This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

High-performance aqueous Na–Zn hybrid ion battery boosted by “water-in-gel” electrolyte

PLEASE CITE THE PUBLISHED VERSION

<https://doi.org/10.1002/adfm.202008783>

PUBLISHER

Wiley

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

This is the peer reviewed version of the following article: PAN, W. ... et al, 2021. High-performance aqueous Na–Zn hybrid ion battery boosted by “water-in-gel” electrolyte. *Advanced Functional Materials*, doi:10.1002/adfm.202008783, which has been published in final form at <https://doi.org/10.1002/adfm.202008783>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Pan, Wending, Yifei Wang, Xiaolong Zhao, Yan Zhao, Xinhua Liu, Jin Xuan, Huizhi Wang, and Dennis Yiu Cheong Leung. 2021. “High-performance Aqueous Na–zn Hybrid Ion Battery Boosted by “water-in-gel” Electrolyte”. Loughborough University. <https://hdl.handle.net/2134/14131892.v1>.

High-performance aqueous Na-Zn hybrid ion battery boosted by “water-in-gel” electrolyte

*Wending Pan, Yifei Wang, Xiaolong Zhao, Yan Zhao, Xinhua Liu, Jin Xuan, Huizhi Wang, D.Y.C Leung**

W. D. Pan, Dr. Y. F. Wang, X. L. Zhao, Prof. D.Y.C Leung
Department of Mechanical Engineering, the University of Hong Kong, 999077, China.
E-mail: ycleung@hku.hk

Dr. Y. Zhao, Dr. H.Z. Wang
Department of Mechanical Engineering, Imperial College London, London, UK.

Dr. X. H. Liu
School of Transportation Science and Engineering, Beihang University, Beijing, 100083, China.

Prof. J. Xuan
Department of Chemical Engineering, Loughborough University, Loughborough, UK

Keywords: Water-in-gel, CuHCF cathode, Na-Zn hybrid ion, dual ion battery, high voltage, high specific capacity

Abstract: Aqueous hybrid Na-Zn ion batteries (ASZIBs) are promising for large-scale energy storage due to low cost and potential for high output voltage. However, most ASZIBs show limited discharge voltage ($<2.0\text{V}$) and capacity ($<100\text{ mAh g}^{-1}$) due to inefficient usage of the dual ions. In this study, a novel large-electrochemical-window “water-in-gel” electrolyte based CuHCF-CNT/Zn Na-Zn hybrid battery is proposed, which achieves a high extraction voltage of Na ion ($2.1\text{V vs Zn/Zn}^{2+}$), together with a large discharge specific capacity (260 mAh g^{-1}) thanks to Zn-ion insertion, delivering a superior energy density of 440 Wh kg^{-1} . The hybrid battery also shows a high capacity retention of 96.8% after 450 cycles. Moreover, an ultrahigh discharge capacity of 1250 mAh g^{-1} is achieved when further coupled with the Zn- O_2 reaction, delivering the promising application of the ion intercalation and metal-air hybrid battery.

1. Introduction

Rechargeable ion batteries are regarded as the most promising energy storage system for the next generation renewable energies, such as wind and solar energy. Lithium-ion battery is the most successful secondary battery system so far, which is widely used in daily life.^[1] Nevertheless, the limited resource of lithium and flammable organic liquid electrolyte make lithium-ion battery systems high-cost together with safety concerns, such as potential explosion and toxicity. Therefore, the research on non-lithium ion batteries with aqueous electrolyte has gained considerable attention in recent years. Among all potential candidates, the aqueous Na-ion batteries (ASIBs) and the aqueous Zn-ion batteries (AZIBs) are promising to be the next-generation ion batteries due to their superior in cost, theoretical high capacity and inherent safety.^[2]

By the similar chemical nature of sodium to lithium, Na-ion batteries (SIBs) show a high theoretical specific capacity compared with Li-ion battery. Aqueous Na-ion batteries (ASIBs) further promotes the safety and cost, making it a promising choice for large-scale energy storage. However, the decomposition of water greatly restricts its stable electrochemical window. Thus, the state-of-the-art full-cell applications of ASIB are limited although lots of cathode materials show good performance in half-cell system, such as CoHCF^[3] and Na₂CoFe(CN)₆^[4]. To address this issue, lots of high-performance anode materials were developed^[5], such as NaTi₂(PO₄)₃^[6], Prussian blue analogues^[5a] and polymers^[7]. Among these efforts, the Prussian blue-like electrodes (Na₂Mn[Fe(CN)₆]/KMn[Cr(CN)₆]) based battery^[8] demonstrated the highest voltage of 2.5V, indicating the potential of ASIB for high output voltage. However, it also showed a limited specific capacity of 34 mAh g⁻¹, making it far from practical application.

By the meantime, due to the advantage of low activity of zinc metal anode, significant progresses in the development of aqueous Zn-ion batteries (AZIBs) has been witnessed in recent years, which show both high capacity and high cyclability. For instance, a high discharge capacity of 190 mAh g⁻¹ was obtained by a VS₂/Zn AZIB^[9], however, a limited

OCV of 0.9V was obtained. Although a lot of efforts have been devoted to the development of high-performance cathode materials^[10], the discharge voltage of most AZIBs was below 1.8V.

Thus, aqueous hybrid Na-Zn hybrid ion battery (ASZIB) was proposed recently, which achieved a high OCV of 2.0V by the high intercalation potential of Na⁺ in Prussian blue analogue (PBA) cathode against Zn anode^[11]. And the intercalation of Na⁺ in PBAs in the hybrid battery system was further investigated^[12], suggesting a high energy storage ability of PBAs. However, the reported hybrid batteries only showed sloping region instead of discharge plateau at high voltage region as the intercalation of Na⁺ ion were restricted by the intrinsically narrow electrochemical window of the aqueous electrolytes. Besides, most hybrid batteries^[11-13] show limited discharge specific capacity (< 100 mAh g⁻¹) compared with AZIBs due to lack of intercalation of Zn ion. Thus, the state-of-art hybrid batteries are far from even compared ASIBs and AZIBs.

Herein, a water-in-gel boosted high-performance Na-Zn hybrid ion battery was demonstrated, which utilized CuHCF/CNT composite as cathode and Zn metal as anode. A novel “water-in-gel” NaCl/ZnSO₄/sodium alginate electrolyte (NaCl/ZnSO₄/SA) was developed, providing a suitable electrochemical window for high-voltage ZnCl₄²⁻/Na⁺ (de-)intercalation. The hybrid battery takes the advantage of both Na and Zn ions insertion/extraction on the cathode, achieving a high specific capacity of 260 mAh g⁻¹ together with a high discharge voltage plateau of 2.1V, corresponding to a high energy density of 440 Wh kg⁻¹, far more than previous reported ASZIBs^[11-14]. The ASZIB also shows a stable cycling performance, which retains a high capacity retention of 96.8% after 450 cycles. Moreover, the hybrid delivered an ultrahigh discharge capacity of 1250 mAh g⁻¹ when the Zn-O₂ reaction was introduced. The result shows a promising future of aqueous hybrid ion batteries which are superior in both capacity and voltage.

2. Results and discussion

2.1. Characterization of copper hexacyanoferrate (CuHCF) and CuHCF/CNT composite cathode

Copper hexacyanoferrate (CuHCF) and single-wall carbon nanotube (SWCNT) composite (with a mass ratio of 8:1) was firstly investigated for aqueous Na-Zn hybrid battery. The XRD spectrum of synthesised CuHCF is shown in [Figure 1a](#), in which the as-prepared CuHCF nanoparticles show a high crystallinity degree and all the reflections are indexed as the face-centred cubic $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (PDF #02-0381). Due to its Prussia Blue analogues (PBAs) layer structure¹, CuHCF shows outstanding potential for Na and Zn ion storage because monovalent and divalent cations can be facile to be inserted into the PBAs framework¹⁷. And CuHCF was reported a higher redox voltage by monovalent ion intercalation compared with pristine FeHCF^[15], suggesting a higher performance. The morphology and microstructures of as-prepared CuHCF were observed by field emission scanning electron microscopy (SEM) and high-resolution TEM (HRTEM), where the CuHCF nanoparticles show a uniform size of 50-70 nm ([Figure 1b & Figure S1](#)). Its high crystallinity degree was further confirmed by selected area electron diffraction (SAED), where clear diffraction pattern of polycrystalline was shown ([Figure 1c](#)). The calculated *d*-spacing values are 0.50nm, 0.35nm, 0.25nm and 0.22nm, which match the *d*-spacing values of (200), (220), (400) and (420) crystal planes of CuHCF, respectively. To enhance the conductivity and capacity, CNT was also added to from the CuHCF/CNT composite, of which the morphology and the microstructure were also observed by SEM, TEM and elemental mapping. The CuHCF particles attached to SWCNT fibres uniformly ([Figure 1d & e and Figure S2 a & b](#)), which was further confirmed by uniform element distribution of C, Fe and N ([Figure 1f](#)). The uniform distribution of CuHCF and SWCNT can benefit the battery performance by achieving efficient intercalation of Na^+ and Zn^{2+} in CuHCF and SWCNT. Besides, compared with aggregated acetylene black additive ([Figure S2c](#)), SWCNT can improve electrochemical active surface due to its

conductive framework, decreasing electron transmission resistance, thus improve the cathode performance. Thus, the electrons transfer from cathode to current collector would be greatly improved by the CuHCF/CNT composite as [Figure S2d](#) shows, where SWCNT shows high conductive and adhesive features.

2.2 *Intercalation chemistry and Electrolyte Study*

2.2.1. Multi-ion (de-)intercalation achieved in the water-in-gel electrolyte

As shown in [Figure 2a](#), CuHCF shows a fine storage capacity for both Na^+ and Zn^{2+} in NaCl and ZnCl_2 solution, respectively, where the intercalation of Na^+ occurs at a high reduction voltage of 0.96V vs Ag/AgCl (corresponding to 2.25V vs Zn/Zn^{2+} , [Figure S3](#)), while intercalation of Zn^{2+} occurs at 0.75V and 0.21V vs Ag/AgCl (corresponding to 1.65V and 1.05V vs Zn/Zn^{2+} , [Figure S3](#)). As a higher intercalation voltage of Na^+ was shown, it is possible to promote the discharge voltage of CuHCF/Zn cell by introducing Na^+ ions. However, only a low discharge voltage (0.9V vs Ag/AgCl, [Figure 2b](#)) was obtained in 1M NaCl solution, which is not higher than that of 1M ZnCl_2 solution (0.9V vs Ag/AgCl). It is evident that the oxygen evolution reaction (OER) that precluded the de-intercalation of Na^+ in the aqueous electrolyte due to the narrow electrochemical stability window (1.5V for cathode in 1M NaCl solution, [Figure 2a](#)). Therefore, no stable discharge voltage was found although a high intercalation voltage of Na^+ (0.9 vs Ag/AgCl) was shown in previous report^[11]. Moreover, although a higher intercalation voltage of Na^+ (1.01V vs Ag/AgCl) was reported in aqueous organic electrolyte ($\text{NaCF}_3\text{SO}_3/\text{Zn}(\text{CF}_3\text{SO}_3)_2$)^[13b] for ASNIB, a low discharge capacity is found due to insufficient of intercalation of Zn ions. Thus, appropriate electrolytes with large electrochemical window together with high-performance cathodes are in great demand for ASNIBs.

Thus, inspired by “water-in-salt” electrolyte, a high-stability “water-in-gel” (WIG, [see supplementary methods](#)) electrolyte was proposed, in which the weight of solute, e.g. salt and

polymer, overcomes the weight of water. The water-in-gel NaCl/Sodium Alginate has showed an enlarged electrochemical stability window of 2.72V, which is much larger than 1.01V of NaCl solution (Figure 2c and Figure S4). Therefore, a promoted intercalation voltage of Na⁺ ion at 1.1V vs Ag/AgCl was achieved. Besides Na⁺ ion, other Zn ions, including Zn²⁺ and ZnCl₄²⁻ were also proved to be intercalated in the CuHCF cathode, showing a promoted performance than previous ASNIBs. To further investigate on the multi intercalated ions, the electrochemical behaviours of CuHCF cathode were comprehensively investigated by ion exchange membranes (Figure 2d), which can distinguish the storage of cation and anion. Thus, a high intercalation peak of Na⁺ (2.3V vs Zn/Zn²⁺) and an intercalation peak of Zn²⁺ (1.6V vs Zn/Zn²⁺) were obtained by a cation exchange membrane (CEM) covered CuHCF cathode, while reduction peaks at 1.9V and 1.6V (vs Zn/Zn²⁺, Figure 2d) were shown by an anion exchange membrane (AEM) covered CuHCF cathode, indicating the de-intercalation of ZnCl₄²⁻ [16] and Cl⁻ [17]. To further distinguish the (de-)intercalation of Cl⁻ and ZnCl₄²⁻, CV curves in HCl and ZnCl₂ electrolytes were investigated and compared. An obvious pair of redox peaks of (de-)intercalation of Cl⁻ was shown in 1M HCl at 0.7/1.1V vs Ag/AgCl, and a two reduction peaks at 0.9V and 0V vs Ag/AgCl in WIS-ZnCl₂ electrolyte were observed (Figure S5). Discharge curves Besides, two reduction peaks showed at 0.5V and 0.7V vs Ag/AgCl, indicating the Zn²⁺ and Cl⁻ can co-exist with ZnCl₄²⁻ ions in WIS-ZnCl₂ electrolyte. Moreover, a WIS-NaCl/ZnCl₂ based Na-Zn battery was proposed (Figure S6), further confirmed that Cl⁻ and ZnCl₄²⁻ would co-exist in WIG NaCl/ZnSO₄/SA electrolyte and thus co-intercalate into cathode materials. Thus, the multi-ion (Na⁺, Zn²⁺, Cl⁻ and ZnCl₄²⁻) intercalation chemistry was confirmed in the WIG electrolyte based CuHCF/Zn battery system, showing a realized concept of Na-Zn hybrid battery.

As a low electrochemical response for Zn²⁺ intercalation (0.38V vs Ag/AgCl, Figure 2c) was found by CUHCF cathode, SWCNT was added to form a CuHCF/CNT composite cathode to achieve a higher output, and the composite cathode shows high electrochemical

activity at both 1.6V-1.2V (for Zn^{2+} intercalation) and 2.1V (for Na^+ intercalation) in WIG- $\text{NaCl}/\text{ZnSO}_4/\text{SA}$ electrolyte (Figure 2e). Although SWCNT shows a lower capacity for Na^+ intercalation at 2.1V vs Zn/Zn^{2+} , a higher capacity for Zn^{2+} intercalation was shown at 1.4V vs Zn/Zn^{2+} (Figure 2f), which can strengthen the weakness of CuHCF. Moreover, the induced SWCNT improve the electrical conductivity in the cathode, lower the polarization, and thus achieve a higher discharge plateau at 2.15V vs Zn/Zn^{2+} (Figure 2f). Therefore, the CuHCF and SWCNT can cooperate well for a higher intercalation capacity (Figure S7) due to the enhanced conductivity, active surface area and diffusion kinetics, promoting the battery performance significantly.

2.2.2. Characterization and mechanism study of water-in-gel electrolyte

Although WIS- NaCl obtained a large electrochemical window by limited water, it shows a low conductivity of 9.32 mS/cm compared with highly conductive aqueous NaCl solution (85 mS/cm of 1M NaCl)^[18]. The low conductivity was resulted from weakened second hydration shell at high ion concentration^[19], which is significant for ion transportation in aqueous system^[20]. Besides, the WIS- NaCl electrolyte based hybrid battery showed low stability (Figure S8), as the free water was consumed at the interface between electrolyte and electrodes. Thus, the water-in-gel (WIG) electrolyte was developed to achieve robust performance (Figure S8) as SA has a strong affinity with water by formed hydrogen bonds between water molecules and polar groups (including OH and COO^-) along SA chains^[21], enabling the free water restored inside the WIG electrolyte rather than directly attached to the electrode (somewhat like binder^[22]), expanding the electrochemical window and decreasing loss of water by decomposition. The conductivity of WIG electrolyte was also promoted to 62.2 mS/cm, even higher than that of previously reported NaCl polymer^[23]. Although a relatively more free water existed within the WIG electrolyte, providing a suitable environment for ion transportation, a large electrochemical stability window was also obtained (Figure S4) as the electrodes were attached by an interface of sodium alginate, decreasing their direct contact with H_2O .

To further examine the structure of the WIG electrolyte, the Fourier-transform infrared spectroscopy (FTIR) spectra of pristine, reacted WIG electrolyte samples, along with free salt phases are presented in Figure 3a. The intensive bonds at 3460 cm^{-1} (Na-Cl)^[24] was readily

observed in the electrolytes of salt and WIG electrolyte (pristine and reacted), and so it is the S-O (1009cm^{-1}) bond, indicating the existence of Zn^{2+} . And C-O (1060 cm^{-1}), O-C-O (1418 cm^{-1}) and COO^- (1628 cm^{-1}) functional groups of SA was shown in the WIG electrolyte ^[25]. Thus, the coordinate bonds between the carboxylate groups and Na/Zn ions ^[26] can be built, providing a “pass-way” for cation transportation (Figure 3b). And due to random coil conformation of alginate chains affected by dissolved ions, the 3D-fibrillar, porous polymer network ^[27] will assure the uniform distribution and efficient transportation of Na, Zn ions in aqueous environment. (Figure 3b). Interestingly, Zn-Cl bond ^[28] (of ZnCl_4^{2-}) was found by cycled WIG electrolyte, which shows no evidence in pristine ZnSO_4 , revealing the formation of ZnCl_4^{2-} during cycles. As ZnCl_4^{2-} only occurs at concentrated Zn salt electrolyte^[16], this finding suggests that WIG electrolyte shows similar nature as WIS electrolyte.

To further reveal the effect of the additive of SA, a specific parametric analysis on the WIG-NaCl/SA electrolyte was conducted. With the addition of increasing amount of SA, the CV profiles retain their shapes (Figure 3c), indicating the same intercalation chemistry. And a lower resistance was found by WIG electrolyte (Figure 3d), confirming the high conductivity of the WIG electrolyte with an appropriate amount of SA additive^[27b, 29]. However, redox current intensity varied with different ratios of NaCl and SA, where peak current intensity reached the highest at the ratio of 1:0.1, then it decreases with increasing SA additive. The battery resistance was also increased with raised amount of SA (Figure 3d), indicating a lower conductivity. These results revealed that overloaded SA will hamper the reaction activity due to fewer free water inside the electrolyte. Nevertheless, the WIG-NaCl/SA with less SA additive (at a mass ratio of 1:0.1) shows the highest redox intensity (Figure 3c) but also a poor cyclability (Figure S7), indicating that electrolyte decomposition happens due to too much free water inside the WIG electrolyte.

Thus, the WIG-NaCl/SA at the mass ratio of 1:0.3 shows the best balance between conductivity and stability, which retained high stability with the additive of ZnSO_4 (Figure

S7). The reacted WIG electrolyte was investigated by SEM-EDX mapping (Figure 3e), where Na, Zn, C, O, Cl elements distributed uniformly, confirming the multi ion intercalation chemistry of the Na/Zn hybrid battery.

2.2.3. Further investigation on the multi-ion intercalation chemistry in the water-in-gel electrolyte

To further understand the $\text{Na}^+/\text{Zn}^{2+}$ ion storage behaviour of the CuHCF/CNT composite cathode, CV measurements were carried out. At 10 mV s^{-1} , 5 reduction peaks located at 2.0V (peak 1 for intercalation of Na^+), 1.85V (peak 2 for de-intercalation of ZnCl_4^{2-}), 1.65V (peak 3 for de-intercalation of ZnCl_4^{2-} and Cl^-), 1.2V (peak 4 for intercalation of Zn^{2+}) and 0.89V (peak 5 for de-intercalation of ZnCl_4^{2-}) were found (Figure 4a), indicating a complicated multi-ion storage process. To show the electrochemical dynamics of CuHCF and SWCNT separately, they were tested at various scan rates from 1 to 10 mV s^{-1} . With the continuous increase of scan rates, the CV profiles retain their shapes and gradual broaden peaks can be observed. Generally, an approach for analysing the electrochemical kinetics process can be described as following:

$$i = av^b$$

where a and b are adjustable parameters, i is the current, and v is the scan rate. Normally, the coefficient b varies in the range 0.5-1.0 where a value of 0.5 represents a diffusion-limited process, while 1.0 indicates a capacitive behaviour. For SWCNT, all the b -values are around 0.8 (Figure 4b), demonstrating that the intercalation/de-intercalation processes of SWCNT are both diffusion controlled and diffusion limited. The dynamical analysis suggests that the same intercalation type for small cations, e.g., Na^+ and Zn^{2+} , and large anion group, ZnCl_4^{2-} into carbon layers of SWCNT. For CuHCF, the b -values of the two major reduction peaks are 0.76 at 2.1V and 0.94 at 1.9V (Figure 4c). Interestingly, the reduction peak at 1.9V showed a mainly capacitor-like kinetics, indicating a different intercalation type happens for ZnCl_4^{2-} ion group, which may be interlayer intercalation rather than directly inserting into CuHCF crystals. The discharge behaviours were greatly affected by intercalation dynamics, that is, the discharge capacity of high voltage plateau ($>1.9\text{V}$) is highly dependent on current density (Figure S9a, b). Less ZnCl_4^{2-} was detected at low-current-density charged CuHCF, while

almost 5 times amount of ZnCl_4^{2-} was found at high-current-density charged CuHCF by TEM-EDX (Figure S9c-e). Noted that almost the same amount of ZnCl_4^{2-} remained in CuHCF after low-current-density discharge, indicating the existence of a diffusion barrier for (de-)intercalation of large ZnCl_4^{2-} anions. Besides, the CuHCF/CNT possessed enhanced diffusion kinetics as the value b decreased to around 0.6 (Figure S10) from mostly 0.8 of CuHCF (Figure S11), which can be attributed to the uniformly distributed CNT particles among SWCNT framework, achieving efficient ion exchange behaviours by increased interface area between CuHCF particles and electrolyte. Thus, more diffusion-controlled and less capacitive processes were obtained by CNT additive, where CuHCF/CNT composite shows a synergistic effect more than due to the enhanced conductivity, active surface area and diffusion kinetics^[30].

To investigate the multi-ion intercalation mechanism during charging and discharging process, ex-situ XRD experiments were conducted at a series of stages during charge and discharge stages (Figure 4b). As shown in Figure 4c, CuHCF maintains high crystallinity degree and no new peaks appeared after charging and discharging. This confirms a single-phase reaction for the (de-)intercalation of CuHCF. Different from the monotonic peak shifting obtained from XRD spectrum of sole-ion battery^[31], the Na-Zn hybrid battery shows a complicated procedure, where both intercalation of anion and de-intercalation of cation may occur at the same charge/discharge process. As shown in Figure 4c, the diffraction peak of (200) and (220) planes shifted lower after fully charge from 1.75V stage, during which Na^+ was extracted from and ZnCl_4^{2-} was inserted into the cathode, indicating that the large-radius ZnCl_4^{2-} anions may play a more important role in expanding the lattice dimension of CuHCF by intercalation. Also, a more specific study was conducted on discharge processes. From fully charged stage to 1.9V stage (intercalation of Na^+), the diffraction peak shifted to a slightly lower diffraction angle, indicating the slightly expanded lattice dimension^[32]. Afterwards, when discharged from 1.9V stage to 1.6V stage (de-intercalation of ZnCl_4^{2-} and Cl^-), an obviously increasing peak shift was shown, confirming the de-intercalation of ZnCl_4^{2-} greatly affects the lattice structure of CuHCF, while Na^+ shows less effect due to its smaller size. Moreover, the intercalation of Zn^{2+} was also shown by XRD spectrum as the diffraction peak shifted lower when it continued to discharge to 0.9V stage. Although SWCNT shows weak signal due to its limited amount, the XRD reflections of (111) planes of SWCNT (Figure S12c) shows the same movement pattern, indicating the ion intercalation to the layers of SWCNT^[33]. Thus, the XRD spectrum confirmed the reversible intercalation of multi ions in the Na-Zn hybrid battery.

The storage of Na and Zn ions in the CuHCF/CNT was further investigated by ex-situ XPS (Figure 4d-h). Na and Zn were found on CuHCF/CNT, where Na 1s and Zn 2p peaks decreased and shifted higher after charging (Figure 4d and e), indicating the intercalation process. Besides cations, Cl element was also observed taking part in the reaction (Figure 4f), where organic Cl 2p_{3/2} peak enhanced after charging, suggesting the intercalation of ZnCl_4^{2-} and Cl^- . To have a closer look at the intercalation mechanism, the valence change of the CuHCF was investigated. Peaks representing Cu^{1+} (952.8 and 932.6eV) and Fe^{2+} (720.1, 713.2 and 708.6eV) raised after discharge, while Cu^{2+} and Fe^{3+} became dominant after charge (Figure 4h and g), indicating that a lower valence of Cu and Fe elements was obtained due to the intercalation of Na^+ and Zn^{2+} . The intercalation chemistry was further confirmed by TEM-EDX mapping (Figure 4i, j), where Na and Zn elements found in the discharged cathode (Figure 4i). Besides, Zn and Cl elements were found in the charged cathode, indicating the intercalation of ZnCl_4^{2-} and Cl^- , while no Na element was found due to Na^+ de-intercalation.

2.3 Electrochemical Result

2.3.1. WIG-NaCl/SA electrolyte boosted Na/Zn battery

By developing the robust WIG-NaCl/SA electrolyte, high-performance Na-Zn hybrid ion battery was demonstrated (Figure 5). At a current density of 1 A g^{-1} , a high discharge capacity of 260 mAh g^{-1} was obtained, delivering a superior energy density of 440 Wh kg^{-1} . It also shows a high discharge capacity retention of 96.8% and a high coulombic efficiency of 85% after 450 cycles (Figure 5a). The hybrid battery also shows an excellent cyclability at a high current density of 5 A g^{-1} (Figure 5b), where the efficiency gradually increased due to cathode activation. The high efficiency can be attributed to the discharge plateau of (de-) intercalation of multi ions, including Na^+ , Zn^{2+} , Cl^- and ZnCl_4^{2-} (Figure S13). Moreover, stability of SWCNT and CuHCF were tested (Figure S14) as a control group, where CuHCF shows a

slightly decreased capacity, confirming the adding of SWCNT is also significant to the battery stability.

Different from other ion batteries, the Na-Zn hybrid ion battery shows an excellent performance under high current density. To be more specific, higher discharge capacity at high discharge voltage plateau of $>1.9\text{V}$ was obtained by higher current density (Figure 5c), which is caused by the current-density sensitive intercalation/de-intercalation of ZnCl_4^{2-} as mentioned previously. Similar phenomenon also happens in the large AlCl_4^- anion based Al-ion batteries^[34], indicating the higher diffusion barriers of large anion (de-)intercalation. Other discharge plateaus, for instance, the discharge plateau at 1.4V for Zn^{2+} intercalation, showed lower capacity under high current density due to over potential effect.

Self-discharge is a key issue for ion batteries, and thus it was tested by WIG and other aqueous electrolytes. Compared with other common aqueous electrolytes, such as ZnSO_4 and NaCl , the WIG electrolyte exhibits the lowest self-discharge, of which the voltage decreased from 2.14V to 1.80V after 4 hours (Figure S15). Due to lack of study on full cell research, such as separator^[35] and metal anode corrosion^[36], it is hard to avoid slight internal micro-short circuit, capacitive capacity loss and thus loss of intercalated ions. And it would be investigated in our further study to suppress the self-discharge.

2.3.2. Zn-O₂ boosted Na/Zn battery

Zn-O₂ reactions can also occur in the dilute NaCl/SA gel electrolyte, which can greatly promote the discharge capacity of Na/Zn hybrid batteries. Normally, the Zn-O₂ reaction was not involved in CuHCF/Zn cell due to a lack of OH^- . However, the Zn-O₂ reactions would be boosted by the dilute NaCl/SA gel electrolyte because of the hydrolysis of SA, leading to a weak alkaline environment (Figure S16). After sufficient O₂ was accumulated by a high-current-density charge process, a ultrahigh discharge capacity of 1300 mAh g^{-1} (based on cathode active material mass, Figure 5e) was obtained with a high discharge plateau voltage of 2.4V at first cycle in the dilute NaCl/SA gel electrolyte, corresponding to a ultrahigh

energy density of 1660 Wh kg⁻¹. Although the capacity decreased with number of operation cycles, the battery still maintained a high capacity of 600 mAh g⁻¹ (a retention of 46%) and a high energy density of 725 Wh kg⁻¹ after 50 cycles (Figure 5e and Figure S17). This finding shows a promising strategy of a reversible Zn-O₂ reaction boosted Na/Zn battery to promote the battery performance.

The high capacity was attributed to the discharge plateau at 1.2V vs Zn/Zn²⁺, where Zn-O₂ reactions rather than ion intercalation occurs as not much Na or Zn elements were found after discharge (see cathode examined by TEM-EDX, Figure S18). Further investigation was conducted by a 3-electrode system, which provides a closer look at the anode. Galvanostatic charge and discharge curves (vs Ag/AgCl) are greatly different due to Zn-O₂ reactions, where stripping/deposition of Zn occurs in WIG-NaCl/SA electrolyte (stable potential can be seen at -1.03V and -1.14V vs Ag/AgCl, respectively, Figure S19a), while ZnO was formed and reduced in dilute NaCl/SA gel electrolyte (gradually changed voltage can be seen at -1.22 to -1.42V and -1.41 to -1.10V vs Ag/AgCl, respectively, Figure S19b).

Different previous sole Na⁺ ion inserting/extracting on cathode, the intercalation of multi ions (Na⁺, Zn²⁺, Cl⁻ and ZnCl₄²⁻) occurs on the CuHCF/CNT cathode in the WIG electrolyte. Thus, a high-performance hybrid battery was proposed, outperforming most state-of-art aqueous Na-Zn hybrid batteries, aqueous Na-ion batteries and aqueous Zn-ion batteries (Figure 5f).

2.4 Dendrite formation on zinc anode

Dendrite formation is a serious problem in Zn-ion batteries and Zn-O₂ batteries, which easily causes battery failure. Thus, the formation of dendrite was investigated in the present Na/Zn hybrid system. Due to the ion-confinement by internal coordinate bonds of Zn²⁺ and SA [24c], the deposited Zn on zinc anode formed uniformly on the zinc surface, where zinc flakes were found by SEM observation (Figure 6a and b). Although thin Zn nanowires were

formed under high current density charge (Figure 6c), no large dendrite^[37] was found. Despite ZnO would be formed on the zinc anode using dilute NaCl/SA gel electrolyte, there is also no full-sized dendrite found (Figure 6d and e), compared with long dendrites found in 1M NaOH solution electrolyte (Figure 6f and g), indicating the dendrite free advantage of the gel electrolyte.

3 Conclusion

In summary, the present hybrid battery utilized a low-cost WIG-NaCl/ZnSO₄/SA electrolyte, achieving high capacity, high voltage and good stability. A high discharge voltage of 2.1V against Zn anode was achieved by sufficient intercalation of Na⁺ by the large electrochemical window of WIG electrolyte. Similar to previous reported WIS electrolyte, ZnCl₄²⁻ insertion into CuHCF/CNT cathode also takes places in WIG electrolyte, contributing to a high anion de-intercalation plateau at $\approx 1.9\text{V}$ vs Zn/Zn²⁺. Attributed to multi-ion intercalation/de-intercalation, the hybrid battery delivered a high capacity of 260 mAh g⁻¹ and a high energy density of 440 Wh kg⁻¹. The WIG electrolyte also enabled stable cycling, which shows a high capacity retention after 450 cycles. Moreover, taking advantage of the Zn/O₂ reaction, an ultrahigh discharge capacity of 1250 mAh g⁻¹ was achieved with a high discharge plateau of 2.4V. The low-cost WIG electrolyte offers a full-cell solution for high-performance hybrid battery, which is promising for practical applications.

4 Experimental Methods

Synthesis of copper hexacyanoferrate (CuHCF) and CuHCF/CNT composite cathode: CuHCF nanoparticles were synthesised by a simple one-step method. Cu(NO₃)₂·3H₂O (120 mL, 0.1M, 99%, Aladdin) was dropped into K₄Fe(CN)₆·3H₂O (120mL, 0.05M, 99%, Aladdin) solution carefully. After stirring for 30 min, the solution turned into a brown color. Then, the solution was sonicated for 20 min and stayed for 6h. The product was then centrifuged and washed with deionized water and ethanol for at least 3 times. Finally, the product was

obtained after heating in an oven at 60°C overnight. CuHCF/CNT composite cathode was obtained by mixing synthesised CuHCF and commercial SWCNT (OCSiAl) with a mass ratio of 8:1. The composite was sonicated for 1 h to achieve a uniform distribution with ethanol solvent.

Preparation of electrodes and Morphology Characterization: CuHCF/CNT composite was used as cathode active material. The cathode ink comprised of active material (CuHCF and SWCNT) and PVDF (HSV900, Arkema) (9:1), dissolved in absolute ethanol (VWR International), which was then treated in a supersonic bath for 20 min. The ink was dropped onto a carbon paper (HCP120, Hesen) substrate, then dried at 80°C for 2 h in air. Commercial graphite (AR grade, Aladdin) was also used as cathode by the same procedure. High purity zinc foil (99.9%, Qinghe guantai Metal) was used as anode material. The microstructure and chemical probing of the CuHCF cathode and the Zinc anode was examined by HR-TEM (FEI Tecnai G2) with TEM-EDX (Oxford Instruments X-Max 80T EDS Detector) and FE-SEM (Hitachi S-4800) analysis equipped with a EDX detector (Oxford Instruments X-Max 80 EDS Detector), respectively.

Electrochemical Measurements: Aqueous NaCl and ZnCl₂ electrolyte was prepared by NaCl (AR purity, Dieckmann) and ZnCl₂ (Laboratory reagent grade, Fisher Chemical) powder with D.I water (18.2 MΩ cm), respectively. The water-in-gel electrolyte was prepared by mixing salt and sodium alginate (SA, AR purity, viscosity of 350-550 mPa.s for 1% in H₂O, Brookfield LV, 20 °C, Aladdin) with D.I water, where the weight of solute (salt and SA) outnumbers the weight of water. To study the effect of the addition of SA, a series of mass ratios of 1:0.1:0.8, 1:0.3:0.8 and 1:0.5:0.8 of NaCl, SA and D.I water was utilized, while a more dilute electrolyte with a higher ratio of water (1:0.3:1.2 of NaCl, SA and D.I water) was also used. A mass ratio of 1:1:0.3:0.8 of NaCl, ZnSO₄·7H₂O (AR purity, Macklin), SA and D.I water was utilized for battery performance test. To solve the self-discharge problem, the

electrolyte additive has been studied, where $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (AR purity, Guoyao) was added at the same amount as ZnSO_4 . The electrical conductivity was measured by a commercial conductivity meter (Mettler Toledo Ltd.) with accuracy of 0.5% over the range of $0.1 \mu\text{S cm}^{-1}$ to 199.9 mS cm^{-1} . To avoid potential corrosion, the batteries were assembled with PMMA shells in a 2-electrode system. To examine the intercalated ions, cation/anion exchange membranes (Huamo Tech) were utilized, which were set between the electrolyte and the cathode. The batteries were then cycled at various current densities by a battery testing system (CT2001A, Wuhan Land). As the electrochemical behaviour of high-voltage intercalation of ZnCl_4^{2-} is highly affected by the concentration^[38], unstable charge voltage was obtained in the WIS/WIG electrolyte. Thus, charge capacity was controlled with constant voltage rather than setting a charge voltage cut-off to achieve suitable charge. (A discharge cut-off voltage of 0.85V was set.) A control group by charge cut-off voltage (2.12V and 2.115V were set with a current density of 500 mA/g) was shown in Figure R20, which suffered insufficient and over charge. For long-term cycling stability tests, a cell using the WIG electrolyte was charged for 300 mAh g^{-1} /250 mAh g^{-1} at 2.2V and discharged at a current density of 1000 mA g^{-1} /5000 mA g^{-1} . To test the rate capability of the Zn-Na battery, the discharge current densities varied from 500 to 4000 mA g^{-1} with a constant voltage charge at 250 mAh g^{-1} . In addition, for the Zn/O₂ hybrid battery test, controlled galvanostatic charge with certain capacity was used to accumulate O₂ under high current density. 3-electrode system based experiments were also conducted with Ag/AgCl as reference electrode and Pt as counter electrode, respectively. Galvanostatic discharge and charge, and CV curves were tested by an electrochemical workstation (CHI 660, Shanghai Chenhua).

XRD and Ex situ XPS characterization: Synthesised CuHCF product was tested by an X-ray Diffractometer (Rigaku SmartLab 9kW). The CuHCF/CNT cathodes, which were attached on Pt plate substrates, were charged/discharged to a series of stages to show the multi ion intercalated processes. The cathodes were rinsed with ethanol and DI water and baked at

80°C to remove the water and ethanol before XRD measurement. The cells were fully charged/discharged at a current density of 500 mA g⁻¹ for X-ray photoelectron spectroscopy (XPS) analysis. The cathodes were washed and sonicated with ethanol and DI water at least 3 times to remove residual electrolyte, then baked at 80°C to remove the water and ethanol. XPS spectra was collected on a Thermo Scientific™ K-Alpha™+ spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) operating at 100 W. Samples were analysed under vacuum ($P < 10^{-8}$ mbar) with a pass energy of 150 eV (survey scans) or 25 eV (high-resolution scans). All peaks were calibrated with C1s peak binding energy at 284.8 eV for adventitious carbon. The experimental peaks were fitted with Avantage software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to acknowledge the CRCG grant of the University of Hong Kong (201711160009) and the SZSTI of Shenzhen Municipal Government (JCYJ20170818141758464) for providing funding support to this project.

Conflict of Interest

The authors declare no conflict of interest.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] a) L. Mai, Q. Wei, Q. An, X. Tian, Y. Zhao, X. Xu, L. Xu, L. Chang, Q. Zhang, *Advanced Materials* **2013**, 25, 2969; b) J. Bai, X. Li, G. Liu, Y. Qian, S. Xiong, *Advanced Functional Materials* **2014**, 24, 3012.
- [2] a) M. Pasta, C. D. Wessells, N. Liu, J. Nelson, M. T. McDowell, R. A. Huggins, M. F. Toney, Y. Cui, *Nature communications* **2014**, 5, 1; b) Y. Wang, J. Liu, B. Lee, R. Qiao, Z. Yang, S. Xu, X. Yu, L. Gu, Y.-S. Hu, W. Yang, *Nature communications* **2015**, 6, 1; c) Z. Li, D. Young, K. Xiang, W. C. Carter, Y. M. Chiang, *Advanced Energy Materials* **2013**, 3, 290.

- [3] T. Shao, C. Li, C. Liu, W. Deng, W. Wang, M. Xue, R. Li, *Journal of Materials Chemistry A* **2019**, 7, 1749.
- [4] X. Wu, M. Sun, S. Guo, J. Qian, Y. Liu, Y. Cao, X. Ai, H. Yang, *ChemNanoMat* **2015**, 1, 188.
- [5] a) X.-y. Wu, M.-y. Sun, Y.-f. Shen, J.-f. Qian, Y.-l. Cao, X.-p. Ai, H.-x. Yang, *ChemSusChem* **2014**, 7, 407; b) L. Sharma, K. Nakamoto, R. Sakamoto, S. Okada, P. Barpanda, *ChemElectroChem* **2019**, 6, 444; c) B. H. Zhang, Y. Liu, Z. Chang, Y. Q. Yang, Z. B. Wen, Y. P. Wu, R. Holze, *Journal of Power Sources* **2014**, 253, 98; d) G.-M. Weng, J. Kong, H. Wang, C. Karpovich, J. Lipton, F. Antonio, Z. S. Fishman, H. Wang, W. Yuan, A. D. Taylor, *Energy Storage Materials* **2020**, 24, 557; e) Y. Liu, Y. Qiao, X. Lou, X. Zhang, W. Zhang, Y. Huang, *ACS Applied Materials & Interfaces* **2016**, 8, 14564.
- [6] X. Wu, Y. Cao, X. Ai, J. Qian, H. Yang, *Electrochemistry Communications* **2013**, 31, 145.
- [7] a) W. Deng, Y. Shen, J. Qian, H. Yang, *Chemical Communications* **2015**, 51, 5097; b) X. Dong, L. Chen, J. Liu, S. Haller, Y. Wang, Y. Xia, *Science Advances* **2016**, 2, e1501038.
- [8] K. Nakamoto, R. Sakamoto, Y. Sawada, M. Ito, S. Okada, *Small Methods* **2019**, 3.
- [9] P. He, M. Yan, G. Zhang, R. Sun, L. Chen, Q. An, L. Mai, *Advanced Energy Materials* **2017**, 7, 1601920.
- [10] a) B. Wu, G. Zhang, M. Yan, T. Xiong, P. He, L. He, X. Xu, L. Mai, *Small* **2018**, 14, 1703850; b) H. Li, Q. Yang, F. Mo, G. Liang, Z. Liu, Z. Tang, L. Ma, J. Liu, Z. Shi, C. Zhi, *Energy Storage Materials* **2019**, 19, 94; c) M. Liu, Q. Zhao, H. Liu, J. Yang, X. Chen, L. Yang, Y. Cui, W. Huang, W. Zhao, A. Song, Y. Wang, S. Ding, Y. Song, G. Qian, H. Chen, F. Pan, *Nano Energy* **2019**, 64, 103942; d) D. Kundu, B. D. Adams, V. Duffort, S. H. Vajargah, L. F. Nazar, *Nature Energy* **2016**, 1, 16119; e) L. Ma, N. Li, C. Long, B. Dong, D. Fang, Z. Liu, Y. Zhao, X. Li, J. Fan, S. Chen, S. Zhang, C. Zhi, *Advanced Functional Materials* **2019**, 29, 1906142.
- [11] T. Gupta, A. Kim, S. Phadke, S. Biswas, T. Luong, B. J. Hertzberg, M. Chamoun, K. Evans-Lutterodt, D. A. Steingart, *Journal of Power Sources* **2016**, 305, 22.
- [12] L.-P. Wang, P.-F. Wang, T.-S. Wang, Y.-X. Yin, Y.-G. Guo, C.-R. Wang, *Journal of Power Sources* **2017**, 355, 18.
- [13] a) W. Li, K. Wang, M. Zhou, H. Zhan, S. Cheng, K. Jiang, *ACS Applied Materials & Interfaces* **2018**, 10, 22059; b) C. Liu, Y. Sun, J. Nie, D. Dong, J. Xie, X. Zhao, *New Journal of Chemistry* **2020**, 44, 4639.
- [14] a) K. Lu, B. Song, J. Zhang, H. Ma, *Journal of Power Sources* **2016**, 321, 257; b) J. Huang, X. Chi, J. Yang, Y. Liu, *ACS Applied Materials & Interfaces* **2020**, 12, 17583.
- [15] E. Targholi, S. M. Mousavi-Khoshdel, M. Rahmanifara, M. Z. A. Yahya, *Chemical Physics Letters* **2017**, 687, 244.
- [16] Q. Guo, K. i. Kim, H. Jiang, L. Zhang, C. Zhang, D. Yu, Q. Ni, X. Chang, T. Chen, H. Xia, *Advanced Functional Materials* **2020**, 2002825.
- [17] Q. Yin, D. Rao, G. Zhang, Y. Zhao, J. Han, K. Lin, L. Zheng, J. Zhang, J. Zhou, M. Wei, *Advanced Functional Materials* **2019**, 29, 1900983.
- [18] D. E. Goldsack, R. Franchetto, A. Franchetto, *Canadian Journal of Chemistry* **1976**, 54, 2953.
- [19] S. Chowdhuri, A. Chandra, *The Journal of Chemical Physics* **2001**, 115, 3732.
- [20] J. Peng, D. Cao, Z. He, J. Guo, P. Hapala, R. Ma, B. Cheng, J. Chen, W. J. Xie, X.-Z. Li, P. Jelínek, L.-M. Xu, Y. Q. Gao, E.-G. Wang, Y. Jiang, *Nature* **2018**, 557, 701.
- [21] L. Hou, P. Wu, *Carbohydrate polymers* **2019**, 205, 420.
- [22] L. Ling, Y. Bai, Z. Wang, Q. Ni, G. Chen, Z. Zhou, C. Wu, *ACS Applied Materials & Interfaces* **2018**, 10, 5560.

- [23] S. Masood, M. Rehan, *INTERNATIONAL JOURNAL OF PHARMACEUTICAL AND CHEMICAL SCIENCES* **2012**, 1, 1591.
- [24] R. Liu, H. Lu, L. Wang, M. Tian, W. Sun, *Minerals* **2019**, 9, 41.
- [25] S. Bashir, Y. Y. Teo, S. Ramesh, K. Ramesh, M. Rizwan, *Journal of the Chilean Chemical Society* **2019**, 64, 4571.
- [26] a) E. M. Adams, B. A. Wellen, R. Thiriaux, S. K. Reddy, A. S. Vidalis, F. Paesani, H. C. Allen, *Physical Chemistry Chemical Physics* **2017**, 19, 10481; b) J. Mirtič, J. Ilaš, J. Kristl, *Carbohydrate Polymers* **2018**, 181, 93; c) Y. Tang, C. Liu, H. Zhu, X. Xie, J. Gao, C. Deng, M. Han, S. Liang, J. Zhou, *Energy Storage Materials* **2020**, 27, 109.
- [27] a) A. Doderio, S. Vicini, M. Alloisio, M. Castellano, *Rheologica Acta* **2020**, 59, 365; b) Y. O. Iwaki, M. H. Escalona, J. R. Briones, A. Pawlicka, *Molecular Crystals and Liquid Crystals* **2012**, 554, 221.
- [28] V. A. Macrae, J. C. Green, T. M. Greene, A. J. Downs, *The Journal of Physical Chemistry A* **2004**, 108, 9500.
- [29] S. Mohanapriya, S. D. Bhat, A. K. Sahu, A. Manokaran, R. Vijayakumar, S. Pitchumani, P. Sridhar, A. K. Shukla, *Energy & Environmental Science* **2010**, 3, 1746.
- [30] S. Li, X. Song, X. Kuai, W. Zhu, K. Tian, X. Li, M. Chen, S. Chou, J. Zhao, L. Gao, *Journal of Materials Chemistry A* **2019**, 7, 14656.
- [31] C. D. Wessells, R. A. Huggins, Y. Cui, *Nature Communications* **2011**, 2, 550.
- [32] Y. You, X.-L. Wu, Y.-X. Yin, Y.-G. Guo, *Journal of Materials Chemistry A* **2013**, 1, 14061.
- [33] H. Sun, W. Wang, Z. Yu, Y. Yuan, S. Wang, S. Jiao, *Chemical Communications* **2015**, 51, 11892.
- [34] a) M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, *Nature* **2015**, 520, 324; b) X. Yu, B. Wang, D. Gong, Z. Xu, B. Lu, *Advanced materials* **2017**, 29, 1604118.
- [35] M. Soltani, S. H. Beheshti, *Journal of Energy Storage* **2020**, 102019.
- [36] B. Tang, L. Shan, S. Liang, J. Zhou, *Energy & Environmental Science* **2019**, 12, 3288.
- [37] M. Biton, F. Tariq, V. Yufit, Z. Chen, N. Brandon, *Acta Materialia* **2017**, 141, 39.
- [38] X. Wu, Y. Xu, C. Zhang, D. P. Leonard, A. Markir, J. Lu, X. Ji, *Journal of the American Chemical Society* **2019**, DOI: 10.1021/jacs.9b00617.

Figure 1. Characterisation of CuHCF and CuHCF/CNT composite cathode. a) XRD spectrum, b) SEM and c) SAED images of synthesised CuHCF. d) SEM, e) TEM images and f) SEM mapping of CuHCF/CNT composite cathode, where CuHCF nanoparticles attached on CNT fibres.

Figure 2. Electrochemical behaviours of the CuHCF (CuHCF/CNT) cathode in different electrolytes. a-c) Cyclic voltammetry (CV) and galvanostatic charge and discharge curves of CuHCF cathode in 1M NaCl, 1M ZnCl₂ and WIG-NaCl/SA electrolytes. d) CV curves obtained by cation exchange membrane and anion exchange membrane covered CuHCF/Zn cell in WIS-NaCl electrolyte. e) CV curves of Na-Zn battery with CuHCF and CuHCF/CNT cathode. f) galvanostatic discharge curves of Na-Zn battery with CuHCF, CNT and CuHCF/CNT cathode.

CuHCF/CNT cathode.

Figure 3. a) FTIR spectrum of WIS-NaCl, WIS-ZnSO₄ and WIG-NaCl/ZnSO₄/SA electrolytes. b) Schematic figure of ion transportation in water-in-gel electrolyte. c, d) Cyclic voltammetry (CV) and electrochemical impedance spectroscopy EIS of Na-Zn batteries under a series ratio of NaCl/SA electrolytes. e) SEM-Mapping of the WIG-NaCl/ZnSO₄/SA electrolyte.

Figure 4. Mechanism of Na & Zn intercalation into the cathode material of CuHCF/CNT. a) CV curves of CuHCF/CNT. b) Schematic figure of different stages during charge and discharge and c) corresponding ex-situ XRD spectrum. d-h) XPS data of Na 1s, Zn 2p, Cu 2p and Fe 2p, respectively. i, j) TEM-Mapping of CuHCF/CNT cathode at charged and discharged state.

Figure 5. Electrochemical performance of WIG electrolyte-based Na-Zn hybrid battery. a, b) Cycling stability test at 1 A g^{-1} and 5 A g^{-1} , respectively. c) Cyclical stability for charge/discharge capability and coulombic efficiency at various current densities. d) Constant voltage charge and galvanostatic discharge curves at different current density. e) Galvanostatic charge and discharge curves of a Zn/ O_2 boosted CuHCF/Zn cell, where high charge current density and low discharge current density were adopted. f) Electrochemical parameters including open circuit voltage, discharge capacity, energy density and cycle life for various AZIBs, ASIBs and ASZIBs.

Figure 6. Cross section and enlarged images of zinc anode at reacted states (after 50 cycles) in WIG NaCl/ZnSO₄/SA electrolyte (a-c), dilute NaCl/SA gel electrolyte (d and e) and 1M NaOH electrolyte (f and g).

Table of content:

The “water-in-gel” electrolyte boosted Na-Zn hybrid battery achieved a multi-ion (Na^+ , Zn^{2+} , Cl^- and ZnCl_4^{2-}) intercalation chemistry on the CuHCF/CNT cathode, while only the stripping/deposition of Zn/Zn^{2+} happens on the anode. The battery delivered both a high voltage and a high discharge capacity.

A high-performance aqueous Na-Zn hybrid ion battery boosted by “water-in-gel” electrolyte

W. D. Pan, Y. F. Wang, X. L. Zhao, Y. Zhao, X. H. Liu, J. Xuan, H. Z. Wang, D.Y.C Leung*

© Copyright 2020. WILEY-VCH GmbH.

Supporting Information

A high-performance aqueous Na-Zn hybrid ion battery boosted by “water-in-gel” electrolyte

*Wending Pan, Yifei Wang, Xiaolong Zhao, Yan Zhao, Xinhua Liu, J. Xuan, Huizhi Wang, D.Y.C Leung**

Figure S1. TEM image of synthesised CuHCF.

Figure S2. (a-b) TEM images of CuHCF/CNT, where sufficient attachment sites provided by the large specific surface area SWCNT and (c) CuHCF cathodes. (d) Schematic figure of SWCNT and carbon as conductive additive.

Figure S3. Cyclic voltammetry (CV) of CuHCF/Zn cell in 1M NaCl, 1M ZnCl₂ and WIG-NaCl/SA electrolytes.

Figure S4. Electrochemical stable window tested by cyclic voltammetry of a 3-electrochemical system with Pt cathode, Pt anode and Ag/AgCl reference electrode in 1M NaCl and WIG-NaCl/ZnSO₄/SA electrolytes.

Figure S5. (a) CV curves of CuHCF/CNT cathode in 0.5M H₂SO₄, 1M HCl and WIS-ZnCl₂ electrolytes, which were conducted by 3-electrode system, where Pt was used as counter electrode and Ag/AgCl was used as reference electrode.

Figure S6. (a) CV curve and (b) stability test of WIS-NaCl/ZnCl₂ electrolyte based Na/Zn hybrid battery, where the battery shows decreased performance due to the hygroscopic ZnCl₂. (c) Corresponding charge and discharge curves during cycles, where a standard discharge plateau was shown at 1.8V vs Zn/Zn²⁺ (de-intercalation of ZnCl₄²⁻) at first, however, only a sloping region was found after the electrolyte concentration getting lower with cycles, indicating Cl⁻ was de-intercalated rather than ZnCl₄²⁻ in the low concentration electrolyte.

Figure S7. (a) Discharge curves of CuHCF, CNT and CuHCF/CNT cathodes WIG electrolytes, a computational curve by adding CuHCF and CNT curves as the mixing ratio of 8:1 was also shown, while a higher discharge capacity was obtained by CuHCF/CNT, indicating CuHCF/CNT composite shows a synergistic effect due to the enhanced conductivity, active surface area and diffusion kinetics

Figure S8. Cyclability of Na-Zn batteries in WIS-NaCl, WIG-NaCl/SA (Mass ratio of 1:0.1 and 1:0.3) and WIG-NaCl/ZnSO₄/SA (Mass ratio of 1:1:0.3) electrolytes.

Figure S9. Galvanostatic charge and discharge curves at varied current densities: (a) Charged and discharged at 0.5 A g^{-1} . (b) Charged and discharged at 2.5 A g^{-1} and discharged at 0.5 A g^{-1} . And element composition analysis of CuHCF cathode at corresponding states: (c) At low-current-density charged state. (d) At low-current-density discharged state. (e) At high-current-density charged state.

Figure S10. CV curves of a) SWCNT and b) CuHCF at different scan rates.

Figure S11. (a) CV curves of CuHCF/CNT cathode in WIG electrolyte at a series of scan rates and b) electrochemical dynamics analysis.

Figure S12. (a) Schematic figure of different stages during charge and discharge and (b) corresponding ex-situ XRD spectrum. (c) Specific XRD spectrum at small range.

Figure S13. Galvanostatic charge and discharge curves during cyclicality test at discharge current density of a) 1 A g^{-1} and b) 5 A g^{-1} .

Figure S14. (a and b) Stability test of SWCNT and CuHCF and (c) corresponding charge and discharge curves in WIG electrolyte, where the computational curve of 85% the 1st discharge cycle (Obtained by 0.85*capacity of 1-cycle curve) is mostly the same as that of the 200th cycle, indicating the same intercalation reactions happened but lower amount of CuHCF was remained. This suggests the material loss and contact loss of CuHCF cathode during cycles without SWCNT.

Figure S15. The self-discharge test of CuHCF/CNT cathode in 1M ZnSO_4 , 1M NaCl and WIG- $\text{NaCl}/\text{ZnSO}_4/\text{SA}$ electrolytes.

Figure S16. Photos of (a) WIG- NaCl/SA and (b) dilute NaCl/SA gel electrolytes; (c, d) corresponding pH value tested by pH test paper, where (d) dilute NaCl/SA gel showed alkaline, and (c) WIG- NaCl/SA showed no change due to little amount of water in the electrolyte.

Figure S17. Cyclicality test of a Zn/O₂ boosted CuHCF/Zn cell, where high charge current density and low discharge current density were adopted.

Figure S18. (a) Galvanostatic charge and discharge curves of dilute NaCl/SA gel based CuHCF/Zn cell, where a long discharge plateau at 1.2V was shown, indicating a Zn/O₂ reaction. And element composition analysis of CuHCF cathode at corresponding states: (b) At charged state and (c) At discharged state.

Figure S19. Galvanostatic charge and discharge curves of Zn anode in (a) WIG-NaCl/SA electrolyte and (b) dilute NaCl/SA gel electrolyte.

Figure S20. (a) Stability test of CuHCF/CNT based Na-Zn battery with cut-off voltage of charge and (b) corresponding charge and discharge curves.