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# A salt-concentrated electrolyte for aqueous ammonium-ion hybrid batteries†

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The development of aqueous ammonium-ion batteries (AAIBs) is currently attracting great attention because of the interesting electrochemical features induced by the charge carrier  $\text{NH}_4^+$ . One possible way to improve the performance of AAIBs is increasing the salt concentration in the electrolyte. Yet, few studies focus on the complex electrode–electrolyte interface behaviors in highly concentrated electrolytes, which affect the electrochemical performance of AAIBs significantly. Herein, we aim to understand the impact of  $\text{CH}_3\text{COONH}_4$  electrolyte concentration on the  $\text{NH}_4^+$  storage performance of a bimetallic hydroxide material. Experimental and theoretical simulation results indicate that the acetate anion will participate in the construction of the solvated  $\text{NH}_4^+$  in a highly concentrated electrolyte, facilitating the adsorption of the solvated  $\text{NH}_4^+$  cluster on the electrode surface. Besides, a new partial de-solvation model is also proposed, demonstrating an energy favorable de-solvation process. Finally, an ammonium-ion hybrid battery is designed, which provides a high average discharge voltage of 1.7 V and good energy density of  $368 \text{ W h kg}_{(\text{cathode})}^{-1}$ , outperforming most of the state-of-the-art aqueous batteries. This work provides new understanding about the electrode's interfacial chemistry in different concentrated  $\text{CH}_3\text{COONH}_4$  electrolytes, establishes a correlation between the electrolyte concentration and the electrode's performances, and demonstrates the superiority of the hybrid ammonium-ion battery design.

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## Introduction

Aqueous ammonium-ion batteries (AAIBs) using non-metallic ammonium ions ( $\text{NH}_4^+$ ) as charge carriers are receiving increasing attention, due to the fast diffusion kinetics of  $\text{NH}_4^+$  and the interesting H-bonding chemistry between  $\text{NH}_4^+$  and host materials.<sup>1–4</sup> Current research in AAIBs mainly focuses on fabricating high-performance electrode materials, such as metal oxides,<sup>5–9</sup> polyanionic compounds,<sup>10</sup> conducting polymers,<sup>11,12</sup> Prussian blue analogues,<sup>13–16</sup> etc. Yet, the systematic study of electrolytes which are compatible with these  $\text{NH}_4^+$  hosting materials is still lagging, limiting the development of competitive AAIBs.

A recent breakthrough in electrolyte engineering is achieved by simply increasing the salt concentration in aqueous solution, offering distinct merits over dilute electrolytes.<sup>17</sup> In a highly concentrated aqueous electrolyte, the content of free  $\text{H}_2\text{O}$  molecules decreases, leading to less corrosion (dissolution) of electrode materials and a wider electrochemical stability window (ESW) of the electrolyte.<sup>18</sup> For instance, active material's dissolution was significantly suppressed in an AAIB using the concentrated electrolyte [5.8 m  $(\text{NH}_4)_2\text{SO}_4$ ], exhibiting 72% capacity retention and good coulombic efficiency over 1000 cycles. The ESW was also broadened from 1.34 to 2.39 V upon increasing the electrolyte concentration from 1 to 5.8 m.<sup>18</sup> Recently, Niu *et al.*<sup>19</sup> reported a highly concentrated  $\text{NH}_4\text{CF}_3\text{SO}_3$  electrolyte (24 m) for high performance AAIBs.  $\text{H}_2\text{O}$  molecules in the electrolyte were confined by  $\text{NH}_4^+$  and  $\text{CF}_3\text{SO}_3^-$  ions in the solvation sheath structure, weakening the water activity, and thus resulting in a large ESW and good cycling stability.

It is known that battery performance is highly associated with the solvation sheath structure of cations.<sup>20</sup> In AAIBs, the high population of anions in a concentrated electrolyte will force them into the solvation sheath of  $\text{NH}_4^+$ , leading to the formation of a new  $\text{NH}_4^+$ -anion- $\text{H}_2\text{O}$  solvation sheath structure.<sup>19</sup> The unique solvated  $\text{NH}_4^+$  clusters would adsorb and get de-solvated at the electrolyte–electrode interface, making it the center of charge transfer reactions.<sup>21</sup> Different from other metal

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cations,  $\text{NH}_4^+$  could interact with  $\text{H}_2\text{O}$  molecules, anions and electrode materials *via* H bonding, constituting unusual energy barriers for  $\text{NH}_4^+$  de-solvation and intercalation, resulting in distinct physical and electrochemical properties for ammonium-ion batteries.<sup>22</sup> Though previous reports have studied the solvation sheath structures of  $\text{NH}_4^+$  in highly concentrated electrolytes [*i.e.*,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{CF}_3\text{SO}_3$ ],<sup>18,19</sup> the complicated electrolyte-electrode interface processes, including the solvated  $\text{NH}_4^+$  adsorption and de-solvation, have never been studied, to the best of our knowledge.

In this work, starting from the concentration of electrolyte, we discussed how various concentrations of ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) electrolytes led to different electrochemical performances of an electrochemically activated Co-Ni double hydroxide material (A-CoNi DH). Electrochemical and spectroscopic studies combined with theoretical simulations indicated that the enhanced  $\text{NH}_4^+$  storage performance in 15 m  $\text{CH}_3\text{COONH}_4$  electrolyte was mainly due to the facilitated adsorption/de-solvation processes of the unique solvated  $\text{NH}_4^+$  on the electrode surface. Compared to the diluted electrolyte (1 m  $\text{CH}_3\text{COONH}_4$ ), the solvated  $\text{NH}_4^+$  exhibited stronger adsorption on the electrode surface in the concentrated electrolyte. In addition, a partial de-solvation model was also proposed to demonstrate an energy favorable de-solvation process in the highly concentrated  $\text{CH}_3\text{COONH}_4$  electrolyte. To illustrate the practical application of the highly concentrated electrolyte, an ammonium-ion hybrid battery [ $\text{Zn}|15\text{ m CH}_3\text{COONH}_4 + 2\text{ m Zn}(\text{CH}_3\text{COO})_2|\text{A-CoNi DH}$ ] was assembled and delivered a high energy density of  $368\text{ W h kg}_{(\text{cathode})}^{-1}$ , which is better than those of the assembled Zn-ion battery [ $\text{Zn}|2\text{ m Zn}(\text{CH}_3\text{COO})_2|\text{A-CoNi DH}$ ] and other reported ammonium-based batteries, indicating the superiority of the highly concentrated  $\text{CH}_3\text{COONH}_4$  electrolyte and the hybrid ammonium-ion battery design.

## Results and discussion

### Electrochemistry of A-CoNi DH in $\text{CH}_3\text{COONH}_4$ electrolytes with different concentrations

As a study prototype, an electrochemically activated Co-Ni double hydroxide (A-CoNi DH) was deposited on a 3D exfoliated graphite substrate (EG, Fig. S1†) using an electrochemical method reported before.<sup>21</sup> The electrochemical activation strategy could significantly enhance the electrochemical performance of the double hydroxide material (Fig. S2 and S3†).<sup>23,24</sup> Ultrathin nanosheets were uniformly grown on the exfoliated graphene/graphite sheets, forming a hierarchically porous structure (Fig. S4†). The XRD pattern of the A-CoNi DH electrode indicates the amorphous structure of the deposited material (Fig. S5a†). The chemical composition of A-CoNi DH was further characterized *via* energy dispersive X-ray spectroscopy (EDX, Fig. S5b†), Fourier transform infrared spectroscopy (FTIR, Fig. S5c†) and X-ray photoelectron spectroscopy (XPS, Fig. S5d–f†). The results suggest that the possible composition of A-CoNi DH is  $\text{Co}_{0.78}\text{Ni}_{0.22}\text{O}_{0.6}(\text{OH})_{1.27}(\text{NO}_3)_{0.05}$  (for details please see ESI, Fig. S5†).

To investigate the effect of salt concentration on aqueous  $\text{NH}_4^+$  storage, we first tested the electrochemical performance of A-CoNi DH in a three-electrode cell using ammonium acetate electrolytes with different concentrations [1 to 20 mol  $\text{kg}^{-1}$  (m)], and a saturated calomel electrode (SCE) as the reference electrode. Interestingly, we observe that the concentration of the electrolyte significantly affects the  $\text{NH}_4^+$  storage performance of the A-CoNi DH electrode (Fig. 1a). The electrode tested in the concentrated 15 m electrolyte exhibits the optimized performance, delivering a high capacity of  $220\text{ mA h g}^{-1}$  at a current density of  $0.85\text{ A g}^{-1}$ , which is much higher than that of  $172\text{ mA h g}^{-1}$  obtained in 1 m electrolyte (Fig. 1b and S6†). Further increasing the electrolyte concentration to 20 m would lead to capacity decay at a high discharge rate, which could be due to the high viscosity and poor ion conduction in the highly concentrated solution.<sup>25</sup>

The charge storage mechanism of A-CoNi DH in  $\text{NH}_4\text{Ac}$  electrolyte was studied using FTIR and XPS. Upon charging from 0 to 0.8 V *vs.* SCE (Fig. S7†), the intensity of the N–H vibration at  $1410\text{ cm}^{-1}$  decreased, and recovered during the subsequent discharging process from 0.8–0 V *vs.* SCE (Fig. 1c). This result indicates that  $\text{NH}_4^+$  participated in the charge storage of A-CoNi DH. XPS Co 2p (Fig. 1d) and Ni 2p (Fig. 1e) spectra indicate that both Co and Ni atoms are active sites for charge storage. XPS O 1s spectra of the samples can be fitted into three O containing components, *i.e.*, Co/Ni–O (529.8 eV), Co/Ni–O–H (531.4 eV), and H–O–H (533 eV), as shown in Fig. S8.† Upon discharging from 0.8 to 0 V *vs.* SCE, the content of Co/Ni–O (529.8 eV) slightly decreased, suggesting that a small number of Co/Ni–O species were converted to Co/Ni–O–H due to the inevitable  $\text{H}^+$  insertion in aqueous electrolyte. These results suggest that A-CoNi DH experienced a  $\text{NH}_4^+/\text{H}^+$  co-insertion mechanism, and  $\text{NH}_4^+$  is the main charge carrier in this work, which could be due to the highly concentrated  $\text{NH}_4^+$  as well as the neutral pH value of the electrolyte. These results are also in accordance with our previous studies.<sup>26,27</sup>

### Solvation structure of the concentrated ammonium acetate electrolytes

The above results suggest that the concentration of the electrolyte significantly affects the  $\text{NH}_4^+$  storage performance of the A-CoNi DH electrode (Fig. 1a). Therefore, we studied the structural features of the electrolytes with different concentrations. Fig. 2a indicates that the  $\text{CH}_3\text{COONH}_4$  electrolytes from 1 to 20 m all exhibit good ionic conductivity (higher than  $60\text{ mS cm}^{-1}$ ), which is higher than those of most of the concentrated aqueous electrolytes, such as 10 m  $\text{NH}_4\text{CF}_3\text{SO}_3$  ( $18\text{ mS cm}^{-1}$ ),<sup>19</sup> 30 m  $\text{ZnCl}_2$  ( $3\text{ mS cm}^{-1}$ ),<sup>28</sup> and 5 M  $\text{Zn}(\text{ClO}_4)_2$  ( $46\text{ mS cm}^{-1}$ ).<sup>29</sup> The high ionic conductivity of the electrolytes ensures fast ion transfer during charge/discharge processes.

In addition to ionic conductivity, the solvation structure of  $\text{NH}_4^+$  in these electrolytes plays an important role in the promising electrochemical  $\text{NH}_4^+$  storage performances, which is further studied *via* Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and theoretical simulation. The specific infrared active bending modes of  $\text{NH}_4^+$  and  $\text{CH}_3\text{COO}^-$



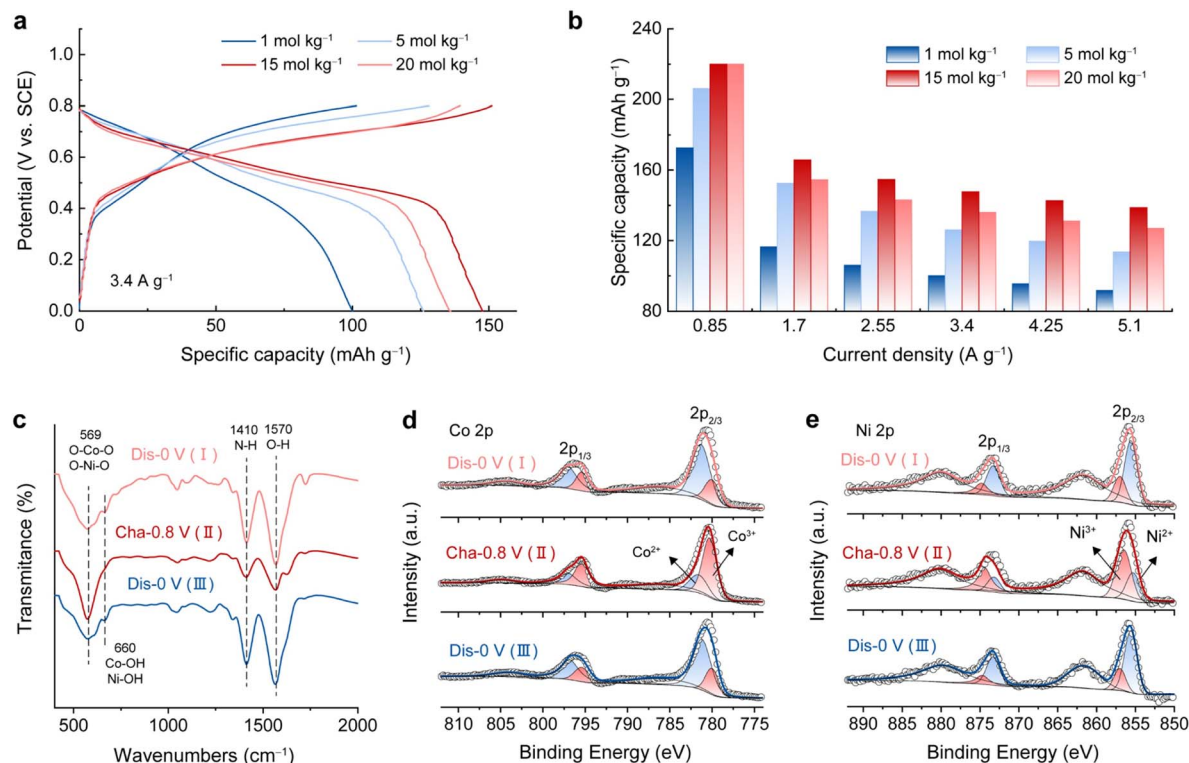


Fig. 1 (a) Galvanostatic charge/discharge curves of the A-CoNi DH electrode in different concentrations of ammonium acetate electrolyte at the current density of  $3.4 \text{ A g}^{-1}$ . (b) Rate performance of the A-CoNi DH electrode in different electrolytes. (c) FTIR, (d) XPS Co 2p, and (e) XPS Ni 2p spectra of the A-CoNi DH electrode at different states of charge.

were observed at  $1414 \text{ cm}^{-1}$  and  $1552 \text{ cm}^{-1}$  for  $1 \text{ m CH}_3\text{COONH}_4$  electrolyte, respectively (Fig. 2b).<sup>26,30</sup> Interestingly, as the electrolyte concentration increased from 1 to 20 m, the N-H vibration shifts to lower wavenumbers (from  $1414$  to  $1407 \text{ cm}^{-1}$ ), while the C-O mode moves to higher wavenumbers (from  $1552$  to  $1562 \text{ cm}^{-1}$ ). These results indicate a strong interaction between  $\text{NH}_4^+$  and  $\text{CH}_3\text{COO}^-$  in the electrolytes, and this interaction is strengthened by increasing the concentration of  $\text{CH}_3\text{COONH}_4$ .<sup>31</sup> In order to obtain more band-related information of the overlapped O-H, N-H, and C-H stretching bands at high-wavenumber positions (Fig. 2b), we classified these peaks in Fig. S9† and the results are summarized in Fig. 2c. For O-H components, the higher wavenumber peak at  $3620 \text{ cm}^{-1}$  can be attributed to the non-hydrogen bond. Two intermediate vibrations at  $3515 \text{ cm}^{-1}$  and  $3350 \text{ cm}^{-1}$  are assigned to the weak hydrogen bond, and the lowest wavenumber at  $3195 \text{ cm}^{-1}$  is labeled as the strong hydrogen bond (Fig. S9†).<sup>32,33</sup> With the increase of  $\text{CH}_3\text{COONH}_4$  concentration, the proportion of strong and weak hydrogen bonds decreased, and non-hydrogen bonds increased, indicating that the H bond network of the aqueous solution was broken, due to the high proportion of solute in the highly concentrated electrolytes.<sup>19</sup> Besides, the peaks for H bonded  $\text{NH}_4^+$  (N-H...O) shifted to lower wavenumbers when the concentration of  $\text{CH}_3\text{COONH}_4$  increased (Fig. 2b right column and Fig. S9†). In addition to the H bonds between N-H and  $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$  can also interact with  $\text{CH}_3\text{COO}^-$  upon increasing the  $\text{CH}_3\text{COONH}_4$  concentration, resulting in

the N-H...O peak shift and intensity enhancement. This strong interaction of  $\text{NH}_4^+$  with  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{COO}^-$  in the electrolytes plays a crucial role in constructing the solvation structure. In the concentrated electrolytes,  $\text{CH}_3\text{COO}^-$  participates in the construction of the  $\text{NH}_4^+$  solvation sheath and expels water molecules. Moreover, as indicated by Raman spectroscopy (Fig. S10†), when the  $\text{CH}_3\text{COONH}_4$  concentration increased, the characteristic peaks for N-H and C-O shifted, and the water activity reduced, in agreement with the FTIR results.<sup>34,35</sup>

*Ab initio* molecular dynamics (AIMD) simulation was performed to further study the  $\text{NH}_4^+$  solvation structures in different electrolytes. As study prototypes, we selected 1 and 15 m  $\text{CH}_3\text{COONH}_4$  aqueous solutions to conduct the calculation. The snapshots in Fig. 2d and e show the simulated  $\text{NH}_4^+$  solvation structures. In 1 m  $\text{CH}_3\text{COONH}_4$  electrolyte,  $\text{NH}_4^+$  coordinated with five  $\text{H}_2\text{O}$  molecules, and four  $\text{H}_2\text{O}$  molecules bonded with  $\text{NH}_4^+$  via H bonding, forming a long-lived tetrahedral cage. The fifth  $\text{H}_2\text{O}$  molecule was mobile and flexible exchanging with one of the four  $\text{H}_2\text{O}$  in the tetrahedral cage.<sup>36</sup> The average bond length between the H-bonded water molecules and the central  $\text{NH}_4^+$  in the first solvation sheath is  $1.88 \text{ \AA}$ . The radial distribution function (RDF) result suggests that the number of ligands varied in the range of four to six for N-O interaction ( $\text{NH}_4^+\text{-H}_2\text{O}$ ) in 1 m  $\text{CH}_3\text{COONH}_4$  solution (Fig. 2f, blue lines). The preferred coordination number was five, which was further confirmed by the density functional theory (DFT) results (Fig. S11†). The larger N-C distance and the low





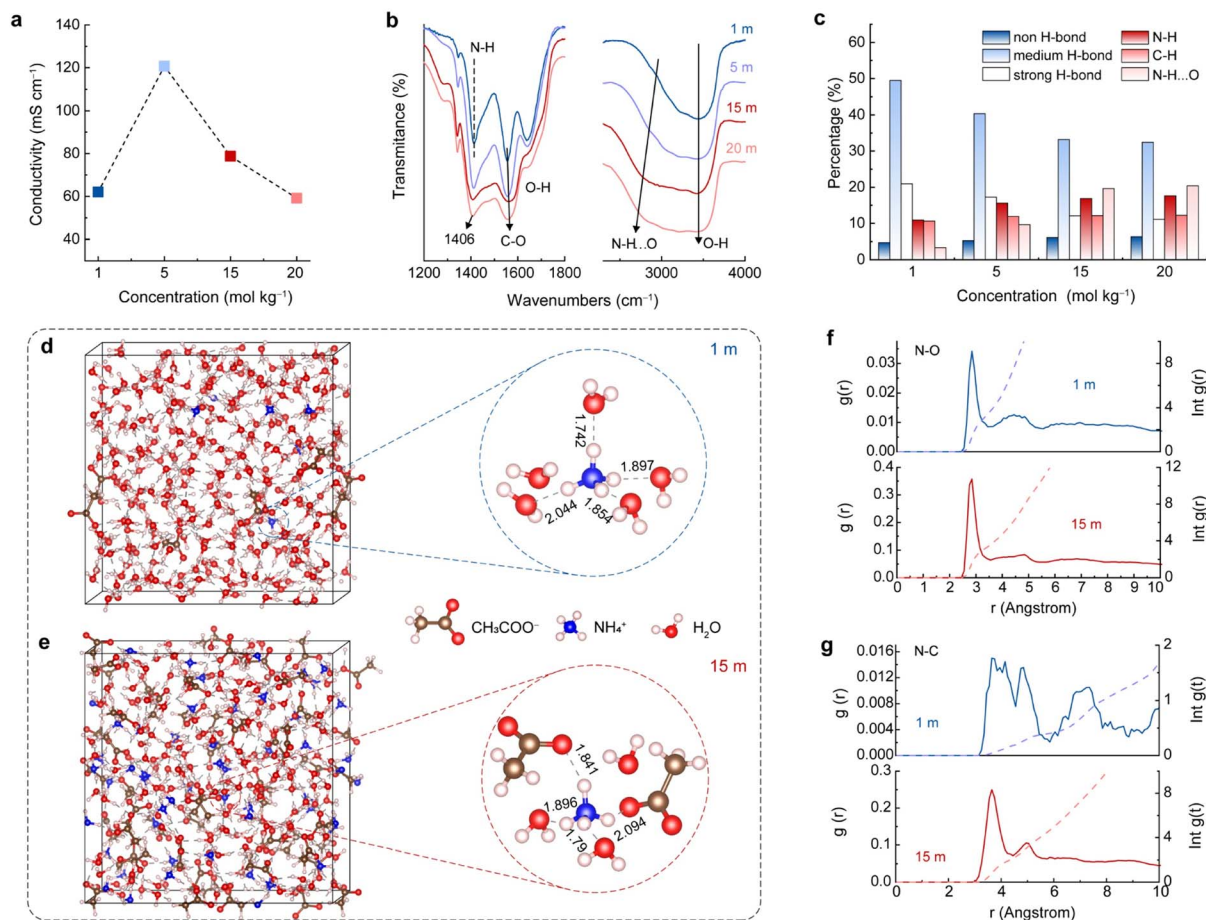


Fig. 2 (a) Electrical conductivity and (b) FTIR spectra of  $\text{CH}_3\text{COONH}_4$  electrolytes with different concentrations. (c) The corresponding percentage of the chemical bonds summarized in Fig. S9† (d) and (e) MD simulation. (f) and (g) RDF plots of N-O and N-C, and the corresponding average coordination number of 1 and 15 m  $\text{CH}_3\text{COONH}_4$  electrolytes.

coordination number as shown in Fig. 2g (blue lines) indicate that  $\text{CH}_3\text{COO}^-$  did not participate in the  $\text{NH}_4^+$  solvation sheath in 1 m  $\text{CH}_3\text{COONH}_4$  solution. By contrast,  $\text{CH}_3\text{COO}^-$  anions tend to supersede partial water molecules and participate in constructing the solvation sheath of the central  $\text{NH}_4^+$  in 15 m  $\text{CH}_3\text{COONH}_4$  electrolyte (Fig. 2e and S12†). RDFs results in Fig. 2f and g (red lines) suggest that one  $\text{NH}_4^+$  is coordinated with three  $\text{H}_2\text{O}$  molecules and two  $\text{CH}_3\text{COO}^-$  in the solvation sheath. The simulation snapshot of 15 m  $\text{CH}_3\text{COONH}_4$  shows that the average distance between  $\text{NH}_4^+$  and the H-bonded species is 1.91 Å, which is larger than that in 1 m electrolyte. The increased distance leads to smaller bonding energy and weaker interatomic bonding interaction, facilitating the subsequent de-solvation process during discharging.<sup>37</sup> The above experimental and theoretical results indicate that a higher electrolyte concentration will promote the  $\text{CH}_3\text{COO}^-$  involving in the first solvation sheath of  $\text{NH}_4^+$ , forming different solvation sheath structures compared with diluted electrolyte. The unique solvated  $\text{NH}_4^+$  clusters would adsorb and get de-solvated at the electrolyte-electrode interface, leading to distinct electrochemical features.

### Solvation structure–electrochemical performance relationship

Electrochemical impedance spectra (EIS) of the A-CoNi DH electrode were collected in different concentrated  $\text{NH}_4\text{Ac}$  electrolytes (Fig. 3a and S13†). The equivalent series resistances ( $R_s$ ,  $Z'$ -intercept) of the plots are almost the same, indicating that the solution resistances of the  $\text{NH}_4\text{Ac}$  electrolytes have little effect on the electrochemical performance. Yet, the charge transfer resistances ( $R_{ct}$ , semicircle diameter) decrease with the increase of electrolyte concentration from 1 to 15 m, and slightly increase when the concentration is higher than 15 m (Fig. S13†). In addition, Fig. 3b and c show that the A-CoNi DH electrode exhibits a much lower redox polarization potential in 15 m  $\text{CH}_3\text{COONH}_4$  electrolyte, suggesting fast reaction kinetics in the highly concentrated electrolyte. These results explain why the A-CoNi DH electrode shows optimized electrochemical performance in 15 m electrolyte.

In general, the electrode's discharging process usually involves ion diffusion in bulk electrolytes, interfacial behaviors (including ion adsorption and de-solvation) on the electrolyte-electrode interface, and subsequent ionic solid-state migration



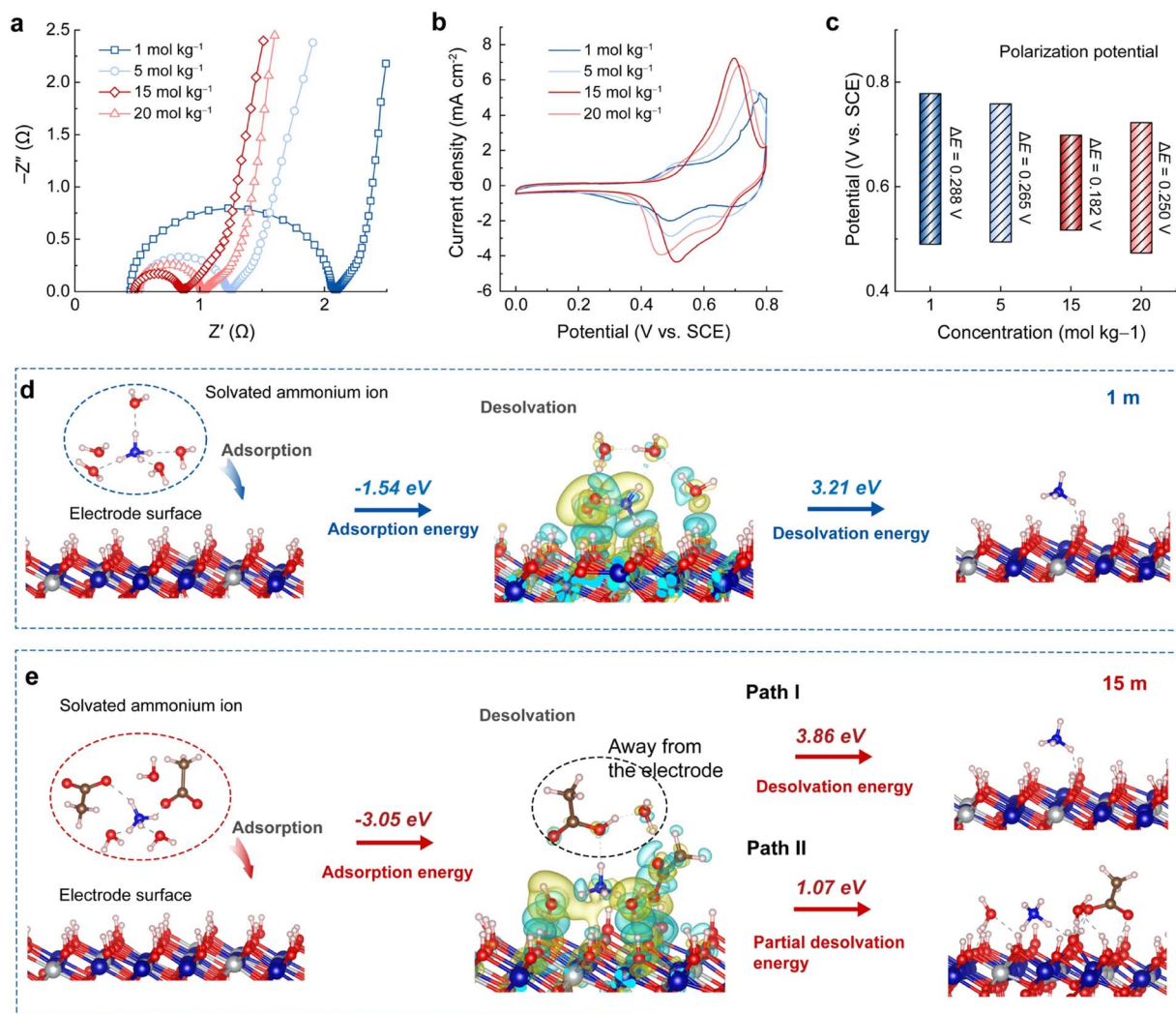


Fig. 3 (a) Nyquist plots of the A-CoNi DH electrode in different concentrated  $\text{CH}_3\text{COONH}_4$  electrolytes. (b) CV curves of the A-CoNi DH electrodes in different electrolytes at the scan rate of  $0.5 \text{ mV s}^{-1}$ . (c) The redox polarization potentials of A-CoNi DH's CV curves (b) in different electrolytes. The simulated electrolyte-electrode interface processes upon discharging in (d) 1 m, and (e) 15 m  $\text{CH}_3\text{COONH}_4$  electrolytes, respectively.

in the electrode matrix. In this work, all the  $\text{CH}_3\text{COONH}_4$  electrolytes exhibit good ionic conductivity, and the electrolyte concentration will not affect the  $\text{NH}_4^+$  solid-state migration in the A-CoNi DH bulk. Therefore, the distinct interfacial processes in different concentrated electrolytes are believed to be the primary factor that affects the electrochemical performances.

To further study the complicated interfacial behavior and disclose the solvation structure-electrochemical performance relationship in aqueous  $\text{NH}_4^+$  storage, we present a specific interfacial model that describes the adsorption and desolvation behaviors of solvated cations ( $\text{NH}_4^+$ ) on the electrode surface. Different from the conventional isolated ion adsorption model,<sup>21</sup> this specific interfacial model could better describe the complicated interaction between cation-anion-solvent and electrode materials. For the diluted electrolyte (1 m  $\text{CH}_3\text{COONH}_4$ , as shown in Fig. 3d), upon discharging, solvated  $\text{NH}_4^+$  (optimized from the solvation

structure of  $\text{NH}_4^+$  in Fig. 2) would attach on the electrode surface, and the adsorption energy is calculated to be  $-1.54 \text{ eV}$ . The differential charge density distribution of the specific adsorption model suggests strong interaction between  $\text{NH}_4^+-\text{H}_2\text{O}$  and the electrode material, which demands extra energy as large as  $3.21 \text{ eV}$  for solvent  $\text{H}_2\text{O}$  molecules de-solvating before  $\text{NH}_4^+$  insertion.

By contrast, in the concentrated 15 m electrolyte, the solvated  $\text{NH}_4^+$  cluster exhibits a much lower adsorption energy of  $-3.05 \text{ eV}$  compared with that in the diluted electrolyte (Fig. 3e). This can be ascribed to the strong coordination effect of acetate ions that participated in the solvation sheath of  $\text{NH}_4^+$  in the concentrated electrolyte, leading to compact interaction between the solvated  $\text{NH}_4^+$  and the electrode surface. As a result, a high de-solvation energy of  $3.86 \text{ eV}$  is required in a complete de-solvation process (Fig. 3e, Path I), which is unfavorable in thermodynamics. However, it is noticed that the solvation structure of  $\text{NH}_4^+$  in 15 m

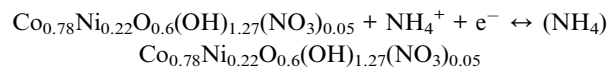


electrolyte is loose due to the large volume of  $\text{CH}_3\text{COO}^-$ , which inspires us to propose a partial de-solvation process. DFT calculations were performed to further study this process. The partial de-solvation model (Fig. 3e, Path II) reveals that the solvated  $\text{NH}_4^+$  loses one  $\text{CH}_3\text{COO}^-$  and one  $\text{H}_2\text{O}$  molecule away from the electrode surface and the interaction between  $\text{NH}_4^+$  and the  $\text{H}_2\text{O}/\text{CH}_3\text{COO}^-$  attached on the electrode surface is broken, demanding only 1.07 eV in energy, which is less than that in the complete de-solvation pathway I. As shown in the model, the strong H bonding between the left  $\text{H}_2\text{O}/\text{CH}_3\text{COO}^-$  and the hydroxide electrode remains (gray dashed lines). These surface adsorbed  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{COO}^-$  will be stable (in the form of  $\text{O}\cdots\text{H}-\text{O}-\text{metal}$ ) even after  $\text{NH}_4^+$  insertion. As shown in Fig. S14,† after discharging, the electrode's XPS C 1s signal at higher binding energy (288~291 eV for  $-\text{COO}^-$ ) was significantly enhanced compared with that of the pristine electrode. Another advantage of the partial de-solvation model is that the  $\text{NH}_4^+$  is closer to the electrode surface due to the surface rearrangement, which is beneficial for the insertion into the electrode material. Therefore, in the highly concentrated electrolyte, acetate anions would participate in the solvation structure of  $\text{NH}_4^+$ , and therefore improve the adsorption thermodynamics of the solvated  $\text{NH}_4^+$  on the electrode surface. The proposed partial de-solvation model also provides an energy favorable  $\text{NH}_4^+$  de-solvation process with low energy cost. All these features lead to the decreased charge transfer resistance and electrochemical polarization, and therefore make the highly concentrated electrolyte attractive in aqueous  $\text{NH}_4^+$  storage.

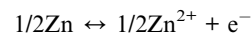
### High-performance $\text{NH}_4^+$ -ion hybrid battery

To test the practical application of the highly concentrated  $\text{CH}_3\text{COONH}_4$  electrolyte, an ammonium ion hybrid battery was assembled using A-CoNi DH as the cathode and a piece of zinc foil as the anode (Fig. 4a). To make sure that there are enough  $\text{Zn}^{2+}$  ions in the electrolyte for Zn deposition, a small amount of anhydrous  $\text{Zn}(\text{CH}_3\text{COO})_2$  was added into 15 m  $\text{CH}_3\text{COONH}_4$  electrolyte to form the optimized hybrid electrolyte, *i.e.*, 15 m  $\text{CH}_3\text{COONH}_4 + 2$  m  $\text{Zn}(\text{CH}_3\text{COO})_2$  (Fig. S15†). SEM, XRD, XPS and EDX results suggest that the  $\text{Zn}^{2+}$  in the hybrid electrolyte did not participate the charge storage of the A-CoNi DH cathode (Fig. S16–S19†). Theoretical simulation was performed to further study the  $\text{NH}_4^+$  solvation structures as well as the cation diffusion barrier (Tables S1 and S2†) in the hybrid electrolyte (Fig. 4b). The snapshot of the solvated  $\text{NH}_4^+$  indicates that the small amount of  $\text{Zn}^{2+}$  additives in the hybrid electrolyte did not change the solvation structure of  $\text{NH}_4^+$ . In addition, the calculated adsorption energy of  $\text{NH}_4^+$  (−0.08 eV) on the electrode surface is lower than that of  $\text{Zn}^{2+}$  (+0.65 eV), suggesting the favorable thermodynamic adsorption of  $\text{NH}_4^+$  on A-CoNi DH. These results explain why  $\text{Zn}^{2+}$  did not participate in the charge storage of A-CoNi DH in the hybrid electrolyte. The possible chemical reactions occurring in the hybrid device are summarized as below:

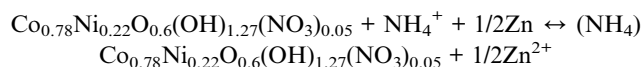
Cathode:



Anode:



Overall:



To demonstrate the superiority of this hybrid electrolyte design, we also tested the electrochemical performance of a Zn-ion battery for comparison, using the 2 m  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolyte, A-CoNi DH cathode and Zn anode, respectively. The hybrid  $\text{NH}_4^+$  ion battery exhibited a high capacity of 216 mA h  $\text{g}^{-1}$  at current density of 1 A  $\text{g}^{-1}$  and 116 mA h  $\text{g}^{-1}$  at 10 A  $\text{g}^{-1}$ , which are higher than those (193.7 mA h  $\text{g}^{-1}$ @1 A  $\text{g}^{-1}$  and 0.2 mA h  $\text{g}^{-1}$ @10 A  $\text{g}^{-1}$ ) of the Zn-ion battery using 2 m  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolyte (Fig. 4c, d and S20†). Importantly, the charge/discharge curves and the corresponding differential capacity profile of the hybrid device display a high discharge plateau around 1.76 V (Fig. 4c and S21†), because of the high  $\text{NH}_4^+$  insertion potential *vs.*  $\text{Zn}^{2+}/\text{Zn}$ . This value is much higher than that of the assembled Zn-ion battery in this work. The electrochemical impedance spectra (EIS) of the A-CoNi DH electrode in the hybrid electrolyte and 2 m  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolyte were collected and are shown in Fig. 4e. The concentrated hybrid electrolyte exhibits a smaller equivalent series resistance ( $R_s$ , the intercept of the x-axis) than 2 m  $\text{Zn}(\text{CH}_3\text{COO})_2$ , indicating the higher electrical conductivity of the hybrid electrolyte. In addition, the electrode in the hybrid electrolyte also shows a much smaller charge transfer resistance ( $R_{ct}$ ) of 0.3  $\Omega$ , which can well explain the superior rate performance of the hybrid device. This hybrid battery can deliver a good capacity retention of 75% after 2000 charge–discharge cycles at the current density of 10 A  $\text{g}^{-1}$  (Fig. 4f). The capacity degradation could be due to the slight dissolution of the active materials in the electrolyte during the charge/discharge processes (Fig. S22†). The average discharge voltage *vs.* the discharge capacity of the hybrid  $\text{NH}_4^+$ -ion battery with other aqueous batteries, including aqueous  $\text{NH}_4^+$ -ion and  $\text{Zn}^{2+}$ -ion batteries, is shown in Fig. 4g and Table S3.† The hybrid battery exhibited a high average voltage of about 1.7 V and a relatively good gravimetric capacity of 216 mA h  $\text{g}^{-1}$ , which are higher than or comparable with those of other aqueous  $\text{NH}_4^+$  and  $\text{Zn}^{2+}$ -ion batteries.<sup>8,9,15,38–50</sup> Therefore, the hybrid device exhibits a high energy density of 368 W h  $\text{kg}_{(\text{cathode})}^{-1}$  at a power density of 1703 and 192 W h  $\text{kg}_{(\text{cathode})}^{-1}$  at an excellent power density of 16 531 W  $\text{kg}^{-1}$ , outperforming most of the reported aqueous batteries (Fig. 4h and Table S4†).<sup>8,15,38–43,49,51</sup>





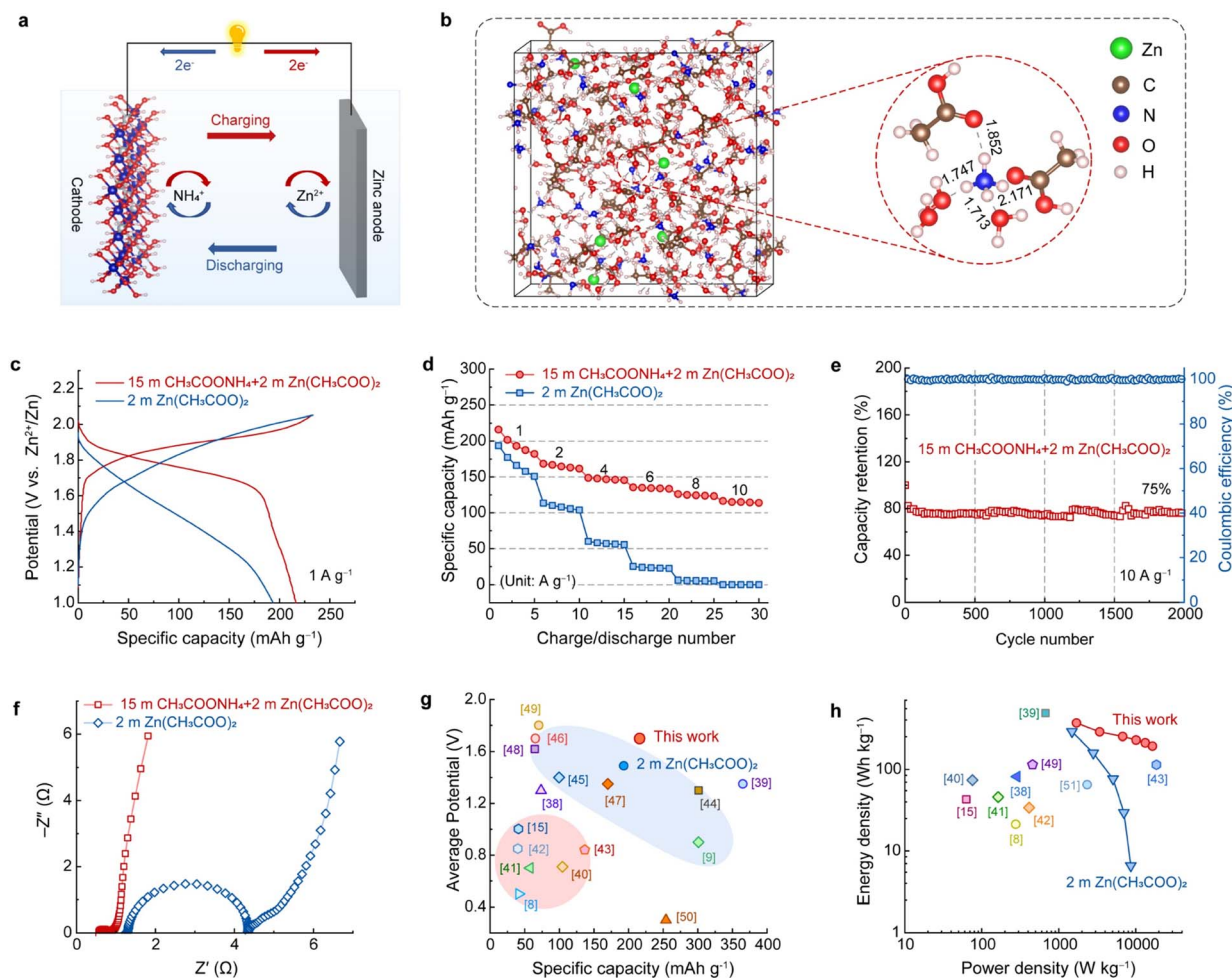


Fig. 4 (a) Schematic illustration of a hybrid ammonium ion battery. (b) MD simulation of 15 m  $\text{CH}_3\text{COONH}_4 + 2 \text{ m Zn}(\text{CH}_3\text{COO})_2$  electrolyte. (c) Galvanostatic charge/discharge curves, and (d) rate performance of the hybrid  $\text{NH}_4^+$ -ion battery and the assembled  $\text{Zn}^{2+}$ -ion battery. (e) Nyquist plots of the A-CoNi DH electrode in 15 m  $\text{CH}_3\text{COONH}_4 + 2 \text{ m Zn}(\text{CH}_3\text{COO})_2$  and 2 m  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolytes. (f) Cycling stability of the hybrid device at the current density of  $10 \text{ A g}^{-1}$ . (g) The average potential vs. discharge capacity, and (h) Ragone plots of the hybrid battery and recently reported aqueous batteries for comparison.

## Conclusions

In summary, we fabricated an electrochemically activated CoNi hydroxide material and tested the electrochemical performances of the electrode in different concentrated ammonium acetate ( $\text{CH}_3\text{COONH}_4$ , from 1 to 20 m) electrolytes. The A-CoNi DH electrode exhibited the optimized electrochemical performance in 15 m  $\text{CH}_3\text{COONH}_4$  electrolyte. The theoretical calculation, and spectroscopic and electrochemical studies established a direct correlation between the  $\text{NH}_4^+$  solvation-sheath structure and the electrode's performances in different concentrated electrolytes. In 15 m electrolyte, acetate will replace water molecules and participate in the  $\text{NH}_4^+$  solvation sheath, leading to a stronger specific adsorption between the solvated  $\text{NH}_4^+$  and the A-CoNi DH electrode. In addition, a partial de-solvation model was proposed, in which the interaction between  $\text{NH}_4^+$  and the surrounding solvated molecules, *i.e.*, acetate and water, was broken. The electrode surface adsorbed acetate and water molecules do not necessarily de-solvated into the electrolytes, but bound to the hydroxide on the electrode surface,

leading to a low energy cost process. To illustrate the practical application of the highly concentrated electrolyte, an ammonium-ion hybrid battery  $[\text{Zn}|15 \text{ m } \text{CH}_3\text{COONH}_4 + 2 \text{ m } \text{Zn}(\text{CH}_3\text{COO})_2|\text{A-CoNi DH}]$  was assembled, which provided a high energy density of  $368 \text{ W h kg(cathode)}^{-1}$ , a high working voltage of 1.7 V and good rate performance, outperforming most of the reported aqueous batteries. This work provides new understanding about the electrode-electrolyte interface processes in differently concentrated  $\text{NH}_4^+$  based electrolytes, opening a viable route to the development of promising  $\text{NH}_4^+$ -ion batteries, which may also be extended to other aqueous batteries.

## Author contributions

J. M., Y. S., and J. W. conceived the project and designed this work. The experiment was performed by J. M. under the guidance of Y. S. and X.-X. L. with the help of P. H., C. L., M. L. and Y. L. carried out the SEM and FTIR tests. J. W. carried out the DFT



calculations. J. M. and Y. S. wrote the manuscript. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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