytes in traditional alkali-metal-ion batteries, aqueous electrolytes always possess higher ionic conductivity. Moreover, they are not sensitive to air humidity, therefore, AIBs can be assembled in air which may reduce the manufacturing costs.[1,2] AIBs has a long history, and it could be traced back to 1859 when Planté proposed a lead-acid battery, where lead dioxide served as the cathode, lead metal as the anode and sulfuric acid as the electrolyte. Until today, this type of lead-acid batteries still retains a market share, and it exhibits an energy density of 30–40 Wh kg⁻¹.

In 1901, Waldemar Jungner developed a nickel–cadmium (Ni–Cd) rechargeable battery, which could deliver a higher energy density up to 60 Wh kg⁻¹. However, in modern days, the energy density of traditional AIBs cannot satisfy the demand for vehicle. In 1973, the fourth Middle East War broke out and caused the Oil Crisis, which pushed United States Government to fund researches relevant to electric vehicles. Finally, Stanley Whittingham proposed a novel lithium-ion battery that composed of Li metal as anode and TiS₂ as cathode in 1978.[3] During operation, Li ion could be reversibly (de)intercalated into (from) TiS₂, which has a much higher energy density than AIBs, and the reaction mechanisms are totally different from traditional battery systems. However, unsafety issues stopped its stepping into market. Two years later, John B. Goodenough discovered a high-potential cathode material-LiCoO₂, in which Li⁺ was stored between layers of structure.[4] In 1991, lithium-ion battery (LIB) was first commercialized by Sony Company after Akira Yoshino paired LiCoO₂ with graphite as anodes, which was much safer than batteries with Li metal as anodes. Since then, LIB triggered a global wave of research on rechargeable batteries based on metal ion shuttling. However, metal ion batteries with nonaqueous electrolytes still have safety issues.[5] Searching for safer and higher energy density batteries is still a big challenge. Batteries with aqueous solutions as electrolytes are hopefully good choices. In 1994, the first aqueous rocking-chair LIB (ALIB) was proposed by Dahn et al., however its energy density and cycling life are not satisfying.[6] In 2010, Xia and co-workers successfully addressed the issue of cycling stability of ALIB, and Wang’s group developed the water-in-salts electrolyte (WISEs) to enlarge voltage window of electrolyte in 2015.[7,8] which arouse researchers’ interests on aqueous metal-ion batteries again. During the past decades, much focus has shifted to Na⁺ and K⁺ batteries due to their high natural abundance and low cost.[9–11] And aqueous multivalent metal-ion batteries (Al³⁺, Zn²⁺, Ca²⁺, Mg²⁺) also received much more attention as they could transfer two or three electrons per ion and perform higher volumetric energy density (Scheme 1).[12–15]

As introduced above, batteries using metal-ions as charge carriers have been studied a lot, however, nonmetal cation batteries received little attention.[16–19] Nevertheless, nonmetal charge carriers have advantages of low-cost and sustainability compared to the reported metal ions. For example, protons are widely used charge carriers in nonmetal cation batteries, and there are only low cost contains of abundant in H₂O and...
H₂SO₄, who supply protons.[20–23] From this aspect, aqueous nonmetal cation batteries are competitive candidates for inexpensive energy storage and grid-level stationary applications.[21,24,25] Generally, it is the charge carrier which is likely to dictate the nature of the battery chemistries.[26] Different properties of charge carriers result in different types of bonding, which affect electrochemical performance. It is regarded to be ionic bonding between metal-ion charge carriers and host materials, while it is hydrogen bonding in nonmetal cation charge carrier batteries. Therefore, non-metal cation charge carrier batteries may achieve good electrochemical performance due to their weak bonding and small radius. Furthermore, the development and study on aqueous nonmetal cation charge carrier batteries may expand views on reaction mechanisms inner battery and enrich knowledges on battery chemistry.

Herein, we systematically review the latest research progresses in electrode materials and newly proposed electrochemical reaction mechanisms in aqueous nonmetal cation charge carrier batteries including proton-, hydronium-, and ammonium-ion batteries. We also highlight the challenges and prospects in AIBs with nonmetal ion charge carriers toward future grid energy storage.

2. Aqueous Batteries with Nonmetal Cations as Charge Carriers

2.1. Proton as the Charge Carrier

Proton has the lightest ionic weight and smallest size among charge carriers with a radius of ≈0.89 or ≈2.1 fm.[27] The application of protons as charge carriers in AIBs is not a new concept and it could be traced to the first lead-acid battery invented by Planté, where the protons converted PbO₂ to PbSO₄.[28] However, lead-acid battery exhibited a low specific power density, poor cycle life, and low Coulombic efficiency. In recent years, proton has been revived as it could be applied as an intriguing ionic charge carrier in proton batteries.

2.1.1. Proton–Host Cathode

Recently, various kinds of materials including Prussian blue analogues, organic materials, and metal oxides were reported as cathode materials in aqueous proton batteries. In the following section, we will introduce the latest advances in these proton–host cathode materials.

Prussian Blue Analogues: Prussian blue analogues (PBAs), as a classification of metal-organic frameworks, have a favorable crystallographic hexagonal cubic structure with a large lattice parameter of 10 Å, facilitating the diffusion of guest ions. Moreover, they exhibit high structural stability against large volume changes. Better structural stability makes PBAs better cathode materials for rechargeable batteries.[29] PBAs as cathode materials have been widely studied in various of AIBs. Generally, only a single species of transitional metal in PBAs participates redox reactions, which limited capacity delivered.[30,31] To address this issue, Chung et al. synthesized V/Fe PBAs via a simple co-precipitation method.[29] By adjusting the pH and molar ratios of the precursor solutions, the resulted materials exhibited a good crystallinity and satisfying performance (Figure 1a,b). Ex situ test methods disclosed that the improved performance of the as-prepared material was ascribed to the multiple-electron redox reactions of V and Fe ions. Ji’s group studied the proton storage behavior of Cu[Fe(CN)]₆·0.63□·0.37 3.4H₂O(CuFe-TBA).[32] At an extra-high current density of 380 A g⁻¹, the as-prepared electrode exhibited half of the capacity acquired at 1C (1C = 95 mA g⁻¹). Amazingly, CuFe-TBA could exhibit a retention rate of 60% of the initial capacity after 0.73 million cycles at 500C. Recently, Ji et al. also demonstrated NiFe-TBA as a proton-host cathode (Figure 1c), which exhibited a capacity of around 65 mAh g⁻¹ and achieved a cycling life of 1000 cycles.[33] By virtue of Grotthuss mechanism (introduced in the following part), it also showed a fast proton conduction under low-temperature (50% of theoretical capacity at 50C, −40 °C). More recently, they reported an aqueous proton battery, which worked well below −78 °C via a 9.5 m H₃PO₄ electrolyte, where CuFe-PBA as a cathode exhibited a good electrochemical performance at different temperatures.

Organic Materials: Organic electrode materials were also applied as cathodes in AIBs due to their “large voids” and “soft” structure, in which large and highly charged cations can transport easily.[34] Charge carriers were stored in them through “ion-coordination” mechanisms.[35] This process will not cause volume changes during oxidation/reduction reactions, which is different from the intercalation/deintercalation mechanisms often accompanied by large volume changes.

Marcilla et al. used catechol as the bioinspired redox core redox-active polymers (RAPs) to coordinate with H⁺.[36] The as-prepared poly(dopamine acrylamide) (P(DA)₁₀₀) only exhibited a reversible capacity of 190 mAh g⁻¹, while the newly formed P(4VC)₁₀₀ could exhibit a capacity of 330 mAh g⁻¹ after 4-vinylcatechol (4VC) substituted the DA repeating units. In Sjödin et al.’s study, an aqueous conducting redox-polymer-based proton battery was built, where 0.5 m H₂SO₄(aq) was used as electrolyte, benzoquinone/hydroquinone (Q/H₂Q) and naphthoquinone/naphthohydroquinone (NQ/NQH₂) as cathode and anode material (Figure 1d).[36] The cathode redox activity relied on the two-electron two-proton (2e₂H) redox process of the pendant. During oxidation process, the cathode material was converted to QH₂ with a discharge capacity of ≈80 mAh g⁻¹ at 3C.

Metal Oxide Materials: Metal oxide materials have been demonstrated to be good candidates for AIBs. However, the study on aqueous proton battery is rarely, one reason is that the metal oxide materials can be corroded by strong acid electrolytes. Recently, Archer et al. reported that orthorhombic V₂O₅ supported highly reversible proton insertion/de-insertion reactions in aqueous Al battery.[37] They used various of ex situ characterization methods together with theoretical analysis to disclose the intercalation process of protons into V₂O₅ in
aqueous media. Tarascon et al. synthesized a new protonic iridate phase $\text{H}_3\text{IrO}_4$ with a layered structure after acid leaching of $\text{Li}_3\text{IrO}_4$.\textsuperscript{[38]} It could achieve $\approx 175$ mAh g$^{-1}$ corresponding to 1.7 H$^+$ per Ir, higher than 150 mAh g$^{-1}$ corresponding to 1.5e$^-$ per Ir in nonaqueous electrolyte. The structural transition in different media is displayed in Figure 1f. Kang et al. synthesized a layered tetragonal titanate which was identified by real-space refinement of the pair distribution function (PDF).\textsuperscript{[39]} This newly formed layered structured materials were stabilized by hydronium ions and water molecules located in the interlayer space (Figure 1g), and they exhibited high proton conductivity. In such prepared materials, proton transferred from hydronium ions to the titanate framework, consistent with the Grotthuss-based mechanism. It exhibited a capacity of $\approx 33$ mAh g$^{-1}$ (0.38 H$^+$ per formula unit) in 25–30 s, demonstrated fast reaction mechanisms. High areal capacity is important for high energy density storage applications. To achieve this, Su et al. made a very thick MoO$_3$ composite electrode with a mass loading up to 90.48 mg cm$^{-2}$ (Figure 1h) and areal capacity of 22.4 mAh cm$^{-2}$.\textsuperscript{[40]} This thick electrodes proton battery provided new insights into high areal capacity batteries.

### 2.1.2. Proton–Host Anode

Anode materials have been the performance-limiting part for aqueous batteries, and for proton batteries as well. The studies...
on anode materials are vital for achieving high-performance aqueous proton batteries.

Organic materials are one kind of the most studied anode materials. Quinones materials are particularly attractive due to their high specific capacity, fast 2e⁻/C⁰ redox reactions and structural diversity.[35] Yao et al. reported pyrene-4,5,9,10-tetraone (PTO, red structure in Figure 2a) as stable anode materials for long cycle life AIBs.[41] It has a high theoretical specific capacity (409 mAh g⁻¹) and low reduction potential (0.5 V versus SHE). And practically, PTO exhibited a capacity of 395 mAh g⁻¹, which was higher than that of AC and Pb (Figure 2b). Moreover, the acidic cell exhibited an energy density of 76 Wh kg⁻¹/161Wh L⁻¹ and a cycle life of more than 1,500 cycles (>1,200 h) without obvious decreasing in capacity. Furthermore, quinone anodes were paired with cathode materials, spinel lithium manganese oxide and Ni(OH)₂, and working well with aqueous electrolytes. Recently, alloxazine (ALO) was studied owning to rapid diffusion of proton and pseudocapacitive character. And the full cell obtained an energy density up to 110 Wh kg⁻¹ at a specific power density of 1650 W kg⁻¹ under −60 °C, showing a very promising low temperature potential application.[42]

Apart from organic materials, inorganic materials have also been demonstrated to be good candidates for proton storage. Yan et al. reported MoO₃ as an anode for hydrogen ion storage with a specific capacity of 88 mAh g⁻¹ at 100°C.[43] The reaction mechanisms were verified by using ex situ X-ray diffraction (XRD), reflection electron energy loss spectroscopy (REELS) and photoelectron spectroscopy (XPS) (Figure 2c–e). In recent studies, MoO₃ was also reported as anode materials in aqueous proton batteries. WO₃ is another widely studied anode material.

Figure 2. a,b) PTO structure and its charge/discharge profile. Reproduced with permission.[41] Copyright 2017, Springer Nature. c) Ex situ Mo 3d XPS spectra. d) Charge/discharge profile at 5C. Reproduced with permission.[43] Copyright 2018, Wiley-VCH GmbH. e) Optical images of Cu and Zn anodes in initial and cycled states. f) Ragone plots of different batteries. g) Cycling performance at 20C. Reproduced with permission.[49] Copyright 2019, Wiley-VCH GmbH.
in aqueous proton batteries and supercapacitor.\textsuperscript{[44–46]} Ji et al. studied the unique proton insertion mechanism of \( \text{WO}_3 \cdot 0.6\text{H}_2\text{O} \), which is introduced in the next section.\textsuperscript{[47]}

Metal (such as Li, Na, and K) is regarded as one of anodes with the highest theoretical capacity and thus energy density.\textsuperscript{[48]} Similar to that, metal also has the highest theoretical capacity as anode in aqueous batteries. However, it is a huge challenge to use them in acidic aqueous battery systems due to the corrosion of metal. Recently, Zhi et al. used Cu as an anode, which achieved nearly 100% deposition-dissolution.\textsuperscript{[49]} After carefully studied the electrochemical behaviors of Cu both in acidic and mild electrolyte, they found that the deposition/dissolution process could be tuned by protons, as they largely improved the reaction kinetics of Cu. Compared to Zn, Cu anode exhibited dendrite-free morphology with long cycling at high current rate (Figure 2f–h). Paired with CuFe-PBA cathode, the full-cell delivered a power density up to 1830 W kg\(^{-1}\) and long-term cycling stability over 5000 cycles at 20C with a retention of 85.2% (Figure 2i,j). Moreover, a Cu-based fiber-shaped battery was fabricated as a flexible power supply for electronics. This work showed the promising of Cu as an anode in acidic batteries. Apart from these materials, carbon-based materials for hydrogen ion insertion were also studied.\textsuperscript{[50,51]}

2.2. Aqueous Hydronium-Ion Batteries

Protons as charge carriers in alkaline electrolytes have been investigated for a long time, where protons come from ionization of water. Normally, it’s hard to use naked protons as charge carriers in aqueous Brønsted–Lowry acids, instead they might be hydronium ions (\( \text{H}_3\text{O}^+ \)) or other hydrated forms (\( \text{H}_x \text{O}^{+x} \)), as thedehydration energy of \( \text{H}_3\text{O}^+ \) is 11.66 eV, which is too high.\textsuperscript{[52,53]} And the radius of \( \text{H}_3\text{O}^+ \) is 0.148 nm, though it has the smallest hydrated ionic radius (0.282 nm), which facilitates fast ion diffusion in aqueous environment. Ji and co-workers firstly demonstrated that hydronium ions could be reversibly stored in a structure of crystalline 3,4,9,10-pyrenetetracarboxylic dianhydride (PTCD A) (Figure 3a).\textsuperscript{[53]} In that study, they observed reversible lattice expansion during \( \text{H}_3\text{O}^+ \) intercalation through ex situ XRD, which confirmed that the intercalant species is hydronium ion instead of naked proton in 1 M \( \text{H}_2\text{SO}_4 \). It evoked the enthusiasm for constructing hydronium-ion batteries and extended the boundaries of intercalation chemistry for battery. Later on, Wang et al. further broadened the knowledge of hydronium-ion battery chemistry.\textsuperscript{[52]} They reported another hydronium-ion battery, where pyrene-4,5,9,10-tetraone (PTO) used as an anode and graphite felt (GF) as a cathode (Figure 3b). However, the reaction mechanism was totally different from Ji’s work. During the charging process, \( \text{Mn}^{2+} \) in electrolyte would be oxidized to form \( \text{MnO}_2 \) and deposited on GF electrode with formation of \( \text{H}_3\text{O}^+ \) (Equation 1) on the cathode side. Meanwhile, the \( \text{H}_3\text{O}^+ \) in electrolyte would be intercalated into PTO to form hydroquinone (HQ) through the reaction shown in Equation 2 on the anode side. The whole charge/discharge reaction progress was as follows

\[
\text{Mn}^{2+} + 6\text{H}_2\text{O} \leftrightarrow \text{MnO}_2 + 4\text{H}_3\text{O}^+ + 2\text{e}^- \quad (1)
\]

\[
\text{PTO} + 2\text{e}^- + 2\text{H}_3\text{O}^+ \leftrightarrow \text{PTO}^-2\text{H} + 2\text{H}_2\text{O} \quad (2)
\]

![Figure 3. a) Simulated PTCDA unit cell incorporated with two \( \text{H}_3\text{O}^+ \) ions. Reproduced with permission.\textsuperscript{[23]} Copyright 2017, Wiley-VCH GmbH. b) Schematic illustration of working mechanism for the PTO//\text{MnO}_2@GF hydronium-ion battery. Reproduced with permission.\textsuperscript{[52]} Copyright 2020, Springer Nature. c) Schematic illustration of the selective \( \text{H}_3\text{O}^+ \)-intercalation chemistry for WP-MoO_3. Reproduced with permission.\textsuperscript{[54]} Copyright 2021, Wiley-VCH GmbH.](https://www.advancedsciencenews.com)
This new hydronium-ion battery achieved a high energy density (132.6 Wh kg\(^{-1}\)) and supercapacitor-like power density (30.8 W kg\(^{-1}\)), which were approximated to those of aqueous lithium-ion battery.

Generally, pure H\(_3\)O\(^+\) existed in corrosive acidic electrolytes, rather than in mild neutral electrolytes. Zhang et al. demonstrated the feasibility of H\(_3\)O\(^+\) reversible intercalation in MoO\(_3\) by using neutral ZnCl\(_2\) as an electrolyte.\(^{[54]}\) The reason for choosing MoO\(_3\) was that it has a typical layered structure with distorted [MoO\(_6\)] octahedra bilayers bonded by Vander Waals force, which has a theoretical capacity of 372 mAh g\(^{-1}\). They proposed a H\(_3\)O\(^+\)-intercalation chemistry as shown in Figure 3c. The water and proton co-inserted into \(\alpha\)-MoO\(_3\) (WP-MoO\(_3\)), which tackled the issues of low-capacity, poor-rate, and short-life of pristine \(\alpha\)-MoO\(_3\) with Zn\(^{2+}\)-intercalation chemistry. The H\(_2\)O molecules, which were embedded in WP-MoO\(_3\) interlayers, increased the Zn\(^{2+}\) intercalation energy barrier and facilitated H\(_3\)O\(^+\) diffusion within WP-MoO\(_3\) interlayers through Grotthuss mechanism. As a result, WP-MoO\(_3\) exhibited an enhanced specific capacity of 356.8 mAh g\(^{-1}\) and a good stability (83% retention over 1000 cycles). Sun and co-workers also reported that H\(_3\)O\(^+\) could be reversibly stored in alloxazine (ALO) with a mild electrolyte (1 M Mg(NO\(_3\))\(_2\)).\(^{[55]}\) The experimental and DFT calculation analyses showed that Mg\(^{2+}\) ions have catalytic properties, which could promote H\(_3\)O\(^+\) to transfer as a stable complex with reducing ALO.

2.3. Insights on the Proton Insertion Mechanism

As the lightest and smallest ion charge carrier, reaction mechanism on proton insertion/de-insertion processes arouses researchers’ interests. In this part, we will review the studies on reaction mechanisms in this system.

Ji et al. investigated the mechanism of proton storage in WO\(_3\)\(\cdot\)nH\(_2\)O by using the electrochemical quartz crystal microbalance (EQCM) and ex situ XRD. EQCM is a powerful analytical tool for determining the charge carrier in electrodes. By observing mass evolution of an electrode, the transport behavior of lattice water during the (de)-insertion of proton in WO\(_3\) was studied (Figure 4a).\(^{[47]}\) It proved that proton topochemistry in WO\(_3\) hydrate undergoes three stages: proton intercalation accompanied by lattice water dehydrating, naked proton intercalation, and the intercalation of hydronium.

It has been demonstrated that Grotthuss proton conduction takes place in hydrogen-bonding networks.\(^{[48]}\) Recently, Ji et al. established the connection between the Grotthuss proton conduction and redox reaction.\(^{[32]}\) And they demonstrated that the Grotthuss proton conduction could facilitate the redox reactions to enable a good rate capability and long cycle life for batteries (Figure 4b). In this work, Turnbull blue analogue (TBA), Cu[Fe(CN)\(_6\)]\(_{0.63}\)\(\cdot\)□\(_{0.37}\)\(\cdot\)3.4H\(_2\)O (CuFe-PBA), where □ represents a ferricyanide vacancy, was selected as a Faradaic electrode. Synchrotron X-ray and neutron diffraction, together with the first
principles calculations (Figure 4c), demonstrated that the good capacity of CuFe-TBA derives from its contiguous network of hydrogen bonded lattice water, which facilitated Grotthuss proton conduction. This study explored the limits of high rate topotactic battery chemistry and brought new insights into other charge carriers related to Grotthuss conduction.

2.4. Aqueous Ammonium-Ion Battery

Ammonium ion (NH$_4$\(^+\)) is composed of hydrogen and nitrogen, which is abundant in the Earth’s crust. NH$_4$\(^+\) ion has a hydrated ionic size of 3.31 Å, facilitating fast kinetics during charge transfer.\(^{[56]}\) Cui et al. investigated the effects of insertion species (Li\(^+\), Na\(^+\), K\(^+\), NH$_4$\(^+\)) on the electrochemical behavior of KM[Fe(CN)$_6$] (M=Ni and Cu) and demonstrated that NH$_4$\(^+\) could be reversibly intercalated at high rates.\(^{[57]}\) Ji et al. firstly proposed the “rocking-chair” NH$_4$-ion battery, where ammonium Prussian white analogue, (NH$_4$)$_{1.47}$Ni[Fe(CN)$_6$]$_{0.88}$, was cathode, organic solid, 3,4,9,10-perylenetetracarboxylic dimide (PTCDI) was anode, and 1.0 m aqueous (NH$_4$)$_2$SO$_4$ was electrolyte (Figure 5a).\(^{[58]}\) Meaningfully, this work opened a new paradigm for NH$_4$\(^+\)-based energy storage. As such, ammonium ions (NH$_4$\(^+\)) as nonmetal charge carriers developed in recent years, but the development of aqueous ammonium ion batteries (AAIBs) is still in the infancy. Developing suitable cathode and anode materials for AAIBs are the biggest challenge in building high-performance AAIBs.\(^{[59,60]}\)

2.4.1. Cathode Materials

Metal-Oxide Materials: Wang et al. studied urchin-like NH$_4$V$_4$O$_{10}$ anchored on a carbon fiber (CF@NH$_4$V$_4$O$_{10}$) as cathode (Figure 5a). Reproduced with permission.\(^{[54]}\) Copyright 2017, Wiley-VCH GmbH. b) A schematic of the CF@ urchin-like NH$_4$V$_4$O$_{10}$. c) Galvanostatic charge/discharge measurement for CF@NH$_4$V$_4$O$_{10}$. Reproduced with permission.\(^{[24]}\) Copyright 2020, Elsevier. d) Charge/discharge curves of MnO$_2$ electrodes charged and discharged after 40 cycles in different NH$_4$Ac electrolytes. Reproduced with permission.\(^{[61]}\) Copyright 2021, Wiley-VCH GmbH. e) The first three GCD curves of N-CuHCF at 1C. Reproduced with permission.\(^{[67]}\) Copyright 2021, Elsevier.
materials (Figure 5b).[24] Such CF@NH4V4O10 exhibited a high specific discharge capacity of 103 mAh g⁻¹ at 0.1 A g⁻¹ with an initial coulombic efficiency of 99.1%. After 100 cycles, CF@NH4V4O10 could still deliver 85 mAh g⁻¹ with a retention of 82.5% (Figure 5c). Song et al. investigated NH4⁺ storage behavior and reaction mechanism in electrodeposited MnO₂.[61] They found the concentration of electrolyte played an important role which affected the electrochemical performance. In diluted electrolyte, MnO₂ experiences morphology and phase transformations during charge/discharge, and the transformed MnO₂ with layered structure delivered a capacity of 176 mAh g⁻¹ at 0.5 A g⁻¹ and 66 mAh g⁻¹ at 10 A g⁻¹, respectively. MnO₂₄₀ also achieved a capacity retention of 94.7% after 10 000 cycles. However, high concentration electrolytes (8 M NH₄Ac) suppressed the amorphous-crystalline transformation and induce fast capacity fading in MnO₂ electrodes (Figure 5d). Xu et al. introduced layered iron vanadate (FVO) nanosheets as NH₄⁺ storage electrode.[62] Different from Na⁺ and K⁺ intercalation, iron vanadate nanosheets exhibited an improved pseudocapacitance behavior. At a current density of 5 A g⁻¹, FVO could still deliver a specific capacity of 72.5 mAh g⁻¹ after 500 cycles with a retention of 61%.

Interestingly, cation and proton might both insert, or say “co-insertion” into metal-oxide materials during a discharging process in aqueous electrolyte. More recently, Wang et al. reported a reversible H⁺/NH₄⁺ co-insertion/extraction in an aqueous Zn/MnO₂ battery system.[63] The co-insertion of dual cations provided higher capacity and energy density owning to the synergistic effect between dual cations. Combined various ex situ characterization techniques and density functional theory (DFT) calculations, they discovered that the insertion of NH₄⁺ promoted the reversibility of structure evolution and achieved a long cycle life up to 4000 cycles. The nonmetallic ions co-insertion chemistry enriches electrochemical knowledge and broaden the boundary of aqueous-ion batteries.

**Prussian Blue Analogues and Polymer.** Berlin green (BG) was a kind of fully oxidized PBA compounds with a formula of Fe₃[FeII(III)(CN)₆] and Ji’s Group studied NH₄⁺ topotactic chemistry of Berlin Green (BG).[64] They used Prussian white Na₅Fe[Fe(CN)₆]₅ as a cathode and conducted comparative studies on Na⁺ and K⁺ ions storage to highlight the topochemistry of NH₄⁺. The results showed that the retention of capacity is 87% over 4000 cycles for NH₄⁺ battery, much higher than K⁺ (48% over 1000 cycles) and Na⁺ (72% over 1000 cycles) batteries, which implied good structural compatibility and stability between BG framework and NH₄⁺ ions. Xia et al. explored the intercalation of NH₄⁺ into iron hexacyanoferrate (Fe₄[Fe(CN)₆]₀). The NH₄⁺ storage mechanism in Fe₄[Fe(CN)₆]₀ was different from other results, and it is discussed in the next section. It exhibited a very good cycling stability (with a retention of 87.5% over 500 cycles at 1C and 88.9% over 2000 cycles at 3C). And the combination of vanadium with metal organic framework was also studied by Xing et al. In that study, they synthesized novel K-V-Fe Prussian blue analogues nanocubes (PBAs NCs) by using oxalic acid as reducing agent.[65] The K-V-Fe PBAs NCs could deliver a good specific capacity of 92.85 mAh g⁻¹ (at 2 A g⁻¹), excellent cyclability with a retention of 91.4% over 2000 cycles (at 2 A g⁻¹) and outstanding rate capability of 46.2 mAh g⁻¹ at 5 A g⁻¹. The strategy of combining vanadium element with metal organic framework provided a new way to improve the performance for electrochemical energy storage batteries. To improve NH₄⁺ storage property, Zhang et al. studied NH₄⁺-rich copper hexacyanoferrate (N-CuHCF).[67] In aqueous NH₄NO₃ electrolyte, N-CuHCF exhibited an excellent rate performance (60.0 mAh g⁻¹ at 1C, and 59.0 mAh g⁻¹ at 50C) (Figure 5e). And the cycling stability is also remarkable. After 17 000 and 20 000 cycles at 100 and 180C, the capacity retentions were 91.5% and 86.5%, respectively. Characterizations including XRD, FTIR and XPS unveiled that the highly reversible redox reaction was attributed to the stable structure of N-CuHCF, which was based on Fe³⁺/Fe²⁺ and Cu²⁺/Cu⁺ redox couples. In their recent work, they studied the performance of NH₄⁺ intercalation in copper hexacyanoferrate (CuHCF), and there was nearly no capacity fading after 3000 cycles. Moreover, a new NH₄⁺ diffusion mechanism was proposed,[68] which was also discussed in the following section. Wang and co-workers studied NH₄⁺ intercalation in emeraldine salt polyaniline (ES-PANI). In the study, they prepared Cl⁻ doped ES-PANI on the carbon felts through a facile solution method. As-prepared ES-PANI delivered a highly reversible capacity of 160 mAh g⁻¹ at 1 A g⁻¹ and a high-capacity retention of 82% after 100 cycles at 5 A g⁻¹.[69]

### 2.4.2. Anode Materials

On anode materials, Ji’s group synthesized an amorphous titanic acid with the formula of TiO₂.x(OH)₀.₁₀x.₀.₈₂H₂O via a facile solgel method.[59] The titanic acid electrode exhibited reversible storage capacities of 70 and 50 mAh g⁻¹ at 1 A g⁻¹ in 25 m and 1 M AmAc respectively (Figure 6a,b). Ma et al. studied alloxazine (ALO) as another kind of anode material for AAIBs.[70] Owning to the positive pseudocapacitive effect and good diffusion kinetics of NH₄⁺, it exhibited a specific capacity of 120 mAh g⁻¹ at 10 A g⁻¹. Moreover, after paired with Prussian white anodes cathode, the ALO anode in full cell could still deliver a capacity of 110 mAh g⁻¹ without obvious capacity fading over 10, 000 cycles at 5 A g⁻¹. Furthermore, it could exhibit a high energy density of 122.5 Wh kg⁻¹ and power density of 5, 055 W kg⁻¹ (Figure 6c). Zhang et al. studied NH₄⁺ storage behavior in n-type polyimide (PI) (Figure 6d).[71] which exhibited a capacity retention of 69% when current density increased from 0.5 to 10 A g⁻¹. And PTCDI and MoO₃ were also studied as anode materials for NH₄⁺ storage in AAIBs.[25,58,65]

### 2.5. The Hydrogen Bonding Between NH₄⁺ and Host Materials

It is generally accepted that the ionic bonding exists between the metal ion charge carrier and host electrode, while less attention is paid to explore other forms of bonding, like nonionic chemical bonding. Hydrogen bonding is a typical kind of nonionic chemical bonding, which is strong and may play a vital role in affecting the electrochemical performance of electrodes.[26] Ji et al. studied and compared NH₄⁺ and K⁺ storage behaviors in bilayered V₂O₅ electrodes. In that work, they observed a strong H bonding between NH₄⁺ and V₂O₅, and a distinct pseudocapacitive behavior. While it was ionic bonding between K⁺ and V₂O₅.[72] The different types of bonding resulted in the large different
electrochemical performance. The pseudocapacitive behavior of NH₄⁺ storage was much stronger and faster than that of K⁺. Moreover, a monkey-swinging model was proposed, which elaborated rich bonding chemistry among electrode hosts (Figure 7a).

More recently, Zhi et al. explored anode materials and studied the bonding chemistry for NH₄⁺ ion storage.[25] Due to large ionic channels and pseudocapacitive dominated behaviors for fast kinetics, hexagonal molybdenum oxide (h-MoO₃) as an anode for NH₄⁺ storage exhibited a capacity of 32 mAh g⁻¹ at 150 °C (Figure 7b), and an ultralong cycle life over 100,000 cycles with a retention of 94% (Figure 7c). Experimental and first-principal calculation results demonstrated that NH₄⁺ inserted and diffused into MoO₃ framework by forming/breaking of hydrogen bonds in a monkey-swinging model (Figure 7d). This work again highlighted the importance of hydrogen-bonding between ion-electrode in facilitating NH₄⁺ storage.

Xia et al. systematically analyzed the storage performance of NH₄⁺ in iron hexacyanoferrate (Fe₄[Fe(CN)₆]₃).[65] From the experimental and calculation results, a novel intercalation mechanism was discovered. The hydrogen bonds formed between NH₄⁺ and N species of Fe₄[Fe(CN)₆]₃, which promoted the stabilization of the system. Furthermore, the density of states (DOSs) results of Fe₄[Fe(CN)₆]₃ with and without NH₄⁺ insertion demonstrated the formation of covalent bonds, which was responsible for the structural stability of the materials. Zhang et al. also found an interesting hydrogen chemistry in CuHCF when NH₄⁺ inserted.[68] As discussed above, the excellent reversible performance of NH₄⁺ intercalation in PBA s has achieved. To excavate the mechanisms, a joint theoretical and experimental study were applied to analyze the results. And NH₄⁺ diffusion mechanisms in CuHCF was attributed to continuously forming and fracturing of hydrogen bonds (Figure 7e,f). This is fundamental for fast charge transfer and excellent ammonium ion storage.

2.6. Other Aqueous Cation-Ion Battery

Small nonmetal cations, including proton, H₃O⁺, and NH₄⁺, have been certified as competitive charge carriers in AIBs. Though the possibility of nonmetal molecular as charge carrier is less explored. Wang et al. demonstrated that the quaternary alkyl ammonium cations (QAAs) could also be stored in graphite electrode when using organic electrolyte, and inspired by this work, scientists started studying the intercalation of nonmetal molecular into the host material in aqueous environment.[73] Recently, Ji’s group and our group found that methyl viologen (MV²⁺), which is a large molecular dication, could be reversible intercalated into 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), which has been used as electrode host for various ions discussed in the early part (Figure 8a,b).[74] As far as we know, this is the largest charge carrier nonsolvated ever reported for insertion into batteries. The kinetic mechanism of MV²⁺ is attractive and the capacity retention is 60% at an increased current rate of 2000 mA g⁻¹ (Figure 8c). The results showed that the phase of PTCDA was transformed after the insertion of MV²⁺, and the chemical bonding between MV²⁺ and PTCDA was polar covalent bonding. The DFT results showed that the MV²⁺ didn’t compromise the capacity of PTCDA, and so didn’t the rate capability. This work extends the boundary of knowledge of nonmetal charge carrier to molecular and provide a new perspective to consider the ion/electrode nonionic interactions (Figure 8e).
3. Conclusions

The AIBs with nonmetal charge carrier has been reviving and widening the boundary of aqueous rechargeable batteries. As the benefits of wide availability, and negligible cost, aqueous batteries with nonmetal charge carrier have potential to be candidates for future scalable energy storage applications. Although in recent years, this field has attracted much attention, it is still at an early stage compared to aqueous metal-ion batteries. Improvement on the electrochemical performance and energy density are essential to meet the requirements of applications. In this part, we will focus on the challenges of aqueous nonmetal cation batteries and come up with the possible solution ways for high performance aqueous nonmetal cation batteries.

3.1. Comparison of Different Nonmetal Charge Carriers

Considering one energy system, the most important factors are energy density, power density and specific capacity. Among these charge carriers, proton has the smallest size, which makes it...
possible to deliver high power density as its fast kinetics com-
pared to other larger-size nonmetal cations.[42] Moreover, recent
studies have demonstrated that the aqueous proton batteries
could exhibit encouraging performance even at and below
−90 °C, showing promising applications in extremely cold area
and deep space.[36,42,52] NH₄⁺ ions as charge carriers have
received much attention due to the abundant sources and low
cost. It has a small hydrated ionic size and could promote faster
kinetics. Its interaction with the electrode is similar to proton.
However, AAIBs is more stable and easier to obtain long cycling
life, which can be attributed to the friendly environment for
active materials when using mild electrolyte.

3.2. the Issues of Aqueous Nonmetal Cation Batteries

Various types of cathode materials for aqueous nonmetal cation
batteries have been introduced in the preceding part. Though
there are plenty of progresses, some issues still remain.
Owing to the large lattice parameter of 10 Å and high structural
stability, Prussian blue analogues (PBAs) was the most applied
cathode materials for aqueous nonmetal cation batteries, but the
delivered specific capacity is limited (≤100 mAh g⁻¹) thus the
energy density is very low, which could be attributed to the lack-
ing of electrochemical active sites and storage sites. Metal
oxide was widely studied in nonaqueous and aqueous metal-
ion batteries,[75] however, it does not receive as much attention
in aqueous nonmetal cation batteries. And the reported electro-
chemical performance of metal oxides for aqueous nonmetal cat-
ion batteries is far from satisfaction. One reason is that the size of
charge carriers is too large, e.g., H₃O⁺ (larger than Li⁺ and close
to Na⁺), NH₄⁺ (larger ionic radius but small hydrated ionic
radius), which limits the insertion of cations into layers of metal
oxides.[23,53,58] Thus how to solve the issues in metal oxides lay-
ered structures is a big challenge. In these years, organic materi-
als become popular in aqueous ion batteries due to their low cost
and good ability to store different sizes of charge carriers.
Impressively, the performance of organic materials will be super-
ior to others if the repeating units are substituted, one example
is the substituted redox-active polymer could exhibit a capacity of
nearly 330 mAh g⁻¹.[34] However, the dissolution of organic
materials in aqueous solution is a tough issue.

Figure 8. Molecular structures of a) MV²⁺ and b) PTCDA; c) GCD potential profiles of PTCDA; d) EQCM curve recorded during a cathodic CV Scan; e) Simulated MV²⁺ inserted PTCDA and the corresponding XRD patterns. Reproduced with permission.[74] Copyright 2019, Springer Nature.
The investigation upon anode materials mainly focuses on organic materials (such as PTO) and metal oxides (MoO₃, WO₃ et al.). And in proton battery, PTO and MoO₃ anodes exhibited attractive performance, and their full cells exhibit very high-energy density and power density when paired with cathode materials. As discussed above, metal anode might be the best choice due to the highest theoretical capacity, but most metal anodes are not stable in aqueous environment. Though Cu anode applied in aqueous proton battery shed light on the metal anode for aqueous nonmetal cation batteries, to develop stable metal anode is still a tough task.

Apart from the electrode materials, electrolyte also plays an important role in affecting the electrochemical performance. The solvent of aqueous electrolyte is water, which only has a theoretically narrow voltage window (<1.23 V), otherwise the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occur.[76] These reactions limited selection and application theoretically narrow voltage window (≤0.3 V) in aqueous batteries.

As for cathode materials, material choice due to the highest theoretical capacity, but most metal oxides (such as PTO) and metal oxides (MoO₃, WO₃) were used. The reason of expanding the voltage window is attributed to extend the potential window of HER and OER.[77] In recent years, the water-in-salts electrolyte (WISEs) is developed to expand the voltage window to improve energy density of the battery. The reason of expanding the voltage window is attributed to little free water in the electrolyte.[8,78,79] After that, more research focus on developing new WISEs to improve the electrochemical performance. However, the increasing of concentration may reduce the ion diffusion rate while increase the cost as more salts were used.

In summary, aqueous nonmetal cation battery is an exciting and promising field, though some challenges remain to be overcome. For grid scale applications, aqueous nonmetal cation batteries with high energy and power density are essential. More important, the cost need to be cut down. To meet these demands, the aqueous nonmetal cation battery has a long way to go, and relevant reaction mechanisms need to be further explored. Therefore, to promote the development of aqueous nonmetal cation battery, we need: (i) develop new aqueous electrolytes, such as new hydrogel electrolyte to suppress the water activity and optimize the WISEs to reduce the cost; (ii) explore more cathode materials after expansion of the voltage window; (iii) develop high-performance metal anodes and build connections between metal anode and electrolyte to fully utilize the high capacity. We believe this review can give a brief introduction to aqueous nonmetal cation batteries and incite more research along this field.

Keywords
aqueous batteries, charge carriers, hydrogen bonding, nonmetal cations

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Conflict of Interest
The authors declare no conflict of interest.

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