Reversible Electrochemical Energy Storage Based on Zinc-Halide Chemistry

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ABSTRACT: The development of rechargeable Zinc-ion batteries (ZIBs) has been hindered by the lack of efficient cathode materials due to the strong binding of divalent zinc ions with the host lattice. Herein, we report a strategy that eliminates the participation of Zn\(^{2+}\) within the cathode chemistry. The approach involves the use of composite cathode materials that contain Zn halides (ZnCl\(_2\), ZnBr\(_2\), and ZnI\(_2\)) and carbon (graphite or activated carbon), where the halide ions act both as charge carriers and redox centers while using a Zn\(^{2+}\)-conducting water-in-salt gel electrolyte. The use of graphite in the composite electrode produced battery-like behavior, where the voltage plateau was related to the standard potential of the halogen species. When activated carbon was used in the composite, however, the cell acted as a hybrid Zn-ion capacitor due to the fast, reversible halide ion electrosorption/desorption in the carbon pores. The ZnX\(_2\)-activated carbon composite delivers a capacity of over 400 mAh g\(^{-1}\) and cell energy density of 140 Wh kg\(^{-1}\) while retaining over 95% of its capacity after 500 cycles. The halogen reaction mechanism has been elucidated using combinations of electrochemical and in situ spectroscopic techniques.

KEYWORDS: Zn-ion battery, halogen conversion intercalation, halogen conversion adsorption, halogen cathode, carbon–Zn halide composite, Zn-ion capacitor

1. INTRODUCTION

Aqueous rechargeable batteries are a promising class of batteries for grid-scale electrochemical energy storage owing to their low cost, ease of fabrication, high ionic conductivity, and high operational safety.\(^1\) Research on aqueous batteries in recent years has been gaining momentum from application in low-voltage divalent zinc–ion batteries (ZIB) to high-voltage monovalent lithium-ion batteries (LIBs)\(^4\)−\(^6\). In particular, ZIBs have attracted substantial interest as one of the most promising next-generation technologies because: (i) they depend on an Earth-abundant metal, which is air-stable unlike Li; (ii) their low cost, safety, and environmental benignity is attractive for grid-scale energy storage, and (iii) the volumetric energy density is approximately 3 times higher than that of Li.\(^2\)−\(^5\) Due to these favorable properties, zinc has been used as an anode material in a series of battery technologies both in conventional static cells (zinc−manganese dioxide batteries, zinc−air batteries, or Zn-graphite dual ion batteries) and in redox flow configurations (Zn−bromine or Zn−iron cells).\(^9\)−\(^10\)

The development of ZIBs is, however, hindered by a number of factors relating to aqueous electrolytes, the formation of Zn dendrites at the anode, and lack of efficient cathode materials.\(^7\) Furthermore, the codecomposition of water molecules during the deposition of Zn\(^{2+}\) is known to affect the reversibility of the Zn stripping/deposition and depletes the electrolyte due to the sustained water consumption. Wang et al. used water-in-salt electrolytes (WiSEs) to enhance the electrochemical window of water and obtained dendrite-free Zn plating/stripping with near 100% Coulombic efficiency.\(^7\) WiSEs contain a high concentration of the desired salt so that the hydrated ions outnumber free water: as there is no free water to react at the electrode surface, the overall cell voltage can be increased. The combination of small cations and large fluorinated anions in water alters the hydration behavior of the ions where the cation is strongly solvated, but the anion is not. The less solvated fluorinated anions can be reduced to form a passivating solid electrolyte interface (SEI) on the electrode surface.\(^5\) This SEI formation significantly suppresses the hydrogen evolution reaction and is largely responsible for the overall electrochemical stability window of WiSEs.\(^5\) The highest voltage window (4.9 V) recorded at the hydrophobic graphite of WiSEs contains small metal cations (Li\(^+\)) and large fluorinated anions such as bis(trifluoromethanesulfonyl)imide ([TFSI]\(^−\)) and trifluoromethanesulfonate ([TFO]\(^−\)).

Although the electrochemical reversibility of Zn stripping/deposition was enhanced and Zn dendrite formation was...
suppressed using WiSEs, the lack of an efficient cathode material for ZIBs remains a severe challenge.11,12 Some of the cathode materials developed to date are Prussian blue analogs,13,14 manganese oxides,15−18 and vanadium oxides.11,12 Each of these materials suffers from limited specific capacity, far below the theoretical capacity of the Zn anode (820 mAh g−1), a low-voltage plateau (<1.4 V), and a low rate capability due to their poor electronic conductivity. The low performance of these cathodes is mainly attributed to the high polarization of the divalent Zn2+ ions leading to strong binding with the host lattice and sluggish solid-state migration dynamics.1,12 Therefore, the development of efficient cathodes should use different combinations of battery chemistry, for example, reversible deposition and stripping of Zn as the anode half-reaction and reversible atomic intercalation or plating of non-Zn-ion species as the cathode half-reaction. This strategy not only avoids the intercalation of Zn2+ to the host cathode material but also allows the flexibility to fine tune and increase the output voltage, which is the main barrier limiting the overall performance.

Herein, we describe a new class of composite cathode materials that contain Zn halides (ZnCl2, ZnBr2, and ZnI2) and carbons (graphite or activated carbon), where the halide ions act both as charge carriers and as redox centers. It should be noted that our approach differs from the conventional Zn−bromine flow battery, where bromide is oxidized to bromine and stored in an external tank.19 The approach we pursue in the current study uses Zn halide immobilized on carbon hosts as the cathode, where the redox activity of the halides is exploited to store more charge. In other words, the halides

Figure 1. (A) Thermogravimetric analysis (TGA) traces recorded for a WiTS gel electrolyte obtained by ramping the temperature from 30 to 800 °C at a rate of 10 °C min−1 under N2. The inset shows the photographic images of a WiTS gel electrolyte, the scale bar is 5 cm. (B) Cyclic voltammetry (CV) recorded at a 3 mm diameter glassy carbon (GC) electrode at 10 mV s−1 using a WiTS gel electrolyte between −0.2 and 4.2 V. (C) CVs recorded with a symmetrical Zn|Zn cell at 1 mV s−1 in a WiTS gel electrolyte before and after cycling for 40 h using galvanostatic charge−discharge. (D) Galvanostatic charge−discharge curve obtained using a symmetrical Zn|Zn cell in a WiTS gel electrolyte and 2.0 M ZnSO4 (aq) at 0.2 mA cm−2. (E) Scanning electron microscopy (SEM) image of a fully discharged Zn substrate, the scale bar = 20 μm. (F) SEM of a fully charged Zn substrate, scale bar = 20 μm.
undergo a “conversion−intercalation/adsorption” reaction inside the carbon structure when the cell is charged using a Zn\(^{2+}\) conducting water-in-trisalt (WiTS) gel electrolyte. Our approach also removes the halogen cross-over seen in Zn\(^{-}\)bromine cells as the halogen is confined (intercalated or adsorbed) within the carbon structure upon oxidation. The variety of the halogen species means that the cell voltage can be fine-tuned and increased. The standard reduction potentials of I\(^{-}/I_2\), Br\(^{-}/Br_2\), Cl\(^{-}/Cl_2\), and F\(^{-}/F_2\) redox couples are 0.54, 1.09, 1.36, and 2.8 V vs standard hydrogen electrode (SHE), respectively.\(^{20}\) The combination of the zinc-halide−carbon cathode with a Zn anode can therefore generate an open-circuit voltage that ranges between 1.3 and 3.5 V depending on the halide type. The flexible and non-flammable semisolid WiTS gel electrolyte, which is compatible with the halogen cathode, exhibited fast electrode kinetics for Zn oxidation and reduction without the formation of Zn dendrites. We will show that both the identity of the Zn halide and carbon structure in the cathode produces electrochemical energy storage devices that fundamentally differ from one another. The resultant composite electrodes can deliver a capacity of 480 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\) with a corresponding energy density of 140 Wh kg\(^{-1}\).

2. RESULTS AND DISCUSSION

2.1. WiTS Gel Electrolyte Formulation and Characterization. The robust Zn\(^{2+}\) conducting gel electrolyte was formulated from water-in-trisalt (WiTS) electrolyte by mixing ZnSO\(_4\), Zn(TFO)\(_2\), and LiTFSI (in a 1:1:2 mass ratio, respectively) in 20% water using 10% poly(tetrafluoroethylene) (PTFE) polymer binder. The resulting white gel is a highly flexible, yet semisolid, electrolyte that can be molded to any shape (inset of Figure 1A for optical image). Each of the components contributes to the unique properties of the gel. LiTFSI was used as it is soluble in water to a high concentration (when compared to Zn(TFO)\(_2\) or ZnSO\(_4\)) to reach the water-in-salt regime. It is also used as a source of the [TFSI]\(^{-}\) anion since it is believed that the reduction of [TFSI]\(^{-}\) is responsible for the formation of the passivating SEI, which extends the overall electrochemical window.\(^{5,7}\) We also note that in the absence of ZnSO\(_4\) the gel is very sticky to handle, while in the absence of Zn(TFO)\(_2\), a rigid dry material is formed, as excess ZnSO\(_4\) pulls water from the mixture. The thermal decomposition of the gel electrolyte was studied by thermogravimetric analysis (TGA), which shows four mass losses due to the loss of H\(_2\)O (<200 °C), decomposition of [SO\(_4\)]\(^{2-}\) (200−284 °C, ~10%), [TFO]\(^{-}\) (323−450 °C, ~34%), and [TFSI]\(^{-}\) (>450 °C).\(^{21−23}\) The TGA also shows the gel contained about 15% water. The ionic conductivity of the gel electrolyte was determined using alternating current (AC) impedance (Figure S1) and was found to be 6 mS cm\(^{-1}\), which is comparable to that of nonaqueous electrolytes (9.0 mS cm\(^{-1}\)) used in commercial
The electrochemical window of the gel, as well as the reversibility of Zn plating and stripping, was investigated using cyclic voltammetry (CV) at a glassy carbon (GC) disk electrode. The gel electrolyte exhibited fast kinetics for Zn oxidation/reduction and achieved a potential window of 3.0 V (Figure 1B), which is comparable to WiSE-based on 21 m LiTFSI. The long-term electrochemical reversibility of the Zn plating and stripping processes in the WiTS gel electrolyte was investigated using a Zn|Zn symmetric cell under galvanostatic and CV methods. Figure 1C shows the CV obtained before and after several charge–discharge cycles; in each case, the gel electrolyte exhibited reversible Zn redox chemistry with the ratio between the anodic (i\text{pa}) and cathodic peak currents (i\text{pc}) being one which indicates that the Coulombic efficiency of the cell is near 100%. The kinetics of Zn oxidation/reduction, however, significantly improved after cycling, as exemplified by the peak-to-peak (∆Ep) separation that decreased from ~0.4 to 0.2 V. The decrease in ∆Ep with cycling is most likely due to the removal of surface oxides from Zn, which impede electron transfer. In addition, the current due to Zn oxidation/reduction is increased by a factor of 5 after cycling, which could be due to an increase in the active surface area. The charge–discharge curve (Figure 1D) also showed similar behavior where the overpotential (η) for Zn stripping/plating decreased from about 0.6 to 0.2 V after 10 cycles and stabilized at 0.2 V even after the cell was cycled for 40 h at 0.2 mA cm⁻². The cell can operate continuously without short circuiting (no formation of dendrites) for over 400 h at 0.1 mA cm⁻² with a much lower η for Zn|ZnCl₂ redox reactions (see Figure S2). In sharp contrast, in a dilute electrolyte (2 M ZnSO₄), a rapid polarization started to occur after nine cycles most likely due to the formation of Zn dendrites and other associated problems including oxide formation (Figure 1D). These observations demonstrate that the gel electrolyte is an excellent Zn²⁺ conductor with very facile Zn stripping/plating kinetics. Both the stability and the kinetics of the Zn couple in the WiTS gel electrolyte are superior to those in solution-based aqueous and nonaqueous ionic liquid-based electrolytes. The presence or absence of Zn dendrite formation in this gel electrolyte is also examined using SEM after galvanostatic cycling of a Zn|Zn symmetric cell for 40 h. The Zn-plated substrate exhibited a dense and uniform layeredlike structure after Zn stripping, this dense structure is completely removed in contrast, in a dilute electrolyte (2 M ZnSO₄), a rapid polarization started to occur after nine cycles most likely due to the formation of Zn dendrites and other associated problems including oxide formation (Figure 1D). These observations demonstrate that the gel electrolyte is an excellent Zn²⁺ conductor with very facile Zn stripping/plating kinetics. Both the stability and the kinetics of the Zn couple in the WiTS gel electrolyte are superior to those in solution-based aqueous and nonaqueous ionic liquid-based electrolytes. The presence or absence of Zn dendrite formation in this gel electrolyte is also examined using SEM after galvanostatic cycling of a Zn|Zn symmetric cell for 40 h. The Zn-plated substrate exhibited a dense and uniform layeredlike structure after Zn stripping, this dense structure is completely removed. In summary, this Zn²⁺-conducting WiTS gel electrolyte provides the advantage of safety (as it is nonflammable) and enables certain battery components to be removed (such as the polymer separator). The elimination of the separator from the cell will significantly reduce the contact resistance of the interface. Then, we consider the cathode chemistry involving the carbon host.

### 2.2. Aqueous Zn(Graphite–ZnX₂) Cell

The electrochemistry of confined Zn halides within a graphite electrode was examined using the WiTS gel electrolyte in full-cell Zn batteries. The free-standing graphite–ZnX₂ cathodes were prepared by mixing the desired halide and natural graphite at a mass ratio of 1:3 with 5% PTFE binder. Figure 2A shows the CVs recorded at the cathodes of graphite–ZnI₂ (G–ZnI₂), graphite–ZnBr₂ (G–ZnBr₂), and graphite–ZnCl₂ (G–ZnCl₂) combined with Zn anodes in cells using the WiTS gel electrolyte. Significantly, both G–ZnI₂ and G–ZnBr₂ showed reversible redox reactions at the characteristic formal potentials of I⁻/I₂ (1.17 V vs Zn/Zn²⁺) and Br⁻/Br₂ (1.67 V vs Zn/Zn²⁺). The oxidative redox reactions are therefore attributed to the conversion of the halide ion (I⁻, Br⁻) to elemental halogen (I or Br), which is stabilized by sequential intercalation/adsorption into graphite galleries to form a solid graphite intercalation compound (GIC) (eq 1). This oxidation process releases Zn²⁺, which is transported through the gel electrolyte to replace the ions reversibly plated on the Zn anode (eq 2). The reduction process at the cathode is due to the deintercalation and reduction of I²/Br₂ to recombine with Zn²⁺ (n is the molar ratio of carbon atoms to the intercalated/adsorbed halogens in the GIC). The ratio between the i\text{pa} and the i\text{pc} being one in Figure 2A demonstrates the high reversibility of eq 1.

\[
2C_n + ZnX_2 \leftrightarrow 2C_n[X] + Zn^{2+} + 2e^-
\]

(1)

\[
Zn^{2+} + 2e^- \leftrightarrow Zn
\]

(2)

In contrast, the CV obtained using the G–ZnCl₂ cathode showed a lower current and a lower degree of reversibility with a sharp undefined oxidation peak and a small reduction peak. The poor reversibility of G–ZnCl₂ suggests the formation of an irreversible product during battery charging. This is in contrast to G–LiCl which has been reported to display a reversible Cl⁻ conversion–intercalation process in WiSEs. The fact that the conversion–intercalation of ZnCl₂ is irreversible suggests that the metallic counterions have a strong impact on the conversion–intercalation process. It has been shown that the chemical intercalation of ZnCl₂ into graphite forms a strong complex with the carbon species to form ZnCl₂–carbon. Indeed, characterization of a fully charged G–ZnCl₂-containing electrode using XPS showed the formation of C–Zn–C bonds at a low binding energy (283.0 eV) when analyzing the high-resolution Cl 1s spectrum (Figure 2B). Furthermore, the signal due to Zn carbide is still present and increased for the fully discharged cathode, which confirms the irreversibility of the process, manifested in the CV response (Figure 2C). The slight shift to high binding energy (283.5 eV) during discharge indicates a change in the environment of Cls presumably due to the increase in the concentration of chloride along with Zn inside the carbon. This data demonstrates that ZnCl₂-based cathode materials cannot be combined with sp²-carbon to form a secondary ZIB.

Figure 2D presents the discharge curves at 50 mA g⁻¹ of the ZIB full cells with the WiTS gel electrolyte for different halide-based cathodes. As expected, G–ZnCl₂ showed a very low capacity with the absence of any useable voltage plateau due to the irreversible reaction. The G–ZnI₂ and G–ZnBr₂ cathodes showed voltage plateaus that correspond to their respective redox reactions, G–ZnI₂ at 1.17 V and G–ZnBr₂ at 1.67 V vs Zn/Zn²⁺, in agreement with the CV data. The cathode made from the equimolar mixture of ZnCl₂ and ZnBr₂ showed two discharges voltage plateaus; a small one at 1.90 V, due to the Cl⁻/Cl₂ redox reaction, and the other at 1.67 V due to the Br⁻/Br₂ redox reaction. Nonetheless, the specific capacity of each cathode is much lower than the theoretical capacity of a halogen GIC (309 mAh g⁻¹ for MBr₂ and 632 mAh g⁻¹ for MCl₂). Among the cathodes tested, the best specific capacity (55 mAh g⁻¹) was obtained using G–ZnCl₂–ZnBr₂ with the
others being lower than 30 mAh g\(^{-1}\). However, the capacity decayed by more than 50% after 200 cycles due to the continual formation of zinc carbide species (Figure S4). The specific capacity quoted is based on the total mass of the cathode (mass of graphite plus mass of halide).

In \textit{in situ} Raman spectroscopy was used to understand the halide intercalation mechanism and to rationalize the poor performance of the G--ZnX\(_2\) using the WiTS gel electrolyte. Figure 3 shows the fully charged--discharged Raman spectra for each cathode. The free-standing sample for each cathode showed a similar response at open-circuit potential (OCP), with the characteristic graphite bands, G-band at 1580 cm\(^{-1}\) and a small D-band at \(\sim 1350\) cm\(^{-1}\), being shown and no other bands associated with Zn halides. The fully charged G--ZnI\(_2\) electrode displayed an intense Raman signal at 172 cm\(^{-1}\) due to surface-bound iodine species.\(^{34,35}\) However, the absence of a G-band splitting suggests that there is no intercalation of the iodide species into the graphite galleries (see the inset of Figure 3A). While other halogens including chlorine and bromine intercalate into graphite, iodine has a strong affinity for adsorption rather than intercalation.\(^{36,37}\) G--ZnBr\(_2\) also exhibited similar behavior when fully charged where it showed a signal at 240 cm\(^{-1}\) due to the stretching mode of Br\(_2\)\(^{-}\). The G-band of the material, however, was split into two Raman modes: the E\(_{2g2b}\) mode at \(\sim 1580\) cm\(^{-1}\) due to the interior unintercalated original layers and the E\(_{2g2b}\) at 1604 cm\(^{-1}\) due to the bounding layers next to the intercalants. The fact that the intensity of the E\(_{2g2b}\) mode is twice that of the E\(_{2g2b}\) together with the higher wavenumber for the E\(_{2g2b}\) reflects the dilute staging of bromine species into graphite galleries.\(^{38}\) The opposite trends were observed during discharge that involves the desorption/deintercalation of the halogen at each cathode (Figure 3B) characterized by the absence of halogen-related bands, further confirming the reversibility of the process. This \textit{in situ} Raman spectroscopy data shows that reversible surface adsorption/desorption is the dominant reaction mechanism in G--ZnI\(_2\) and G--ZnBr\(_2\) electrodes. This observation is similar to Na chemistry at a graphite electrode where Na plates are on the graphite surface rather than intercalating due to its size and weaker chemical interaction with the graphite planes.\(^{39}\) The use of hard carbon in the composite may improve the cell performance.

The electrode that contained ZnCl\(_2\) (neat or mixed with ZnBr\(_2\)) on the other hand showed a more intense E\(_{2g2a}\) at 1609 cm\(^{-1}\), approximately twice that of the E\(_{2g2b}\) a characteristic of the formation of a stage-3 GIC.\(^{39}\) However, the G-band splitting remained after the battery was fully discharged, which demonstrates that the intercalation process is nonreversible, in agreement with the XPS analysis (inset of Figure 3B). Furthermore, the fully charged G--ZnCl\(_2\) or G--ZnBr\(_2--\) ZnCl\(_2\) did not show the band associated with Cl\(_2\) (expected in the region of 530--570 cm\(^{-1}\)) intercalant due to the reaction of ZnCl\(_2\) with the graphite host as previously discussed. Figure 3C shows the Raman spectrum response for the G--ZnI\(_1--\) ZnBr\(_2\) composite electrode. It is interesting to note that significant Raman frequency shifts for both iodide and Br-species were observed when analyzing the G--ZnI\(_1--\) ZnBr\(_2\) sample. When the cell was charged to 1.4 V, a broad band at 172 cm\(^{-1}\) due to surface-bound iodine species (also the case for G--ZnI\(_2\) charged to 1.9 V) was seen. When the voltage was increased to 1.9 V, sharp bands at 180 and 189 cm\(^{-1}\) were observed along with the G-band splitting. The formation of these new bands is most likely due to the formation of interatomic IBr intercalants.\(^{41}\) A frequency downshift is often observed for surface-bound halogen when compared to free halogen due to the interaction of halogen with host materials, which weakens the interatomic bonds of the intercalants.\(^{41,42}\) In contrast, the G--ZnCl\(_2--\) ZnBr\(_2\) sample did not show the BrCl formation due to the reaction of ZnCl\(_2\) with the graphite (Figure 3A).

Overall, the analysis of Raman spectra indicates that the size of halogens significantly impacts the reaction mechanism at the graphite cathode. The conversion--adsorption process occurs when the halogen is larger, for example in G--ZnI\(_2\), and the conversion--intercalation process occurs for smaller halogens such as G--ZnCl\(_2\). Even though ZnCl\(_2\) can reach a reasonably high intercalation staging, the irreversible reaction is the hindering factor for use in practical ZIBs. The low capacity of

![Figure 3](https://dx.doi.org/10.1021/acsami.0c020622)  
**Figure 3. In situ** Raman spectral series of a Zn|G--ZnX\(_2\) cell in the WiTS gel electrolyte during full (A) charge and (B) discharge. The insets in (A) and (B) show the graphite G-band region. (C) Comparison of Zn|G--ZnX\(_2\) at different voltages.
the full-cell battery at each electrode is explained by the conversion–adsorption reaction mechanism, which needs a high surface area carbon rather than the low surface area graphite.

2.3. Aqueous Zn(Activated Carbon–ZnX₂) Cell. Given that the conversion–adsorption process is the dominant reversible process in Zn halide–carbon composites, the working hypothesis was that variation of the surface area of carbon would determine the extent of cell performance. To this end, various Zn halides were mixed with high surface area-activated carbon (AC) and their performance was tested in full-cell coin cells. Figures 4A and S5 show the representative charge–discharge curves of Zn|AC–ZnX₂ batteries using the WiTS gel electrolyte at various current densities between 0.1 and 2.0 V. Significantly, the charge–discharge curves possess a near-triangular shape with little deviation from an ideal capacitor response. This implies that the kinetics of the halogen conversion–adsorption reaction at the activated carbon electrode is extremely facile in the WiTS gel electrolyte. However, the CV response at each electrode was not strictly pseudocapacitive due to the presence of redox peaks (see Figures 4D and S6A). The specific capacities for Zn|AC–ZnCl₂, Zn|AC–ZnBr₂, and Zn|AC–ZnI₂ cells are approximately 281, 232, and 196 mAh g⁻¹, respectively, at a current density of 0.05 A g⁻¹ (compared to <100 mAh g⁻¹ for bare AC in the same electrolyte). These capacities decreased to 102, 90, and 65 mAh g⁻¹ when the current density was increased to 1.0 A g⁻¹, and the corresponding capacity fade is over 60% for each cell (Figure 4B). The capacity loss is most likely due to the low conductivity of the activated carbon and future work will focus on the use of conducting additives, such as carbon black, to further optimize the performance. The capacities obtained at these electrodes are nonetheless higher than Zn-ion capacitors using an activated carbon cathode and Zn anode.42,43

The AC composite cathode made from the combination between ZnCl₂, ZnBr₂, and ZnI₂ with the equimolar ratio of the halides achieved specific capacities twice that of individual ZnX₂ at all current densities studied (Figure 4B). The improved capacity in the Zn|AC–ZnCl₂Br₂I₂ cell relative to pure Zn|ZnX₂ could be due to a denser adsorption of halide ions on the carbon microstructure. The enhancement in performance of the mixed halide cathode is possibly due to the reduction of Coulombic repulsion of the adsorbed halides and an electrocatalytic effect. It has been shown that the intercalation/adsorption density of halogen on a carbon surface is approximately twice as large as Li–GIC. This is because the oxidation state of the halogen is close to zero, which reduces the average effective charge per halogen atom. This minimizes the Coulombic repulsion and, in turn, increases the adsorption density of halogen on the carbon pore. Furthermore, the Coulombic repulsion is expected to be
Figure 5. (A) ZnAC−ZnCl2Br2I2 coin cells charged at 1.0 A g⁻¹ (left-hand vertical axis) and discharged at 0.05 A g⁻¹ (right-hand vertical axis) using the WiTS gel electrolyte and (B) capacity retention and Coulombic efficiency of the ZnAC−ZnCl2Br2I2 cell cycled at 0.75 A g⁻¹ using the WiTS gel electrolyte.

The gravimetric capacitances of ZnAC−ZnCl2Br2I2 ranged from 400 to 930 F g⁻¹ depending on the applied current density (Figure 4C). This figure also demonstrates the importance of the Zn halides to the cathode chemistry, proving that the cathodic process involved the immobilized Zn halides. Based on the mass of the cathode (mass of activated carbon plus mass of ZnX2), the energy densities of 422 and 160 Wh kg⁻¹ at power densities of 122.8 and 1071.7 W kg⁻¹ were obtained. These values are higher than the energy density of all other cathode materials reported to date for ZIBs including MnO2, V2O5, Zn3V2O7, CuHCF, and VS2 nanosheets. The cell energy density varies between 30 and 90 Wh kg⁻¹ depending on the applied current density within a pouch cell configuration is a third of the total mass of the cell. These values are much higher than those of typical commercial supercapacitors (5−10 Wh kg⁻¹), lead-acid batteries (30−40 Wh kg⁻¹), and Zn-ion capacitors (17−30 Wh kg⁻¹). The energy density of the ZnAC−ZnCl2Br2I2 cell is even higher than a Li-ion capacitor, where the energy density varies between 30 and 90 Wh kg⁻¹. Li-ion capacitors often use intercalation-type anodes and adsorption-type cathodes (adsorption of large complex anions ([PF6]⁻, [TFSI]⁻, [BF4]⁻, etc.), where their overall energy density is limited by the capacitor-type electrode. The advantages of using halide ion conversion−adsorption within carbon cathodes are (i) they are smaller than most organic anions so that the migration/diffusion of ions is faster, (ii) they are inside the carbon structure so that they do not have to diffuse to the surface from bulk electrolyte, and (iii) they undergo reversible fast redox reactions, which substantially provide an extra charge, unlike inert anions. The combination of these factors is responsible for the high performance of the ZnAC−ZnCl2Br2I2 cell. The cell also truly combines the characteristic high energy density of a battery with the high power density of a supercapacitor device. For example, this cell can be fully charged within a few minutes (6 min) at high power and can be discharged for over 5 h at lower rates (see Figure 5A).
The Zn1AC−ZnCl2 Br−I− cell also exhibited excellent cyclic stability when the cell was cycled at 0.75 A g−1. The cell capacity retention is 95% after 500 cycles with 99% Coulombic efficiency throughout the cycles (Figure S5B). Although the capacity initially decreased by 10%, a subsequent increase in capacity was observed after 250 cycles and the ohmic drop of the cell decreased with increasing cycling (Figure S10). The increase in capacity could be due to the gradual activation of the electrode, which increases the number of active electrochemical sites for ion adsorption. Finally, the WiTS gel electrolyte performance was tested using a traditional α-MnO2 cathode and Figure S11 shows the charge−discharge curve obtained for a ZnIr−MnO2 cell. The gel electrolyte exhibited a Coulombic efficiency of over 99% with specific capacities that were increased from 162 to 210 mAh g−1 after 50 cycles. This indicates that the WiTS gel electrolyte is as efficient as traditional aqueous electrolytes (such as 1 M ZnSO4), but with additional advantages such as the absence of parasitic water reduction reactions, elimination of the need for a separator, and other advantages that semisolid state devices provide, e.g., flexibility. The combination between the WiTS gel electrolyte and ZnX2−carbon composite cathode in conjunction with aqueous gel electrolytes offers the tantalizing possibility of solving the issues of poor ZIB performance. This study also provided the very first fundamental understanding of halogen conversion chemistry inside crystalline and amorphous carbon.

3. CONCLUSIONS

A Zn-conducting water-in-trisalt gel electrolyte and halogen-incorporating cathode have been successfully developed and used in Zn-based electrochemical energy storage for the first time. The benefits of using confined halogen within the carbon structure as a cathode are (i) elimination of the irreversible binding of Zn2+ to the host structure within the cathode chemistry, (ii) the provision of substantial extra charge through their conversion−intercalation/adsorption process, and (iii) obviating the need for ions to diffuse to the surface from bulk electrolyte as they are already inside the carbon structure. The most significant findings emerging from this study are that the identity of the Zn halide and carbon structure in the cathode composite produces electrochemical energy storage devices that are fundamentally different from each other (battery vs supercapacitor). The use of graphite in the composite electrode produced battery-like behavior, where the voltage plateau was related to the standard potential of the halogen species. In situ Raman spectroelectrochemistry revealed that the identity of halides determines the mechanism of charge storage, intercalation vs electrosorption. In contrast, when activated carbon was used in the composite, the cell acted as a hybrid Zn-ion capacitor due to the fast reversible halogen species electrosorption/desorption in the carbon pores. In this case, the overall capacity is related to the number (binary or ternary) of Zn halides present; and the Zn(activated carbon−ZnCl2 Br−I−) cell exhibited a high specific capacity and energy density as well as good cycling stability. The combination of the Zn(activated carbon−ZnCl2 Br−I−) cell with the WiTS gel electrolyte is promising for the development of high-performing, low-cost, and environmentally friendly energy storage device based on Zn. Future work should focus on the microstructural design of carbon pores to match the size of halogens as well as investigating other carbon structures such as heteroatom-doped carbon or high surface area hard carbon materials.

4. EXPERIMENTAL METHODS

4.1. Materials and Apparatus. All chemicals are of analytical grade and obtained from Sigma-Aldrich, Fluorochrome or Alfa Aesar and used as received. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al Kα X-ray source (E0 = 1486.6 eV, 10 mA emission). Scanning electron microscope (SEM) analysis was carried out using a FEI Quanta 650 FEG environmental SEM. Powder X-ray diffraction analysis was performed using a Philips Xpert PRO diffractometer with Cu Kα radiation (λ = 0.154 nm) and operating at 40 kV and 30 mA.

4.2. WiTS Gel Electrolyte Preparation. Two grams of ZnSO4·7H2O (99.99%, Sigma-Aldrich), 2 g of zinc trifluoromethanesulfonate (98%, Fluorochrome), and 4 g of lithium bis(trifluoromethanesulfonyl)-imide (99%, Fluorochrome) were mixed together with 1.5 g of ultrapure water (Milli-Q, 18 MΩ cm resistivity) in a mortar and pestle until a uniform white paste formed. Subsequently, 1.3 g (10% of total salt) of a 60% PTFE suspension was added and mixed with a mortar and pestle. The mixture was then heated at 80 °C on a hot plate for 30 min to remove any excess water. A semisolid elastic gel was formed, which can be changed into any desired shape (Figure 1A).

4.3. Electrode Preparation. For the preparation of the carbon−ZnX2 cathode, first the desired amount of ZnX2 (anhydrous ZnCl2, ZnBr2, ZnI2, or mixture of two or more halides) was dissolved in 0.5 g of water followed by slow addition of natural graphite (−325 mesh, 99.8%, Sigma-Aldrich) or activated carbon (YEC-8B, Fuzhou Yihuan Carbon Co., Ltd) while mixing homogeneously with a mortar and pestle. The mass ratio between ZnX2 and carbon was 1:3. PTFE suspension (5% with respect to the mass of carbon) was added to the thick slurry and mixed to uniformly coat the mixture with the polymer binder. The excess water was removed by heating the mixture on a hot plate. The resulting carbon−ZnX2 clay was quite flexible and could be made as a free-standing film or rolled onto a prepatterned (15 mm diameter) titanium (99.99%, Alfa Aesar) foil current collector. The composite electrode was dried in a vacuum oven at 80 °C overnight. The typical mass loading of the carbon−ZnX2 composite electrode ranged from 2 to 5 mg cm−2.

4.4. Battery Assembly and Electrochemical Measurements. The full cells were assembled in CR2032-type coin cells using carbon−ZnX2 as the cathode and Zn foil as the anode. The flexible gel electrolyte was spread onto the Zn foil with an approximate thickness of 0.5−1.0 mm and acted as both the electrolyte and separator. The coin cell was sealed using a hydraulic crimping machine (MSK-160D) in an ambient atmosphere. Three-electrode cell electrochemical measurements were conducted using a WiTS gel electrolyte that was rolled onto a micrography glass slide for electrode connection. A glassy carbon working electrode, stainless steel wire counter electrode, and Zn metal reference electrode were used. Electrochemical measurements were performed using an Autolab potentiostat (model PGSTAT302N, Metrohm Autolab, The Netherlands). The charge−discharge battery tests were carried out using a Basytec Cell Test System (BasY Tec GmbH, Asselingen, Germany) with 32 independent test channels. The average capacity of three different coin cells was used to report capacity/capacitance.

4.5. In situ Raman Spectroscopy Measurement. Raman spectra were obtained using a Renishaw inVia microscope with a 532 nm excitation laser operated at a power of 0.274 mW with a grating of 1800 lines/mm and 50× objective. The in situ Raman cell was obtained from ECC-Opto-Std (EL-Cell GmbH, Hamburg, Germany) and the cell was comprised of a free-standing carbon−ZnX2 positive electrode and a Zn foil negative electrode with a WiTS gel electrolyte. A titanium foil that contained a small hole in its middle (diameter ca. 1 mm) was used as a current collector for the positive electrode. The exciting laser beam was shone through a thin glass window onto the rear of the free-standing carbon−ZnX2 film through the small hole in the center of the Ti foil. Spectral scans were collected in a backscattering configuration. The Raman measurements were collected at various voltages as the cell charged and discharged at 1 mV s−1.
Cyclic voltammograms and galvanostatic charge–discharge curves of various electrodes, XPS, Raman spectroscopy and SEM of charged electrodes, and AC electrochemical impedance spectroscopy of water-in-salt gel electrolyte (PDF)

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**Notes**

The authors declare the following competing financial interest(s): A patent application on a Zn-halogen secondary battery has been filed by the University of Manchester.

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