Safety and cost are the key metrics for large-scale energy storage. Due to the use of nonaqueous electrolytes and transition metal oxides in current lithium-ion battery technologies, safety, cost, and environmental issues are a significant cause for concern. Graphite is a promising cathode material for dual-ion batteries due to its high operating potential, low cost, and high safety. Nevertheless, it is challenging to find a suitable aqueous electrolyte due to the narrow electrochemical stability window (1.23 V). This work presents a graphite \( || \) zinc metal aqueous dual-ion battery of \( \approx 2.3 \)–\( 2.5 \) V, a remarkably high voltage in aqueous zinc batteries, achieving >80% capacity retention after 200 cycles and delivering \( \approx 110 \) mAh g\(^{-1}\) at a charge/discharge current of 200 mA g\(^{-1}\). A capacity of nearly 60 mAh g\(^{-1}\) is achieved at a charge/discharge current of 5000 mA g\(^{-1}\). Natural graphite is enabled as a reversible cathode using a highly concentrated lithium-free bisalt aqueous electrolyte.

1. Introduction

Widespread installation of renewable energy sources, such as wind and solar\([1–3]\) has been delayed by the lack of suitable stationary energy storage solutions. The metrics for large-scale storage batteries are vastly different from batteries for portable electronics and transportation batteries\([4–6]\) where top priorities in storage batteries should be low acquisition and minimum maintenance cost, while a high energy density is not of major importance.\([7]\) As sustainable solutions, these systems cannot afford the usage of rare elements (e.g., cobalt and nickel), which directly results in high material cost, and must exhibit extremely long cycle and calendar life. Lithium-ion batteries (LIBs) currently lead the market of high-energy and high-power batteries for portable electronics and transportation purposes\([4,5]\). Nevertheless, LIBs face the challenges of high cost, material abundance, and sustainability for the stationary market.\([8]\) In recent years, several emerging battery technologies have attracted considerable attention for large-scale stationary energy storage, e.g., sodium-ion\([9]\) and potassium-ion batteries;\([10]\) systems that are key to transforming the energy infrastructure to overcome the intermittency of renewable energy.

Among different aforementioned battery technologies, dual-ion batteries (DIBs) can be very competitive in terms of cost, material abundance, and sustainability for large-scale stationary storage because both the positive (cathode) and negative
electrode (anode) can be made of low-cost redox-amphoteric carbonaceous materials.[7,11–15] Such special types of DIBs are also known as dual-carbon or dual-graphite batteries;[16–18] DIB cells do not operate by the rocking-chair principle, which is well-known for LIB cells; DIB cells are rather based on their cathode and anode simultaneously incorporating anions and cations from the electrolyte, respectively, in an “accordion” fashion during charging.[11,18] The enabler for DIB cells in nonaqueous electrolytes is the cathode, which is primarily graphite to date, proposed more than three decades ago.[19–21] Thus far, the major challenge that arises when using graphite cathodes is that they operate in a potential range of ≥4.5 V versus Li\textit{||}Li\textsuperscript{+}. Up to now, very few nonaqueous electrolytes have been reported to “survive” such high potentials without being oxidized and decomposed.[18,22–25] Where the usage of expensive ionic liquids or highly concentrated electrolytes might become a necessity, as these electrolytes can offer a high oxidative stability.[18,22–24,26,27] Nevertheless, graphite remains the primary choice of anion storage electrodes.[28] Despite recent works using oxides, metal-organic frameworks, hydrocarbons, and organic molecules.[29–35]

Recently, aqueous electrolytes have been a topic of high interest for different battery systems, such as aqueous LIBs[36] especially due to their increased safety aspects and low cost: two crucial metrics for large-scale energy storage. However, high graphite cathode potentials far above oxygen evolution potentials render developing graphite cathodes for aqueous systems immensely challenging. Recently, a fundamental study by Abe and co-workers[37] demonstrated the formation of a graphite intercalation compound (GIC; discharge capacity of ≈20 mAh g\textsuperscript{−1}) in a highly oriented pyrolytic graphite electrode using a water-in-salt electrolyte (WiSE; 19 M NaFSI). Wroge mann et al. proved that a hybrid nonaqueous/aqueous electrolyte (21 M LiTFSI in H\textsubscript{2}O; 9.25 M in dimethyl carbonate; wt ratio 1:1) could also be used to host anions intercalating into synthetic graphite.[38] Moreover, a new anion conversion-intercalation mechanism (using graphite as the cathode) was discovered by Xu and co-workers[39] allowing a remarkable specific capacity of up to ≈240 mAh g\textsuperscript{−1}. WiSE systems were first introduced by Xu and co-workers in 2015,[36] where they successfully expanded the electrochemical stability window (ESW) of an aqueous electrolyte to 3.0 V, much higher than the thermodynamic limit of ≈1.23 V. More recently they could expand the ESW up to 4.0 V by using a hydrophobic coating on the graphite anode side, allowing a reversible operation in an aqueous solution.[40] WiSE systems have also made their way into the zinc (Zn)-ion battery realm, where the Zn metal anodes become highly reversible,[41,42] and systems material performance is transformed by using 30 M ZnCl\textsubscript{2} WiSE.[43,44]

In this work, we report on a natural graphite || zinc metal dual-ion battery (ZnG-DIB) system enabled by a “water-in-bisalt” electrolyte (WiBSE), which is free of expensive lithium salts (e.g., LiPF\textsubscript{6} or LiTFSI). Natural graphite (NG), being a low-cost and highly abundant material, would be an optimal choice for large-scale stationary energy storage applications. NG is enabled at high potentials (≈1.95 V vs standard hydrogen electrode, equivalent to ≈5.0 V vs Li\textit{||}Li\textsuperscript{+}) in an aqueous electrolyte system as the anion host intercalating/deintercalating anions, while simultaneously in an “accordion” fashion.[30] Zn is plated/stripped at the anode. Zn metal also serves as a current collector resulting in a lighter anode and improving the specific energy of the system; not to mention the high capacity (820 mAh g\textsuperscript{−1}), intrinsic safety of Zn, high abundance, low toxicity, and low operating potential that allow a high cell voltage for operation of the DIB cell.

As we begin to understand high-voltage aqueous NG cathodes, we report our initial fundamental insight of the anion storage into NG facilitated by the WiBSE, where a system based on NG || activated carbon (AC) enables a reversible capacity of ≈100 mAh g\textsuperscript{−1} at a specific charge/discharge current of 200 mA g\textsuperscript{−1}, and shows fast kinetics where at 5000 mA g\textsuperscript{−1}, we still observe reversible capacity of ≈50 mAh g\textsuperscript{−1}. Furthermore, to investigate practicability of this DIB system, we paired the NG cathode with a Zn metal anode, where we observe even higher capacities (≈110 mAh g\textsuperscript{−1} at 200 mA g\textsuperscript{−1} and ≈60 mAh g\textsuperscript{−1} at 5000 mA g\textsuperscript{−1}), stable cycling stability of the Zn anode, and a stable voltage range of the NG cathode, observing above 80% capacity retention over 200 charge/discharge cycles. In a NG || Zn metal DIB full-cell, we are able to obtain a cell voltage of ≈2.3–2.5 V due to the conditioning of the graphite, and an average discharge voltage of ≈2.25 V, one of the highest cell voltages reported in a Zn system, with a specific energy of nearly 200 Wh kg\textsuperscript{−1} based on the cathode material (without including other cell components such as the electrolyte). With a suit of complementary characterization techniques, we can understand the graphite cathode high-voltage aqueous anion intercalation mechanism from a WiBSE in order to fulfill its potential for large-scale grid-level energy storage.

2. Results and Discussion

2.1. Graphite as a Cathode for TFSI\textsuperscript{−}/FSI\textsuperscript{−} Anion Intercalation from an Aqueous Electrolyte

We chose 20 mol kg\textsuperscript{−1} (M) NaFSI + 0.5 M Zn(TFSI)\textsubscript{2} WiBSE as the electrolyte where the high concentration of NaFSI reduces the amount of “free” water in the electrolyte, reducing onset of oxygen evolution reaction (OER) allowing the graphite to be oxidized, and provides FSI\textsuperscript{−} anions. The motivation behind selection of this specific electrolyte was to use a sufficiently high concentration of lithium-free salt to enable redox of NG in an aqueous system, while being able to dissolve a secondary salt for the Zn metal anode (full-cell discussed in detail in Section 2.4). Therefore, solubility of the salts played a crucial role and NaFSI offers an exceptional solubility in water, significantly higher than other low-cost sodium salts, such as NaTOF, NaTFSI, NaClO\textsubscript{4}, and Na\textsubscript{2}SO\textsubscript{4}. Further, Zn(TFSI)\textsubscript{2} was chosen due to its anion TFSI\textsuperscript{−} having similar intercalation energies into the graphite cathode as FSI\textsuperscript{−} (discussed in Section 2.3); Zn(TFSI)\textsubscript{2} could not be used on its own as its solubility was simply not high enough to create a suitable WiSE. At any rate, the Zn(TFSI)\textsubscript{2} dissolved into the NaFSI WiSE offers Zn\textsuperscript{2+} cations and TFSI\textsuperscript{−} anions as active ion sources to enable Zn metal as an anode material. When evaluated in a half-cell setup (three-electrode configuration, and with an excess amount of electrolyte: ≈0.2 mL) the WiBSE provides an ESW of ≈2.7 V, which pushes the OER potential beyond 1.81 V versus Ag|AgCl (5.05 V vs Zn|Zn\textsuperscript{2+}). Therefore, this stability enables
graphite electrochemical oxidation, compared to the dilute 1 M NaFSI + 0.5 M Zn(TFSI)₂ electrolyte (Figure 1a), which is only stable up to 1.41 V versus Ag | AgCl (4.65 V vs Li|Li⁺ and 2.37 V vs Zn|Zn²⁺), well below the graphite oxidation potential (Table S1, Supporting Information). Synergistically, the expanded ESW (due to the lack of free water), along with the Nernstian relationship, lowering graphite’s oxidation potential, enables NG to be oxidized and reversibly intercalate anions. Based on the Nernst Equation

\[ E = E^\circ - \frac{RT}{nF} \ln(a_{\text{anion}}) = E^\circ - \frac{RT}{nF} \ln(c_{\text{anion}}) \gamma_{\text{anion}} \]

a varied concentration will yield different onset potentials for oxidation, especially in a far from dilute (ideal) solution where anion activity plays a crucial role. As the electrolyte concentration, \( c_{\text{anion}} \), is drastically increased (\( \gamma_{\text{anion}} \) being the activity coefficient), the anion activity (\( a_{\text{anion}} \)) would then increase accordingly, therefore the graphite intercalation potential (\( E \)) is consequently decreased. ¹⁵ As shown in the galvanostatic charge-discharge (GCD) profiles (Figure 1b) of a half-cell (information regarding electrochemical setup can be found in the Experimental Section, Supporting Information), the NG electrode shows a high reversible capacity of \( \approx 100 \) mAh g⁻¹ at 200 mA g⁻¹, giving a 1.30 V | 1.25 V (vs Ag|AgCl) potential for the intercalation/deintercalation of anions, this being equivalent to \(-4.70 V \) | \(-4.45 V \) versus Li|Li⁺, indicating the reduced onset potential for graphite oxidation, according to the Nernstian relationship. Naturally, in the dilute electrolyte, the NG gives a very low capacity of \( \approx 12 \) mAh g⁻¹ and gradually increases with electrolyte concentration increase (Figure S1, Supporting Information), which is why we chose 20 M NaFSI + 0.5 M Zn(TFSI)₂ as the electrolyte. It is notable that the Coulombic efficiency (\( C_{\text{Eff}} \)) of intercalation/deintercalation of anions into NG is low, only \(-50\% \), where the corresponding irreversible capacity is derived from parasitic side reactions at the surface of the positive electrode, such as unwanted oxidation of the graphite introducing CO|C functional groups, as shown via Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis (Figures S2 and S3 and Table S2, Supporting Information), which can be found in the Supporting Information. Furthermore, potentially competing OER at such high potentials could be catalyzed by the impurities in the NG. This is supported by the fact that a higher specific capacity is observed at higher charge/discharge current of 200 mA g⁻¹ (Figure 1b) versus 100 mA g⁻¹ (Figure S4, Supporting Information), meaning that less time is allowed for parasitic side reactions, which may have a negative impact on the intercalation behavior, such as electrolyte decomposition. However, as the charge/discharge current continues to increase (Figure 1c), the capacity decreases again as expected, making 200 mA g⁻¹ the optimal charge/discharge current. A similar behavior was found for the reversible capacity in graphite || Li metal DIB cells using an ionic liquid-based electrolyte, in which a low charge/discharge
current can reduce the specific capacity.\textsuperscript{[27]} From our previous publication on anion intercalation from hybrid aqueous/non-
aqueous electrolytes,\textsuperscript{[38]} it is known that one has to find the most suitable balance between high discharge capacity and high Coulombic efficiency (= reduced decomposition of the electrolyte at higher potentials) to achieve the best performance, which can, e.g., be achieved by choosing an optimized anodic cut-off potential for anion storage. Here, we chose relatively harsh cut-off conditions for anion storage in order to maximize the overall capacity, resulting in a decreased $C_{\text{Eff}}$. Nevertheless, by various adjustments in terms of optimized materials, electrolytes, and cycling conditions such as cut-off potentials, the $C_{\text{Eff}}$ can be further improved.

Certainly, more parasitic side reactions are avoided (although not entirely) by using higher specific currents, where we observed a high $C_{\text{Eff}}$ of $\sim$90\% at 2000 mA g\textsuperscript{-1} and $\sim$95\% at 5000 mA g\textsuperscript{-1} with high discharge capacities of $\sim$60 and $\sim$50 mAh g\textsuperscript{-1}, respectively, indicating the extremely fast kinetics in this system (Figure 1c). Thus, due to the fast kinetics, if less time is allowed for parasitic side reactions (kinetically slower), anion intercalation becomes even more prevalent at the electrode, rendering higher capacities at 200 versus 100 mA g\textsuperscript{-1}. To support the hypothesis of fast kinetics, cyclic voltammetry (CV) curves were recorded at different scan rates, revealing distinct redox peaks attributed to the electrochemical oxidation (= anion intercalation) and reduction (= anion deintercalation) of the NG (Figure 1d). These measurements provide real-time reaction information, that can be analyzed using the equation $i = a v^b$, where $i$ is the current, $v$ is the scan rate, and $a$ is a coefficient. The kinetic parameter $b$ indicates the dominating reaction mechanism. In the limiting cases where the kinetics are diffusion-controlled (faradaic contribution) or perfectly non-diffusion-controlled (normally capacitive contribution), the exponent $b$ would be either 0.5 or 1.0, respectively.\textsuperscript{[35]} Impressively, the anodic and cathodic $b$ values are 0.82 and 0.98 (Figure 1e), respectively, indicating the almost entirely non-diffusion-controlled behavior of anion (de)intercalation into/from NG. The concentrated electrolyte (20 M NaFSI + 0.5 M Zn(TFSI)\textsubscript{2}) provides irreversible intercalation/deintercalation of anions, in which the NG electrode retains $\sim$76\% of its original discharge capacity after 90 cycles (Figure 1f) in a NG || AC DIB cell.

The expansion of the graphite layers is the largest energy barrier, but no significant energy is associated with graphite contraction during deintercalation of the anions.\textsuperscript{[22,27]} This promising behavior of fast rates (fast kinetics) could partially be attributed to the ion network formation in the electrolyte, as supported by nuclear magnetic resonance (NMR) (Figure 2; Figure S5, Supporting Information) and density functional theory (DFT) simulations (discussed in theory and simulation section). There are differences in the diffusion behavior between water and NaFSI, which is quite similar to the LiTFSI WiSE that forms an ion network and nanomeric water channel partitioning.\textsuperscript{[46]} Therefore, we can assume that the 20 M NaFSI +0.5 M Zn(TFSI)\textsubscript{2} WiSE system may have a similar nanophase separation between the NaFSI/Zn(TFSI)\textsubscript{2} 3D extended ion networks and the water channels based on the similar diffusion behavior (Figure S5, Supporting Information). It is also noticeable that with Zn(TFSI)\textsubscript{2} introduced into the electrolyte, the water diffusion becomes slower as seen by the decrease in the ratio $D_{\text{H}_2\text{O}}/D_{\text{Na}}$ (compared to $D_{\text{Na}}/D_{\text{FSI}}$) in 20 M NaFSI + 0.5 M Zn(TFSI)\textsubscript{2} versus just 20 M NaFSI (Figure S5d vs b, Supporting Information, respectively).

Furthermore, $^{67}$Zn NMR spectra (Figure 2a) provide crucial information regarding the effect of increasing concentration on the Zn\textsuperscript{2+} ion mobility. The results show that approximately two-thirds of the Zn\textsuperscript{2+} ions in the electrolyte are “invisible” to liquid NMR, indicating they are part of a larger network of ions. This is determined by looking at the actual number of Zn\textsuperscript{2+} ions per unit volume compared to the normalized peak intensities, which indicate the mobile (visible) species (Figure 2b). These results, together with slower water diffusion, could suggest water coordination to Zn\textsuperscript{2+} ions (later shown in Section 2.3), both of which are incorporated in a larger ion network, slowing their mobility. Attributable to the confinement of both anions and Zn\textsuperscript{2+} ions in these large ion networks, the non-diffusion limited transfer of ions into the electrodes is a possibility, as the ion transfer might behave similar to the Grotthuss mechanism described in proton batteries\textsuperscript{[47]} where anions and cations could “hop” within the network into their respective electrodes. Simultaneously, water channels would allow the fast transport of Na\textsuperscript{+} cations to the Zn metal anode surface for protection, similar to the facilitated Li\textsuperscript{+} cation diffusion in the WiSE composed of LiTFSI/H\textsubscript{2}O.\textsuperscript{[46,48]} See Supporting Information for more detail.

![Figure 2](image-url)
To further investigate the rate-limiting step, we performed rate-capability measurements by keeping the charge current constant and varying the discharge current, and vice versa (Figure 3). Due to the large graphite layer expansions upon charge, electrochemical anion intercalation is bound to have the largest energy penalty and has been observed in previous studies on anion intercalation into graphite.\[27\] We can observe this behavior when charging at 200 mA g\(^{-1}\) and discharging at varying currents, the capacities are close to one another, indicating that charging is the rate-limiting process. This phenomenon was also observed in the works of Placke et al. when charging at varying currents and discharging at a constant current. Capacities vary more significantly although the results are similar to those of charging and discharging at varying rates, still indicating the capability of fast discharge.\[27\]

Electrochemical impedance spectroscopy (EIS) was performed to show further evidence of the rate-limiting step. Upon initial charging of the graphite electrode, the charge transfer resistance is significantly lower than in the following discharge (of the same electrode) (Figure S6a, Supporting Information), indicative of the fact that ion transfer into and out of the graphite is easier when graphite is in the fully charged state. This appears to indicate that anion intercalation is more difficult when graphite is in the discharged state, as graphite layers must expand, making the charge process \((=\) anion intercalation\) the rate-limiting step, further confirmed by Figure 3b. Furthermore, the absence of the Warburg element for fresh samples, which is possibly due to the initial expansion of the graphite layers that became irreversible over time, as anions might not be completely de-intercalated upon cycling. From another study on DIB cells, it is also well known that a certain portion of anions can remain irreversibly intercalated upon prolonged cycling.\[49\] This could signify the graphite layers becoming permanently expanded causing crystallinity to be significantly reduced, making anion intercalation and deintercalation similarly feasible. At this stage, since charge transfer kinetics is faster, mass transfer limitation can be observed as seen from the appearance of the Warburg element. The loss of crystallinity in NG is further discussed and characterized via X-ray diffraction (XRD) in the full-cell section (Section 2.4). Moreover, with crystallinity reduced, especially with parasitic side reactions involved that may consume electrolyte, the concentration of anions will decrease in the surrounding electrolyte inducing a diffusion limitation, where a Warburg element then becomes evident.

2.2. Structural and Chemical Characterization of Anion Intercalation into Graphite

To prove that FSI\(^{-}/\)TFSI\(^{-}\) anions are indeed being intercalated into the NG, in situ XRD measurements were performed during a CV experiment using a two-electrode setup (NG || AC DIB cell) between a cell voltage of –0.2 and 2.3 V. For further information, see the Supporting Information text and the Experimental Section in the Supporting Information. Figure 4a shows the first cycle of the in situ XRD investigations and the correlating CV measurement. Up to a cell voltage of \(\approx 1.4\) V, the NG electrode shows no change of the structure and the (002) reflection is clearly visible at \(2\theta = 26.55^\circ\). Upon further charging, the dominant (002) reflection vanishes and two new reflections appear. This “reflection splitting” phenomena of the (002) reflection of the pristine NG breaking up to the \((00n+1)\) and \((00n+2)\) reflections, suggests the formation of a stage-\(n\) GIC.\[50,51\] By calculation of the \(d_{(n+2)}/d_{(n+1)}\) ratio and each other. Therefore, the overarching point here is that the charge transfer resistance has decreased significantly compared to fresh samples, which is possibly due to the initial expansion of the graphite layers that became irreversible over time, as anions might not be completely de-intercalated upon cycling.

![Figure 3](image-url)
correlation to stage pure GICs (Table S3, Supporting Information), the dominant stage phase of the formed GIC can be determined.\(^{50–52}\) The first observable dominant intercalation stage is 5 at a cell voltage of 1.69 V (lower red dotted line), whereas at the end of charge (upper red dotted line), a stage-3 GIC with a gallery height \(d_h\) of 8.08 Å is achieved (see Table S3 and Equation (S1), Supporting Information). The achieved stage 3 goes in line with previous ex situ XRD studies at higher scan rates (Figure S7, Supporting Information). Upon discharge, we see the totally reversible deintercalation process of the anions; however, the reflection intensity is reduced after a full discharge (Figure S8, Supporting Information), indicating a more disordered structure of the NG after anions have been deintercalated. Furthermore, it is important to note that since order/crystallinity is being reduced and anion intercalation involves well-ordered structures, that not all of the reversible capacity observed is exclusively due to anions being intercalated, where they can also be partially adsorbed/desorbed onto the NG surface, as in a (super) capacitor electrode. This is also the reason sloping regions are observed in the charge and discharge profiles as cycling continues; potentially explaining why the proposed stage-3 structure does not correlate exactly with the measured capacity; however, from what is actually being intercalated, the in situ data proves to form a stage-3 GIC and that the anions intercalated are reversibly de-intercalated. It is important to consider the limitations of this characterization technique, as the mass loading is heavier for the electrodes and the rate of charge is significantly slower compared to the cells made to test for performance, in order to detect the structural changes happening; therefore, once again, the stage formation from these results may not directly correlate with the high capacities obtained in the full cell section, since different testing parameters were needed.

To provide chemical evidence of anions being present within the graphite structure, we performed chemical characterization via inductively coupled plasma (ICP) mass spectrometry analysis (Table S4, Supporting Information). Three samples were analyzed for sulfur content as the anions in questions contain sulfur. ICP analyses of a pristine, a pristine-soaked sample, and a fully charged (intercalated) NG sample contained 0.105, 0.060, and 17.35 ppm of sulfur, respectively. All samples were washed with deionized water; therefore, we noticed the clear indication that the sulfur signal coming from the anions was not merely surface residue, but intercalated anions inside the graphite.

Additionally, to supply strong evidence of the presence of anions within the structure of the NG and to understand the nature of anion intercalation, X-ray absorption near edge spectroscopy (XANES) at the S K-edge was employed. XANES measurements were carried out in beamline 9-BM at the Advanced Photon Source (Figure 4b). Ex situ S K-edge of the fully charged (= intercalated) sample was compared with dilute salt solutions of NaFSI (0.3 M) and Zn(TFSI)\(_2\) (0.5 M), solutions from both salts present in the WiBSE. The reason for the comparison to both salts is two-fold: to determine whether anions are indeed intercalated in the NG sample and to see which anion is preferably intercalating into the graphite, as both types are present in the electrolyte.

From these results, it is evident that sulfur is present within the graphite and likely a result of anion intercalation. A comparison of the S K-edge for the two neat solutions shows obvious differences. For the FSI\(^-\) sample, the S K-edge absorption white line was shown to split into two large features of similar intensity (note the ratio of the peaks, where the first peak at 2477 eV is smaller compared to the second peak at 2480 eV). For sulfur originating from TFSI\(^-\), only a single white line feature appeared at 2477 eV. This difference in XANES structure likely originates from differences in the local electronic structure—particularly the presence of S—F bonds in FSI that cause a splitting of the main, broad transition into two, sharp transitions. The S K-edge spectra from the fully charged...
XANES would illustrate a 20:1 molar ratio of FSI$^-$ to TFSI$^-$ were intercalation of TFSI$^-$ is truly remarkable considering the sea of NaFSI intercalation of TFSI$^-$ and FSI$^-$ were purely random, the sulfur XANES would illustrate a 20:1 molar ratio of FSI$^-$ to TFSI$^-$ were (shown in Figure 4b, green trace) and provide a nearly identical ratio of edge features to that of neat FSI$^-$. Predominant intercalation of TFSI$^-$ is truly remarkable considering the sea of FSI$^-$ anions present in the electrolyte compared to TFSI$^-$ (20 M NaFSI + 0.5 M Zn(TFSI)$_2$). In an attempt to explain this, theory and modeling were used to take a look at the environment created by the WiBSE and the resulting GIC. This is discussed in more detail in the following section.

2.3. Theory and Modeling: A DFT Study of Anion Intercalation into Graphite

Supported by in situ XRD data, a stage-3 GIC was modeled to determine whether there are differences in FSI$^-$ and TFSI$^-$ interactions with graphite to elucidate the origin of preferential TFSI$^-$ intercalation (Figure 5). DFT, however, revealed only a very small difference between FSI$^-$ and TFSI$^-$ binding energies to stage-3 GIC. Surface groups present in NG, which were found by XPS analysis (Figure S3, Supporting Information), were included in the calculations to simulate a more realistic environment, where the optimized configurations of the anions on non-ideal graphite were then calculated and compared to ideal pristine graphite (Figure S9, Supporting Information). The calculated energies, which are not significantly different from the ideal graphite (Table S5, Supporting Information), are $-2.93$ and $-2.83$ eV for FSI$^-$ and TFSI$^-$, respectively, suggesting that anion-graphite interactions are most likely not the source for a more predominant intercalation of TFSI$^-$ anions versus intercalation of FSI$^-$ anions. However, using these data, we also calculated the free energy change required to intercalate each anion (Table S5, Supporting Information), meaning the barrier the anion has to overcome to go from the electrolyte into the graphite; the calculated intercalation voltage is $-2.37$ V for FSI$^-$ and $-0.48$ V for TFSI$^-$ intercalation into graphite. This is a significant difference, indicating TFSI$^-$ anions would intercalate more feasibly than FSI$^-$ anions, making the TFSI$^-$ the predominant species intercalated.

An alternative hypothesis we propose is that predominant TFSI$^-$ intercalation can be linked to the unique structure of the concentrated electrolyte, which dictates different mobilities of FSI$^-$ and TFSI$^-$ anions under electrochemical driving force. To verify this hypothesis, we considered possible solvation structures of cations in the electrolyte by FSI$^-$, TFSI$^-$, and water. The results revealed significant differences in solvation energies (Table S6, Supporting Information) for Zn$^{2+}$ by FSI$^-$, TFSI$^-$ anions, and hydrated TFSI$^-$ with solvation energies per anion in Zn(TFSI)$_2$, Zn(TFSI)$_2$(H$_2$O)$_2$, and Zn(FSI)$_2$ complexes equal to $-1.71$, $-2.35$, and $-1.70$ eV, respectively. In contrast, interaction energies between Na$^+$ and anions in the electrolyte are similar for FSI$^-$ and TFSI$^-$ and equal to $-5.3$ and $-5.1$ eV, respectively. These results suggest that in the 20 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolyte, Na$^+$ cations will be strongly coordinated by FSI$^-$ anions. This prediction can support the NMR results, discussed above, pointing to the formation of a large 3D ion network. Weaker solvation forces in Zn complexes (vs Na) (Table S6, Supporting Information) and higher electrostatic

![Image of simulated anion intercalation into graphite and cation solvation structure in WiBSE. Optimized structure (C$_{72}$:TFSI) of stage-3 graphite with intercalated TFSI$^-$ anions (left) and schematics of 20 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolyte based on optimized first solvation shells of Na$^+$ and Zn$^{2+}$ (right). Desolvation of Zn-(TFSI)$_2$-2H$_2$O under applied potential is shown schematically. Carbons are shown as brown, O as red, N as blue, F as light blue, S as yellow, Zn as gray, Na as gold, and H as white spheres. A top-down view of the GIC is provided in the Supporting Information (Figure S9c, Supporting Information).]
driving force for Zn$^{2+}$ diffusion compared to that for Na$^+$ point to Zn$^{2+}$ cations and TFSI$^-$ anions as dominating diffusing species in the concentrated NaFSI bulk electrolyte. The structure of the 20 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolyte and the mechanism of Zn$^{2+}$ and TFSI$^-$ diffusion requires further in-depth study. However, based on previous molecular dynamics simulations and the current study of the possible first solvation shells of Zn$^{2+}$ cations, the aforementioned mechanism of coupled TFSI$^-$ and Zn$^{2+}$ diffusion can be proposed. Previous simulations of the structure of 20 M LiTFSI + 1 M Zn(TFSI)$_2$ electrolyte predict that first solvation shell of Zn$^{2+}$ consists almost exclusively of Zn-(TFSI)$_3$ with TFSI$^-$ binding to Zn$^{2+}$ in a bidentate configuration (Figure 5). Given the strength of Zn-TFSI interactions is 0.8 eV higher than that of Zn-FSI, a similar Zn solvation structure is expected to be predominant in the absence of an applied voltage in the 20 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolyte, considered here. More details regarding the zinc solvation prediction leading to TFSI$^-$ predominant intercalation can be found in the Supporting Information.

Based on the model and NMR data, we are inclined to believe that the NaFSI in the electrolyte serves largely as the atmosphere/environment for the WiBSE (removal of free water), while the predominant electrolyte for the DIB system is the Zn(TFSI)$_2$. More insights are detailed in the Supporting Information.

### 2.4. Full-Cell Performance of Natural Graphite || Zn Metal Dual-Ion Batteries

We first evaluated the Zn metal anode stability in Zn metal || Zn metal symmetrical cells with excessive Zn on both electrodes by plating/stripping for 10 min using a current density of 0.1 mA cm$^{-2}$ in the 20 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolyte (Figure 6a). The Zn electrode shows highly stable GCD profiles over 365 h with few overpotential fluctuations in the electrolyte that actually becomes more stable over time. For different electrolyte concentrations, the plating/striping behavior is less stable and eventually short circuits at ≈160, ≈240, and ≈315 h for the Zn electrode in the more dilute 5, 10, and 15 M NaFSI + 0.5 M Zn(TFSI)$_2$ electrolytes, respectively (Figure S10, Supporting Information). Moreover, scanning electron microscopy (SEM) of the Zn electrodes clearly shows the improved plating and stripping stability as the concentration is increased in the electrolyte (Figure S11, Supporting Information), where at high concentrations, the morphology is dominated by smooth Zn metal deposits, as opposed to ZnO (at low concentrations of 1 and 5 M) and dendritic Zn metal growth (at intermediate concentration of 10 M) with additional ZnO impurities as seen via XRD (Figure S12, Supporting Information). Furthermore, we believe that the high concentration of Na$^+$ ions in the electrolyte is aiding in the dendrite-free deposition of Zn$^{2+}$ ions on the Zn metal anode. Due to the lower reduction potential of Na$^{-}$/Na, once the Zn$^{2+}$ plates onto the Zn metal, the Na$^+$ ions may serve as a positively charged electrostatic shield around the initial Zn deposited growth, similar to the mechanism proposed by Ding et al. regarding dendrite-free lithium deposition. Based on the exceptional reversibility of the Zn anode (Figure 6a), we coupled NG with Zn metal to form a DIB full-cell, in which anion (de)intercalation happens at the NG cathode, whereas the Zn(TFSI)$_2$ dissolved into the NaFSI offers Zn$^{2+}$ cations for Zn plating/stripping at the anode, forming a ZnG-DIB. Figure 6b shows the CV curves of the three-electrode cell (also with an excess amount of electrolyte: ≈0.2 mL), where the anode and cathode curves were obtained simultaneously using the same cell. Figure 6c shows the GCD profiles at 200 mA g$^{-1}$ of the NG || Zn metal DIB cell, where we observe high discharge capacities of ≈110 mAh g$^{-1}$ based on anion (de)intercalation. Importantly, we are able to obtain a cell voltage of ≈2.3 to ≈2.5 V (since end of charge criterion is capacity, as graphite is conditioned, the upper voltage cutoff can change), and an average discharge voltage of ≈2.25 V, which is one of the highest voltages reported in an aqueous Zn system, while the plating and stripping of Zn remains remarkably stable, as shown with the three-electrode cell results (Figure 6d). The high discharge capacity and average discharge voltage of this NG || Zn DIB cell reveal a high specific energy of nearly 200 Wh kg$^{-1}$ based on the NG cathode. We would like to note, however, that this is not considering all components of the cell and is only based on the capacity of the NG cathode and the achieved cell voltage. Therefore, if all components were considered, i.e., considering that the electrolyte is also active, the practical energy content would be lower. In this work, we wanted to focus on the promising performance of the NG.

Similar to the half-cell, the ZnG-DIB shows excellent discharge capacity (at 200 mA g$^{-1}$: ≈110 mAh g$^{-1}$, limiting charge to 200 mA h g$^{-1}$) and rate capability. It is important to note the lower C$_{Eff}$ due to parasitic side reactions at such high potentials for an aqueous system; however, high capacities and cycling can still be achieved. As shown in Figure 6e, from 200 to 2000 mA g$^{-1}$, the reversible capacity is still a high ≈88 mAh g$^{-1}$ and only drops about half that of 200 mA g$^{-1}$, remaining at ≈60 mAh g$^{-1}$ at 5000 mA g$^{-1}$ (Figure S13, Supporting Information), and then the cell can cycle for over 200 cycles at above 80% capacity retention. To further support the fast kinetics of anion intercalation, we notice that in these full-cell rate capability measurements, higher capacities were obtained for cycles at higher rates of charge/discharge, with capacities of ≈113 and ≈124 mAh g$^{-1}$ at 300 and 500 mA g$^{-1}$, respectively, indicating that side reactions were mitigated by the fast rate of charge. The fast kinetics of the system allowed graphite to continue to electrochemically oxidize (for anion intake) and, since the side reactions are kinetically slower, this allowed the graphite electrochemical oxidation to take predominance and intercalate more anions, even at faster rates. We also observe above 80% capacity retention over 200 cycles at the representative 200 mA g$^{-1}$ rate (Figure 6f). The capacity decay was determined to originate from the NG cathode as the Zn metal does not show signs of degradation via XRD (Figure S14a, Supporting Information) like the NG does (Figure S14b, Supporting Information), where crystallinity is significantly reduced, which is also supported by the EIS results reported in an earlier section; insights can be found in the Supporting Information. Inspired by this work, we studied Zn salt alternatives that would drive the cost of the system down. We have tested 1 M Zn(TOF)$_2$ and 1 M Zn(ClO$_4$)$_2$ (both using 20 M
NaFSI) with similar capacities and so far can run for >80 cycles using a charge and discharge current of 200 mA g\(^{-1}\) (Figure S15, Supporting Information).

3. Conclusion

NG has been successfully enabled in a WiBSE using a high-concentration 20 M NaFSI solution acting as the enabling supporting and mildly active electrolyte while the 0.5 M Zn(TFSI)\(_2\) acts as the predominantly active salt in the electrolyte, as supported by NMR, DFT simulations, and XANES. Electrochemical and XRD characterizations prove that the NG has indeed been enabled in full-cell based on an aqueous electrolyte. NG, as the anion intercalation host, was paired with a Zn metal anode in a full-cell, delivering capacities of \(\approx 110\) mAh g\(^{-1}\) at 200 mA g\(^{-1}\) and \(\approx 60\) mAh g\(^{-1}\) at 5000 mA g\(^{-1}\), displaying remarkable kinetics of the system. Furthermore, stable cyclability of the Zn anode was observed in the electrolyte with stable overpotentials for over 365 h. In the full NG || Zn DIB, a full-cell voltage of \(\approx 2.3–2.5\) V was recorded, a remarkably high voltage for an aqueous (or nonaqueous) Zn system. Over 200 cycles above 80% capacity...
retention were observed, with a specific energy of nearly 200 Wh kg⁻¹ based on the cathode, pointing toward the promise of this infant system, especially for grid storage applications. Further advances are needed to develop a more stable electrolyte and electrode surface to reduce parasitic side reactions and increase OER overpotentials. In particular, further improvements in terms of energy density and cost are needed for this graphite || Zn metal DIB cell, e.g., by future systematic studies on advanced electrolyte systems using optimized electrolyte amounts, salt combinations, concentrations, etc. Therefore, it is evident that optimization of this system is needed; however, this work showcases a promising, intrinsically safe, and cost-effective system for large-scale energy storage geared toward grid-level applications based on aqueous DIB technology.

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

Acknowledgements
This work was conducted under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. I.A.R.-P. is grateful for the support of the Linus Pauling Distinguished Postdoctoral Fellowship program. Simulation work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Materials Sciences and Engineering, Synthesis and Processing Sciences Program FWP 12152. Computational, NMR, and XPS resources were provided by EML, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research under contract no. DE-AC02-76SF00515 and located at Pacific Northwest National Laboratory. NMR and XAS studies were supported by the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. This research used resources of the Advanced Photon Source, a U.S. Department of Energy Office of Science User Facility operated by Argonne National Laboratory under contract no. DE-AC02-06CH11357. The authors are thankful for the ICP results provided by Zimin Nie, the help from Aaron Hollas in obtaining FTIR results, and the help from Nathan Canfield in obtaining SEM and EDX results: all in the Energy and Environment Directorate at Pacific Northwest National Laboratory. The authors from University of Münster thank the Ministry of Economic Affairs, Innovation, Digitalization and Energy of the State of North Rhine-Westphalia (MWiDE) for funding this work in the project “GrEEn” (313-W044A). The authors are also thankful for the graphical abstract/cover art provided by Hongkyung Lee, an assistant professor in the Department of Energy Science and Engineering in the Daegu Gyeongbuk Institute of Science and Technology, Republic of Korea.

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
I.A.R.-P. and T.P. directed the research. I.A.R.-P. conceived the idea and both I.A.R.-P. and T.P. designed this work. I.A.R.-P. performed electrochemical measurements. I.A.R.-P. and J.M.W. performed XRD measurements, ex situ and ex situ, respectively. D.M.D., M.B., and J.L.F. performed XANES measurements. M.L.S. performed simulation work. K.S.H. and V.M. performed NMR characterization. V.V.V contributed to the electrochemical impedance measurements and interpretation. M.H.E. performed XPS work. All authors revised the manuscript and supported ideas providing intellectual contribution. I.A.R.-P., L.Z., J.M.W., and T.P. wrote the article with edits and approval from all the authors.

Keywords
anion intercalation, aqueous batteries, dual-ion batteries, water-in-bisalt electrolytes, zinc anodes

Received: April 11, 2020
Revised: July 7, 2020
Published online: September 28, 2020

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