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Reversible Multi-electron Transfer I/IO$_3^-$ Cathode enabled by Hetero-halogen for Ultra-high Energy Density Aqueous Batteries

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Abstract: The ever-increasing need for more energy-dense batteries is fuelling global research and innovations in new redox chemistry and device design. Lithium-ion batteries adopting organic electrolytes have the potential to deliver high energy densities, however, they usually have to compromise on safety—a metric of equal importance. Here, we show an aqueous battery that exhibits a volumetric energy density far beyond the state of the art, together with long cycling life and excellent power performance. The high energy density is realized by employing highly concentrated hetero-halogen electrolytes that contain I$^-$ and Br$^-$, which can realize a multi-electron transfer process of I$^-$/IO$_3^-$ with high reversibility and excellent kinetics. The intermediate bromide species can enhance the reaction kinetics and alleviate overpotential, leading to reversible and fast multi-electron transfer. Using a 6 M halogen electrolyte to achieve more than 30 M electron transfers per litre (the highest reported so far is 9 M), the I$^-$/IO$_3^-$ cathode displayed super high specific capacity of 830 Ah L$^{-1}$. A battery with Cd/Cd$^{2+}$ as anode demonstrated an energy density of >1200 Wh L$^{-1}$ catholyte, which is by far the highest value for aqueous batteries. Even at a current density of 120 mA cm$^{-2}$ an energy efficiency of 72% can be obtained. Our work demonstrates that safe aqueous batteries with high energy density are possible, offering a new and evolutional option for grid scale energy storage and electric vehicles.

The ever-increasing energy demand and climate change require the exploration of sustainable energy alternatives, renewable energies in particular. With wide deployment of renewable energies, batteries are essential for grid-scale electrical energy storage and transport applications. As one of the most important indices for batteries, energy density (Wh kg$^{-1}$ or Wh L$^{-1}$) tells us how much energy a battery contains in proportion to its weight or volume, which in turn, indicates how long the battery lasts. Traditional nonaqueous lithium-ion batteries (LIBs) possess superior energy density (~300 Wh kg$^{-1}$ or 700 Wh L$^{-1}$) but their nonaqueous carbonate electrolyte is highly flammable$^{2,3}$. On the contrary, aqueous batteries have the potential to address this issue naturally, however, their energy densities are low (< 200 Wh L$^{-1}$)$^{4,5}$, limited by the narrow potential window (~2 V vs. 5 V for nonaqueous) and the low specific capacity (~100 mAh g$^{-1}$ or 170 Ah L$^{-1}$), which are a compelling technology only for large-scale stationary energy storage such as flow batteries. For a battery, the energy density is mainly determined by the concentration of redox species and
the number of electron transfers per molecular. For example, the concentration of Li$^+$ in the cathode of LIB exceeds 20 M e.g. LiFePO$_4$, while the vanadium ions in vanadium flow battery electrolyte is only 1.5 M. With a fixed concentration, the energy density almost depends on the number of electron transfers in each mediator molecular. For example, using 0.5 M P$_2$W$_{18}$O$_{62}$ as reactant, Conner et al. realized an 18-electron transfer reaction to obtain an energy density of 225 Wh L$^{-1}$. While multi-electron transfer redox pairs such as methyl-viologen (MV) are common in organic systems, the electron transfer is limited to only two per molecular hitherto, which results in only minor improvement in energy density.

An alternative strategy to obtain high-energy-density batteries is to combine high concentration electrolyte and multi-electron transfer reactions. Among the numerous aqueous batteries, the single electron transfer iodide/iodine (I/I$_2$) redox couple is most well-studied for high energy density batteries because it is highly soluble (10 M I$^-$) and has excellent reversibility and activity. However, it is difficult to obtain energy density that is comparable to LIBs. Nonetheless, in addition to I$_2$, the stable high valence (+5) iodine of iodate (IO$_3^-$) suggests that a six-electron transfer process from I$^-$ to I$_2$ and on to IO$_3^-$ is possible (oxygen atoms come from water). Combined with a high solubility of I$^-$ (10 M), the theoretical specific capacity for I$^-$/IO$_3^-$ couple can reach 1608 Ah L$^{-1}$ (Supplementary Fig. 1), which is much higher than LIBs (LiCoO$_2$ cathode~575 Ah L$^{-1}$) and comparable to lithium metal batteries (Li metal anode ~2000 Ah L$^{-1}$). However, the problem is the electrochemical process of I$_2$/IO$_3^-$ is highly polarized with poor kinetics. During charging, the transformation of I$_2$ to IO$_3^-$ results in serious overpotential, because it is difficult for the oxygen atom in H$_2$O molecule to attack the positive charge center of symmetrical I$_2$ (Eq. 1 and Supplementary Fig. 2a). For the discharge process, severe polarization also occurs because the direct reduction of IO$_3^-$, in fact, is a “chemical-electrochemical” hybrid process (Supplementary Fig. 2a). Residual I$_2$ is firstly reduced to I$^-$ (electrochemical reaction, Eq. 2), then it was oxidized by IO$_3^-$ to I$_2$ (chemical reaction, Eq. 3) and continues to participate in discharge (electrochemical reaction, Eq. 2), which results in severe discharge polarization due to the large potential gap between I$^-$/I$_2$ (0.54 V vs. SHE) and I$_2$/IO$_3^-$ (1.19 V vs. SHE). In this case, the high specific capacity and energy density of multi-electron transfer are difficult to fully exert.

\[
\begin{align*}
\text{Charge: } & \quad I_2 + 6H_2O - 10e^- \leftrightarrow 2IO_3^- + 12H^+ \quad E = 1.19 \text{ V vs. SHE} \\
\text{Discharge: } & \quad I_2 + 2e^- \leftrightarrow 2I^- \quad E = 0.54 \text{ V vs. SHE} \\
& \quad 5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad \text{Chemical Process}
\end{align*}
\]

To promote the kinetics of I$_2$/IO$_3^-$ and reduce the polarization, we tuned the electrolyte chemistry by introducing Br$^-$ into the I$^-$ solution. During charging, the reaction between I$_2$ and Br$^-$ generates a highly polar intermediate bromide of IBr (due to the difference in electronegativity between halogens) (Step 2 in Fig. 1a; Supplementary Fig. 2B) that eases the nucleophilic attack of I by H$_2$O molecules to form Br$_2$I$^-$/IO$_3^-$, reducing the charging overpotential (Step 3 in Fig. 1a; Supplementary Fig. 2b). For the discharge process, Br$_2$I$^-$ is reduced to Br$^-$ firstly and then the Br$^-$ is oxidized by IO$_3^-$ to produce Br$_2$ and IBr, which continue to participate in the discharge (Step 4 and 5 in Fig. 1a). Because the redox potentials of Br$_2$/Br$^-$ (1.08 V vs. SHE) and IBr/I$_2$ (0.97 V vs. SHE) are closer to IO$_3^-$/I$_2$ (1.19 V vs. SHE), the discharge overpotential is significantly lowered. Accordingly, the overpotential of discharge is expected to decrease. It should be noted that capacity contribution through Br$_2$ or IBr via chemical-electrochemical processes needs to be analyzed in detail.
Fig. 1. Multi-electron transfer process of I$_2$/IO$_3^-$ made reversible through addition of Br$^-$. (a) Schematic of the charge (steps 1-3)-discharge (steps 4-6) process of I$_2$/IO$_3^-$ in the presence of Br$^-$. Generation of IBr intermediate (step 2) reduces charging overpotential (step 3) and the closer redox potentials of Br$_2$/Br$^-$ (1.08 V) and IBr/I$_2$ (0.97 V) lowers the discharge overpotential. X represents the amount of IO$_3^-$ reduced and the value is between 0~1. The capacity contribution of the step 4 and 5 needs to be analyzed under specific circumstances, especially the composition of the electrolyte. (b) Schematic of an assembled battery with multi-electron transfer cathode (green side) and metal cadmium as anode (yellow side). Electrolyte of the metal anode flows while electrolyte of the cathode stays in the electrode cavity. (c) Energy density of our cathode reaches >1200 Wh L$^{-1}$, far better than other cathodes. All data are calculated from the output energy and the volume of catholyte or the solid cathode. Intercalation-type: lithium-ion battery (LiFePO$_4$); Zinc iodine flow...
battery (ZIB); polyoxoanion bromine flow battery (Polyoxoanion); aqueous lithium-ion batteries (LiMnO2); Vanadium flow battery (VFB). (d) Charge-discharge plot of 6 M (green) I- electrolyte at 30 mA cm\(^{-2}\). (e) CV curve of 1 M HI + 1 M HBr + 1 M H\(_2\)SO\(_4\) electrolyte at 1 mVs\(^{-1}\) with a potential range of 0.8–2.1 V versus Cd\(^{2+}\)/Cd show 6 distinct steps. Compared with HI+HBr, the reduction current of electrolyte only containing HBr is much lower, indicating that step 4 involves chemical-electrochemical process. The insertion diagram is the CV test of Cd\(^{2+}\)/Cd at 50 mV s\(^{-1}\) (electrolyte: 50 mM CdSO\(_4\)+1 M H\(_2\)SO\(_4\)). (f) CV curves of electrolyte with different concentration of HBr and the results indicate that steps 4 were greatly inhibited with decreasing HBr concentration. (g) CV measurements of the electrolyte in potential range of 0.8–2.1 V at 1 mV/s and 10 mV/s respectively. At different scan rates, the obvious step 2 and the corresponding reduction step 5 indicate the high reversibility and electrochemical kinetic of IBr (Electrolyte composition:100 mM HI-100 mM HBr-100 mM H\(_2\)SO\(_4\)). (h) Photographs of the electrolyte and their corresponding charge-discharge plot at different steps. Samples in the bottles are products of each step. Electrolyte composition:1 M HI + 1 M HBr + 1 M H\(_2\)SO\(_4\)+1 M CdSO\(_4\).

Using a high concentration hetero-halogen electrolyte containing I\(^-\) and Br\(^-\) in strong acid (denoted as IBA), a reversible multi-electron transfer redox couple of I/OI\(_3^-\) could be realized. With IBA as catholyte and Cd\(^{2+}\)/Cd as anolyte (IBA-C) (Fig. 1b), we obtained an aqueous battery with an ultra-high energy density of 1200 Wh L\(^{-1}\) (Fig. 1c-d) based on the volume of catholyte, which even more than most solid electrode materials (e.g. LiFePO\(_4\) in theory) and enables the design of high-energy-density aqueous batteries possible. Cyclic voltammograms (CVs) of IBA clearly show six distinct processes (Fig. 1e), in agreement with the mechanism described in Fig. 1a. And compared with HBr electrolyte, IBA shows a more obvious step 4 (Br\(_2\)/Br\(^-\) \(i_0\): -2 vs. -13 mA) due to the chemical-electrochemical discharge of HIO\(_3\) via Br\(^-\). Further, step 4 is inhibited as the HBr concentration decreases (Fig. 1f) due to the restricted chemical reaction. Meanwhile, the crucial intermediate IBr exhibits excellent electrochemical kinetic and reversibility (Fig. 1g). The enlarged charge-discharge profiles of the assembled battery display six steps and changes in the electrolyte at each step can be visually observed by optical microscope (Fig. 1h). In this case, the capacity contributions of the step 4 and 5 are three electron transfers, respectively.

**Results and discussion**

**Six-electron transfer mechanism of hetero-halogen electrolyte (IBA)**

To verify the possibility of multi-electron transfer mechanism of IBA, we began with ex-situ characterization to simulate the formation of IBr in step 2 by mixing I\(_2\)(aq) with Br\(_2\)(aq) at different molar ratios. Raman (214 cm\(^{-1}\)\(^{14-16}\) and ultraviolet (UV) (253 nm)\(^{17}\) spectra confirmed the formation of IBr (Fig. 2a and Supplementary Fig. 3). At high molar ratios of Br\(_2\) to I\(_2\) (>2:1), the generated IBr dissolved in excess Br\(_2\) and formed a homogenous and stable solution (Supplementary Fig. 4a). At low ratios, I\(_2\) precipitates were clearly observed (Supplementary Fig. 4b and c). Furthermore, IBr also rapidly dissolved in a 1:1 mixture of IBr and Br\(_2\) (Supplementary Fig. 4d). These results confirmed the charging-formed IBr as outlined in step 2 (Fig. 1a). The binding energy combined with molecular electrostatic potential (ESP) indicate the interaction between IBr and H\(_2\)O is much higher than that of I\(_2\) (Fig. 2b), which facilitates the subsequent generation of IO\(_3^-\). Furthermore, the charge density difference also means that IBr is easier to absorb on the surface of carbon electrode and gain or lose electrons (Fig. 2b and Supplementary Fig. 5 and 6), which corresponds to the Bader charge analysis results (oxidation state: 0.03 for I in I\(_2\)@C; 0.15 for I and −0.17 for Br in IBr\(_2\)@C).

As for discharge, we also simulated the reduction process of IO\(_3^-\) during discharge by mixing HIO\(_3\) and HBr at different molar ratios. Raman spectroscopy showed that IO\(_3^-\) can easily oxidize Br\(^-\) into Br\(_2\) and IBr, following the chemical-electrochemical process outlined in step 4 and 5 (Fig. 2c). Simulated electrolytes composed of different ratios of HI to HIO\(_3\) demonstrated that as the depth
of discharge increases, IBr precipitates from Br₂ to form deposits on the electrode that trigger step 5 (Supplementary Fig. 7).

![Raman spectra](image)

**Fig. 2. Characterization of multielectron transfer of halogen electrolytes IBA.** a) Raman spectra of mixed solutions of I₂(1) and Br₂(1) at different molar ratios. Raman vibration signals were assigned to IBr (215 cm⁻¹), Br⁻ (168 cm⁻¹) and Br₂⁻ (270 cm⁻¹). Formation of Br₂n+1⁻ follows equations 1~3: Eq.1: I₂+Br₂=2IBr; (hydrolysis) Eq.2: 5IBr+3H₂O=HIO₃+5HBr+2I₂; Eq.3: HBr+nBr₂=HBr₂n+1⁻. b) The molecular electrostatic potential (ESP) (isosurface=2.6 kJ mol⁻¹) and charge density differences of IBr and I₂ on the carbon electrode (I₂@C and IBr@C). c) Raman spectra of mixed solutions of HIO₃ and HBr at different molar ratios. Signals for Br⁻ and Br₂ seen in the 1:1 and 1:2 solutions indicate that IO₃⁻ can easily oxidize Br and then participate in the discharge process. At higher proportions of HBr (HIO₃: HBr 1:3), IBr signal is seen, which would participate in discharge process. d and e) In-situ Raman spectra (100~1000 cm⁻¹, left) and the corresponding charge-discharge plot (right) of IBA (d) and ex-situ XRD spectra of products from each step (e). All steps in d corresponding to the Raman curves are marked with colored points in the charge-discharge plot. Vertical dotted lines in d indicate vibrational modes of Raman signals. Raman tests recorded signals every 100 seconds. XRD spectra was obtained at 2θ range of 20~60°. Scan mode (θ, diffraction angle) was applied with Cu Kα radiation at wavelength of 1.5418 Å. Peaks marked with an asterisk correspond to signals in standard cards shown in the Figure. Products of each step were measured as is without additional treatment.

Electrolyte composition in d and e: 1 M HI+1 M HBr+1 M H₂SO₄+1 M CdSO₄.
To solidify these *ex-situ* observations, we used *in-situ* Raman spectroscopy (Fig. 2d) and X-ray diffraction (XRD) (Fig. 2e) to follow the multi-electron transfer chemistry of the entire charge-discharge process of IBA. During initial charging, we observed I2 signal from step 1 at 180 cm$^{-1}$\textsuperscript{118,19}. Further charging formed a new peak at 219 cm$^{-1}$, which was assigned to the stretching vibration of I-Br. Strong peaks at 300-400 cm$^{-1}$ and 700-800 cm$^{-1}$ were attributed to the formation of IO$_3^-$ in step 3\textsuperscript{20,21}. The formed IO$_3^-$ precipitates with Cd$^{2+}$ to form Cd(IO$_3$)$_2$ ($K_{sp} = 2.5 \times 10^{-8}$) (Supplementary Fig. 8). Meanwhile, the signal at 290 cm$^{-1}$ was assigned to the formation of Br$_4^-$ (complex between Br$_2$ and Br$^{-}$)\textsuperscript{22,23}. Following discharge, signals for IO$_3^-$ and Br$_n^-$ corresponding to the chemical-electrochemical processes (step 4 and 5 in Fig. 1a) were clearly observed. Signal of IBr at step 5 can be further confirmed by *Ex-situ* Raman spectroscopy (Supplementary Fig. 9) because it would be overlaid with Cd(IO$_3$)$_2$ during *in-situ* process. The disappearance of I$_2$ signal confirmed step 6. XRD analysis of products from each of the 6 steps corroborated the presence of key compounds (Fig. 2e). It is important to note that the signal of IBr (Supplementary Fig. 10) was strengthened by introducing Cs$^+$ into the solution to precipitate CsIBr at step 2 and 5 (Fig. 2e). Together with the *ex-situ* experiments, these results demonstrate that the charge-discharge of IBA is reversible, and the process involves 6 steps as outlined in Fig. 1a.

We also inspected the charge-discharge process with an *in-situ* microscope (Fig. 3 and Supplementary Movie 1). During initial charging (step 1), spindle-shaped I$_2$ particles were seen on the electrode (Fig. 3b). “Oil droplets” that formed upon further charging (step 2) indicate the presence of IBr (Fig. 3c). In step 3, most of the IBr droplets were converted into a mist of Cd(IO$_3$)$_2$ that covered the electrode surface (Fig. 3d). Upon discharge, the misty Cd(IO$_3$)$_2$ gradually disappeared and the spindle-shaped I$_2$ re-generated (step 4-5) (Fig. 3e-f) (IBr will be overlaid with Cd(IO$_3$)$_2$). At the end of discharge (Fig. 3g), I$_2$ particles gradually dissolved. Only a little I$_2$ particles were remained on the electrode surface at the end of the process.

In contrast to IBA, the charge-discharge of halogen electrolyte without Br$^-$ (IA) displayed 4 distinct steps with serious polarization (~880 mV vs. 480 mV for IBA) (Supplementary Fig. 11). We studied the electrochemical mechanism by *in-situ* Raman spectroscopy (Supplementary Fig. 12) and *ex-situ* XRD (Supplementary Fig. 13) as well. Consistent with the literature, Raman signals of I$_2$ (180 cm$^{-1}$) and IO$_3^-$ (300-400 cm$^{-1}$ and 700-800 cm$^{-1}$) were observed upon charging in step 1 and 2, respectively. During discharging in step 3, IO$_3^-$ signal gradually weakened, while the intensity of I$_2$ increased, indicating the gradual conversion of IO$_3^-$ to I$_2$. Upon further discharging to step 4, I$_2$ is completely reduced to I$^-$ as shown by the disappearing I$_2$ signal. *In-situ* microscopy confirms this process as well (Supplementary Fig. 13 and Supplementary Movie 2). Only needle-shaped I$_2$ and Cd(IO$_3$)$_3$ mists corresponding to the four steps were seen. XRD spectra of the products in each step were consistent with the *in-situ* Raman data (Supplementary Fig. 14). Together, these results demonstrate the mechanism that the introduction of Br$^-$ can effectively reduce the polarization in IA.
Fig. 3 In-situ observation of charge-discharge process of IBA under an optical microscope. (a-g), Optical microscope images of electrode surface morphology at different charge and discharge stages. Step 1: spindle-shaped I$_2$ particles form; step 2: oil droplets of IBr form; step 3: conversion of IBr to Cd(IO$_3$)$_2$ mist; step 4: disappearance of Cd(IO$_3$)$_2$; step 5: disappearance of Cd(IO$_3$)$_2$ and reappearance of spindle-shaped I$_2$ particles; step 6: dissolution of I$_2$ particles. All images correspond to the charge discharge state marked in h. i) Schematic of the in-situ microscope experimental setup. CE, counter electrode; RE, reference electrode; WE, working electrode. (Battery performance limited by homemade devices)

**High-energy-density batteries with hetero-halogen electrolyte**

To demonstrate the feasibility of our IBA, we assembled a single flow battery with IBA as catholyte and Cd/Cd$^{2+}$ as anode (IBA-C) (Supplementary Fig. 15). The anode was used as flow
mode to prevent dendrite formation in Cd²⁺/Cd platting/stripping. Polarization curves for various state of charge (SOC) of IBA-C showed that, when SOC is 90%, the peak power density can reach 474 mW cm⁻² at a current density of 640 mA cm⁻² (Fig. 4a). The energy efficiencies decreased from 82% to 63% as the current density increased from 20 to 160 mA cm⁻¹ (Fig. 4b and Supplementary Fig. 16). Even at a high current density of 120 mA cm⁻², an energy efficiency of 72% was obtained. Compared with the battery with IA, the energy density of a battery with IBA is two times higher (250 vs. 120 Wh L⁻¹ for 1 M electrolyte) due to its higher discharge voltage (~1.49 V for IBA vs. ~1.23 V for IA) and specific capacity (184 versus 106 Ah L⁻¹) (Supplementary Fig. 17, A, B, D and E). Further, the energy efficiency of IBA-C can reach 75% (vs. 58% for IA) (Supplementary Fig. 17, C and F). Increasing the I⁻ concentration in IBA from 1 M to 6 M, the energy density increased from 234 to 1222 Wh L⁻¹ (Fig. 4c-d and Supplementary Fig. 18 A-B) and the electron transfer concentration reached ~32 mol L⁻¹ (Fig. 4e). However, due to the increase in electrolyte viscosity, the energy efficiency of the battery dropped from 75% (1 M at 80 mA cm⁻²) to 67% (6 M at 30 mA cm⁻²) (Supplementary Fig. 19). Using a high concentration anolyte (4.5 M CdCl₂) with 6 M IBA catholyte, energy density of the full cell (based on catholyte + anolyte) with ~186 Wh L⁻¹ was obtained (Supplementary Fig. 20). These results show IBA is a very promising catholyte for high energy density battery design.

**Capacity contributions in Steps 4 and 5 of IBA**

We also evaluated the performance of batteries assembled with IBA containing different concentrations of HBr. Increasing the Br⁻ to I⁻ ratios from 1:1 (1 M HBr:1 M HI) to 3:1 (3 M HBr:1 M HI), we found that the capacity contributed by step 2 increased from ~30 to ~82 Ah L⁻¹, almost linearly with the amount of Br⁻ (Supplementary Fig. 21A). This is because in step 2, I₂ and Br⁻ will preferentially form IBr, and excess Br⁻ will be oxidized to form Br₂. However, during discharge, we found that as Br⁻ to I⁻ ratios increased from 1:1 to 3:1, the discharge capacity of step 4 gradually increased from ~78 to ~172 Ah L⁻¹, while step 5 gradually decreased from ~70 to ~25 Ah L⁻¹ (Supplementary Fig. 21B). Because step 5 starts with the precipitation of IBr(s) from Br₂(l), higher concentrations of Br⁻ to I⁻ generates more Br₂ in the electrolyte. The excess Br₂ dissolves IBr and delays step 5. As a result, the capacity contributed by step 4 increases, while that of step 5 decreases. For the electrolyte with same concentrations of Br⁻ and different concentrations of I⁻, the capacities of step 4 were almost constant, while the capacities of step 5 were increased obviously, which also proves the above conclusion (Supplementary Fig. 18 C-D). Employing IBr dissolved in Br₂ as electrolyte, the abnormal short discharge time of Br₂ (step 4) also prove the precipitation of IBr will trigger step 5 (Supplementary Fig. 22).

**Cycling stability of HIBA-based batteries**

Battery cycle tests show that IBA is highly stable. At a current density of 40 mA cm⁻², IBA-C with 2 M I⁻ can run continuously for more than 300 cycles with an energy efficiency >78% and specific capacity of 215 Ah L⁻¹ (Fig. 4f and Supplementary Fig. 23A). Increasing I⁻ concentration in IBA to 3 M, more than 90 cycles could be obtained with an energy efficiency of 74% and specific capacity of 315 Ah L⁻¹ (Fig. 4g and Supplementary Fig. 23B). When the working current density increased to 80 mA cm⁻², the cycle stability decreased to no more than 100 cycles (Supplementary Fig. 24). The main reason is that the uneven cadmium deposition will cause short circuit, which limits the cycle life of the battery (Supplementary Fig. 25).
Fig. 4. Single flow aqueous battery using IBA as catholyte (a-g) Cd/Cd$^{2+}$ or (h-i) silicotungstic acid (SWO) as anode shows superior performance. (a) Polarization curves of the assembled battery at different SOCs. All data were collected with 1 M HI + 1 M HBr + 1 M H$_2$SO$_4$ +1 M CdSO$_4$ solution for catholyte and anolyte. (b) Battery efficiencies at current densities between 20~160 mA cm$^{-2}$ with cut-off voltage of 2.1 V and 0.1 V. (c) Charge-discharge plots of the battery assembled with different concentrations of I$^-$ in IBA catholyte. (d) Energy density of assembled batteries with different concentrations of electrolyte. (e) Measured (grey) and theoretical (green) concentration of transferred electron (mol L$^{-1}$) for different concentrations of I$^-$ in IBA. (f and g), Cycling performance of the battery with 2 M IBA (1 M CdI$_2$ + 2 M HBr + 3 M H$_2$SO$_4$) (f) and 3 M IBA (1 M NaI +1 M CdI$_2$ + 2 M HBr + 3 M H$_2$SO$_4$) (g) at 40 mA cm$^{-2}$. The capacity of each I$^-$ to transfer 4 electrons was used as the charge cut-off condition and the discharge voltage cut-off was 0.1 V. (h) Charge-discharge plot of the assembled IBA-SWO battery at 80 mA cm$^{-2}$. (i) Cycling performance of IBA-SWO battery at 80 mA cm$^{-2}$. Both catholyte and anolyte are 1 M HI+1 M HBr + 0.5 M SWO. Battery was charged and discharged between 0.1~1.6 V. (i) Cycling performance of IBA-SWO battery at 80 mA cm$^{-2}$. Capacity cut-off condition of charging is 4-electron transfer of each I$^-$ and cut-off for discharge is 0.1 V.

We also investigated the stability of our IBA catholyte by pairing it with silicotungstic acid (SWO) (IBA-SWO) and PbSO$_4$/Pb anodes (IBA-P). The SWO anode demonstrated good electrochemical reversibility and was free of dendrites$^{24}$ (Supplementary Fig. 26; H$_4$[SiW$_{12}$O$_{40}$]...
As a result, the IBA-SWO battery can stably operate for more than 1000 cycles at a current density of 80 mA cm\(^{-2}\) (Fig. 4h-i and Supplementary Fig. 27). Furthermore, a static battery assembled with Pb/PbSO\(_4\) as anode displayed an energy density of more than 800 Wh L\(^{-1}\) (Supplementary Fig. 28), which can effectively power LED lights (Supplementary Fig. 29 and Supplementary Movie 3).

**Cost-efficient performance**

Our IBA-C battery with working current density reaching 120 mA cm\(^{-2}\) and actual power density exceeding 150 mW cm\(^{-2}\) outperforms many current aqueous battery systems (mostly < 100 mW cm\(^{-2}\)) (Fig. 5a). Further, its energy density of over 1200 Wh L\(^{-1}\) is 3 times higher than the current reported aqueous batteries (Fig. 5b) and comparable to some solid electrode materials such as LiFePO\(_4\) (Fig. 5c). Most importantly, the realization of six-electron transfer property with IO\(_3^-/I^-\) means the amount of I\(^-\) required per kWh is significantly lower than the I\(^-\)/I\(^2\) single electron transfer reaction. This brings the cost down to ~$29 kWh\(^{-1}\), which is comparable to LiFePO\(_4\) (~$26 kWh\(^{-1}\)) (Fig. 5d). We expect the iodine multielectron transfer system to broaden the application of aqueous batteries.

![Fig. 5 IBA-based batteries outperform current battery systems](image-url)

(a and b) Current density of IBA-based batteries reach 120 mA cm\(^{-2}\) and their power density exceed 150 mW cm\(^{-2}\) (a). Energy density is 3 times higher than most aqueous batteries (b). Data such as working current density and electrolyte concentration are from the literature (see Methods for references). Voltage values are standard voltage of the battery systems. (c) Energy density of IBA is better than most electrode materials and comparable to LiFePO\(_4\). Values from our work are based on actual energy density of 5–6 M IBA (1.3–1.4 g mL\(^{-1}\)) and the theoretical energy density of 10 M IBA (2.1–2.5 g mL\(^{-1}\)). Intercalation-type: aqueous lithium-ion battery (AqLIB); zinc ion battery (ZIB); lithium-ion battery (LIB); Zinc-Nickel battery (ZNB). (d) Compared with other common positive electrodes, the cost of our cathode ($29 kWh\(^{-1}\)) comes close to LiFP (~$26 kWh\(^{-1}\)). Cost of cathode is calculated according to the price of active materials. LiFP; LiFePO\(_4\); LMO; LiMn\(_2\)O\(_4\); LAc: Lead-acid battery; ZIFB: Zinc iodine flow battery; VFB: Vanadium flow battery; Our work: based on HI.
Conclusion

We developed a high energy density aqueous battery system using a high hetero-halogen based electrolyte. Reversible multi-electron transfer reaction in I$_2$/IO$_3^-$ couple was achieved by introducing Br$^-$ into the I$^-$ solution. Combined with the advantages of a high electrolyte concentration and multi-electron transfer process, the energy density of our catholyte can exceed 1200 Wh L$^{-1}$ with Cd$^{2+}$/Cd as anode. Even at a high current density of 120 mA cm$^{-2}$, the battery had an energy efficiency of 72%. Compared with Cd/Cd$^{2+}$ anode, the cycle life of silicotungstic acid improved to over 1000 cycles, demonstrating significant stability. Combined with high energy density, power density and superior stability, our multi-electron transfer battery system offers a good reference for the development of next-generation high energy density and safe rechargeable aqueous batteries.

Methods

Preparation of electrolytes. For the IBA electrolytes, 1 M electrolyte refers to 1 M HI (Sinopharm Chemical Reagent) +1 M HBr (Tianjin Kemiou Chemical Reagent) +1 M H$_2$SO$_4$ (DAMAO Chemical Reagent) +1 M CdSO$_4$ (Aladdin Reagent), and 2 M electrolyte refers to 1 M CdI$_2$ (Sinopharm Chemical Reagent) +2 M HBr+ 3 M H$_2$SO$_4$, the composition of the 3 M electrolyte was optimized as 1 M CdI$_2$+1 M NaI (Sinopharm Chemical Reagent) +2 M HBr+ 3 M H$_2$SO$_4$. For 4~6 M electrolyte, the catholyte compositions are 4 M NaI+1 M HBr, 3 M NaI+2 M HI+ 1 M HBr and 3 M NaI+3 M HI+ 1 M HBr respectively, and the anolyte is 1 M CdI$_2$ +2 M HBr+ 1 M H$_2$SO$_4$. For the Pb-I battery, the positive electrolyte is 2.8 M HI+2.8 M NaI+2 M HBr (the electrolyte needs to be heated at 60°C to dissolve), and the negative electrolyte is 2 M H$_2$SO$_4$. For the IA electrolyte without HBr, 1 M electrolyte refers to 1 M HI + 1 M H$_2$SO$_4$ + 1 M CdSO$_4$; 2 M electrolyte refers to 2 M HI + 1 M H$_2$SO$_4$ + 1 M CdSO$_4$.

Cyclic voltammetry test. The cyclic voltammetry test was performed through a typical three-electrode device with a compressed sandwich structure (a mini battery), in which the working electrode was carbon felt (Liaoyang J-Carbon Materials Co., Ltd., China) with a radius of 3 mm, and the counter electrode and reference electrode were 9 cm$^2$ cadmium plates (Tianjin Xinjia Weiye Steel Trade Co., Ltd). The electrolyte was stored inside the porous electrode. A Nafion 115 membrane was used to separate the positive and negative electrodes. The cyclic voltammetry test was performed by a Gamary Interface 1000 at scan rates from 1~10 mV/s at room temperature.

In situ Raman Spectra. In situ Raman spectra testing was a combination of Raman and electrochemical detection. The assembled battery was charged and discharged through an electrochemical workstation (CHI) with a constant current of 10 mA. The positive and negative electrodes of the evaluated battery were carbon felts with areas of ~0.25 cm$^2$ (0.5 cm*0.5 cm) and 1 cm$^2$ (1 cm*1 cm), respectively. The self-made in-situ test device was shown in Supplementary Figure 30. The battery was assembled with Nafion 115 membrane with electrolyte stored inside the carbon felt, which connected to the electrochemical workstation by titanium wires. The Raman signal was collected from the positive electrode surface under the quartz window, which was recorded by a LabRAM HR 800 Raman spectrometer with a 532 nm laser. The Raman scanning range was 100~1000 cm$^{-1}$, and the signal was collected every 100 s.

Ex-situ Raman Spectra. For Ex-situ Raman Spectra measurement, the test solution was contained in a nuclear magnetic tube. The Raman spectra were measured by an inVia microscope (Leica) and Raman spectroscopy system (Renishaw). A diode-pumped solid-state laser (532 nm) was used as the excitation source. The scanning range was 50~1000 cm$^{-1}$ at room temperature.

In situ optical microscopy. In situ optical microscopy detection was carried out by using a homemade electrochemical device, which is similar to the in-situ Raman test device. A glassy carbon electrode with the size of 1cm*1cm and a piece of Cd plate with the thickness of 1mm were served as positive and negative electrodes respectively. A piece of Nafion 212 was used as membrane. The battery is charged and discharged via an electrochemical workstation (LANHE) at a current of 5 mA. An optical microscope (Leica microsystems CMS GmbH) was used to detect the change in surface morphology of electrode.
**XRD determination.** XRD detection was performed to detect the product composition on the electrode, when the battery was charged or discharged to a certain state. The electrode products were sealed by a piece of polyimide (PI) film to inhibit the volatilization of bromine. XRD detection was performed by a Rigaku Ultima IV Equipped with a D/teX-Ultra detector and Cu Ka radiation from 20–60° and the scanning rate was 10° per minute.

**Battery assembly.** The battery assembly is similar to that of our previous articles. To inhibit corrosion of the electrode, a titanium plate (1 mm) and a graphite plate were used as positive and negative collectors respectively. Graphite felt with a thickness of 1 mm was used as electrode (size 6 cm×8 cm) with a compression rate of ~50%. In addition, a cadmium plate with a thickness of 1 mm was placed between the negative collector and the electrode to ensure full discharge at cathode. The positive and negative electrodes were separated by a piece of Nafion 115. It is important to note that the electrolyte on the negative side was in a flowing mode to prevent dendrite issues caused by concentration polarization of Cd<sup>2+</sup>, while the electrolyte on the positive side was stored in the positive carbon felt. For the cycling test, a glass fiber separator (AGM Zaozhuang Dongchang Fiber glass Industry Co., Ltd) with a thickness of 1.6 mm was placed between the negative collector and carbon felt to prevent the short circuit caused by cadmium dendrites. And a carbon felt with a thickness of 1 mm was placed between the negative collector and cadmium plate to improve the contact between the negative cadmium plate and collector.

**Battery performance evaluation.** The battery was charged and discharged under constant current density, and the cut-off condition of charging was constant capacity. For the discharge process, the cut-off voltage was 0.1 V. To meet the high capacity of the cathode, a single-flow battery was assembled, where the catholyte was sealed in the positive cavity, which is approximately 2 mL in general, and an excess volume of anolyte was flowed through anode. The volume of catholyte can be determined by the charging capacity of step 1 (i.e., I<sub>1</sub>/I<sub>0</sub>) and concentration of I<sub>−</sub> in IBA or IA. The positive and negative electrolytes need to be mixed regularly to prevent the imbalance of ions caused by osmotic pressure and cross-mixing.

**Deposition morphology.** The deposition morphology on the electrode was detected by scanning electron microscope (JEOL JSM-7800F). Before test, the anode plates, which were charged to a certain state, were freeze-dried at -50°C.

**Energy density calculation.** Calculation of energy density E (Wh L<sup>−1</sup>) in Fig. 1e was based on the volume of electrolyte of at one side (ZIB, polyoxoanion, VFB) or the volume of solid active materials (LiFePO<sub>4</sub>, aq-LiMn<sub>2</sub>O<sub>4</sub>). The calculation of LiFePO<sub>4</sub> is based on the theoretical specific capacity of LiFePO<sub>4</sub> C (170 mAh g<sup>−1</sup>) and battery voltage V (3.2 V vs. Li<sup>+/Li</sup>); tap density ρ (1.0 g cm<sup>−3</sup>). The energy density of aqueous lithium-ion battery (LiMn<sub>2</sub>O<sub>4</sub>) was mainly based on LiMn<sub>2</sub>O<sub>4</sub>-VO<sub>2</sub> system. The theoretical specific capacity was ~148 mAh g<sup>−1</sup>, the voltage is about ~1.5 V and the tap density<sup>27</sup> could reach 2.67 g cm<sup>−3</sup>.

The energy density of solid material: \[ E = C \times V \times \rho \] (4)

For zinc iodine flow battery (ZIB), bromine-Li<sub>i</sub>[P<sub>2</sub>W<sub>18</sub>O<sub>49</sub>] flow battery (polyoxoanion) and VFB battery, the calculation of energy density is mainly based on the electrolyte volume of the positive side<sup>25,28</sup>.

**Cost calculation.** For the cost of cathode materials such as LIF (LiFePO<sub>4</sub>), LMO (LiMn<sub>2</sub>O<sub>4</sub>) was obtained from the related references<sup>29</sup>. The cost of LAC (lead acid battery $44 kWh<sup>−1</sup>), ZIFB (zinc iodine flow battery $162 kWh<sup>−1</sup>) and all vanadium flow battery (VFB $117 kWh<sup>−1</sup>) systems was based on our experimental data.

**Comparison of battery power and energy density.** The power density and energy density in Fig. 5a-b were obtained by the following references: Tin-iodine flow battery (Sn-I)<sup>30</sup>; Zinc-iodine flow battery (Zn-I)<sup>31</sup>; Alkaline zinc-iodine flow battery (Alkaline Zn-I)<sup>32</sup>; Hydrogen-manganese battery (H-Mn)<sup>33</sup>; sulfurred-iodine flow battery (S-I)<sup>34</sup>; Zinc-iodine-Manganese flow battery (Zn-I-Mn)<sup>35</sup>; Zinc-Manganese flow battery (Zn-Mn)<sup>36</sup>; Methyl-Viologen-ferrocene flow battery (MV-Fe)<sup>37</sup>; N,N,N,N',N'-dimethyl-4,4-bipyridinium dichloride flow battery (TEMPTA-MV)<sup>38</sup>; polyoxoanion-Bromine flow battery (PWO-Br)<sup>39</sup>; Zinc Bromine flow battery (ZBB)<sup>39</sup>

In Fig. 5C, the energy density of flow batteries that including ZBB, ICB and VFB is mainly based on the volume or mass of electrolyte on one side.<sup>40</sup> All the data about the flow battery come from the actual evaluations of our group, which were close to the reported data as well<sup>40</sup>. For the volumetric energy density of different solid...
materials, such as LiFePO$_4$; LiMn$_2$O$_4$; Ni(OH)$_2$; MnO$_2$; aqua-LiMn$_2$O$_4$, it was calculated based on Eq. 4 and table S1.

**DFT calculation.** The ESP analysis and binding energy were calculated using density functional theory (DFT) in Gaussian 16 package. The structures were optimized at B3LYP hybrid functional with Def2-TZVP basis set including the atom-pairwise dispersion correction (DFT-D3) with Becke-Johnson (BJ) damping. The implicit universal solvation model based on solute electron density (SMD) was applied during the structure optimization. The optimized structures were checked by vibrational frequency analysis at the same calculation level to ensure they were on the local minima of potential energy surface. The ESP was analyzed by Multiwfn package and was drawn by VMD package. The binding energy ($E_{\text{binding}}$) was calculated by the following Eq.

$$E_{\text{binding}} = E(\text{H}_2\text{O}-\text{B}) - E(\text{H}_2\text{O}) - E(\text{B})$$

Where $E$ represents the electronic energy of the component. B represents I$_2$ or IBr.

The absorption of I$_2$ and IBr on carbon electrode were carried out by Vienna Ab-initio Simulation Package (VASP) with the projector-augmented wave (PAW) method. All calculations were based on the same generalized gradient approximation (GGA) method. Perdew-Burke-Ernzerhof (PBE) functional was applied to deal with the exchange-correlation term. Van der Waals interaction was taken into account at DFT-D3 with Becke-Jonson (BJ) damping level. The plane wave cutoff was set to 500 eV. The Brillouin zone integration was carried out with $2 \times 2 \times 1$ Gamma point. The convergence thresholds for energy was set as $10^{-5}$ eV during ion relaxation, and the convergence thresholds for force was set as 0.02 eV Å$^{-1}$. Charge density differences was analyzed by Vaspkit package.

**References**

15. Boyle, P. D. et al. Further structural motifs from the reactions of thioamides with diiodine and the...
interhalogens iodine monobromide and iodine monochloride: an FT-Raman and crystallographic study†.


Kaiho, T. Iodine chemistry and applications. (Wiley Online Library, 2014).

An, Y. et al. Synthesis, structure and characterization of M(IO\textsubscript{3})\textsubscript{2}(HIO\textsubscript{3}) (M = Ca, Sr) as new anhydrous alkaline earth metal bis-iodate hydrogeniodate compounds. Dalton Trans. 48, 13074-13080, (2019).

Bushiri, M. J., Kochuthresia, T. C., Vaidyan, V. K. & Gautier-Luneau, I. Raman scattering structural studies of nonlinear optical M(IO\textsubscript{3})(M = Fe, Ga, α-In) and linear optical β-In(IO\textsubscript{3}). J. Nonlinear Opt. Phys. Mater. 23, 1450039, (2014).


Easton, M. E. et al. The Formation of High - Order Polybromides in a Room - Temperature Ionic Liquid: From Monoanions ([Br\textsubscript{3}]\textsuperscript{-} to [Br\textsubscript{11}]\textsuperscript{-}) to the Isolation of [PC\textsubscript{16}H\textsubscript{35}]\textsuperscript{2+} [Br\textsubscript{25}] as Determined by van der Waals Bonding Radii. Chem. - Eur. J. 21, 2961-2965 (2015).


Guo, D. et al. Electrochemical performance of solid sphere spinel LiMn\textsubscript{2}O\textsubscript{4} with high tap density synthesized by porous spherical Mn\textsubscript{3}O\textsubscript{4}. Electrochim. Acta 123, 254-259, (2014).


Gaussian 16 Rev. A.03 (Wallingford, CT, 2016).


Data availability: The data that support the plots depicted in this manuscript and other findings of this study are available upon request from the corresponding author.

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C.W. and Q.F; T.L have completed relevant theoretical calculations; X.L. supervised the work, discussed the results and revised the manuscript.

**Competing interests:** The authors declare no competing financial interests.

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Supplementary Files

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