A High-Voltage, Dendrite-Free, and Durable Zn–Graphite Battery

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The intrinsic advantages of metallic Zn, like high theoretical capacity (820 mAh g⁻¹), high abundance, low toxicity, and high safety have driven the recent booming development of rechargeable Zn batteries. However, the lack of high-voltage electrolyte and cathode materials restricts the cell voltage mostly to below 2 V. Moreover, dendrite formation and the poor rechargeability of the Zn anode hinder the long-term operation of Zn batteries. Here a high-voltage and durable Zn–graphite battery, which is enabled by a LiPF₆-containing hybrid electrolyte, is reported. The presence of LiPF₆ efficiently suppresses the anodic oxidation of Zn electrolyte and leads to a super-wide electrochemical stability window of 4 V (vs Zn/Zn²⁺). Both dendrite-free Zn plating/stripping and reversible dual-anion intercalation into the graphite cathode are realized in the hybrid electrolyte. The resultant Zn–graphite battery performs stably at a high voltage of 2.8 V with a record midpoint discharge voltage of 2.2 V. After 2000 cycles at a high charge–discharge rate, high capacity retention of 97.5% is achieved with ≈100% Coulombic efficiency.

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Herein, we report a high-voltage and durable Zn–graphite battery (ZGB), which is enabled by a hybrid electrolyte consisting of Zn(TFSI)$_2$ and LiPF$_6$. The anodic dissolution and electrolyte decomposition of Zn electrolyte (Zn(TFSI)$_2$) are efficiently suppressed by LiPF$_6$ addition. The hybrid electrolyte with a wide electrochemical stability window of 4.0 V (vs Zn/Zn$^{2+}$) renders efficient Zn plating/stripping on the anode and reversible dual-anion intercalation/deintercalation into/from graphite cathode. As the result, the fabricated ZGB can be stably operated in a voltage range of 0.7–2.8 V and output a high midpoint discharge voltage of 2.2 V, outperforming those of the reported Zn batteries. Moreover, the ZGB presents an impressive rate capability (charge within 3 min at a loading of 2 mg cm$^{-2}$) and long-term cycling stability (>97% capacity retention after 2000 cycles).

As shown in Figure 1a, the ZGB consists of a graphite cathode, a Zn anode, and a hybrid electrolyte comprising of Zn(TFSI)$_2$ and LiPF$_6$. During the charge process, both of PF$_6^-$ and TFSI$^-$ are intercalated into graphite cathode. And simultaneously, Zn$^{2+}$ is electrochemically reduced and deposited as metallic Zn due to high redox potential of Zn (−0.76 V vs standard hydrogen electrode (SHE)) compared to Li (−3.04 V vs SHE). In the discharge process, reverse reactions take place with PF$_6^-$/TFSI$^-$ and Zn$^{2+}$ diffusing back into the electrolyte. Due to the high working voltage of graphite cathode, the resultant ZGB, as confirmed experimentally, with quasi-symmetric charge–discharge curves outputs a midpoint discharge voltage ($V_m$) as high as 2.2 V (Figure 1b), which is the highest value among the reported Zn batteries (Figure 1c). Another merit of ZGB lies in its excellent cycling performance: high capacity retention of 97.5% can be attained after 2000 cycles, which is also superior to Zn batteries based on other conventional cathodes (Figure 1d). The performance details of ZGB are provided below.

The stable operation of ZGB demands an electrolyte with a wide electrochemical stability window. The oxidation stability of various electrolytes was first investigated using linear sweep voltammetry (LSV) on stainless-steel (SS) electrodes. Conventional Zn(TFSO$_3$)$_2$/acetonitrile, Zn(TFSI)$_2$/acetonitrile, and Zn(TFSI)$_2$/ethyl methyl carbonate (EMC) electrolytes were unstable against oxidation with rapid current increase above 2.0, 2.2, and 2.3 V (vs Zn/Zn$^{2+}$), respectively (Figure 2a). Inspired by a high electrochemical stability window above 6.0 V (vs Li/Li$^+$) for LiPF$_6$/EMC electrolyte and the capability of LiPF$_6$ to stabilize Al and SS current collectors,[10g,12] we considered that the addition of LiPF$_6$ might solve the stability issue of Zn electrolytes. We found that the addition of LiPF$_6$ into Zn(TFSI)$_2$/EMC, forming transparent liquid without any precipitate (Figure S1, Supporting Information), could efficiently suppress the anodic oxidation and shift the oxidation voltage over 3.0 V. Low anodic current was observed even at 4.0 V for the hybrid electrolytes (0.5–1M Zn(TFSI)$_2$+2M LiPF$_6$). A more aggressive floating test at 3 V was further carried out to confirm the electrolyte stability (Figure 2b). The pure Zn(TFSI)$_2$/EMC electrolyte delivered extremely high anodic current of 30–100 mA cm$^{-2}$, which is 10$^2$–10$^5$ times higher than that of Zn(TFSI)$_2$+2M LiPF$_6$.
for the hybrid ones and accompanied with severe corrosion of SS electrode (Figure S2, Supporting Information). For the hybrid electrolyte 1M Zn(TFSI)$_2$+1M LiPF$_6$, although the anodic current was largely suppressed, large current fluctuations were still observed, which would trigger sudden failure of full cells. At the same condition, the electrolyte 0.5M Zn(TFSI)$_2$+2M LiPF$_6$ displayed the lowest anodic current among all the hybrid electrolytes investigated, which suggested the highest anodic stability. Hereafter, 0.5M Zn(TFSI)$_2$+2M LiPF$_6$ was employed as the hybrid electrolyte in the following sections unless otherwise stated. The above results indicated that the hybrid system promoted the electrochemical stability of Zn electrolyte at high voltage, and the stability was influenced by the ratio between Zn(TFSI)$_2$ and LiPF$_6$. The anodic dissolution problem noticed in the pure TFSI$^-$-based electrolytes was well resolved by the optimal LiPF$_6$ addition (Figures S2 and S3, Supporting Information). It should be noted that our hybrid electrolyte design principle (suppressing anodic oxidation at high voltage) is totally different from that reported recently to stabilize Si anode by forming stable Li–M–Si ternaries.[13]

The Zn plating/stripping behavior in the hybrid electrolyte was evaluated in a symmetric Zn//Zn cell. At a current density of 1 mA cm$^{-2}$, Zn anode demonstrated stable voltage profiles with small polarization (Figure 2c). The detailed plating–stripping curves at 1st, 100th, and 200th cycle well overlapped with each other, indicating a high reversibility of Zn plating/stripping in the hybrid electrolyte (Figure S4a, Supporting Information). Flat voltage plateaus were observed on both charge and discharge curves, which is different from sloping voltage profiles in aqueous electrolytes.[2a] The polarization for Zn plating/stripping was found sensitive to the current density, varying from 16 mV at 0.2 mA cm$^{-2}$ to 286 mV at 5 mA cm$^{-2}$ (Figure S4b, Supporting Information). After the cycling test, the scanning electron microscopy (SEM) image of Zn anode showed a dense spherical morphology without dendrite formation (Figure 2d, and Figure S4c,d, Supporting Information). In the pure Zn(TFSI)$_2$/EMC electrolyte, the deposited Zn consisted of large domains, however, with many vertical nanoprotrusions on the surface (Figure S4e,f, Supporting Information), which may penetrate through the separator and cause short circuit of cells. The dendrite-free morphology of Zn anode in the hybrid electrolyte can be ascribed to an electrostatic shield effect[14] of Li$^+$. The X-ray diffraction (XRD) pattern of Zn anode confirms retention of metallic Zn after the long-time cycling experiment (Figure S5, Supporting Information). Besides, a galvanostatic charge–discharge measurement on Zn//Cu cells also verified the high reversibility of plating/stripping with a high initial CE of 93.9% (Figure S6, Supporting Information). Then the CE quickly increased to 98–100% and remained stable afterward. These results reveal the high reversibility of Zn plating/stripping in the hybrid electrolyte and no parasitic reaction is involved in this process.

To examine whether graphite cathode can efficiently perform in the hybrid electrolyte, a ZGB was constructed with Zn nanosheets deposited on carbon cloth (Zn/CC, Figure S7, Supporting Information) as anode and commercial micrometer-sized graphite (10–80 µm, Figure S8, Supporting Information) as cathode. The selection of Zn/CC instead of Zn foil...
is due to its higher surface area and better kinetics (Figure S9, Supporting Information). In a cyclic voltammetry (CV) measurement, the ZGB showed a group of redox peaks in the voltage range of 1.50–2.60 V (Figure S10, Supporting Information), indicating reversible Faradaic reactions associated with graphite cathode. In a galvanostatic charge–discharge measurement, the charge curve of ZGB can be divided into three segments (Figure 1b), namely, quasi-linear region at 1.90–2.39 V, plateau region at 2.39–2.44 V and linear region at 2.44–2.70 V. Another three segments (2.67–2.32, 2.32–1.98, and 1.98–1.60 V) are also identified on the discharge curve. This result suggests a staging intercalation/deintercalation process of graphite cathode.

To elucidate structural evolution of graphite cathode during the galvanostatic charge–discharge measurement, XRD patterns of graphite cathodes at different charging states were recorded. Charging graphite cathode induced splitting of original graphite (002) peak at 26.45° into two new peaks located at 22°–25° and 30°–35° (Figure 3a), corresponding to the (00n) and (00n+1) peak of graphite intercalation compounds. The appearance of the (00n+1) peak is a clear sign of anion intercalation into graphite cathode. Based on formulas $d_{00n} = l_c/n = \lambda/(2\sin\theta_{00n})$ and $d_{00n+1} = l_c/(n+1) = \lambda/(2\sin\theta_{00n+1})$, stage information of graphite cathode can be calculated (Table S1, Supporting Information). During the charge process, graphite cathode gradually transforms to a Stage 2 compound at the end of quasi-linear region (1.90–2.39 V), and further evolves to a Stage 1 structure after plateau region (2.39–2.44 V), and maintains Stage 1 in the subsequent linear region (2.44–2.70 V). The charge stored in the linear region can be ascribed to a solid solution transition from dilute Stage 1 to dense Stage 1 structure (Figure S11, Supporting Information). Upon discharging, the Stage number varies in a reverse way until recovery of unintercalated graphite. A mix stage structure (Stage-2 and Stage-3) was noticed at 1.9 V, which is associated with stage transition. The Raman spectra also corroborate anion intercalation into graphite cathode by the appearance of $E_{2g}^{2(b)}$ mode (Figure 3b), which originates from symmetry variation of the boundary graphene layer and electronic effects of the intercalated anions.

Solid-state $^{19}$F nuclear magnetic resonance spectroscopy (NMR) was conducted to probe the intercalated species in the charged graphite. Before the measurement, graphite cathode was charged to 2.7 V (vs Zn/Zn$^{2+}$) at a current density of 0.1 A g$^{-1}$ and then rinsed with anhydrous dimethyl carbonate to remove the excess electrolyte. As shown in Figure 3c, the solid-state $^{19}$F NMR spectrum of charged graphite shows three broad signals at −68.3, −69.2, and −74.2 ppm, which indicate the presence of F-containing species in the charged graphite. In contrast, the spectrum of the hybrid electrolyte measured by solution-state NMR presents three sharp peaks at −72, −73.5, and −78.2 ppm, which originate from PF$_6$ and TFSI$^-$, respectively. The broadening of the lines arises from the restrictions in the tumbling motion of these ions in the graphite. The fact that the line observed only moderate narrows with increasing magic-angle-spinning (MAS) sample spinning implies a significant contribution from inhomogeneous broadening (disorder in the environment). The shift of the entire spectrum with respect to the organic solvent is indicative of the different environment, and $^{19}$F chemical is highly sensitive to the environment. Both
Figure 4. Anion diffusion in the hybrid electrolyte and graphite cathode. a) Molecular structure of PF$_6^-$ and TFSI$^-$. b) Anion diffusion coefficients determined by PFG NMR. c) The optimized anion diffusion path in the graphite layers. d) The optimized anion energy barriers in the graphite layers.

The broadening of the line and the changed chemical shift indicate interaction between PF$_6^-$ /TFSI$^-$ anions and the graphite electrode. In addition, the X-ray photoelectron spectrum of the charged graphite cathode shows apparent F1s, P2p, S2p, and N1s peaks (Figure S12, Supporting Information), confirming dual-anion (PF$_6^-$ and TFSI$^-$) intercalation into graphite cathode. After discharging, the residue F1s, P2p, S2p, and N1s signals observed in the electrode can be ascribed to the trapped or adsorbed species in graphite samples. The energy-dispersive X-ray spectrum (Figure S13, Supporting Information) and SEM elemental mapping images of the charged graphite cathodes also exhibited the pronounced F, P, and S signals in the whole electrode (Figure 3d).

To gain insight into the high electrochemical stability of the hybrid electrolyte and the dual-anion intercalation mechanism of graphite cathode, anion diffusion in electrolyte and graphite cathode is analyzed from the aspects of diffusion kinetics, which, however, was not well understood thus far despite the utilization of PF$_6^-$ and TFSI$^-$ electrolytes in dual-ion batteries. Pulsed-field-gradient (PFG) diffusion NMR has been performed for the pure and hybrid electrolytes. In the stimulated echo PFG NMR experiment, the strength of a pair magnetic field gradient pulses is incremented between each step in the experiment and signals from diffusing species are successively attenuated. From the signal decay, the diffusion is derived by the Stejskal–Tanner equation. In all cases a monoexponential decay and a monodisperse size for each species are observed (Figure 4b). Both diffusion coefficients ($D$) of PF$_6^-$ and TFSI$^-$ in hybrid electrolyte were found much lower than those in pure cases, which are mainly attributed to the enhanced viscosity of hybrid electrolyte. $D$(PF$_6^-$) in the hybrid electrolyte was determined as 3.6–3.8 × 10$^{-11}$ m$^2$ s$^{-1}$ and is higher than 3.3 × 10$^{-11}$ m$^2$ s$^{-1}$ for $D$(TFSI$^-$). When an electric field is applied, it is kinetically faster for PF$_6^-$ to diffuse in the hybrid electrolyte and to accumulate on the cathodes than TFSI$^-$. The accumulated PF$_6^-$ can thus protect the SS electrodes by the formation of passivation film, which will separate direct contact of TFSI$^-$ with SS electrodes. In such way, the anodic oxidation of Zn(TFSI)$_2$ electrolyte is efficiently suppressed, resulting in a 4.0 V (vs Zn/Zn$^{2+}$) electrochemical stability window.

Density functional theory calculations were carried out to investigate the anion intercalation processes in graphite. The anion diffusion paths on the unit cell of graphite were optimized (Figure 4c) and both anions need to pass the C–C bond to reach the next stable point along the [110] direction. As the anions are embedded between the interlayers of graphite, the corresponding charge density difference isosurfaces are obtained (Figure S14, Supporting Information). For both anions, there is a large charge deficiency around the anions and charge excess at graphite, suggesting strong electron transfer between graphite and anions. It means that the bonding between graphite and anions has a significant ionic character. The optimized PF$_6^-$ diffusion barrier (0.25 eV) in graphite layers is lower than that (0.54 eV) for TFSI$^-$ as shown in Figure 4d, indicating a higher diffusion rate of PF$_6^-$ in intact graphite. We hypothesize that at the initial charge stage, PF$_6^-$ is more kinetically preferable than TFSI$^-$ to intercalate into graphite, which will expand the interlayer spacing of graphite cathode, especially at the edge sites. Note that the average intercalant gallery heights of PF$_6^-$ and TFSI$^-$ are close (7.89 vs 7.99 Å). Both PF$_6^-$ and TFSI$^-$ are thus facilitated to intercalate into the above pre-expanded graphite cathode until full in-plane packing within the Stage-1 structure is established, leading to dual-anion intercalated graphite.

Electrochemical performance of ZGB was evaluated by galvonostatic cycling tests within SS coin-type cells.
A voltage window of 0.7–2.7 V was applied to ZGB. At the current density of 0.1 A g\(^{-1}\), the ZGB delivered a specific capacity of 105 mAh g\(^{-1}\) based on the mass of graphite (2 mg cm\(^{-2}\)) in cathode. No capacity fading was noticed during the cycling (Figure 5a). The CE was determined to be 93.2% for the first cycle and quickly stabilized at \(\approx 98\%\) after a few cycles, indicating high reversibility of ZGB and negligible side reaction. In sharp contrast, the ZGB with pristine Zn(TFSI)\(_2\) electrolyte suffered from an endless charging process (Figure S15, Supporting Information). Due to insufficient protection of current collector, the ZGB with non-optimal hybrid electrolytes (1M Zn(TFSI)\(_2\)+1M LiPF\(_6\)) experienced a sudden failure during the cycling (Figure S16, Supporting Information). As Li\(^+\) was present in the hybrid electrolyte, the capacity contribution of Li\(^+\) was surveyed in a similar battery configuration (Zn/CC//graphite) but with pure LiPF\(_6\) electrolyte (2M LiPF\(_6\) in EMC). This battery showed a limited capacity of 0.5–0.7 mAh g\(^{-1}\) under the same condition (0.7–2.7 V and 0.1 A g\(^{-1}\), Figure S17, Supporting Information), implying negligible capacity contributed from Li\(^+\) in the hybrid electrolyte.

The rate performance of ZGB was investigated at various current rates ranging from 0.1 to 2 A g\(^{-1}\). Under accelerated current, the capacity of ZGB demonstrated very slight decay and polarization of charge–discharge curves (Figure S18, Supporting Information). High reversible capacities of 102, 101, 99, 98 and 97 mAh g\(^{-1}\) could be retained at 0.2, 0.4, 0.8, 1, and 2 A g\(^{-1}\), respectively (Figure 5b). Particularly, the capacity fully recovered when the current was switched back to 0.1 A g\(^{-1}\). The long-term cycling stability test of ZGB was further assessed at 1 A g\(^{-1}\). After 2000 galvonostatic cycles, the ZGB still maintained a capacity of 96 mAh g\(^{-1}\), corresponding to a capacity retention up to 97.5% (Figure 5c). The charge–discharge curves at different cycles well overlapped with each other, indicating no polarization deterioration during continuous operation (Figure S19, Supporting Information). Notably, an average CE is as high as 99.64%, which is the highest value achieved in graphite cathode-derived batteries (Table S2, Supporting Information). After the long-term cycling test, the graphite cathode maintained its sheet-like morphology and crystalline structure (Figure S20a–c, Supporting Information). No exfoliation of graphite was observed. The Zn/CC anode evolved from smooth nanosheets to a rougher surface yet preserved metallic Zn phase (Figure S20d–f, Supporting Information).

High active mass loading is essential for practical high-capacity applications. The areal capacity of ZGB can be readily enhanced by increasing the areal mass loading of graphite cathode. Within an expanded voltage window of 0.7–2.8 V to compensate voltage polarization, the areal capacity of ZGB reached 1.97 mAh cm\(^{-2}\) with graphite loading up to 21 mg cm\(^{-2}\) (Figure 5d), corresponding to a specific capacity of 94 mAh g\(^{-1}\). After 10 cycles at C/3 (nC means charge/discharge in 1/n h), the areal capacity was still over 1.90 mAh cm\(^{-2}\) (Figure S21, Supporting Information). At lower mass loadings of 9 and 5.5 mg cm\(^{-2}\), areal capacities of 0.92 and 0.56 mAh cm\(^{-2}\) were achieved and remained stable during cycling (Figure S21, Supporting Information).

Figure 5. Electrochemical performance of ZGB. a) Cycling performance at 0.1 A g\(^{-1}\). b) Rate performance at various current densities. c) Long-term cycling stability at 1 A g\(^{-1}\). d) Charge–discharge curves of ZGB with different graphite mass loadings at C/3. All cells were first cycled in a voltage range of 0.7–2.5 V for three cycles. Voltage windows of 0.7–2.7 and 0.7–2.8 V were then applied to ZGB with mass loading of 5.5 and 9/21 mg cm\(^{-2}\), respectively. The current density and specific capacity of ZGB were calculated on graphite mass.
ZGB also shows an excellent cycling stability (Table S3, Supporting Information). Neither Zn dendrite nor side reactions are detected on Zn anode due to the use of organic hybrid electrolyte. The graphite cathode with a unique dual-anion intercalation mechanism performs efficiently in ZGB without exfoliation and disintegration, surpassing conventional cathode materials for Zn batteries in structural stability,[66] cost and sustainability.[23] Based on the mass of electrolyte, anode, and cathode, the ZGB delivers an energy density of 68 Wh kg\(^{-1}\) at a power of 64 W kg\(^{-1}\) and retains 56.7 Wh kg\(^{-1}\) at the power of 1.2 kW kg\(^{-1}\). The energy density of ZGB is close to 70 Wh kg\(^{-1}\) of Li–LiMn\(_2\)O\(_4\) hybrid cell[23] and higher than 30–65 Wh kg\(^{-1}\) of Al–graphite battery,[24][24] but it is inferior to that of state-of-the-art rocking-chair Zn batteries (Figure S22, Supporting Information). Considering the low cost, long cycling life, and moderate energy density, our ZGB is promising for scalable stationary application rather than for automobile application.

In summary, we have demonstrated a high-voltage, dendrite-free and durable ZGB with assistance of a LiPF\(_6\)-containing hybrid electrolyte. The addition of LiPF\(_6\) resolves the anodic oxidation problem of Zn(TFSI)\(_2\) electrolyte, which stems from the diffusion kinetics difference between PF\(_6^-\) and TFSI\(^-\). The hybrid electrolyte exhibits a wide electrochemical stability window of 4 V (vs Zn/Zn\(^2+\)), making it possible to construct high-voltage Zn batteries. Further, PF\(_6^-\) participates in anion intercalation process together with TFSI\(^-\), leading to a dual-anion intercalated graphite cathode. In contrast to PF\(_6^-\), Li\(^+\) in the hybrid electrolyte contributes negligible capacity due to its low redox potential (−3.04 V vs SHE). Benefiting from the highly stable hybrid electrolyte, dendrite-free Zn plating/striping and fast dual-anion intercalation process, the ZGB displays high working voltage, excellent rate capability and long-term cycling stability. For potential stationary application of ZGB, more electrolyte optimization will be carried out in the future to enhance the safety properties of organic electrolyte and to further replace LiPF\(_6\) with other cheaper salts. Moreover, our findings on hybrid electrolyte and dual-anion intercalation mechanism will inspire the future development of novel metal–graphite batteries and other high-energy rechargeable batteries.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

anion intercalation, dendrite-free, dual-ion batteries, graphite cathodes, Zn batteries
