Development of Safe and Sustainable Dual-Ion Batteries Through Hybrid Aqueous/Nonaqueous Electrolytes

Jens Matthies Wrogemann, Sven Künne, Andreas Heckmann, Ismael A. Rodríguez-Pérez, Vassilios Siozios, Bo Yan, Jie Li, Martin Winter,* Kolja Beltrop, and Tobias Placke*}

In this study, a new dual-ion battery (DIB) concept based on an aqueous/non-aqueous electrolyte is reported, combining high safety in the form of a nonflammable water-in-salt electrolyte, a high cathodic stability by forming a protective interphase on the negative electrode (non-aqueous solvent), and improved sustainability by using a graphite-based positive electrode material. Far beyond the anodic stability limit of water, the formation of a stage-2 acceptor-type graphite intercalation compound (GIC) of bis(trifluoromethanesulfonyl)imide (TFSI) anions from an aqueous-based electrolyte is achieved for the first time, as confirmed by ex-situ X-ray diffraction. The choice of negative electrode material shows a huge impact on the performance of the DIB cell chemistry, i.e., discharge capacities up to 40 mAh g\(^{-1}\) are achieved even at a high specific current of 200 mA g\(^{-1}\). In particular, lithium titanium phosphate (Li\(_{2}\)(PO\(_4\))\(_3\); LTP) and lithium titanium oxide (Li\(_4\)Ti\(_5\)O\(_{12}\); LTO) are evaluated as negative electrodes, exhibiting specific advantages for this DIB setup. In this work, a new DIB storage concept combining an environmentally friendly, transition-metal-free, abundant graphite positive electrode material, and a nonflammable water-based electrolyte is established, thus paving the path toward a sustainable and safe alternative energy storage technology.

The inexorable progress of technology in the field of mobile communication and individual mobility is closely linked with achievements in the broad field of energy storage devices in general, and, in particular, in the global battery sector segment.[5] Due to an outstanding mix of high energy density, high power density, and long cycle life, lithium ion batteries (LIBs) are dominating the battery market for various application purposes.[11,2] However, the currently used organic solvent-based electrolytes may raise concerns related to safety, eco-friendliness, and cost.[3] In recent years, aqueous and/or mixtures of aqueous and organic-based electrolytes have become an emerging and highly interesting research field to tackle the disadvantages of state-of-the-art non-aqueous electrolytes.[3,4] Particularly noteworthy in this context are the pioneering works of Xu and co-workers, presenting encouraging approaches to expand the (electro-)chemical stability window (ESW) of water-based electrolytes against decomposition by proposing a “water-in-salt” electrolyte (WiSE) with a 21 m (mol [salt] kg\(^{-1}\) [solvent]) solution of LiTFSI in water for high-voltage aqueous LIBs.[6] This concept has been continuously developed into “hydrate-melt electrolytes,”[6] “water-in-bisalt (WiBS),”[7] “water-in-ionomer,”[8] and “hybrid aqueous/non-aqueous electrolytes (HANE),” yielding outstanding ESWs up to 4.1 V (Figure 1) and enabling a 3.2 V battery output voltage using Li\(_4\)Ti\(_5\)O\(_{12}\) (LTO) and LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_{4}\) (LNMO) as active electrode materials.[9] By following an “inhomogeneous additive” approach, even 4.0 V aqueous LiB were realized[10] and further combined with a new halogen conversion–intercalation chemistry in graphite.[11] The concept of highly concentrated electrolytes (HCE) and especially the high anodic limit of ≈5.1 V versus LiLi\(^+\),[11] demonstrated for HANE may open the pathway to aqueous-based dual-ion batteries (DIBs).[9,12] In contrast to LiB, the DIB is characterized by the simultaneous uptake and release of both, anions and cations from the electrolyte into the respective host materials.[13] In several studies, graphite was considered to be the material of choice for the positive electrode due to its ability to reversibly form acceptor-type graphite intercalation compounds (GICs) with a variety of organic and inorganic anions from non-aqueous electrolytes.[14] The development of aqueous DIB cells seems to be not only of interest from scientific point-of-view, but also for industry, as an “aqueous dual-ion secondary battery” (graphite|titanium oxide cell) has been recently patented by Toyota.[15] Detailed studies dealing with anion intercalation...
Here, we report for the first time a DIB concept based on an aqueous/non-aqueous electrolyte combining high safety in form of a nonflammable WiSE with high cathodic stability by forming a protective solid electrolyte interphase (SEI) at the negative electrode (with the help of a non-aqueous solvent) and a sustainable positive intercalation-electrode material in terms of graphite. Therefore, a commercially available synthetic flake-type graphite is used for the positive electrode or working electrode (WE) (see Supporting Information). For cyclic voltammetry (CV) experiments as well as for ex situ X-ray diffraction studies (XRD), activated carbon (AC) was used as counter electrode (CE) in a half-cell setup (three-electrode configuration). The AC’s high working potential (3.0 – 1.5 V vs Li\text{Li}^+) its capacitive behavior, and its fast kinetics do not influence the graphite-based WE or lead to any significant reductive decomposition reactions of the electrolyte. In further steps, due to the cathodic limit (1.0 V vs Li\text{Li}^+; \sim 2.4 V vs Ag\text{AgCl}) of the water-based hybrid electrolyte (HANE; 21 m LiTFSI in H\text{H}_2\text{O}, 9.25 m in DMC, wt. ratio 1:1; Figure 1), the impact of two different negative electrode materials, i.e., LTP or LTO, on the electrochemical performance was investigated. Detailed information regarding synthesis of LTP, graphite characteristics, and experimental details for the electrode preparation as well as for electrochemical methods can be found in the Supporting Information. In order to verify the reversible intercalation/de-intercalation of TFSI\text{–} anions into the graphitic positive electrode from the chosen hybrid electrolyte, CV investigations of graphite (WE) \parallel AC (CE) cells with different cut-off potentials at a scan rate of 0.1 mV s\textsuperscript{–}1 were performed in a half-cell setup (three-electrode configuration). Thus, to achieve the most suitable balance between high discharge capacity and reduced decomposition of the water-based electrolyte at higher potentials, an optimized anodic cut-off potential was set to 1.85 V versus Ag\text{AgCl}, as determined from CV studies (Figure S1, Supporting Information). For a first proof of concept, CV

**Figure 1.** Schematic overview of active materials for aqueous LIBs (white) and DIBs (yellow) with respect to their redox potentials versus Li|Li\textsuperscript{+} and versus Ag|AgCl (0 V vs Ag|AgCl = 3.24 V vs Li|Li\textsuperscript{+}) and practical capacities related to the ESWs of water-based electrolytes; for further information and references see Tables S2 and S3 (Supporting Information).
experiments were performed for the graphite || AC cell in a potential range of 0–1.85 V versus Ag|AgCl with a scan rate of 0.1 mV s\(^{-1}\) for two cycles followed by increasing scan rates. Figure 2a shows the first two cycles of a graphite || AC cell, exhibiting reversible redox activities. In the 1\(^{st}\) cycle, oxidative currents were measured at an onset potential (arbitrarily defined as the potential at which the specific current reached \(0.01\) A g\(^{-1}\)) of \(\approx 1.33\) V versus Ag|AgCl shifted in the following cycle to slightly lower potentials (\(\approx 1.30\) V vs Ag|AgCl), which is most likely caused by an “activation” of the graphitic structure in the 1\(^{st}\) cycle, as observed previously for anion intercalation from ionic liquid electrolytes.\(^{14d}\) At higher potentials of \(\approx 1.75\) V versus Ag|AgCl, a second peak can be observed, representing the well-known “stage formation” behavior of acceptor-type GICs.\(^{13a}\) In comparison to the onset potentials for the formation of TFSI-GICs from ionic liquids (IL; 4.4 V vs Li|Li\(^+\)) and organic HCEs (4.3 V vs Li|Li\(^+\)), the onset potential in the aqueous electrolyte is shifted to slightly higher potentials (4.6 V vs Li|Li\(^+\)).\(^{12,13}\) This shift may be induced by stronger solvent–salt interactions in the water-based electrolyte in comparison to organic HCEs. Figure 2a shows the first two cycles of a graphite || AC cell, exhibiting reversible redox activities. In the 1\(^{st}\) cycle, oxidative currents were measured at an onset potential (arbitrarily defined as the potential at which the specific current reached \(0.01\) A g\(^{-1}\)) of \(\approx 1.33\) V versus Ag|AgCl shifted in the following cycle to slightly lower potentials (\(\approx 1.30\) V vs Ag|AgCl), which is most likely caused by an “activation” of the graphitic structure in the 1\(^{st}\) cycle, as observed previously for anion intercalation from ionic liquid electrolytes.\(^{14d}\) At higher potentials of \(\approx 1.75\) V versus Ag|AgCl, a second peak can be observed, representing the well-known “stage formation” behavior of acceptor-type GICs.\(^{13a}\) In comparison to the onset potentials for the formation of TFSI-GICs from ionic liquids (IL; 4.4 V vs Li|Li\(^+\)) and organic HCEs (4.3 V vs Li|Li\(^+\)), the onset potential in the aqueous electrolyte is shifted to slightly higher potentials (4.6 V vs Li|Li\(^+\)).\(^{12,13}\) This shift may be induced by stronger solvent–salt interactions in the water-based electrolyte in comparison to organic HCEs. However, in order to state and quantify this effect, further investigations are mandatory. In the cathodic scan, reductive currents can be observed in a potential range of 1.3–1.0 V versus Ag|AgCl attributed to a reversible de-intercalation of TFSI\(^{-}\) anions. For a closer look on the kinetics of the electrode reaction, different scan rates were applied. Figure 2b shows an increase of the current peak maximum for both, anodic and cathodic specific currents with increasing scan rate. The shift of the cathodic peak maximum (\(\approx 0.33\) V between a scan rate of 0.1 and 20 mV s\(^{-1}\)) hints at a quasi-reversible reaction. Based on the power-law expression

\[
i_p = a v^b
\]

where \(i_p\) is the maximum peak current and \(v\) is the sweep rate, the value of \(b\) can be used to distinguish between nondiffusion controlled (capacitive; \(b = 1.0\)) and diffusion controlled (Faradaic; \(b = 0.5\)) contributions (see Supporting Information).\(^{23}\) By plotting \(\log(i_p)\) versus \(\log(v)\) (Figure S2a, Supporting Information), a \(b\)-value for the graphite || AC setup of 0.77 for the anodic current and 0.74 for the cathodic current was determined, indicating a Faradaic character of the reaction with capacitive contribution and therefore, fast electrode kinetics. The linear correlation between the maximum specific peak current and the square root of the scan rate provides additional evidence for a charge transfer reaction (Figure S2b, Supporting Information).\(^{23}\) In order to investigate the structural changes of graphite during intercalation/de-intercalation of TFSI\(^{-}\) from a water-based electrolyte, ex situ XRD studies of a graphite || AC half-cell setup were performed at different states-of-charge (SOCs). Figure 2c shows the potential profiles of the second cycle at a constant current of 50 mA g\(^{-1}\) and d) correlated ex-situ XRD measurements of graphite positive electrodes.

**Figure 2.** a,b) CV investigations of the graphite || AC cell of the first two cycles at a scan-rate of a) 0.1 mV s\(^{-1}\) and of different scan rates from b) 0.1 to 20 mV s\(^{-1}\). Maximum peak currents (\(i_p\)) are marked by a vertical line. c) Potential profiles of the second cycle of a graphite || AC cell setup at 50 mA g\(^{-1}\) and d) correlated ex-situ XRD measurements of graphite positive electrodes.
staging mechanism, which is proposed for anion intercalation and well-studied for TFSI\(^-\) intercalation via in situ XRD from ionic liquid electrolytes, the most dominant staging phase can be determined by calculating the ratio of the \(d_{(n+2)}/d_{(n+1)}\) peak positions (see Supporting Information), as reported by Schmueling et al.\(^{[24]}\). The ratio for the charged graphite electrode corresponds to a value of 1.23, which can be attributed to a dominant stage-3 GIC. However, with the ongoing charging up to 1.85 V versus Ag\(\mid\)AgCl, the reflections further shift to 23.41° and 31.16° \(2\theta\) demonstrating a formation of stage-2 GIC. The periodic repeat distance (\(I_c\)), the gallery height (\(d_i\)), and the gallery expansion (\(\Delta d\)) were calculated and are shown in Table S4 (Supporting Information). During discharge, the deintercalation mainly starts at the observed plateau at \(\approx 1.2\) V versus Ag\(\mid\)AgCl and the staging mechanism is going “backwards” ending up with the formation of a distinctive graphitic (002) reflection again at 0 V versus Ag\(\mid\)AgCl. The results show that the electrochemical data correlate well with the structural changes and a reversible staging mechanism can clearly be observed.

In order to achieve maximum voltage in a water-based electrolyte, we investigated possible negative electrode materials which show lower potentials than AC. Therefore, we combined LTP as well as LTO as negative electrode material with graphite. To gain a deeper understanding of both DIB cells, CV studies (see Figure S3, Supporting Information), constant current cycling (CCC) investigations, and ex situ XRDs were conducted. Experimental details can be found in the Supporting Information. The electrochemical performance of LTP and LTO was also characterized by cyclic voltammetry versus activated carbon as CE (see Figures S5, S6, and S7, Supporting Information).

Figure 3 shows the results for the graphite \(\parallel\) LTP system. Different specific charge/discharge currents were applied to investigate the rate capability of the system, while also the advantage of the HANE electrolyte compared to the WiSE electrolyte in terms of improved capacity and Coulombic efficiency can be clearly pointed out (Figure S4a, Supporting Information). After five cycles at a specific current of 50 mA g\(^{-1}\), the following charge/discharge experiments were performed at 10, 20, 50, 100, 200, and 300 mA g\(^{-1}\) for five cycles each in the graphite potential range of \(-0.2\) V to 1.85 V versus Ag\(\mid\)AgCl. A discharge capacity up to 36 mAh g\(^{-1}\) is reached at 10 mA g\(^{-1}\), which decreases with higher specific currents down to 27 mAh g\(^{-1}\) at 300 mA g\(^{-1}\).

In the first cycle, the DIB cell suffers from a low Coulombic efficiency (\(C_{\text{eff}}\)) of 65% (50 mA g\(^{-1}\)), which may be caused by parasitic decomposition reactions of the water-based electrolyte. With increasing specific currents, an enhanced \(C_{\text{eff}}\) up to 98.8% at 300 mA g\(^{-1}\) can be observed (Figure S4a, Supporting Information). This behavior was already described in our former studies of various DIBs, caused by a reduced time at higher potentials. Therefore, a decreased decomposition of the electrolyte and/or decreased dissolution of the current collector at high SOC occurs, as displayed by a high \(C_{\text{eff}}\).\(^{[13a, 14b]}\)
In comparison to organic-solvent based systems, the impact of the applied current is more pronounced in the mixed solvent solution, presumably related to an increased decomposition of HANE (C_{eff} of ≈81% at 10 mA g⁻¹).[12,14b] The positive electrode potential profiles for different specific currents, shown in Figure 3a, exhibit a charge plateau at ≈1.6 V versus Ag|AgCl slightly shifted to higher values with higher specific currents. This shift goes in line with the observed quasi-reversible behavior in Figure 2b. The discharge profile starts with a sloping behavior, followed by a plateau at ≈1.3 V versus Ag|AgCl, which decreases with increased specific current and ends up again with a sloping behavior. This sloping or quasi-capacitive contribution is supported by our previously calculated b-value of 0.74. The difference between the graphite positive electrode potential and the potential of the LTP negative electrode, which indicates a reversible lithiation and de-lithiation of LTP, results in an average discharge cell voltage of ≈1.5 V (Figure 3b). Considering the improved C_{eff} at high currents, long-term cycling studies at high specific current (200 mA g⁻¹) were conducted, as displayed in Figure 3c. After 500 cycles, a capacity retention of 71% and an average C_{eff} of ≈95% (cycle 50–500) was achieved (Figure 3c). Post mortem analysis via SEM of the graphite positive electrode after 500 cycles shows no hint for exfoliation and, thus, no hint for any severe co-intercalation of water or DMC molecules (Figure S8, Supporting Information), indicating a high stability of graphite. These results are also supported by thermogravimetric analysis (Figure S9, Supporting Information), showing that the cycled graphite exhibits only a slightly enhanced amount of water in the mass spectrum than the pristine graphite. Further, the analysis shows an increase of CO₂ and SO₂ evolution referring to intercalated TFSI⁻. In order to confirm the anion intercalation into graphite, ex situ XRD measurements were performed. Figure 3d displays the XRD patterns for the pristine graphite electrode and the ex situ pattern after charging to a cut-off potential of 1.85 V versus Ag|AgCl with a constant current of 10 mA g⁻¹ in the first cycle. The distinctive graphitic (002) reflection at 26.5° 2θ is clearly observable for the pristine electrode. After charging, the (002) reflection completely disappeared and two new reflections at 23.57° and 30.84° 2θ arose. The ratio for the charged electrode corresponds to a value of 1.30, which can be attributed to a dominant stage-2 GIC. The periodic repeat distance (I_c), the gallery height (d_i), and the gallery expansion (Δd) were determined and are shown in Table S4 (Supporting Information). In conformity to in situ studies by Schmuelling et al., the values go in line with a stage-2 GIC formed from ionic liquid-based electrolytes, especially with the achieved capacity of ≈40 mAh g⁻¹.[24]

The investigated graphite || LTP DIB cell shows a promising performance for a water-based system regarding cycling stability at higher currents, but exposes a low cell voltage (1.5 V). In order to increase the cell voltage and, thus, the energy density, LTP was substituted by LTO, exhibiting a redox potential close to the lower border of the ESW of the HANE (Figure 1). For a fair comparison of both DIB cell systems, the same electrochemical and XRD studies were conducted for the graphite || LTO DIB cell, as depicted in Figure 4 and Figure S4b.
(Supporting Information). Similar to the LTP-based cell, the LTO-based cell suffers from a low first cycle C_{eff} (~59%), most likely due to enhanced decomposition of the electrolyte. However, especially in the first cycles and for low specific currents (10 mA g\(^{-1}\)), C_{eff} is even lower (~62%; Figure S4b, Supporting Information) due to the fact that the working potential of LTO (~1.55 V vs Li|Li\(^+\)) is directly at the border of the cathodic stability of the HANE, as observed by CV studies (Figure S5, Supporting Information). Electrolyte decomposition and gas evolution might also explain the non-smooth potential profiles in Figure 4a. Nevertheless, ex situ XRD measurements show a similar behavior for the LTO setup (2\(\theta\) (003) = 23.48\(^\circ\); 2\(\theta\) (004) = 31.01\(^\circ\)), confirming the formation of a stage-2 GIC \((d_{(n+2)}/d_{(n+1)} = 1.31)\) (Figure 4d, Table S4, Supporting Information). The C_{eff} values increase with increasing specific current, rising up to nearly ~99% at 300 mA g\(^{-1}\) by reaching a capacity of 27 mAh g\(^{-1}\), clearly demonstrating fast kinetics of the system (Figure S4b, Supporting Information). Taking the lower working potential of LTO into account, an average discharge cell voltage of ~2.5 V can be achieved (Figure 4b). However, owing to the control of the positive electrode potential during cycling, the uneven ratio of parasitic reactions on the negative and positive electrode sides as well as the nonoptimized balancing between the negative and the positive electrodes (N/P ratio) lead to an ongoing polarization of the LTO during discharge (Figure 4b), as it has also been observed in previous publications.\(^{[13]}\) Heidrich et al. recently reported on the capacity fading mechanism in DIB cells, unraveling this issue in detail by introducing an electron inventory model.\(^{[25]}\) Nevertheless, the potential control of the graphite WE has been chosen in this work to primarily study the behavior of the positive graphite electrode within a DIB full-cell setup, having the advantage of a fixed graphite potential range over cycling. For further studies, in particular in terms of practicality, the performance has to be evaluated in cell voltage-controlled DIB cells, while using optimized active materials and electrolytes.

Investigating the cycling stability, a capacity retention of 84% after 50 cycles based on the first cycle and a C_{eff} up to 98.6% at an increased specific current of 200 mA g\(^{-1}\) were achieved (Figure 4c). In general, the graphite || LTO DIB cell shows a promising working voltage on the cost of a higher amount of parasitic reactions. By applying high specific currents, the parasitic reactions attributed to the cathodic stability limit of the electrolyte can be reduced. In 2012, we reported on graphite || LTO DIB cells using a non-aqueous electrolyte, i.e., a Pyr\(_{14}\)TFSI/LiTFSI-based electrolyte.\(^{[13]}\) For comparison, a discharge capacity of up to ~84 mAh g\(^{-1}\) and a C_{eff} up to 97.4% could be achieved by this ionic liquid electrolyte (specific current: 50 mA g\(^{-1}\); average discharge voltage: ~2.7 V), which clearly points out the importance of a high electrolyte stability.

Overall, these initial results on aqueous DIB cells will pave the path toward a novel battery type, which is based on a graphite intercalation positive electrode and a water-based electrolyte. This study shows a first proof of concept toward a promising environmentally friendly (“greener”) energy storage technology. Further comprehensive and systematic studies related to the stability of the aqueous-based electrolyte and an optimization of the negative/positive electrode capacity balancing (N/P ratio) as well as a cell-voltage controlled DIB setup are necessary to further elaborate this innovative DIB concept.

In summary, we introduced a novel DIB concept based on a HANE and an environmentally friendly, low-cost graphite positive electrode combined with either LTO or LTP as the negative electrode material, respectively. To the best of our knowledge and confirmed by ex situ XRD measurements, the formation of a stage-2 acceptor-type GIC of TFSI anions from an aqueous-based electrolyte is reported for the first time. In case of LTP as negative electrode material, a long-term stable cycling performance with an initial discharge capacity of ~42 mAh g\(^{-1}\) and a capacity retention of 71% after 500 cycles at a specific current of 200 mA g\(^{-1}\) and with 1.5 V average discharge cell voltage was achieved. Combining graphite with LTO as the negative electrode, the average discharge voltage is increased to 2.5 V. With this work, we hope to encourage the scientific community to develop a deeper understanding and further improvements of advanced aqueous electrolyte DIB technologies toward sustainable energy storage.

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

Acknowledgements
The authors thank the German Federal Ministry of Education and Research (BMBF) and the Ministry of Economic Affairs, Innovation, Digitalization and Energy of the State of North Rhine-Westphalia (MWIDE) for funding this work in the projects “Dual-Carb” (03XP0118) and “GrEEn” (313-W044A), respectively. A portion of the research described in this paper 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. The authors also thank Andre Bar for his graphical support.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
anion intercalation, aqueous batteries, dual-ion batteries, graphite intercalation compounds, hybrid aqueous/nonaqueous electrolytes

Received: August 20, 2019
Revised: October 15, 2019
Published online: January 15, 2020

1\(^{[1]}\) a) R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, Nat. Energy 2018, 3, 267; b) G. E. Blomgren, J. Electrochem. Soc. 2017, 164, A5019; c) M. Winter, B. Barnett, K. Xu, Chem. Rev. 2018, 118, 11433.
