Fast constructing polarity-switchable zinc-bromine microbatteries with high areal energy density

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Microbatteries (MBs) are promising candidates to provide power for various miniaturized electronic devices, yet they generally suffer from complicated fabrication procedures and low areal energy density. Besides, all cathodes of current MBs are solid state, and the trade-off between areal capacity and reaction kinetics restricts their wide applications. Here, we propose a dual-plating strategy to facilely prepare zinc-bromine MBs (Zn-Br2 MBs) with a liquid cathode to achieve both high areal energy density and fast kinetics simultaneously. The Zn-Br2 MBs deliver a record high areal energy density of 3.6 mWh cm−2, almost an order of magnitude higher than available planar MBs. Meanwhile, they show a polarity-switchable feature to tolerate confusion of cathode and anode. This strategy could also be extended to other battery systems, such as Zn-I2 and Zn-MnO2 MBs. This work not only proposes an effective construction method for MBs but also enriches categories of microscale energy storage devices.

INTRODUCTION

Microscale energy storage devices have attracted increasing research interests due to their potential applications in various miniaturized electronics, such as microrobots, implantable medical devices, and Internet of Things (1–3). To date, microsupercapacitors (MSCs) have been extensively studied due to high power density and ease of fabrication, as their two electrodes could be the same materials (4–10). However, the low energy density, fast self-discharge, and unstable voltage output limit their practical applications (11–13). Microbatteries (MBs) could effectively overcome these challenges (14).

Although substantial progresses have been made in recent years, current planar MBs still suffer from tedious and complicated construction procedures as it is a considerable challenge to prepare and match cathode and anode at a microscale (15–23). For example, a multistep mask-assisted filtration strategy was proposed to construct a planar sodium-ion MB, which required at least six procedures (24), including preparation of cathode and anode active materials, and then step by step build current collector, cathode, and anode on the nylon substrate with the help of a prepared interdigitated mask, adding the gel electrolyte for the final encapsulation. Besides, current planar MBs are limited to solid cathodes and generally deliver unsatisfactory areal capacity and energy density (most are lower than 300 μAh cm−2 and 500 μWh cm−2) due to inferior power density originated from a too thick solid electrode (25–28). Furthermore, current MBs contain an excess amount of anode (typically more than 10 times than the cathode), which results in a decreased overall performance and is not applicable in practice.

Here, we propose a dual-plating strategy to fast construct zinc-bromine (Zn-Br2) MBs with a liquid cathode, which not only gets rid of the complicated and time-consuming procedures of traditional methods but also helps the planar MB access high areal energy density and power density. The electrolyte is the key point, and it contains redox-active cations (Zn2+) and anions (Br−). During the charging process, Zn2+ gain electrons and then get deposited on the negative current collector to form the zinc anode; concomitantly, Br− loss electrons to generate Br2 that work as the cathode on the positive current collector. The Br2 cathode and the Zn anode return to soluble Br− and Zn2+, respectively, during the discharging process (29). The cathode and anode are generated one by one, and no one electrode is excessive, enabling the maximization of the overall electrochemical performance. The dual-plating and stripping reactions are as follows:

Cathode: 2Br− − 2e− ↔ Br2 E0 = 1.06 V versus SHE (1)

Anode: Zn2+ + 2e− ↔ Zn E0 = −0.76 V versus SHE (2)

The Zn-Br2 MBs shows an electrode-less feature, and it only requires an interdigitated current collector and a redox-active electrolyte, eliminating the synthesis of active materials, which is a necessary procedure for previous MBs. It also bypasses the challenge of precisely coat or deposit cathode and anode on different microelectrodes. Moreover, the troublesome and time-consuming mass matching of the cathode and anode procedure could also be ingeniously avoided, because they always generate one by one (30). It is worth mentioning that, to the best of our knowledge, the Zn-Br2 system have not yet been introduced into the field of microscale energy storage, because it is hard to manipulate liquid Br2 through previous methods. The new MB is expected to achieve high energy density and power density at the same time due to the liquid nature of the
Br$_2$ cathode. For traditional MBs, increasing areal loading to pursue higher energy density could result in long ion transfer distance in solid active materials and lead to decreased power density. The liquid feature of the Br$_2$ cathode could circumvent the trade-off between energy density and power density due to fast reaction kinetics in the liquid medium. Benefiting from these merits, the Zn-Br$_2$ MBs deliver record high areal capacity and areal energy density (2220 µAh cm$^{-2}$ and 3645 µWh cm$^{-2}$) and maintain an excellent power density of 26.2 mW cm$^{-2}$ (even better than most MSCs). It is worth mentioning that these electrochemical performances are obtained without any excess of cathode or anode. They also have good flexibility, maintaining almost the same galvanostatic charge-discharge (GCD) curves under different bending states. Meanwhile, the Zn-Br$_2$ MBs show a unique feature of switchable polarity, allowing self-rectification on possible faulty operations such as wrongly connecting cathode and anode during charging. This work provides a new simple but efficient method to fast construct in-plane MBs, which is applicable for both solid and liquid microelectrodes. The Zn-Br$_2$ MB as a novel MB not only enriches the microscale energy storage devices but also sets a new benchmark for in-plane MBs.

**RESULTS**

**Construction of Zn-Br$_2$ MBs**

The preparation of Zn-Br$_2$ MBs is shown in Fig. 1A. A flexible and hydrophilic carbon nanotube (CNT) paper (about 10 µm in thickness) is first stuck on the insulating tape (fig. S1) and then patterned into interdigitated electrodes (the area is about 0.18 cm$^2$ based on all fingers and gaps) through the laser carving method. The microelectrode is flexible and could be easily integrated (Fig. 1B). The Zn-Br$_2$ MBs are obtained after covering a redox-active gel electrolyte containing Br$^-$ and Zn$^{2+}$ on the interdigitated electrodes. The prepared Zn-Br$_2$ MBs are at the discharging state. Once a bias (1.85 V is used here) is applied, the Br$_2$ and Zn could be in situ plated on the CNT microelectrodes to act as the cathode and anode (Fig. 1C), respectively, and then to provide power for miniaturized electronics.

**Choice of electrolyte**

The redox-active electrolytes greatly affect the electrochemical performance of the Zn-Br$_2$ MBs (Fig. 2, A to C). The composition of the redox-active electrolyte is first optimized through a homemade cell (fig. S2). When ZnBr$_2$ is used as the Zn and Br sources, the Zn-Br$_2$ battery delivers a low Coulombic efficiency of about 40% due to the diffusion of soluble Br$_3^-$ spontaneously formed from Br$_2$ and Br$^-$ during the charging process (Fig. 2D and fig. S3) (31–33), and its diffusion process can be witnessed by the slow percolation of light yellow colored Br$_3^-$ into the electrolyte (fig. S4). Tetrabutylammonium bromide (TBABr; C$_{16}$H$_{36}$BrN) has been reported as an efficient complexing agent for Br$_3^-$ to impede the cross-diffusion of Br$_3^-$ (33). When TBABr is selected as the Br source and ZnSO$_4$ is used as the Zn source in the electrolyte to construct the Zn-Br$_2$ MBs, the Coulombic efficiency of MBs is improved to 78% (Fig. 2E), but the polarization between charging and discharging processes substantially increases to 822 mV, suggesting the slow reaction kinetics of solid TBABr$_3$ complex (fig. S5).

Instead, 1-methyl-3-propylimidazolium bromide (MPIBr; C$_7$H$_{13}$BrN$_2$) is found to provide high Coulombic efficiency and fast reaction kinetics at the same time. MPIBr is an ionic liquid composed of MPI$^+$ cation and Br$^-$ anion, and its molecular structure is shown in fig. S6. The device prepared with a 1 M MPIBr + 1 M ZnSO$_4$ electrolyte shows a high Coulombic efficiency of 99% and a low polarization of 144 mV (Fig. 2, F and G). The Raman spectra, ultraviolet-visible (UV-vis) spectra, $^1$H nuclear magnetic resonance (NMR) spectra, $^{13}$C NMR spectra, and electrospray ionization mass spectrometry spectra indicate that the MPIBr$_3$ liquid cathode is formed during the charging process (figs. S7 to S10). The Zn anode is also generated at the same time (fig. S11). The UV-vis spectra were used to detect the Br$_3^-$ in the electrolyte. During the charging process, a strong Br$_3^-$ signal is found in the ZnBr$_2$ electrolyte (Fig. 2H), but there is no obvious signal of Br$_3^-$ in the electrolyte containing MPIBr and ZnSO$_4$ (Fig. 2I and fig. S12), further demonstrating that MPI$^+$ could effectively complex with Br$_3^-$ (MPI$^+$ + Br$_3^-$ $\rightarrow$ MPIBr$_3$). When MPIBr or TBABr is added to a solution containing Br$_3^-$ (fig. S13),...
the solution immediately becomes turbid (figs. S14 and S15 and movie S1), suggesting that MPI + and TBA + could form insoluble complex compounds with Br 3−. In contrast, no change is noticed when ZnBr 2 is added to the solution (fig. S16).

Meanwhile, the concentration of Br− in the electrolyte also affects the electrochemical performance of the Zn-Br 2 MBs. The electrolyte with 1.5 M MPIBr + 1.5 M ZnSO 4 shows the fastest plating rate (fig. S17), and a further increase to 2.0 M leads to incomplete dissolution of MPIBr (fig. S18). Therefore, unless otherwise specified, the electrolyte with 1.5 M MPIBr + 1.5 M ZnSO 4 is used in the following electrochemical tests.

**Theoretical understanding of the advantages of MPIBr**

To uncover the origins of high Coulombic efficiency and fast kinetics of MPIBr, first-principle calculations are performed. Here, the key issue is to compare the binding energy of various bromides (such as MPIBr, MPIBr 3, TBABr, etc.) to hydration energy of Br− and Br 3−. The binding energy per Br in compound ABn is defined as

\[ E_b(\text{Br}, A B_n) = \frac{E(A B_n) - E(A) - n \times E(\text{Br})}{n} \]

where \( E_b \) and \( E \) represent the binding energy and energy, respectively. The binding energy of Br in various bromides is shown in Fig. 3A. Both binding energies of Br in MPIBr 3 (−3 eV) and TBABr 3 (−3.4 eV) are lower than that of ZnBr 4 (−2.6 eV), ensuring the preference of Br 2 to form MPIBr 3 or TBABr 3 in the charging process and accumulate on the positive electrode. In the meantime, these values are also lower than the hydration energy of Br 3− (−2.91 eV), implying that both MPIBr 3 and TBABr 3 can retain Br 3− from dissociation. For comparison, the binding energy of Br in ZnBr 4 is higher than the hydration energy of Br−, leading to the observed low Coulombic efficiency of 44% in the ZnBr 2 battery system. Moreover, the difference between binding energy of Br in MPIBr 3 (−3.71 eV) and hydration energy of Br− (−3.71 eV) is larger than the difference between TBABr 3 (−3.4 eV) and hydration energy of Br− (−3.71 eV), suggesting that the driving force in the MPIBr system is larger than that in the TBABr, demonstrating the fast reaction kinetics in the MPIBr system.

Microstructure greatly affects the reaction kinetics. To investigate the possible assembling form of MPIBr 3 and TBABr 3, their chain configurations are established (Fig. 3B). MPIBr 3 and TBABr 3 are supposed to form chain structures, which further consist spatial networks, as they have lower binding energies than their separated form. For MPIBr 3, its quasi–one dimensional molecular chain leads to a relative loose network structure. In contrast, the TBABr 3 molecule features a tetrahedral symmetry and has multiple equivalent directions to

**Fig. 2. Selection and optimization of the electrolyte.** (A) Schematic of the fast diffusion of Br 3− from current collector when ZnBr 2 solution is used as the electrolyte. (B) When TBABr is used as the electrolyte, solid-state TBABr 3 complex is generated, which shows slow reaction kinetics. (C) When MPIBr is used as the electrolyte, the oily phase MPIBr 3 complex is formed, which not only prevents the Br 3− from dissolving into the electrolyte but also shows fast reaction kinetics. GCD curves of Zn-Br 2 batteries with (D) ZnBr 2, (E) TBABr, and (F) MPIBr electrolytes. These cells are tested in the homemade cells at 1 mA cm−2. (G) The Coulombic efficiency and polarization comparisons of Zn-Br 2 batteries with different electrolytes. Error bars represent the SD of five independent batteries. UV-vis spectra of (H) ZnBr 2 and (I) MPIBr electrolytes after charging to 0.1, 0.2, and 0.4 mAh cm−2.
continue its chain structure, which contributes to the eventual formation of a dense network. This configurational difference is also reflected by the fact that MPIBr$_3$ and TBABr$_3$ exist in liquid and solid states, respectively, and the loose network structure apparently endows the MPIBr$_3$ system with fast reaction kinetics.

The energy barrier is another factor to determine the reaction kinetics. To correctly estimate the energy barrier during the discharging process of MPIBr$_3$, the liquid form of MPIBr$_3$ should be considered. In this scenario, it is not necessary for Br$_2$ to be first dissociated from MPIBr$_3$ (i.e., MPIBr$_3$ → MPIBr + Br$_2$) and then diffuse all the way to the interface for the reaction Br$_2$ + 2e$^-$ → 2Br$^-$. With discharging process proceeding and the breakdown of the interfacial MPIBr$_3$ network, new interface could form at a short time due to its liquid form, which ensures fast reaction kinetics. Figure 3C shows the energy variation of the two reactions, and their combination at different paces is shown in Fig. 3D. Note that different $l_t$ (the separated distance at the end of the reaction; see the Supplementary Materials for details) values are taken, and their corresponding energy curves are marked by different colors in Fig. 3D. The most possible combination in reality should be the one that gives minimum energy barrier, which is equal to 0.075 eV in terms of our calculation (details could be found in Materials and Methods). This ultralow energy barrier helps Zn-Br$_2$ MBs to realize extreme fast reaction kinetics.

**Visualization of the dual-plating/stripping process**

The in operando microscopy was used to study the dual-plating and dual-stripping working mechanisms of Zn-Br$_2$ MBs (Fig. 4A). Because it is hard to observe the MPIBr$_3$ complex on the black CNT microelectrode, here, Pt and Au wires (1 mm in diameter) were used as the positive and negative current collectors, respectively. Their smooth surface allows easy observation of the deposited electrodes. The Pt and Au wires both show a smooth and shiny surface before charging (Fig. 4B). Along with charging begins (0.1 mA cm$^{-2}$), lots of tiny yellow MPIBr$_3$ droplets appear and then gradually merge into larger droplets. The visualization of the dual-plating process is shown in Fig. 4C. These droplets gradually form a interface for the reaction, and eventually, the interface forms a larger surface for the reaction to proceed.
beads on the Pt surface, demonstrating the plating reaction of the MPIBr₃ cathode (Fig. 4, C to F) (34). Meanwhile, the glossy surface of a Au wire turns dark due to continuous Zn metal plating on it. The scanning electron microscopy images of the Au wire after charging for different times further demonstrate the gradual Zn plating process (fig. S19). The discharging procedure was performed after charging for 200 s, and the oily MPIBr₃ complex was stripped to Br⁻ and gradually decreased in size. The discharge ends at 1 V versus Zn²⁺/Zn, and it lasts for 195 s. After discharging, the Au wire becomes shiny again, suggesting that almost all Zn metals have been stripped away. Meanwhile, there is only a little residual of MPIBr₃ complex on Pt (Fig. 4, G to K), demonstrating that the charging-discharging is reversible (Coulombic efficiency is 97.5%). The in operando visualization of the charging-discharging process (4 mA cm⁻²) of Zn-Br₂ MBs based on the CNT paper microelectrode was also performed, where the plating and stripping processes of the zinc anode are quite clear (Fig. 4, L to P, and movie S2). The two in operando observations both demonstrate the dual-plating and dual-stripping working mechanisms of Zn-Br₂ MBs.

**Electrochemical performance and flexibility of Zn-Br₂ MBs**

The dual-plating strategy also endows the Zn-Br₂ MBs with excellent electrochemical performance. Figure 5A shows the cyclic voltammetry (CV) curves of the redox-active electrolyte in the three-electrode system, suggesting that the electrolyte could perform Br⁻/Br₂ and Zn²⁺/Zn redox reactions at the same time (35). Figure 5B shows the CV curves of the constructed Zn-Br₂ MBs, which is consistent with previously reported Zn-Br₂ batteries (36–38), suggesting the successful construction of Zn-Br₂ MBs through the dual-plating strategy.

The Zn-Br₂ MBs were constructed on the basis of the MPIBr gel electrolyte, which shows good ionic conductivity (3.4 S m⁻¹; fig. S20) and mechanical property (660% stretch ratio and 80% compression ratio; fig. S21). The Zn²⁺ transference number of the MPIBr gel electrolyte is 0.83 (fig. S22). The charging voltage strongly influences the electrochemical performance of the Zn-Br₂ MBs, and 1.85 V is applied during the charging process. A lower charging voltage (1.8 V) leads to a longer charging time, while a higher charging voltage (1.9 V) reduces the energy efficiency of Zn-Br₂ MBs (fig. S23). The discharging plateau is at about 1.7 V versus Zn²⁺/Zn at 2 mA cm⁻². It shows an excellent rate performance, retaining about 72% capacity even at 20 mA cm⁻² (Fig. 5C and fig. S24) and a maximum power density of about 26.2 mW cm⁻² (fig. S25), further demonstrating the fast kinetics of the oily MPIBr₃ cathode. It shows a long shelf stability and slow self-discharging due to the inhibition of Br₃⁻ cross-diffusion (fig. S26). It also delivers a stable cycling performance for 1000 cycles at 5 mA cm⁻² with a decay rate of 0.004% per cycle (Fig. 5D and fig. S27), which is the lowest value in the field of MBs (fig. S28). The positive current collector maintained its micromorphology after lone cycling (1000 cycles at 5 mA cm⁻²) due to the liquid nature of MPIBr₃ (fig. S29). The maximum discharging areal capacity and energy density of Zn-Br₂ MBs are further studied. The Coulombic efficiency is more than 95% when charging capacity is less than 2000 µAh cm⁻² (Fig. 5E and fig. S30). After charging to

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**Fig. 4. In operando visualization of the charging-discharging process of Zn-Br₂ MBs.** (A) Schematic of observation of the dual-plating process through the in operando microscope. The platinum (Pt) and gold (Au) wires are used as the positive and negative current collectors, respectively. (B to F) Time-lapse microscope images show oily MPIBr₃ complex that gradually forms on the Pt wire, and Zn generates on the Au wire during the charging process. (G to K) Time-lapse microscope images show oily MPIBr₃ complex on the Pt wire and Zn on the Au wire that gradually decrease during the discharging process. (L to P) The digital photographs show zinc plating and stripping processes of Zn-Br₂ MBs. Scale bars, 2 mm.
2500 μAh cm$^{-2}$, the discharging areal capacity and energy density are up to record high values of 2220 μAh cm$^{-2}$ and 3645 μWh cm$^{-2}$ (Fig. 5F), respectively, which are even one magnitude higher than those of most reported planar MBs (Fig. 5, G and H; fig. S31; and table S1). It also shows high volumetric performance of 8 mAh cm$^{-3}$ and 13.1 mWh cm$^{-3}$ (based on the total volume of current collectors and gel electrolyte). Note that these high values are achieved under a considerably large current density and power density, further demonstrating the fast kinetics of the liquid cathode. It is worth mentioning that, unlike previous MBs with an excess of anode, the electrochemical data are obtained on the basis of the case of no electrode excess, which shows important implications for practical applications. As a proof of concept, a single Zn-Br$_2$ MB could power an electric fan and a red light-emitting diode (fig. S32).

The Zn-Br$_2$ MBs also show excellent flexibility as all of their components are highly flexible in nature (fig. S33). They deliver almost the same GCD curves under different bending angles (45°, 90°, and 180°), and they could suffer 1000 times bending without obvious changes (fig. S34, A to D). They also show a good cycling performance of 500 cycles at a bending angle of 180° (fig. S34E). The Zn-Br$_2$ MBs can be easily integrated to provide higher voltage or energy output (figs. S35 and S36). Three Zn-Br$_2$ MBs in series could deliver a 5.1-V voltage output, which could power most miniaturized electronic devices. The dual-plating strategy could also be extended to constructing Zn-I$_2$ and Zn-MnO$_2$ MBs (figs. S37 to S42).

**Polarity-switchable function**

Despite with the asymmetrical cathode and anode, the polarity of the Zn-Br$_2$ MB can be easily switched due to the dual-plating/stripping process. For a constructed Zn-Br$_2$ MB, the Br$_2$ cathode and the Zn anode completely change into soluble Br$^{-}$ and Zn$^{2+}$ and then dissolve into the electrolyte after discharging. The MPIBr$_3$ could deposit on the other current collector where Zn was previously plated once an opposite bias is applied, thus the cathode and anode of the microdevice are switched (Fig. 6A).

In operando technology could visualize such a process. The two microelectrodes are black before charging (Fig. 6B). The left one changes to white due to Zn anode deposition after charging at 1.85 V for 2 min (Fig. 6C), and it returns to black color after discharging to 0 V through CV at a scan rate of 5 mV s$^{-1}$ (Fig. 6D). When the right
microelectrode is scanned from 0 to −1.85 V and held at −1.85 V for 2 min, it changes to white color (Fig. 6E), showing the polarity-switchable process. To clearly visualize the switch process of the MPIBr₃ cathode, the Pt and Au are used as the current collectors (Fig. 6F). The MPIBr₃ cathode is plated on the upper wire during the charging process (Fig. 6G), and it gradually disappears and lastly gets deposited on the lower wire with continuous discharging (Fig. 6, H to I, and movie S3).

The CV curves between −1.85 and 1.85 V show centrosymmetric features, further demonstrating the polarity switch of Zn-Br₂ MBs (Fig. 6J). The Zn-Br₂ MB could deliver a stable cycling performance of 500 cycles with switching cathode and anode every 100 cycles (Fig. 6K). Because a small portion of the MPIBr₃ cathode remains on the current collector during the GCD test, it reacts directly with the Zn anode when cathode and anode are switched, resulting in a lower discharging capacity with each polarity switch. It also could endure repeatedly reversing the polarity for 100 cycles (Fig. 6L and fig. S43), demonstrating that it could tolerate the misdeeming of cathode and anode, which usually results in complete damage or even safety issue in other batteries (39, 40). Besides, the Zn-I₂ and Zn-MnO₂ constructed through the dual-plating strategy also have polarity-switchable functions (figs. S44 and S45). To the best of our knowledge, it is the first time that microscale energy storage devices show polarity-switchable functions.

DISCUSSION
In conclusion, we propose a dual-plating strategy to fast construct MBs with excellent electrochemical performance. This strategy eliminates complicated and time-consuming manufacture procedures of available MBs, bypasses the challenge of constructing and matching cathode and anode at a microscale, and enables the construction of liquid microelectrodes otherwise impossible by previous methods. We construct the first aqueous Zn-Br₂ MBs with a liquid cathode through using a novel redox-active MPIBr, which not only prevent diffusion of Br⁻ but also show fast kinetics during charging and discharging. The constructed Zn-Br₂ MBs show the zero excess of cathode and anode configuration and deliver a record high areal capacity and energy density (2.2 mAh cm⁻² and 3.6 mWh cm⁻²), more than 10 times of most planar MBs. The Zn-Br₂ MBs also show polarity-switchable capability, making them tolerate some wrong operations. This work offers new insights for constructing MBs and is promising to promote the development of miniaturized electronics.

MATERIALS AND METHODS
Materials
All materials, including free-standing CNT paper (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences), MPIBr (99%; Meryer), ZnSO₄ (99.5%; Aladdin), ZnBr₂ (98%; Aladdin), TBABr (99.5%; Aladdin), NaBrO₃ (99.5%; Aladdin), HBr (AR, 40%; Aladdin), KBr (99%; Aladdin), 1-methyl-3-propylimidazolium iodide (MPII; C₇H₁₃IN₂, 99%; Meryer), Mn(AC)₂·4H₂O (99%; Tianjin Fucheng), Zn(AC)₂·2H₂O (99%; Tianjin Fucheng), acrylamide (99%; Acros Organics), ammonium persulfate (98%; Sigma-Aldrich), N,N′-methylenebisacrylamide (99%; Energy & Chemicals), and carbon cloth (Suzhou Wingrise Energy Technology Co. Ltd., HCP330N) are used without further purification.
Characterization of materials

The morphology and microstructure analysis of the synthesized materials were examined using field-emission scanning electron microscopy (ZEISS SUPRATM 55 SAPPHIRES) and transmission electron microscopy (FEI Tecnai TF20, USA). Raman spectra were performed by using a Nanofocus Raman Evolution (Horiba Jobin Yvon, France) Raman microscope equipped with a 532-nm laser. The UV-vis absorption spectrum was performed on a 2600-PC spectrophotometer. 1H and 13C NMR spectra were obtained using Bruker Avance III 400-MHz NMR Instruments. The high-resolution mass spectrometer was carried out on a Waters Xevo G2-XP time-of-flight mass spectrometer. The mechanical tensile tests of gel electrolytes were performed on a material testing system (Shimadzu AGS-X). Contact angle was measured by the contact angle measuring instrument (JC-200CD).

Synthesis of quasi-solid-state redox-active electrolyte

Dry polyacrylamide (PAM) gel is first prepared. In a typical synthesis, 2.9 g of acrylamide monomer, 14.3 mg of ammonium persulfate, and 1.8 mg of N,N′-methylenebisacrylamide were added into 20 ml of deionized water. After stirring for 0.5 hours, the mixture was stored at 60°C for 12 hours to obtain the PAM hydrogel. Then, the PAM hydrogel was dried at 60°C for 12 hours to prepare dry PAM gel. The MPIBr gel electrolyte was obtained after immersing dry PAM gel in 1.5 M MPIBr + 1.5 M ZnSO4 solution for 3 days. The MPIBr gel electrolyte film can be cut into the desired size for the Zn-Br2 MB assembly. Each Zn-Br2 MB uses about 50 μl of electrolyte. The MPII and Mn(AC)2 gel electrolytes were prepared through immersing dry PAM in 0.5 M MPII + 0.5 M ZnSO4 and 0.5 M Mn(AC)2 + 0.5 Zn(AC)2 solutions for 3 days, respectively.

Preparation of solution contains Br5− ions

The solution that contains Br5− was prepared through a previously reported method (32) and could be described as follows

\[ \text{NaBrO}_3 + 5 \text{Br}^- + 6 \text{H}^+ \rightarrow 3 \text{Br}_2(\text{aq}) + 3 \text{H}_2\text{O} \]  

\[ \text{Br}_2(\text{aq}) + \text{Br}^- \rightleftharpoons \text{Br}_3^-(K_{\text{eq}} = 16.1 \text{ M}^{-1}) \]  

Typically, 5 ml of 2 M HBr, 5 ml of 2 M KBr, and 10 ml of 0.1 M NaBrO3 were combined in a glass vial and stirred for 10 min to prepare 20 ml of solution that contains 120 mM Br3−, which shows dark orange.

Optimization of the electrolyte in homemade cell

The tests were performed in a homemade cell, as shown in fig. S2. The carbon cloth was used as the positive and negative current collectors (the distance between the two current collectors is about 1 cm), and about 1 ml of electrolytes (1 M ZnBr2 or 0.1 M TBABr + 1 M ZnSO4 or 1 M MPIBr + 1 M ZnSO4) was used for different redox-active electrolytes. These cells were first charged at 1 mA cm−2 to 500 μA h cm−2 and then discharging at 1 mA cm−2 to 1 V.

Assembly of in-plane Zn-Br2 MB

A flexible free-standing CNT paper (thickness of about 10 μm) was first pasted on the flexible polyimide tape. Then, the interdigital microelectrode was obtained through the laser engraving method. Each microelectrode is about 500 μm in width and 0.3 cm in length, and the distance between adjacent fingers is 300 μm. Last, a redox-active gel electrolyte was put on the microelectrode, and the polyimide tape was used for the packaging. The Zn-I2 and Zn-MnO2 MBs were constructed through the similar method but use MPII and Mn(AC)2 gel electrolytes, respectively.

Ionic conductivity of MPIBr gel electrolyte

The ionic conductivity of MPIBr gel electrolyte is estimated on the basis of the following equation

\[ \sigma = \frac{L}{R \times S} \]

where \( \sigma \) (siemens per meter), \( L \) (meters), \( R \) (ohm), and \( S \) (square meters) are the ionic conductivity, thickness, ohmic resistance, and area, respectively. The ohmic resistance is from the electrochemical impedance spectroscopy (EIS) of Au/MPIBr gel electrolyte/Au cell.

Zn2+ transference number of MPIBr gel electrolyte

The Zn2+ transference number of the MPIBr gel electrolyte is estimated in Zn/MPIBr gel electrolyte/Zn cell based on the following equation (41)

\[ t_{\text{Zn}^{2+}} = \frac{I_{\text{SS}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{SS}} R_{\text{SS}})} \]

where \( \Delta V \) is the applied polarization voltage (10 mV), \( I_0 \) and \( R_0 \) are the initial current and interfacial resistance, and \( I_{\text{SS}} \) and \( R_{\text{SS}} \) are the steady-state current and interfacial resistance, respectively.

Calculation of energy efficiency

It is computed on the basis of

\[ E = \frac{\int_0^{t_{\text{ch}}} U_c I_t \, dt}{\int_0^{t_{\text{dis}}} U_d I_d \, dt} \]

where \( E \), \( t_{\text{ch}} \), \( U_c \), and \( I_t \) are the energy efficiency, discharge time, charge voltage, and discharge current, respectively; \( t_{\text{dis}} \), \( U_d \), and \( I_d \) are the charge time, charge voltage, and charge current, respectively.

Electrochemical measurements

The optimization of the electrolyte was performed in a homemade cell, and the cells were galvanostatic cycled at 1 mA cm−2 on a LAND cycler (Shanghai Chenhua, China). For the Zn-Br2 MBs, these batteries were charged at 1.85 V to different areal capacities and then discharged at different current densities. The CV tests were recorded on a CHI 660C electrochemical workstation (Shanghai Chenhua, China) at a scanning rate of 1 mV s−1. The areal performance was calculated on the basis of the total area of all fingers and gaps (0.18 cm2). The volumetric performance is calculated on the basis of the total volume of current collectors and the gel electrolyte (50 μl). EIS was tested under an AC amplitude of 5 mV at the frequency from 100 kHz to 1 Hz under the open-circuit potential (constant potential). The recording number of data points was 12 (per decade). All electrochemical energy storage tests are carried out in an environmental chamber with a temperature of 25°C ± 0.5°C.

First-principle calculations

The projector augmented wave pseudopotential method implemented in the Vienna Ab initio Simulation Package is used to perform
structural optimization and energy calculation (42). The energy cutoff and the electronic self-consistent step convergence are 400 and 10^{-19} eV, and the structure optimization ends when the total energy change between two steps is less than 0.01% of its total energy. Besides, the local density approximation exchange-correlation potential is applied for all calculations (43–45).

**Barrier minimum estimation**

The energy variation of Br\(_2\) + 2 e\(^-\) = 2 Br\(^-\) is described by

\[
E(x) = \begin{cases} 
\frac{a x^2}{2} + \frac{b x^4}{4}, & x < l_t \\
-\frac{a x^2}{2}, & x \geq l_t
\end{cases}
\]

where \(a = 2\Delta E/l_t^2\) and \(b = a l_t^2\) are determined by the energy decrease \(\Delta E\) (4.05 eV) and separated distance \(l_t\) at the end of the reaction. Note that the energy decrease is obtained via first-principle calculation, while the separated distance is assumed. In Fig. 3C, \(l_t = 0.546\) nm, and, in Fig. 3D, different values are taken for \(l_t\) while the separated distance is assumed.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abo6688

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Acknowledgments: We thank Analysis and Testing Center, Beijing Institute of Technology for material characterizations. Funding: We acknowledge financial supports from NSFC (nos. 21975027, 11972349, 11790292, 22035005, 52073159, 52022051, 22075165, and 22109009) and the Strategic Priority Research Program of the Chinese Academy of Sciences (no. XDB22040503).

Author contributions: L.Q. and Z.Z. led the team and supervised the experiments. C.D., H.C., Y.Z., Z.Z., L.J., and L.Q. conceived the idea. C.D., L.H., X.J., Y.W., R.W., and Y.X. prepared the materials and performed the electrochemical measurements. C.D., X.L., X.Z., L.S., and Y.H. performed the characterizations and analyzed the corresponding data. F.L. contributed to the theoretical calculations. All authors discussed the results and agreed on the submission of the manuscript.

Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 18 February 2022
Accepted 26 May 2022
Published 13 July 2022
10.1126/sciadv.abo6688

Dai et al., Sci. Adv. 8, eabo6688 (2022) 13 July 2022