Optimization of Electrolytes for High-Performance Aqueous Aluminum-Ion Batteries

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ABSTRACT: Aqueous rechargeable batteries based on aluminum chemistry have become the focus of immense research interest owing to their earth abundance, low cost, and the higher theoretical volumetric energy density of this element compared to lithium-ion batteries. Efforts to harness this huge potential have been hindered by the narrow potential window of water and by passivating effects of the high-electrical band-gap aluminum oxide film. Herein, we report a high-performing aqueous aluminum-ion battery (AIB), which is constructed using a Zn-supported Al alloy, an aluminum bis(trifluoromethanesulfonyl)-imide (Al[TFSI]3) electrolyte, and a MnO2 cathode. The use of Al[TFSI]3 significantly extends the voltage window of the electrolyte and enables the cell to access Al3+/Al electrochemistry, while the use of Zn−Al alloy mitigates the issue of surface passivation. The Zn−Al alloy, which is produced by in situ electrochemical deposition, obtained from Al[TFSI]3 showed excellent long-term reversibility for Al electrochemistry and displays the highest performance in AIB when compared to the response obtained in Al2(SO4)3 or aluminum trifluoromethanesulfonate electrolyte. AIB cells constructed using the Zn−AlAl[TFSI]3|MnO2 combination achieved a record discharge voltage plateau of 1.75 V and a specific capacity of 450 mAh g−1 without significant capacity fade after 400 cycles. These findings will promote the development of energy-dense aqueous AIBs.

KEYWORDS: aluminum-ion battery, water-in-salt, aluminum bis(trifluoromethanesulfonyl)imide, Al−Zn alloy anode, MnO2 cathode, electrodeposition

1. INTRODUCTION

The increased demand for improved and low-cost rechargeable electrochemical energy storage (EES) devices is being driven by the expanding quantity of consumer electronic devices and electric cars, as well as the expansion of energy derived from intermittent renewable sources. A novel EES system that employs readily available raw materials with high energy densities and safety is required to meet future energy demand. To date, lead-acid and lithium-ion batteries (LIBs) have dominated the battery market. In particular, LIBs have been the most commonly used EES systems for portable electronic devices and are now making substantial inroads into the vehicle market.1 While humanity’s reliance on LIBs is increasing in our daily life, its major raw materials including lithium, cobalt, and nickel are predicted to be exhausted within the next decade.2 In addition, those raw materials are concentrated in a few regions of the world while demand is growing everywhere.1,3 As a result, there is an urgent need for the development of alternative battery chemistry that utilizes earth-abundant raw materials.

Aluminum-based batteries are regarded as the most promising alternatives due to their wide availability, Al being the third most abundant element in the Earth’s crust, low cost, low intrinsic flammability, and providing ease of processing and recycling. Aluminum has a high theoretical specific capacity per unit mass (2981 mAh g−1) and the highest capacity per unit volume (8056 mAh cm−3) owing to its three-electron reduction process (Al3+/Al).4 These favorable properties have long attracted the attention of researchers with the first use of Al in an electrochemical cell dating back to the 1850s.5 The Al negative electrode has been investigated in both primary and secondary cells employing either aqueous or nonaqueous electrolytes although none of the cells were commercialized to date.6 Of the electrolytes studied thus far at room temperature, the chloroaluminate ionic liquids are the electrolytes that support the reversible Al3+/Al electrochemistry with a high Coulombic efficiency (>99.5%).7−10 A prototype “Al-ion battery” constructed using a chloroaluminate electrolyte, an Al foil negative electrode, and carbon-based cathodes showed stable ultrafast charge−discharge processes with a discharge voltage of ∼2.0 V and a specific capacity of ∼80 mAh g−1.11−13 The high cost, air sensitivity, and severe corrosiveness toward conventional current collectors/battery
packing materials created complexity in battery design when using chloroaluminate electrolytes. In addition, the cell based on this electrolyte exhibited a low energy density due to (i) the intercalation process involving only a one-electron \([\text{AlCl}_4]^−\) transfer instead of intercalating \(\text{Al}^{3+}\) through a three-electron-transfer process; (ii) a limitation due to a lack of suitable positive electrode materials that can accommodate the large \([\text{AlCl}_4]^−\) species with good capacity; and (iii) lack of sufficient electroactive reactant within the electrolyte \([\text{AlCl}_4]^−\) and \([\text{Al}_2\text{Cl}_7]^−\) that limits the capacity of the negative electrode as the anodic half-reaction requires eight \(\text{Al}\) atoms per three electrons instead of one \(\text{Al}\) atom per three electrons.

The realization of reversible \(\text{Al}\) negative electrode electrochemistry using aqueous solution is hindered by several fundamental factors including the passivating oxide film, negative electrode corrosion, and the narrow electrochemical window of water, i.e., water decomposes to hydrogen gas well before \(\text{Al}^{3+}\) reduction occurs \((E^° = \text{Al}^{3+}/\text{Al} = −1.7 \text{ V vs SHE in contrast to } H_2O/H_2 = 0.0 \text{ to } −0.8 \text{ V vs SHE depending on the pH}). Furthermore, \(\text{Al}\) readily forms a high-band-gap passivating oxide film when exposed to air. This oxide coating makes the \(\text{Al}\) surface inaccessible for redox reactions or requires a high driving overpotential to transport ions through the oxide film. However, due to the narrow electrochemical window of water, this potential can easily exceed the thermodynamic limit of water reduction resulting in continuous electrolyte degradation through hydrogen evolution.

Zhao et al. demonstrated that the immersion of \(\text{Al}\) electrode in chloroaluminate ionic liquid could erode the oxide film and create an artificial solid electrolyte interface (SEI) that is stable at ambient atmosphere. Moreover, the interface protects the \(\text{Al}\) surface from further passivation. The treated electrodes exhibited good reversibility in symmetric \(\text{Al}\) cells when combined with an aluminum trifluoromethanesulfonate \((\text{Al}[\text{OTF}]_3)\) electrolyte. Using this pretreated \(\text{Al}\) negative electrode and a \(\text{MnO}_2\) positive electrode with \((\text{Al}[\text{OTF}]_3)\) electrolyte, a discharge voltage of 1.4 V and a high specific capacity of 380 mAh g\(^−1\) were reported. Alternatively, Yan et al. recently showed that a \(\text{Zn}\) substrate can successfully support the reversible electrodeposition of \(\text{Al}^{3+}\) from aqueous \(\text{Al}[\text{OTF}]_3\) electrolytes through the formation of a \(\text{Zn}−\text{Al}\) alloy. The addition of zinc to \(\text{Al}\), to form an alloy, is known to mitigate the passivation film, reduce the self-corrosion of \(\text{Al}\), and may increase the overpotential for the competing hydrogen evolution reaction. The \(\text{Zn}−\text{AllMnO}_2\) cell in \(\text{Al}[\text{OTF}]_3\) electrolytes achieved the highest discharge voltage plateau of 1.6 V and a specific capacity of 460 mAh g\(^−1\).

The hydrogen evolution side reaction is still the main factor hindering the practical development of AIBs due to the Lewis acidity of aqueous \(\text{Al}\)-based electrolytes (pH < 1) coupled with...
the high negative standard potential of Al$^{3+}$/Al. Recent research from aqueous lithium-ion, $^{18-20}$ sodium-ion, $^{21-23}$ magnesium-ion, $^{24}$ and zinc-ion batteries $^{25,26}$ showed that the choice of the electrolytic anions and their concentration significantly impact the electrochemical window of water. In particular, water-in-salt electrolytes based on perfluorinated sulfonimidyl anions such as bis(trifluoromethanesulfonyl)-imide([TFSI]) displayed the highest potential stability and minimal dendrite formation at the metallic negative electrode and formed an effective interfacial layer on the surface of the electrode. $^{25,27,28}$ Dubois et al. demonstrated that the hydroxides generated during initial hydrogen evolution react with the [TFSI] anion to form an SEI that prevents further water reduction at the negative electrode. $^{29}$ An alternative mechanism for the SEI formation was the preferential reduction of [TFSI] anion relative to water reduction leading to the formation of an anion-derived SEI on the negative electrode surface that contributes to the wider electrochemical window stability. $^{15,30}$ These studies strongly indicate that the use of [TFSI]-based electrolytes in AIBs mitigates the critical challenge of the parasitic hydrogen evolution reaction on the negative electrode. To the best of our knowledge, there is no prior report on the use of an aluminum bis-(trifluoromethanesulfonyl)imide (Al[TFSI]) electrolyte for aqueous AIBs, aside from their use as conducting additives in an organic solvent to suppress the anodic dissolution of the aluminum current collectors. $^{31,32}$ Herein, we synthesize Al[TFSI]$_3$ via a simple ion-exchange reaction and use it as an electrolyte for aqueous AIBs. We show that the electrochemical window of aqueous Al[TFSI]$_3$ is at least 1.0 V larger than Al[OTF]$_3$ or Al$_2$(SO$_4$)$_3$ (aq) electrolytes at comparable salt concentration. The use of Al[TFSI]$_3$ electrolytes using Zn–Al negative electrode and MnO$_2$ positive electrode achieved the highest discharge voltage plateau (1.75 V) reported to date with a high specific capacity of 450 mAh g$^{-1}$. Moreover, we also show that the high performance obtained using Al[TFSI]$_3$ electrolytes is attributed to the facile Al$^{3+}$/Al–Zn$_x$ negative electrode electrochemistry, accessibility of a larger potential window without electrolyte decomposition. A combination of electron microscopy and spectroscopic techniques has been used to gain these mechanistic insight processes for each electrolyte as well as the electrode reactions. Finally, we determine the optimum Al[TFSI]$_3$ concentration for good cell performance and present data demonstrating the high stability of cell cycling.

2. RESULTS AND DISCUSSION

2.1. Electrolyte Optimization. The Al[TFSI]$_3$ salt was prepared by reacting neat trifluoromethanesulfonylimide acid [(CF$_3$SO$_2$)$_2$NH] with anhydrous AlCl$_3$ under an Ar-filled glovebox. This reaction also generates hydrogen chloride gas as a byproduct, which was removed by heating in a vacuum oven or, preferably, in a Schlenk line. The complete formation of Al[TFSI]$_3$ and the removal of the HCl impurity are confirmed using X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance spectroscopy (NMR). As shown in Figure S1, XPS revealed the absence of Cl and the presence of Al as well as other elements associated with the [TFSI] anion, which demonstrates the complete reaction to form Al[TFSI]$_3$. Moreover, $^1$H NMR showed the absence of the acidic proton from the reactant and the presence of $^{27}$Al and $^{19}$F confirming the formation of the Al[TFSI]$_3$ (Figure S1C–E).

The suitability of the Al[TFSI]$_3$ electrolyte for AIBs was then assessed by various electrochemical methods and its cell performance compared to those of Al[OTF]$_3$ and Al$_2$(SO$_4$)$_3$ electrolytes. First, the electrochemical deposition and stripping of Al$^{3+}$, as well as the long-term stability, were compared in a symmetrical cell using Zn foil as a substrate. We should note that we used 2m Al[OTF]$_3$ as a comparison as Yan et al. showed that 2m is the optimum concentration in AIB performance. $^{15}$ In addition, 2m Al$_2$(SO$_4$)$_3$ was used, as this is its maximum solubility limit in water. Figure 1A shows the charge–discharge curve obtained using the three electrolytes in a symmetrical Zn|Zn cell at 0.2 mA cm$^{-2}$. In the initial charge–discharge cycle, Al$^{3+}$ is expected to deposit at the negative Zn electrode while the stripping of Zn to Zn$^{2+}$ occurs at the positive electrode. The codeposition of Zn$^{2+}$ along with Al$^{3+}$ is expected to occur during subsequent charge–discharge to form a Zn–Al$_x$ alloy (where “x” represents the stoichiometry of Al electrodeposited). $^{16}$ Cyclic voltammetry was used in a three-electrode cell setup to confirm the electrodeposition of Al$^{3+}$ on a Zn working electrode from the Al[TFSI]$_3$ electrolyte. As shown in Figure S2A, during the first potential scan from an initial potential of −1.4 V vs Ag/AgCl, a reductive current started to flow and peaked at about −1.9 V due to the electrodeposition of Al. In the return scan, a large sharp current due to the stripping of Al was observed. The oxidation of Zn also occurs if the electrode potential is intentionally scanned all the way to zinc stripping potential during this oxidative scan as an additional reductive peak was seen at −1.25 V due to the codeposition of Zn in the subsequent scan. However, the bulk oxidation of Zn$^{2+}$ is less likely to occur during battery operation given that the standard redox potential of Zn$^{2+}$/Zn is too positive when compared to the anode reaction (Zn–Al$_x$ alloy formation). Indeed, determination of the content of Zn in the Al[TFSI]$_3$ electrolyte solution after several charge–discharge processes using inductively coupled plasma atomic emission spectroscopy detected a trace amount of Zn$^{2+}$ (0.3%). Characterization of both the positive and negative electrodes obtained in Al[TFSI]$_3$ after cycling using X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) revealed the formation of Zn–Al$_x$ alloy (Figures S3 and S4). EDX data showed the electrodeposition of Al, while the X-ray diffraction (XRD) pattern shows peaks that match the Zn reference substrate. However, the positions of the diffraction pattern are shifted to a lower angle compared to pure Zn, indicating the alloying effect of Zn with Al. $^{33,34}$ Yan et al. also observed similar behavior when analyzing the XRD pattern obtained from electrodeposition of Al$^{3+}$ on Zn foil from the Al[OTF]$_3$ electrolyte. $^{16}$ In addition, there were no detectable peaks in the XRD pattern due to pure Al even at a high deposition capacity, suggesting that the bulk electrodeposition of Al on the Zn surface is not observed. It was shown that the signal due to the face-centered cubic Al phase was only visible when the alloy contained more than 50% of Al. $^{35}$ In our case, the atomic concentration of the electrodeposited Al was about 5% (see the next section). Note that this percentage was obtained using a MnO$_2$ cathode at a loading of about 2 mg cm$^{-2}$. In theory, the amount of Al on the Zn can be increased by increasing the MnO$_2$ amount on the current collector or by using a thin Zn surface in the range of a tenth of micron to harness the full potential of Al capacity. The XRD patterns of the anode (obtained in Zn|ZnMnO$_2$ cell) show that as the deposition capacity of Al increases, the diffraction peaks of this
alloy monotonically shift toward a low angle, indicating that the lattice constant is dependent on the alloy composition (Figure S4C). The charge−discharge curve shows the lowest potential separation for Al³⁺ deposition and oxidation in Al[TFSI]₃ (red line) and the largest in Al[OTF]₃ (blue line), indicating that the rate of the Al⁴⁺/Al deposition reaction is fastest in Al[TFSI]₃ electrolytes. The Al[TFSI]₃ electrolyte also showed a stable overpotential (0.15 V) throughout the 100 h cycles when compared to Al[OTF]₃, which showed an overpotential of over 1.0 V during the initial 15 h cycles. Furthermore, the Coulombic efficiency (CE) of the alloy formation and stripping in the Al[TFSI]₃ electrolyte was 99.3% (Figure S2B), implying that hydrogen evolution reaction is greatly reduced in the [TFSI]-based anion. We also noted that CE increased initially with increasing charge−discharge cycling, presumably due to the continual formation of a stable interface. On the other hand, even in Al[TFSI]₃ electrolytes (Figure S5A), the electrochemistry of the symmetrical Al cell displayed an overpotential of over 6.0 V after 20 cycles, and subsequently, the cell failed due to the passivating oxide layer and hydrogen evolution side reaction. These data demonstrate that the Zn substrate can successfully support the reversible deposition of Al³⁺ from aqueous Al³⁺-based electrolytes with high efficiency to form Zn−Alₓ surface alloy.

Figure 2. Galvanostatic charge−discharge curves vs capacity obtained at a current density of 25 mA g⁻¹ using Zn−Alₓ and MnO₂ positive electrodes in (A)3m Al[TFSI]₃, (B) 2m Al[OTF]₃, (C) 2m Al₂(SO₄)₃ electrolytes, and (D) CVs recorded at a 3 mm diameter glassy carbon electrode in a three-electrode configuration at 10 mV s⁻¹ using 3m Al[TFSI]₃, 2m Al[OTF]₃, and 2m Al₂(SO₄)₃ electrolytes.

Figure 1C shows the comparison of the charge−discharge curve obtained for the AIBs full cell with the three Al-based electrolytes using an α-MnO₂ cathode. The Al[TFSI]₃ electrolyte displayed the highest performance in terms of discharge capacity and average voltage plateau (1.75 V), and the rate capability is shown in Figure S5C. Specific capacities of 450, 300, and 290 mAh g⁻¹ were obtained in Al[TFSI]₃, Al[OTF]₃, and Al₂(SO₄)₃, respectively. In addition, the average discharge voltage plateau in Al[TFSI]₃ is larger than the other two electrolytes by ∼100 mV, in agreement with the cyclic voltammetry (CV) response, which shows an average potential of 1.9 V when compared to 1.8 V for Al[OTF]₃ (Figure 1D). The CV response of the full cell also showed that the rate of Al⁴⁺/Al reaction is fastest when the Al[TFSI]₃ electrolyte was used, as characterized by a lower peak-to-peak separation of 0.4 V compared to 0.46 V in the Al[OTF]₃ electrolyte. The average voltage plateau obtained in Al[TFSI]₃ electrolytes is, to the best of our knowledge, the highest discharge voltage among all of the reported AIBs based on a manganese oxide cathode. Yan et al. reported a voltage plateau of 1.6 V using Zn−AlAl[OTF]₃|MnO₂ cell, while others reported plateaux below 1.4 V when using a pure Al negative electrode and manganese oxide cathodes. We should also point out that the use of premade Zn−Alₓ is not essential as in situ Al³⁺ deposition occurs on the Zn negative electrode, while the insertion of H⁺/Al³⁺ occurs at the positive electrode (α-MnO₂) during the cell charge−discharge process. In fact, a
significant decrease in cell performance was seen when premade Zn–AlX was used as the negative electrode (see Figure S6), characterized by lower discharge voltage (<1.6 V) and reduced specific capacity.

2.2. Structural and Compositional Characterization of Electrodes and Electrolytes. There are a few reasons for the enhanced performance seen with the Al[TFSI]3 electrolyte. First, as discussed in the context of Figure 1A, the kinetics of Al3+ deposition and stripping on the Zn substrate are more facile than with Al[OTF]3 or Al2(SO4)3 electrolyte. Second, the electrochemical window of the Al[TFSI]3 electrolyte is the highest, when compared to Al[OTF]3 or Al2(SO4)3, enabling the cell to be charged to a higher voltage. As shown in Figure 2A, the cell with the Al[TFSI]3 electrolyte can be charged to 2.1 V without electrolyte degradation and the CE of the cell was over 93%. A significant amount of electrolyte degradation occurred in Al[OTF]3 and Al2(SO4)3 electrolytes when the cells were charged to 2.1 V, characterized by a dramatic decrease in CE to below 50% (Figure 2B,C). Indeed, the overall electrochemical window characterization of the three electrolytes using a glassy carbon disk electrode also revealed that Al[TFSI]3 showed the highest electrochemical window of 4.3 V when compared to that of 3.2 V in Al[OTF]3 and 3.0 V in Al2(SO4)3 (Figure 2D). It is also interesting to note that the larger increase in the electrochemical window of Al[TFSI]3 is obtained by hindering hydrogen evolution, rather than oxygen evolution, when compared to the other two electrolytes, as seen also by the CE data in Figure 1B and S2B. The high electrochemical oxidative stability of the [TFSI]− anion is known from research in various aqueous battery systems.18,24 The reduction of the [TFSI]− anion is believed to form a passivating solid layer interface that increases the overall electrochemical window.24 The surface passivation of [TFSI]− was also shown by a previous study, which compared the adsorption of [TFSI]− and [OTF]− on Pt from neat ionic liquids.25 Finally, the surface morphology of the cycled negative electrode from the full cell also revealed some insight into the different performance. Figure 3A,C shows the scanning electron microscopy (SEM) images of the negative electrode obtained after charge–discharge cycling in the Zn–AlX|MnO2 full cell. The Zn–AlX deposits obtained using Al[TFSI]3 showed uniform and well-defined nanoparticles (Figure 3A). EDX mapping revealed that Al was uniformly deposited across the Zn foil with a 5% average atomic percentage (Figure 3D,F). In contrast, the deposits obtained from Al[OTF]3 and Al2(SO4)3 showed a high-surface-area honeycomb-like structure that can be prone to form dendrites over multiple cycles (Figure 3B,C).

The solvation structure of Al3+, hydrogen evolution side reaction, interaction between water molecules and electrolyte anions, as well as the overall voltage applied to the cell may affect the morphology of the Al electrodeposits. For example, the upper cutoff voltage for Al[TFSI]3 is 2.1 V compared to that of 2.0 V for Al[OTF]3 or Al2(SO4)3. This voltage difference together with the slow Al3+/Al electrode kinetics in the latter electrolytes may produce different growth morphologies. The hydrogen evolution side reaction also affects the growth of electrodeposited nanostructures. In fact, it was shown that the honeycomb morphology is the preferred growth pattern when hydrogen codeposition occurs during
metal electrodeposition. In addition, the solvation structure of the electrolytes can alter the electrodeposition process by influencing their electrochemical window.

The solvation structure of the three Al electrolytes was explored using $^{27}$Al, $^1$H, and $^{19}$F NMR and other spectroscopic techniques. Figure 4A shows that the signal due to $^{27}$Al moved to a lower chemical shift as the Al electrolyte counteranion changed from $\text{SO}_4^{2-}$ (0.71 ppm), $\text{[OTF]}^-$ (0.65 ppm) to $\text{[TFSI]}^-$ (0.2 ppm). This suggests that the Al cation in Al[$\text{TFSI}$]$_3$ is more shielded than the Al$^{3+}$ cation in Al[$\text{OTF}$]$_3$ or Al$_2$($\text{SO}_4$)$_3$ electrolyte. The increase in electronic density around Al$^{3+}$ in [TFSI]-based electrolyte indicates a change in the solvation shell of Al$^{3+}$, perhaps through the formation of ionic aggregates (TFSI-TFSI) and contact ion pairs (TFSI-Al$^{3+}$).

A decrease in the chemical shift of $^{27}$Al was also observed when the concentration of Al[$\text{TFSI}$]$_3$ increased, which results in an increase in the electronic density around Al$^{3+}$ (Figure S7); presumably, water (or hydroxide) is being displaced from the coordination environment of the Al and replaced with the [TFSI] anion. This observation is consistent with the NMR of Li[TFSI] electrolytes. Similarly, a larger decrease in the chemical shift of $^1$H and $^{19}$F was observed for the [TFSI]$^{-}$ anion compared to that of [OTF]$^-$ or $\text{SO}_4^{2-}$ anions, and the extent of shielding increased with increasing [TFSI]$^{-}$ concentration (Figure 4B,D). Fourier transform infrared (FTIR) spectroscopy (Figure S8) also showed that the characteristic water (O–H) stretching mode shifted to higher wavenumbers for Al[$\text{TFSI}$]$_3$ when compared to that for Al[$\text{OTF}$]$_3$ or Al$_2$($\text{SO}_4$)$_3$. In addition, the NMR spectrum due to $^{19}$F showed a coupling pattern with increasing Al[$\text{TFSI}$]$_3$ concentration. The coupling could be with the proton from water or through close Al$^{3+}$–anion interactions, but the fact that the coupling occurs when the concentration of Al[$\text{TFSI}$]$_3$ increased suggests that the contact ion pair (TFSI-Al$^{3+}$) interaction might be the cause. Alternatively, it could be due to the coupling of anion–anion interaction through aggregates of the [TFSI] network. A recent study of [TFSI] solvation structure using synchrotron X-ray scattering showed two coexisting structures: [TFSI]-solvated structure (caused by hydrogen bonding between the bulk water and [TFSI]$^-$) and [TFSI] network (formed through the hydrogen bonding between the interfacial water and [TFSI]$^-$) depending on its concentration. As the concentration of [TFSI]$^{-}$ anions increases, even at relatively low concentration, the [TFSI] network gradually forms, while the [TFSI] solvated structure gradually disappears. The formation of [TFSI] aggregates significantly alters the solvation structure of the electrolyte and is responsible for the increase in the electrochemical window of the electrolyte. Overall, spectroscopic data analysis indicated that the solvation structure of Al$^{3+}$ in [TFSI] anions is considerably different from the other two anions and this is responsible for the difference in electrochemical performance.

A combination of electron microscopy, XRD, and spectroscopic analysis was also carried out to get insights into the solvation structure of Al, which is crucial for understanding the electrochemical performance.
into the electrochemical processes at the positive electrode. The morphology of the fully discharged MnO2 electrode in Al[TFSI]3 was analyzed and compared to pristine MnO2 after washing several times with water to remove the residual electrolyte. The SEM image of pristine MnO2 exhibited rodlike nanostructures with an average length of $\sim 2 \mu m$ (Figure 5A). The morphology of the MnO2 electrode significantly changed when the cell was fully discharged. SEM images showed the presence of smaller nanostructures that range between 100 and 500 nm in size (Figure 5B), presumably due to the insertion of guest species into MnO2 (this will be discussed in the next section). EDX mapping revealed the homogeneous distribution of the Al element on the MnO2 electrode (Figure 5C). A trace amount of Zn2+ was also inserted alongside the Al3+ into the MnO2, with the atomic ratio of Zn/Mn being 0.05. The trace Zn2+ obtained at the positive electrode as well as in the electrolyte is most likely due to the crossover of some of the oxidized Zn2+ during cell discharge, as also seen previously.16 However, it is important to note that Zn2+ does not seem to contribute to the capacity of the cathode given that Zn 2+ chemistry at the MnO2 cathode usually occurs at <1.4 V (Figure S9).

Ex situ hard X-ray photoelectron spectroscopy (HAXPES, 9.25 keV) and conventional XPS (1.486 keV) were used to examine the change in the manganese oxidation state during the cell charge–discharge process (Figures 6 and S10). The sampling depth of MnO2 based on Mn 2p for HAXPES is 34.1 nm compared to only 5.3 nm for XPS.45,46 HAXPES is able to probe below the topmost surface layer and thus can be used to infer information from the material surface toward the bulk.48 Comparing information extracted using the two photon energies therefore enables the assessment of any changes occurring at the surface to subsurface. In addition, HAXPES also enables the use of deeper core levels at relatively higher binding energies, such as Mn 1s ($\sim 6540$ eV BE) and Al 1s ($\sim 1560$ eV). The Mn 1s core level is useful because no multiplet splitting effects are expected; the spectra for the fully discharged, charged, and pristine MnO2 all show one symmetric peak at 6541.0, 6541.2, and 6541.1 eV, respectively (Figure 6A). The lack of difference in binding energy indicates that Mn is present as MnO2 for charge–discharged samples. In addition, Al 1s is present at 1562.5 eV (metallic Al exhibits Al 1s at $\sim 1559.8$ eV45) for the discharged electrode, where the positive binding energy shift compared to the metallic state confirms the insertion of Al3+ (Figure 6B). In the charged MnO2, an additional peak at a higher binding energy of 1566.0 eV is seen, which could be due to the formation of aluminum oxide.

Measurement of the Mn 3s core level is also useful to determine the oxidation state of Mn. Mn 3s splits due to multiplet splitting effects caused by unpaired d-electrons, and the magnitude of the splitting can reveal the oxidation state of Mn.46 HAXPES measurements obtain a 3s core level splitting width of $\sim 4.9$ eV for both charged and discharge samples, suggesting that the oxidation state of Mn remains unchanged.17,48 The XPS spectra for Mn 3s for charged–discharged electrodes, however, are perturbed by additional peaks in this region originating from Al KLL (Auger transition) and trace Zn (Zn 3p), which overlap, as shown in Figure S10C. This makes use of the 3s core level challenging when using XPS. The lack of this structure in HAXPES suggests that Zn is mainly present at the surface as impurities, while the Al Auger transition has been shifted to a different binding energy position as the photon energy has changed. The fact that Zn is absent below the subsurface suggests that Zn does not contribute to the capacity of the cathode. For the discharged and charged cells, the Mn 2P3/2 binding energy positions were 642.3 and 642.5 eV using XPS and 642.4 and 642.6 eV using...
HAXPES. This suggests that the Mn is present as MnO₂ in both samples at the surface as well as in the bulk, i.e., similar HAXPES and XPS binding energy positions may indicate a homogeneous chemical state. Note that we only take the peak position of Mn 2p 3/2; peak fitting of the first two transition-metal 2p core levels is challenging due to multiplet splitting effects caused by unpaired d-electrons. The HAXPES and XPS data indicate that there is little or no change from the surface into the bulk of the material when the MnO₂ electrodes undergo charge-discharge process.

Given that both HAXPES and XPS showed that the oxidation state of Mn remains unchanged during the battery charge-discharge mechanism, what is the active redox species at the cathode then? There are controversies in the literature regarding the active species (Al³⁺ or H⁺) intercalated into MnO₂ during battery discharge. Previous work suggested that the insertion of Al³⁺ into the oxide is accompanied by the cointercalation of water, which form a layered AlₓMnO₂·nH₂O phase. It was believed that this coinserted water crystal is critically important for the reversible intercalation of Al³⁺ into the oxides by insulating the electrostatic interaction between the Al³⁺ ion and the host MnO₂. A similar mechanism was suggested using other multivalent ions including Mg²⁺ and Zn²⁺ during the electrochemical cycling of manganese oxide electrode in aqueous electrolytes. However, recent research has questioned whether Al³⁺ intercalation into MnO₂ occurs at all and, instead, proposed that proton insertion is the dominant reaction mechanism. Wang et al.
studied the charge storage mechanism of $\alpha$-MnO$_2$ in the Al[OTF]$_3$ electrolyte using various electrochemical/spectroscopic characterizations and found that proton intercalation/deintercalation largely contributes to the reversible capacity of the cell, while only a small amount of Al$^{3+}$ could also intercalate into MnO$_2$. It also proposed that a complex surface product containing Al$^{3+}$, OH$^-$, and [OTF]$^-$ was formed during cell discharge and this product dissolves during the charging process. Alternatively, Balland et al. used an in situ spectroelectrochemical methodology to determine the reaction mechanism of Al$^{3+}$ in the MnO$_2$ electrode using the Al[OTF]$_3$ electrolyte. They proposed a mechanism based on the reversible proton-coupled MnO$_2$ to Mn$^{2+}$ conversion where the hydrated Al$^{3+}$ acts as a proton donor. We also investigated the insertion of proton using CV and galvanic charge–discharge curves employing an aqueous acetic acid electrolyte with a similar pH (1.2) value to the 3m Al[TFSI]$_3$ electrolyte investigated the insertion of proton using CV and galvanic charge–discharge curves employing an aqueous acetic acid electrolyte with a similar pH (1.2) value to the 3m Al[TFSI]$_3$ electrolyte. The cell was discharged from the open circuit potential (OCP) value. The interesting points observed were as follows: first, the OCP of the cell was 1.72 V, similar to the Al[TFSI]$_3$-containing electrolyte. Second, when the cell was fully discharged, the battery displayed a similar discharge plateau to the Al[TFSI]$_3$ electrolyte but with a much enhanced discharge capacity of 510 mAh g$^{-1}$ (see Figure 6E). This capacity is close to the theoretical value for the conversion of the Mn$^{4+}$/Mn$^{2+}$ reaction. In addition, CVs showed the reversible insertion of proton into the MnO$_2$ electrode (inset of Figure 6E). To get further insight, we analyzed the discharged MnO$_2$ electrode in aqueous acetic acid solution using HAXPES. We observed that only a trace amount of manganese species detected with an atomic concentration of Mn is 0.3%. This demonstrates that the majority of Mn$^{4+}$ (MnO$_4^-$) was reduced to Mn$^{2+}$, which then dissolves away from the electrode, confirming that proton insertion reduces Mn$^{4+}$ to Mn$^{2+}$ redox reaction. The fact that we observed the presence of Mn species along with Al, during HAXPES analysis for Al[TFSI]$_3$, indicates that the intercalation of proton was not the sole reaction mechanism. Instead, a small amount of Al$^{3+}$ also cointercalates into MnO$_2$ with the atomic ratio of Al to Mn being 0.07 according to HAXPES for the fully discharged sample. This was, however, small enough to alter the oxidation state of Mn to be detected by HAXPES (Al$_{0.07}$MnO$_2$). Given that the theoretical capacity of Al$_{0.07}$MnO$_2$ is only 65 mAh g$^{-1}$, the dominant reaction mechanism occurring at the MnO$_2$ electrode when using Al[TFSI]$_3$ electrolyte is proton insertion donated from hydrated Al$^{3+}$ (eq 1) rather than Al$^{3+}$ insertion (eq 2), which is consistent with the recent work. The MnO$_2$ positive electrode structural reversibility after the charge–discharge process was also examined using ex situ XRD. Figure 7A shows the XRD pattern of pristine MnO$_2$, which was well indexed to the $\alpha$-MnO$_2$ phase. The prominent (130) and (210) peak intensities of MnO$_2$ are weakened, while the other peaks disappeared when the cell was fully discharged. All of the diffraction patterns are recovered when the cell was charged, indicating the structural reversibility of MnO$_2$

$$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (1)$$

$$x\text{Al}^{3+} + \text{MnO}_2 + n\text{H}_2\text{O} \rightarrow \text{Al}_x\text{MnO}_2 . n\text{H}_2\text{O} \quad (2)$$

### 2.3. Effect of Al[TFSI]$_3$ Concentration on Cell Performance and Stability

Given that the performance of Al[TFSI]$_3$ is superior to that of Al[OTF]$_3$ or Al$_2$(SO$_4$)$_3$ when used in AlIBs, the effect of varying Al[TFSI]$_3$ concentrations on the cell performance is further optimized. We prepared Al[TFSI]$_3$ solutions with varying salt concentrations, and the maximum limit of the Al[TFSI]$_3$ solubility in water was found to be 5m. The concentration of electrolytes has a profound effect on the chemistries and cell performance of several batteries including Li-ion, Al-ion, and Zn-ion batteries. It has also been suggested that the electrolyte properties are largely affected by the identity of the anion, rather than the cation, during aqueous electrolyte formulation. In this case, not only the concentration or the nature of anions impacts but also the stoichiometry between the cation and anion should be considered. For example, one may get the same number of [TFSI] ions in a solution of 9m LiTFSI and 3m Al[TFSI]$_3$. 

Figure 7. (A) XRD patterns of MnO$_2$ cathodes at fully discharged and charged states, (B) galvanostatic charge–discharge curve obtained using the symmetrical Zn/Zn electrode at 1.0, 3.0, and 5.0m Al[TFSI]$_3$ electrolytes at 0.2 mA cm$^{-2}$, (C) galvanostatic charge–discharge curves vs capacity obtained at a current density of 25 mA g$^{-1}$ using various Al[TFSI]$_3$ electrolytes.

https://doi.org/10.1021/acsami.1c23278
ACS Appl. Mater. Interfaces 2022, 14, 25232–25245
with a relatively low concentration of Al[TFSI]3, the water-in-salt regime may be achieved. The kinetics of Al3+/Al deposition and stripping of the different Al[TFSI]3 salt concentrations were evaluated in Zn/Zn symmetric cells. Figure 7B displays the typical voltage–time profiles at a constant charge and discharge current density of 0.2 mA cm−2. The charge–discharge profile in the 1m Al[TFSI]3 electrolyte displayed a large overpotential for the Al3+/Al reaction that was increased with cycling until the cell failed within 50 h. This could be due to the formation of water-induced irreversible side reactions including hydrogen evolution and associated surface oxidation. For the 5m Al[TFSI]3 (as well as for the 4m concentration) electrolyte, the symmetric cell also exhibited a large polarization potential although cell failure was not observed. There are a few factors that may contribute to the slow electrode kinetics of Al3+/Al in 5m Al[TFSI]3. The ionic conductivity measurement using AC impedance showed that conductivity decreased from 46.9 mS cm−1 in 3m Al[TFSI]3 to 4.8 mS cm−1 in 5m Al[TFSI]3. The significant conductivity decrease (caused by the associated viscosity increase) may affect the rate of Al3+/Al reaction as well as the diffusion of Al3+. In addition, the surface morphology of the Al electrodeposits obtained using 5m Al[TFSI]3 considerably differs from the 3m, as shown in Figure S11. The data and discussion of further electrolyte characterization using Fourier transform infrared spectroscopy, UV–vis absorption spectroscopy, and Raman spectroscopy are presented in the Supporting Information (SI). Excellent reversibility of Al stripping/plating with the smallest polarization was achieved in the 3m Al[TFSI]3 electrolytes. The reversibility of Al3+ chemistry was also compared using 5m and 3m Al[TFSI]3 salt concentrations as an example. As shown in Figure S12A, the peak-to-peak separation for Al3+/H+ insertion and extraction significantly increased from 0.4 V in 3m to 0.75 V in the 5m Al[TFSI]3 electrolyte. In addition, the current measured was significantly decreased for the 5m electrolyte, which is most likely due to the slow rate of Al3+/Al transport caused by the associated viscosity increase. The AIB cell with the 3m Al[TFSI]3 exhibits the best electrochemical performance. It shows a specific discharge capacity of 450 mA h g−1 at a current of 25 mA g−1 compared to that of <250 mA h g−1 for the other electrolytes. In addition, the discharge voltage plateau and CE decreased as the concentration of Al[TFSI]3 increased from 3m to 5m, mirroring the slower kinetics of Al3+/Al at concentrations >3m. For example, the CE of the 3m system is ~90% compared to that of 74% at 5m. This data highlights that 3m Al[TFSI]3 is the optimum electrolyte concentration for use in AIBs.

Finally, the stability of the AIB cells was examined: Figure 8A shows the capacity retention of Zn−Al3Mn3O4 cell cycled at 0.15 A g−1 using 3m Al[TFSI]3 electrolyte and (B) charge–discharge curve obtained at 0.15 A g−1 at the shown cycling stage.

Figure 8. (A) Capacity retention and Coulombic efficiency of Zn−Al3Mn3O4 cell cycled at 0.15 A g−1 using 3m Al[TFSI]3 electrolyte and (B) charge–discharge curve obtained at 0.15 A g−1 at the shown cycling stage.

increased by 50% during the first 100 cycles and then stabilized at a little more than the initial value. The increment in capacity could be due to the gradual activation of the surface area by the electrodeposition process of the Mn2+ additives. Examination of the charge–discharge showed that the average voltage plateau of the cell during the charging process progressively decreased, while the length of the discharging curve increased with an increase in cycle numbers (Figure 8B). This indicates that the overall rate of H3+/Al3+ insertion/extraction from the positive electrode and Al plating/stripping at the negative electrode are enhanced with cycling. In addition, the CE increased from 94 to 99% with increased cycling. When compared to the Al[TFSI]3 electrolyte, [SO4]2− or [TFO−]− based electrolytes did not exhibit good cycling stability even with Mn2+ additives. This was due to electrolyte degradation to form hydrogen evolution, as evidenced by the low CE (25% in Al2(SO4)3 compared to over 95% in Al[TFSI]3) (Figure S13). We also note that the 3m Al[TFSI]3 electrolyte performed well with the spinel-structured Mn3O4 cathode. As shown in Figure S14, the electrochemical behavior (CV) and the battery performance of Mn3O4 are comparable to the α-Mn3O4 cathode. We believe that these findings may promote the development of energy-dense aqueous AIBs.

3. CONCLUSIONS

The development of novel aqueous aluminum-based electrolytes with the ability to suppress the hydrogen evolution side reaction, and which overcome the issue of Al passivation, is crucially important for the realization of aluminum-ion batteries. We investigated the suitability of three different Al electrolytes in terms of their practicality for aqueous AIBs. Our results showed that the nature of the electrolyte anion has a crucial effect on the electrochemical window of water, the surface morphology of aluminum electrodeposits, the degree of
Al\textsuperscript{3+}/Al reversibility, and the performance of the cell. An Al electrode based on bis(trifluoromethanesulfonyl)imide anion suppressed the hydrogen evolution side reactions and enabled the cell operating window to extend to 2.1 V. The accessibility of the high-voltage window by the Al[\text{TFSI}]\textsubscript{3} allowed the reversible electrochemistry Al\textsuperscript{3+} at the anode, thereby achieving a record discharge voltage of 1.75 V with a high capacity of 450 mAh g\textsuperscript{-1}. In addition, the use of this innovative electrolyte produced Zn–Al alloy electrodeposits that consist of uniform nanostructures that are less prone to dendrite formation with excellent reversibility for Al electrochemistry when compared to the electrodeposits obtained from Al[OTF]\textsubscript{3} or Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} electrolyte. The results of this study can be seen as a proof of concept for further Al electrolyte development. In particular, solid electrolyte interface forming anions based on various perfluorinated sulfonimides and their mixtures should be investigated to further fine-tune the performance of AIBs with an understanding of their interfacial properties. In addition, it is also important to consider the costs when evaluating the feasibility of using [TFSI]-based electrolytes in aqueous batteries. While [TFSI]-based salts remain relatively expensive, such prices will fall as the salt’s popularity grows.

4. EXPERIMENTAL METHODS

4.1. Materials and Apparatus. Anhydrous aluminum chloride (99.99%), aluminum trifluoromethanesulfonate (99.9%), aluminum sulfate (99.99%), K\textsubscript{2}MnO\textsubscript{4} (99%), MnSO\textsubscript{4} \cdot H\textsubscript{2}O, and N-methyl-2-pyrrolidone were obtained from Sigma-Aldrich and used as received. Titanium (99.99%) and aluminum foil (99.99%) were obtained from Alfa Aesar. Trifluoromethanesulfonimide (95%) was obtained from Fluorochem. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al K\textalpha{} X-ray source (E = 1486.6 eV, 10 mA emission). Hard X-ray photoelectron spectroscopy (HAXPES) was performed using an Al K\textalpha{} X-ray source (1486 eV, 20 mA emission at 300 W) for surface-sensitive XPS at the same sample position (although with a larger spot size of ~1 mm diameter). Survey and core level spectra were measured using 200 and 50 eV pass energies, respectively (using a 1.5 mm wide entrance slit), with a total energy resolution approximately 50% compared to HAXPES. Binding energies were determined according to the experimental procedure reported in the literature following eq 1.\textsuperscript{44} In brief, trifluoromethanesulfonimide was fully melted by heating to 60 °C followed by the slow addition of AlCl\textsubscript{3} (1.05:1.0 molar ratio of acid to AlCl\textsubscript{3}, respectively) under an argon-filled glovebox. The mixture was stirred at 60 °C for 12 h. The HCl byproduct was removed by heating under a vacuum oven overnight at 120 °C. It is preferable to use the Schlenk line to avoid damage to the vacuum oven by HCl. The complete reaction and removal of the HCl were confirmed by X-ray photoelectron spectroscopy and NMR spectroscopy. Each of the Al salt solutions was prepared using ultrapure water, and to aid the dissolution of Al[\text{TFSI}]\textsubscript{3} in water, the mixture was heated to 70–80 °C while stirring. The ionic conductivity of the solutions was determined by AC impedance spectroscopy in a U-shaped glass cell that was filled with the desired electrolytes and contained two identical Ag wires held at a fixed distance from each other. The cell constant was determined using a 0.0145 M KCl conductivity standard (Alfa Aesar). The solution resistance (R\textsubscript{s}) was obtained from the horizontal intercept of the Nyquist plot in the high-frequency region and used for ionic conductivity calculation.

\[
\text{AlCl}_3 + 3(\text{CF}_2\text{SO}_3\text{H})\cdot \text{NH} \rightarrow \text{Al}(\text{CF}_2\text{SO}_3\text{H})\text{N}_3 + 3\text{HCl}(g)
\]

4.2. Preparation of AlumInum Bis-(trifluoromethanesulfonimide). Aluminum bis-(trifluoromethanesulfonimide) (Al[\text{TFSI}]\textsubscript{3}) was synthesized according to the procedure reported in the literature following eq 1.\textsuperscript{44} Briefly, 0.50 g of K\textsubscript{2}MnO\textsubscript{4} and 0.21 g of MnSO\textsubscript{4} \cdot H\textsubscript{2}O were added to 32 mL of deionized water to form a homogeneous solution under magnetic stirring for about 10 min. The solution was then transferred to a Teflon-lined stainless steel autoclave and heated in an oven at 160 °C for 12 h. The obtained product was collected by filtration, washed with deionized water, and dried at 80 °C in an oven overnight.

4.4. Electrode Preparation. The Al-MnO\textsubscript{2} slurries were prepared using 0.8 g of Al-MnO\textsubscript{2}, 0.1 g of carbon black/Super P, and 0.1 g of poly(vinylidene fluoride) (Kynar 761 PVDF) binder in a sufficient volume of N-methyl-2-pyrrolidone (NMP). The slurry was stirred overnight and coated over a Ti (99.95%) substrate or nonwoven carbon (Technical Fibre Products, U.K.) substrate using doctor blading. The resulting cast electrodes were dried in a vacuum at 80 °C overnight. The cast electrodes were then punched into small disks of 1 cm diameter for use in a coin cell. The mass loading of the electrodes ranged from 2 to 5 mg cm\textsuperscript{-2}. The Zn–Al anode electrodeposits were prepared in situ by charging the cell from the cell open circuit voltage at a rate of 25 mA g\textsuperscript{-1} using a Zn foil anode, an Al-MnO\textsubscript{2} cathode, and an Al-based aqueous electrolyte.

4.5. Battery Assembly and Electrochemical Measurements. The full cells were assembled in CR2032-type coin cells using Al\textsubscript{3+}/Al as the cathode, Zn foil as the anode, a glass microfiber filter as the separator and 150 \textmu{}L electrolytes. The electrolytes were made by dissolving various Al salts (Al[\text{TFSI}]\textsubscript{3}, Al[OTF]\textsubscript{3}, or Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}) with various concentrations in ultrapure water (Millipore Milli-Q), which was previously purged with Ar gas for 30 min. Coin cells were assembled using a hydraulic crimping machine (MSK-160D) in an ambient atmosphere. For Coulombic efficiency (CE) determination for Al deposition and stripping at the Zn electrode, an asymmetric cell consisting of Zn and carbon electrodes in addition to the Al[\text{TFSI}]\textsubscript{3} electrolyte was used. The cell was set to electrodeposits the alloy for 30 min at 2 mA cm\textsuperscript{-2} and follow the CE by stripping the electrodeposited Al. Three-electrode cell electrochemical measurements were conducted using a 3 mm diameter glassy carbon (GC) disk as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The electrodeposition of Zn on GC was carried out using 0.1 mZnCl\textsubscript{2}(aq) and the GC/Zn electrode was used as the working electrode for the electrochemistry of Al electrodeposition study from the Al[\text{TFSI}]\textsubscript{3} electrolyte (Figure S2A)
**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c23278.

NMR spectroscopy of various elements, XPS, cyclic voltammograms, and galvanostatic charge–discharge curves of various electrodes, Raman and FTR spectroscopy, and SEM (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to thank EPSRC (Grant ref. EP/R023034/1) for funding. The Manchester Hard X-ray photoelectron spectroscopy facility was supported by the Henry Royce Institute funded through EPSRC grants EP/R00661X/1, EP/P025021/1, and EP/P025498/1.

**REFERENCES**

(1) Chen, M.; Ma, X.; Chen, B.; Arsenault, R.; Karlson, P.; Simon, N.; Wang, Y. Recycling End-of-Life Electric Vehicle Lithium-Ion Batteries. Joule 2019, 3, 2622–2646.

(2) Turcheniuk, K.; Bondarev, D.; Singhal, V.; Yushin, G. Ten Years Left to Redesign Lithium-Ion Batteries. Nature 2018, 559, 467–470.

(3) Tarascon, J.-M. Is Lithium the New Gold? Nat. Chem. 2010, 2, 510.

(4) Faegh, E.; Ng, B.; Hayman, D.; Mustain, W. E. Practical Assessment of the Performance of Aluminium Battery Technologies. Nat. Energy 2021, 6, 21–29.

(5) Li, Q.; Bjerrum, N. J. Aluminium as Anode for Energy Storage and Conversion: A Review. J. Power Sources 2002, 110, 1–10.

(6) Tu, J.; Song, W.-L.; Lei, H.; Yu, Z.; Chen, L.-L.; Wang, M.; Jiao, S. Nonaqueous Rechargeable Aluminum Batteries: Progresses, Challenges, and Perspectives. Chem. Rev. 2021, 121, 4903–4961.

(7) Elterman, V. A.; Shevelin, P. Y.; Yolshina, L. A.; Vovkotrub, E. G.; Borozdin, A. V. Effects of Alcl3-1-Ethyl-3-Methylimidazolium Chloride Ionic Liquid Composition on Transport Properties. J. Mol. Liq. 2020, 320, No. 114482.

(8) Lin, M. C.; Gong, M.; Lu, B. G.; Wu, Y. P.; Wang, D. Y.; Guan, M. Y.; Angell, M.; Chen, C. X.; Yang, J.; Hwang, B. J.; Dai, H. J. An Ultrafast Rechargeable Aluminium-Ion Battery. Nature 2015, 520, 324–328.

(9) Zheng, J.; Bock, D. C.; Tang, T.; Zhao, Q.; Yin, J.; Tallman, K. R.; Wheeler, G.; Liu, X.; Deng, Y.; Jin, S.; Marschilok, A. C.; Takeuchi, E. S.; Takeuchi, K. J.; Archer, L. A. Regulating Electrode Morphology in High-Capacity Aluminium and Zinc Battery Anodes Using Interfacial Metal–Substrate Bonding. Nat. Energy 2021, 6, 398–406.

(10) Li, H.; Meng, R.; Gao, Y.; Chen, B.; Jiao, Y.; Ye, C.; Long, Y.; Tadich, A.; Yang, Q.-H.; Jaroniec, M. Reversible Electrochemical Oxidation of Sulfin in Ionic Liquid for High-Voltage Al-S Batteries. Nat. Commun. 2021, 12, No. 5714.

(11) Kravchyk, K. V.; Wang, S.; Piveteau, L.; Kovalenko, M. V. Efficient Aluminum Chloride–Natural Graphite Battery. Chem. Mater. 2017, 29, 4484–4492.

(12) Chen, H.; Xu, H. Y.; Wang, S. Y.; Huang, T. Q.; Xi, J. B.; Cai, S. Y.; Guo, F.; Xu, Z.; Gao, W. W.; Gao, C. Ultrafast All-Climate Aluminum-Graphene Battery with Quarter-Million Cycle Life. Sci. Adv. 2017, 3, No. eaao7233.

(13) Ejigu, A.; Le Fevre, L. W.; Fujisawa, K.; Terrones, M.; Forsyth, A. J.; Dryfe, R. A. W. Electrochemically Exfoliated Graphene Electrode for High-Performance Rechargeable Chloroaluminate and Dual-Ion Batteries. ACS Appl. Mater. Interfaces 2019, 11, 23261–23270.

(14) Long, Y.; Li, H.; Ye, M.; Chen, Z.; Wang, Z.; Tao, Y.; Weng, Z.; Qiao, S.-Z.; Yang, Q.-H. Suppressing Al Dendrite Growth Towards a Long-Life Al-Metal Battery. Energy Storage Mater. 2021, 34, 194–202.

(15) Zhao, Q.; Zachman, M. J.; Al Sadat, W. I.; Zheng, J. X.; Kourkoutis, L. F.; Archer, L. Solid Electrolyte Interphases for High-Energy Aqueous Aluminum Electrochemical Cells. Sci. Adv. 2018, 4, No. eaau8131.

(16) Yan, C. S.; Lv, C.; Wang, L. G.; Cui, W.; Zhang, L. Y.; Ding, K. N.; Tan, H. T.; Wu, C.; Wu, T. P.; Ren, Y.; Chen, J. Q.; Liu, Z.; Srinivasan, M.; Rui, X. H.; Yan, Q. Y.; Yu, G. H. Architecting a Stable High-Energy Aqueous Al-Ion Battery. J. Am. Chem. Soc. 2020, 142, 15295–15304.

(17) Tang, Y.; Lu, L.; Roeksy, H. W.; Wang, L.; Huang, B. The Effect of Zinc on the Aluminium Anode of the Aluminium–Air Battery. J. Power Sources 2004, 138, 313–318.

(18) Suo, L. M.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X. L.; Luo, C.; Wang, C. S.; Xu, K. “Water-in-Salt” Electrolyte Enables High-Voltage Aqueous Lithium-Ion Chemistries. Science 2015, 350, 938–943.

(19) Chen, L.; Zhang, J.; Li, Q.; Vatamanu, J.; Ji, X.; Pollard, T. P.; Cui, C.; Hou, S.; Chen, J.; Yang, C.; Ma, L.; Ding, M. S.; Garaga, M.; Greenbaum, S.; Lee, H.-S.; Borodin, O.; Xu, K.; Wang, C. A 63 M Superconcentrated Aqueous Electrolyte for High-Energy Li-Ion Batteries. ACS Energy Lett. 2020, 5, 968–974.

(20) Ramamujaparam, A. Gordon, D.; Magasinski, A.; Ward, B.; Nitta, N.; Huang, C.; Yushin, G. Degradation and Stabilization of Lithium Cobalt Oxide in Aqueous Electrolytes. Energy Environ. Sci. 2016, 9, 1841–1848.

(21) Reber, D.; Grissa, R.; Becker, M.; Kühnel, R.-S.; Battaglia, C. Anion Selection Criteria for Water-in-Salt Electrolytes. Adv. Energy Mater. 2021, 11, No. 2002913.

(22) Reber, D.; Kühnel, R.-S.; Battaglia, C. High-Voltage Aqueous Supercapacitors Based on Natfsi. Sustainable Energy Fuels 2017, 1, 2155–2161.

(23) Suo, L.; Borodin, O.; Wang, Y.; Rong, X.; Sun, W.; Fan, X.; Xu, S.; Schroeder, M. A.; Cresce, A. V.; Wang, F.; Yang, C.; Hu, Y.-S.; Xu, K.; Wang, C. “Water-in-Salt” Electrolyte Makes Aqueous Sodium-Ion Battery Safe, Green, and Long-Lasting. Adv. Energy Mater. 2017, 7, No. 1701189.
(24) Ma, Z.; Kar, M.; Xiao, C. L.; Forsyth, M.; MacFarlane, D. R. Electrochemical Cycling of Mg in Mg TFSI (2)/Tetraglyme Electrolytes. Electrochem. Commun. 2017, 78, 29–32.

(25) Wang, F.; Borodin, O.; Gao, T.; Fan, X. L.; Sun, W.; Han, F. D.; Faroane, A.; Dura, J. A.; Xu, K.; Wang, S. C. Highly Reversible Zinc Metal Anode for Aqueous Batteries. Nat. Mater. 2018, 17, 543–549.

(26) Zhang, C.; Holoubek, J.; Wu, X.; Daniyar, A.; Zhu, L.; Chen, C.; Leonard, D. P.; Rodríguez-Pérez, I. A.; Jiang, J.-X.; Fang, C.; Ji, X. A ZnCl2 Water-in-Salt Electrolyte for a Reversible Zn Metal Anode. Chem. Commun. 2018, 54, 14097–14099.

(27) Liang, T. T.; Hou, R. L.; Dou, Q. Y.; Zhang, H. Z.; Yan, X. B. The Applications of Water-in-Salt Electrolytes in Electrochemical Energy Storage Devices. Adv. Funct. Mater. 2021, 31, No. 2006749.

(28) Elguja, A.; Le Fevre, L. W.; Dryfe, R. A. W. Reversible Electrochemical Energy Storage Based on Zinc-Halide Chemistry. ACS Appl. Mater. Interfaces 2021, 13, 14112–14121.

(29) Dubouis, N.; Lemaire, P.; Mirvax, B.; Salager, E.; Deschamps, M.; Grimaud, A. The Role of the Hydrogen Evolution Reaction in the Solid–Electrolyte Interphase Formation Mechanism for "Water-in-Salt" Electrolytes. Energy Environ. Sci. 2018, 11, 3491–3499.

(30) Miyazaki, K.; Takenaka, N.; Watanabe, E.; Iizuka, S.; Yamada, Y.; Tateyama, Y.; Yamada, A. First-Principles Study on the Peculiar Water Environment in a Hydrate-Melt Electrolyte. J. Phys. Chem. Lett 2019, 10, 6300–6305.

(31) Krummacher, J.; Balducci, A. Al(TFSI)3 as a Conducting Salt for Solid-Salt Electrolytes. ChemSusChem 2021, 14, 7823–7828.

(32) Chih, M.; Matsumura, S.; Takeda, H.; Higuchi, E.; Inoue, H.; Heshiki, T.; Suzuki, Y.; Aoki, Y.; Kohno, T.; Tani, Y.; Sano, S.; Kamata, S.; Nakamura, T. Highly Active Zn(II) Species in Zn(II)TFSI Electrolyte for Rechargeable Zn Metal Batteries. J. Electrochem. Soc. 2017, 164, A1841–A1844.

(33) Xu, Y.; Cui, X.; Wei, S.; Zhang, Q.; Gu, L.; Meng, F.; Fan, J.; Zheng, W. Highly Active Ziggag-Like Pt-Zn Alloy Nanowires with High-Index Facets for Alcohol Electrocatalysis. Nano Res. 2019, 12, 1173–1179.

(34) Wang, C.; Markovic, N. M.; Stamenkovic, V. R. Advanced Platinum Alloy Electrocatalysts for the Oxygen Reduction Reaction. ACS Catal. 2018, 8, 4857–4863.

(35) Zhang, S.-B.; Ran, Q.; Yao, R.-Q.; Shi, H.; Wen, Z.; Zhao, M.; Lang, X.-Y.; Jiang, Q. Lamella-Nanostructured Eutectic Zinc–Aluminum Alloys as Reversible and Dendrite-Free Anodes for Aqueous Batteries. Adv. Funct. Mater. 2020, 30, No. 18670 – 18680.

(36) Elguja, A.; Farris, K.; Spencer, B. F.; Wang, B.; Terrones, M.; Kinloch, I. A.; Dryfe, R. A. W. On the Role of Trace Metal Impurities in Electrochemical Exfoliation of Graphite: Antioxidants or Metal Oxide Decorators for Energy Storage Applications. Adv. Funct. Mater. 2018, 28, No. 1804357.

(37) Nesbitt, H. W.; Banerjee, D. Interpretation of Xps Mn(2p) Spectra of Mn Oxhydroxides and Constraints on the Mechanism of MnO2 Precipitation. Am. Mineral. 1998, 83, 305–315.

(38) Nam, K. W.; Kim, S.; Lee, S.; Salama, M.; Shterenberg, I.; Gofer, Y.; Kim, J.-S.; Yang, E.; Park, C. S.; Kim, J.-S.; Lee, S.-S.; Chang, W.-S.; Doo, S.-G.; Jo, Y. N.; Jung, Y.; Aurbach, D.; Choi, J. W. The High Performance of Crystal Water Containing Manganese Birnessite Cathodes for Magnesium Batteries. Nano Lett. 2015, 15, 4071–4079.

(39) Li, N.; Li, G.; Li, C.; Yang, H.; Qin, G.; Sun, X.; Li, F.; Cheng, H.-M. Bi-Cation Electrolyte for a 1.7 V Aqueous Zn Ion Battery. ACS Appl. Mater. Interfaces 2020, 12, 13790–13796.

(40) Wang, Y.; Ng, K. L.; Dong, T.; Azimi, G. Investigating Intercalation Mechanism of Manganese Oxide Electrocatalyst in Aqueous Aluminum Electrolyte. Electrochim. Acta 2022, 405, No. 139808.

(41) Ballard, V.; Mateos, M.; Singh, A.; Harris, K. D.; Laberty-Robert, C.; Limoges, B. The Role of Al3+-Based Aqueous Electrolytes in the Charge Storage Mechanism of MnOx Cathodes. Small 2021, 17, No. 2011515.

(42) Chao, D.; Zhou, W.; Ye, C.; Zhang, Q.; Chen, Y.; Gu, L.; Davey, K.; Qiao, S.-Z. An Electrolytic Zn–MnO2 Battery for High-Voltage and Scalable Energy Storage. Angew. Chem., Int. Ed. 2019, 58, 7823–7828.

(43) Zhang, N.; Cheng, F. Y.; Liu, Y. C.; Zhao, Q.; Lei, K. X.; Chen, C. C.; Liu, X. S.; Chen, J. Cation-Deficient Spinel ZnMn2O4 Cathode in Zn(CF3SO3)2 Electrolyte for Rechargeable Aqueous Zn-Ion Battery. J. Am. Chem. Soc. 2016, 138, 12894–12901.

(44) Pan, H. L.; Shao, Y. Y.; Yan, P. F.; Cheng, Y. W.; Han, K. S.; Nie, Z. M.; Wang, C. M.; Yang, J. H.; Li, X. L.; Bhattacharyya, P.; Mueller, K. T.; Liu, J. Reversible Aqueous Zinc/Manganese Oxide Energy Storage from Conversion Reactions. Nat. Energy 2016, 1, No. 16039.

(45) Zhang, N.; Cheng, F. Y.; Liu, J. X.; Wang, L. B.; Long, X. H.; Liu, X. S.; Li, F. J.; Chen, J. Rechargeable Aqueous Zinc-Manganese Dioxide Batteries with High Energy and Power Densities. Nat. Commun. 2017, 8, No. 405.

(46) Yang, J.; Cao, J. Y.; Peng, Y. D.; Yang, W. J.; Barg, S.; Liu, Z.; Kinloch, I. A.; Bissett, M. A.; Dryfe, R. A. W. Unravelling the Mechanism of Rechargeable Aqueous Zn-MnO2 Batteries: Implementation of Charging Process by Electrodeposition of MnO2. ChemSusChem 2020, 13, 4103–4110.
Performance of Aqueous Zn/MnO2 Batteries with Mn2+ Additive.

Mater. Today Energy 2021, 20, No. 100646.

(60) Regoutz, A.; Mascheck, M.; Wiell, T.; Eriksson, S. K.; Liljenberg, C.; Tetzner, K.; Williamson, B. A. D.; Scanlon, D. O.; Palmgren, P. A Novel Laboratory-Based Hard X-Ray Photoelectron Spectroscopy System. Rev. Sci. Instrum. 2018, 89, No. 073105.

(61) Rocher, N. M.; Izgorodina, E. I.; Rüther, T.; Forsyth, M.; MacFarlane, D. R.; Rodopoulos, T.; Horne, M. D.; Bond, A. M. Aluminium Speciation in 1-Butyl-1-Methylpyrrolidinium Bis-(Trifluoromethylsulfonyl)Amide/AlCl3 Mixtures. Chem. – Eur. J. 2009, 15, 3435–3447.

(62) Liang, S.; Teng, F.; Bulgan, G.; Zong, R.; Zhu, Y. Effect of Phase Structure of MnO2 Nanorod Catalyst on the Activity for CO Oxidation. J. Phys. Chem. C. 2008, 112, 5307–5315.