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A tellurium iodide perovskite structure enabling eleven-electron transfer in zinc ion batteries

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The growing potential of low-dimensional metal-halide perovskites as conversion-type cathode materials is limited by electrochemically inert B-site cations, diminishing the battery capacity and energy density. Here, we design a benzyltriethylammonium tellurium iodide perovskite, (BzTEA)₂TeI₆, as the cathode material, enabling X- and B-site elements with highly reversible chalcogen- and halogen-related redox reactions, respectively. The engineered perovskite can confine active elements, alleviate the shuttle effect and promote the transfer of Cl⁻ on its surface. This allows for the utilization of inert high-valent tellurium cations, eventually realizing a special eleven-electron transfer mode (Te⁶⁺/Te⁴⁺/Te²⁺, I⁺/I⁰/I⁻, and Cl⁰/Cl⁻) in suitable electrolytes. The Zn||(BzTEA)₂TeI₆ battery exhibited a high capacity of up to 473 mAh g⁻¹_{Te/I} and a large energy density of 577 Wh kg⁻¹_{Te/I} at 0.5 A g⁻¹, with capacity retention up to 82% after 500 cycles at 3 A g⁻¹. The work sheds light on the design of high-energy batteries utilizing chalcogen-halide perovskite cathodes.

The need for efficient and affordable energy storage devices to manage intermittent renewable energy has kindled immense interest in functional perovskite materials, representing a distinctive class of ionic crystals comprising several oxide and halide structures with similar octahedral features^{1–4}. ABO₃ (A and B are divalent and tetravalent metallic cations, respectively) structured oxide perovskites are known as promising ferroelectric, dielectric, magnetic, and energy storage materials^{5–7}. Owing to the abundance of oxygen vacancies, oxide perovskites have been successfully applied as catalytic electrode materials^{8–11}. Instead, halide perovskites (ABX₃, A is monovalent cation, B is divalent cation, and X is I, Br, or Cl) possess relatively narrower bandgaps due to the large difference in electronegativity between halogens and oxygen, thereby used for optoelectronic applications such as the light absorber and emissive layer in solar cells and light-emitting diodes, respectively^{12–15}. Nevertheless, the study of halide

perovskites in batteries has reached a rudimentary stage, though being contained to a subsidiary role in storage applications.

The research on molecular-level low-dimensional (LD) crystals such as two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) perovskites are advanced in the meanwhile due to demand for structural stability^{16–19}, some of which reflect deficient formation energy at ambient conditions being suitable for multifunctional purposes^{20–22}. Among them, the LD organic-inorganic hybrid perovskites demonstrate a substantial quantum and dielectric confinement due to the breakdown of three-dimensional (3D) frameworks as the inclusion of insulating organic moieties²³. This special lattice ordering promotes improved structural stability and expanded bandgaps that bring out an exciting intersection of the halide and oxide perovskites' applications, including ferroelectricity and energy storage devices^{24–32}.

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Unlike ancillary oxide perovskites that provide oxygen vacancies for metal-air batteries^{33,34}, halide perovskites perform as the halogen reservoir and restrain the shuttle effect by using Van Der Waals forces (hydrogen bonds and halogen bonds) and steric hindrance from A-site organics, eventually realizing a three-electron transfer process³⁵. However, those encouraging attempts to develop halide perovskite cathodes failed to avail the full range of perovskite materials given that the redox reaction of the B-site cations sits electrochemically inert during the conversion process (of halogens). This undermines the whole discharge capacity. In this regard, replacing those noble B-site metal cations with tetravalent chalcogenide cations to construct chalcogen-halide octahedra is expected to offer full utilization of cathode materials and guarantee a reliable multiple electron transfer. Nevertheless, the high-valent hexavalent and tetravalent chalcogen cations are neither stable nor electrochemically active in aqueous electrolytes, causing irreversible redox processes in batteries^{36–40}.

Herein, we designed a benzyltriethylammonium tellurium iodide perovskite, (BzTEA)₂TeI₆, as the cathode material for problem-solving and demonstrated its special chemical processes in aqueous zinc ion batteries. In our design, the high charge density surrounding each tetravalent Te⁴⁺ cation causes the formation of the tellurium-iodide octahedron unit, which is embedded in the A-site organic ligands (BzTEA) matrix and supplies high elemental iodine and tellurium content of over 71 wt.%. The robust Van Der Waals forces such as Te-I...Cl-Te and Te-I...I halogen bonds on the perovskite surface promote the localization of active elements and avert the undesired shuttling of oxidative polyiodide and tellurium polychloride ions, as supported by the density functional theory (DFT) calculations. Consequently, the Zn|| (BzTEA)₂TeI₆ battery delivers a highly reversible eleven-electron transfer mode on account of the two-electron I⁰/I⁺/I and eight-electron Te⁶⁺/Te⁴⁺/Te⁰/Te²⁻ redox reactions, and one-electron Cl⁰/Cl⁻ transfer gained from the chloride electrolyte, all of which favor a high discharge capacity up to

473 mAh g⁻¹_{Te/I} and a large energy density of 577 Wh kg⁻¹_{Te/I} at 0.5 A g⁻¹ represented by five prominent voltage plateaus at 1.81 V, 1.64 V, 1.53 V, 1.26 V, and 0.51 V. The feasibility of the (BzTEA)₂TeI₆ perovskite cathode is further verified by the zinc pouch cells.

Results

(BzTEA)₂TeI₆ perovskite cathode

Chalcogens, such as sulfur, selenium, and tellurium, display a broad spectrum of valence states (-2, 0, +2, +4, +6) and exhibit significant redox potentials (Fig. 1a). This characteristic theoretically renders them suitable for energy storage, while the stability of high-valent chalcogen cations remains a crucial consideration. Halogens, on the other hand, are proven effective in giving high redox potentials in aqueous zinc ion batteries^{41,42}. A proper integration of chalcogen and halogen chemistry should promote problem-solving and actualize high-energy zinc ion batteries. Implementing halogen redox in halide perovskites brings our attention to potential structural design and prompts the exploration of chalcogen halide perovskites as cathode materials. Actually, the typical ABX₃ perovskites consist of corner-sharing [BX₆]⁴⁻ octahedra and offset of A-site atoms in octahedron cavities throughout the whole 3D matrix⁴³. In contrast, the molecular-level LD perovskite materials crystallize in a way where the [BX₆]⁴⁻ octahedron unit is separated by A-site cations in specific directions and upholds a high structural tunability (Supplementary Fig. 1)^{44,45}. As such, we have now aim to replace conventional electrochemically inert B-site cations with tetravalent chalcogenide cations while retaining the octahedral BX₆ motif to enable the formation of A₂B^{IV}X₆ vacancy-ordered perovskites⁴⁶. This change is expected to maximize the utilization of perovskite materials by enabling multivalent reactions (B²⁻/B⁰/B⁴⁺/B⁶⁺) of both chalcogen and halogen elements, as depicted in Fig. 1a. The special lattice arrangement ensures the confinement of chalcogen and halogen elements in the same perovskite structure,

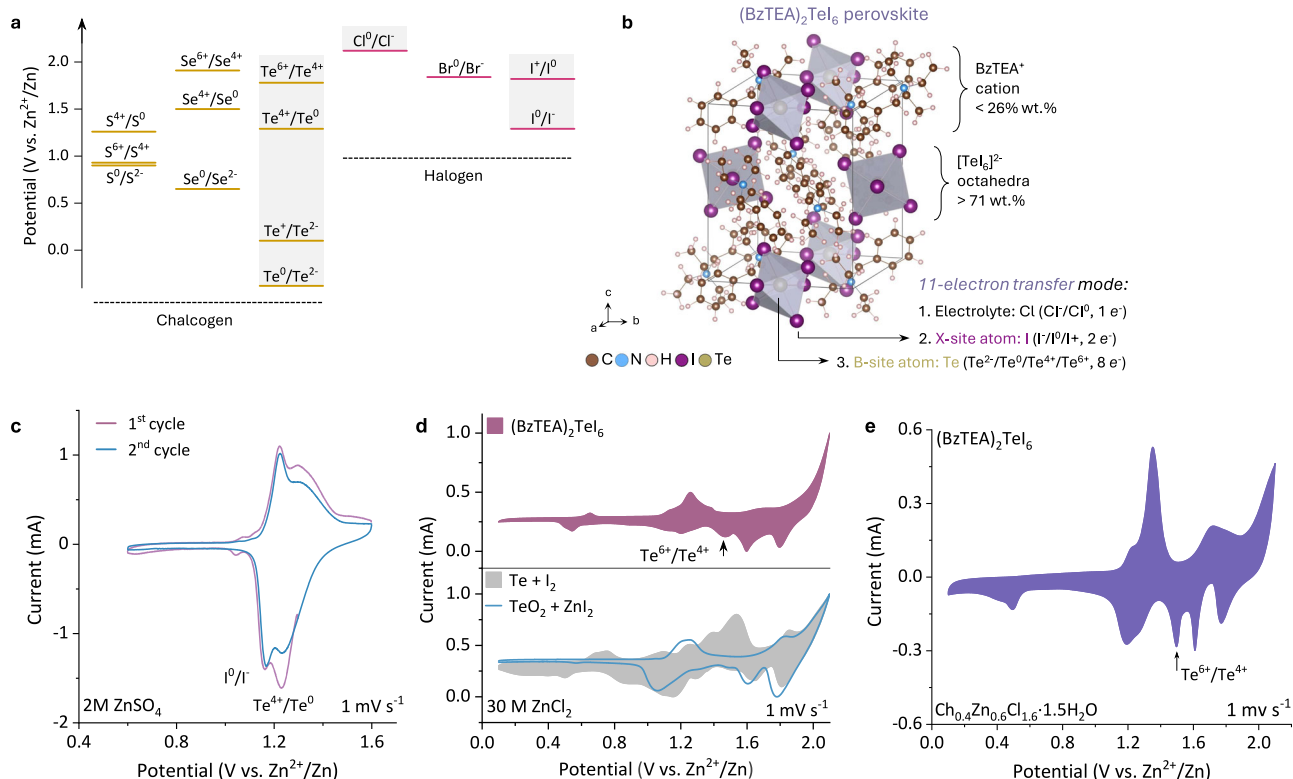


Fig. 1 | Chalcogen halide perovskite structure design and electrochemical properties. **a** Redox potential of chalcogens and halogens. **b** Structural arrangement of low-dimensional (BzTEA)₂TeI₆ perovskite where tellurium and iodine

elements sit as the B- and X-site components, respectively. The CV curves of the perovskite cathode in **c** 2 M ZnSO₄ (first two cycles), **d** 30 M ZnCl₂, and **e** Ch_{0.4}Zn_{0.6}Cl_{1.6}·1.5H₂O.

which creates the platform for chalcogen- and halogen-related redox reactions for high-energy batteries. As summarized in Supplementary Table 1, the cogitation theoretically upholds high redox potential and multiple electron transfer associated with B-site chalcogen and X-site halogens of the perovskite cathode materials, attempting to overcome the deficiency of conventional chalcogen cathodes and enable the electrochemically inert high-valent chalcogen redox^{47,48}. As a proof-of-concept, (BzTEA)₂TeI₆ perovskite, which possesses a high proportion of active elements (>71 wt.%), is thus proposed as conversion-type cathodes for aqueous zinc ion batteries with a special eleven-electron transfer process. (Fig. 1b).

Regardless of the lattice arrangement at molecular levels, (BzTEA)₂TeI₆ microcrystals prepared by a modified saturation recrystallization method crystallized into bulk rod shape with an average length of less than 50 μm, as illustrated in the scanning electron microscope (SEM) image in Supplementary Fig. 2¹⁹. The perovskite microcrystals delivered identical XRD diffractions with the theoretical simulation in Supplementary Fig. 3 and appeared black due to its narrow optical bandgap, aligning with the ultraviolet absorption spectra in Supplementary Fig. 4. SEM-mapping in Supplementary Fig. 5 further revealed the even elemental distribution of (BzTEA)₂TeI₆ microcrystals associated with 14.5 at.% of Te and 85.5 at.% of I according to the energy-dispersive X-ray spectroscopy (EDS) test. Fourier Transform Infrared (FTIR) spectra in Supplementary Fig. 6 indicated the protonation of A-site N-H bond in (BzTEA)₂TeI₆. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves in Supplementary Fig. 7 confirmed the structural stability and hydrophobic feature of the tellurium iodide perovskite according to the negligible weight loss below 211 °C. Raman spectra in Supplementary Fig. 8 reveal symmetric A_{1g} and asymmetric E_g stretching of Te-I bond at approximately 153 cm⁻¹ and 107 cm⁻¹ in (BzTEA)₂TeI₆, resembling the Te-O bond observed in TeO₂⁴⁹.

Tellurium and halogen redox

The halide perovskite cathode was first examined in Zn||2 M ZnSO₄|| (BzTEA)₂TeI₆ Swagelok cells and achieved with two redox peaks, corresponding to I⁰/I⁻ and Te⁴⁺/Te⁰, the latter of which experienced fast decay of current according to the cyclic voltammetry (CV) curves in Fig. 1c. In comparison, 2 M Zn(OTf)₂, 2 M Zn(OAc)₂, and 15 M ZnCl₂ electrolytes all failed to activate the redox reaction of high-valent tellurium cations (Supplementary Figs. 9, 10). 30 M ZnCl₂, containing reduced amount of free water, was then used as the electrolyte with an attempt to stabilize the tetravalent tellurium cations⁵⁰. Surprisingly, it enabled the perovskite cathode with an additional Te⁶⁺/Te⁴⁺ redox at around 1.5 V. It should be noted that the Te⁶⁺/Te⁴⁺ redox was utterly absent in the “TeO₂ + ZnI₂” and “Te + I₂” cathodes (Fig. 1d and Supplementary Fig. 11), which reveals the special structure of (BzTEA)₂TeI₆ for activation of the new redox. The observation also suggested that the activity of water and chloride anions may play an essential role in stabilizing high-valent tellurium cations. Based on that, we introduced choline chloride (ChCl) into the concentrated ZnCl₂ electrolyte to devise the Ch_{0.4}Zn_{0.6}Cl_{1.6} · 1.5H₂O electrolyte, which was found to have limited water activity and enough mobility of chloride ions to coordinate with high-valent tellurium cations during cycling. As shown in Fig. 1e, the activity endowed Zn||Ch_{0.4}Zn_{0.6}Cl_{1.6} · 1.5H₂O|| (BzTEA)₂TeI₆ prominent discharge peaks, including Te⁶⁺/Te⁴⁺ and Te⁴⁺/Te⁰ redox pairs at 1 mV. In sharp contrast, both “TeO₂” and “Te + I₂” cathodes failed to enforce the Te⁶⁺/Te⁴⁺ redox even when coupled with the same modified electrolyte, again highlighting the special chemical design of (BzTEA)₂TeI₆ (Supplementary Fig. 12).

In order to figure out the critical role of (BzTEA)₂TeI₆ perovskite structure for the rich chemistry, we subsequently conducted detailed electrochemical studies of these batteries. As shown in Fig. 2a, the “TeO₂ + ZnI₂” cathode presented two types of redox, including I⁰/I⁻ and Cl⁰/Cl⁻, which experienced an unusual attenuation as the scan rate

increased, together with a mild Te⁶⁺/Te⁴⁺ redox reaction probably due to the catalytic role of iodine atom (Supplementary Fig. 13). The (BzTEA)₂TeI₆ cathode, on the contrary, featured four sharp discharge peaks from the Cl⁰/Cl⁻, I⁰/I⁻, Te⁶⁺/Te⁴⁺, and Te⁰/Te²⁻ redox pairs and one broad peak due to the overlay of Te⁴⁺/Te⁰ and I⁰/I⁻ as will be discussed later (Fig. 2b and Supplementary Fig. 14). Further, as illustrated in Fig. 2c, the surface-controlled process of the battery based on perovskite cathodes gradually grew from 21.5% at 0.5 mV s⁻¹ to 40.2% at 3 mV s⁻¹. In comparison, that for the “TeO₂ + ZnI₂” cathode started from 11.1% at 0.5 mV s⁻¹ to 23.5% at 3 mV s⁻¹ due to weak adsorption of active elements at a high scan rate (Supplementary Fig. 15). The derived *b* value of each cathodic peak generally fell between 0.5 and 1.0 and exhibited a combined action of the faradic and capacitive processes during the conversion reactions (Fig. 2d)⁵¹. However, the *b* values of the control sample were far below 0.5 and turned negative for Cl⁰/Cl⁻, suggesting the poor cycling stability of the “TeO₂ + ZnI₂” cathode and uncontrolled loss of chlorine elements (Supplementary Figs. 15, 16). The summary in Fig. 2e demonstrated their difference in *b* values. It highlighted the importance of (BzTEA)₂TeI₆ and ChCl for properly operating batteries, aside from taking full advantage of the B-site tellurium elements. As a comparison, the Zn||(BzTEA)₂TeI₆ battery in 30 M ZnCl₂ experienced severe degradation under identical test conditions, even though it delivered a Te⁰/Te²⁻ redox pair with a larger *b* value (0.6) and a mild Te⁶⁺/Te⁴⁺ redox pair (Supplementary Fig. 17). Figure 2f presents a typical galvanostatic discharge curve of Zn||(BzTEA)₂TeI₆ battery at 0.5 A g⁻¹, which brought out an eleven-electron transfer process, including three-electron transfer from the iodine element, eight-electron transfer from tellurium element and one from chlorine element, following the result from the differential capacity (dQ/dV) plot in Supplementary Fig. 18.

Mechanism of the eleven-electron transfer

The Raman spectra recorded during the charge and discharge process indicated the presence of I₅⁻ at 169 cm⁻¹, consistent with theoretical calculations, while signals from high-valence tellurium cations were indistinct (Supplementary Fig. 19). This may be due to the overlap of Te⁶⁺ signal with the [ZnCl_{2+x}(H₂O)_y] cluster at around 300 cm⁻¹ and the Te⁴⁺ signal below 100 cm⁻¹ being affected by intense Rayleigh scattered laser light (noise)^{33,40,52,53}. The XRD and its enlarged patterns in Supplementary Fig. 20 reveal a broad peak around 10°, close to the main diffraction peaks of (BzTEA)₂TeI₆ perovskites, whereas the blank electrode consisting solely of Ketjen black and PVDF binder exhibits no characteristic peak at that position. X-ray photoelectron spectroscopy (XPS) measurements were further performed to evaluate the perovskite cathode's conversion reactions. As demonstrated in Fig. 3a, Te⁰ and Te²⁻ dominated at discharge states; the signal of Te⁴⁺ first appeared at 576 eV when charged to 1.2 V and shifted to 576.9 eV, verifying the formation of Te⁶⁺. The presence of Te-O at 579.2 eV is attributed to the oxidation of high-valent tellurium ions in damp air. The Cl 2p_{3/2} core level spectra in Fig. 3b exhibit the signals from lattice Cl⁻ changing from 198.9 eV at 0.5 eV, 199.4 eV at 1.7 V, to 199.6 eV at 1.9 V, contributing to an energy span of over 0.7 eV. Instead, the adsorbed Cl⁻ changed from 198.2 eV at 0.5 V to 198.7 eV at 1.7 V and slightly increased to 198.73 eV at 1.9 V, corresponding to an energy change of 0.5 eV. The energy evolution of the two types of Cl⁻ revealed that a certain degree of (dynamic) halide exchange between iodide and chloride ions could promote a reliable Cl⁰/Cl⁻ redox reaction, consistent with the CV performance discussed above. The I 3d_{3/2} core level spectra in Fig. 3c demonstrate the conversion from I⁻ at 1.7 V, to I⁰ at 1.3 V and I at 0.5 V, verifying the successful operation of the I⁻/I⁰/I redox pairs⁵⁴.

Molecular dynamics (MD) simulations and DFT calculations were subsequently conducted to understand the working principle of the chalcogen halide perovskite cathode. As depicted in Fig. 4a, the ZnCl₂ · 1.4H₂O electrolyte was dominated by tetrahedral [ZnCl₄]²⁻ and octahedral [ZnCl₄(H₂O)₂]²⁻ clusters. Notably, as the inclusion of ChCl,

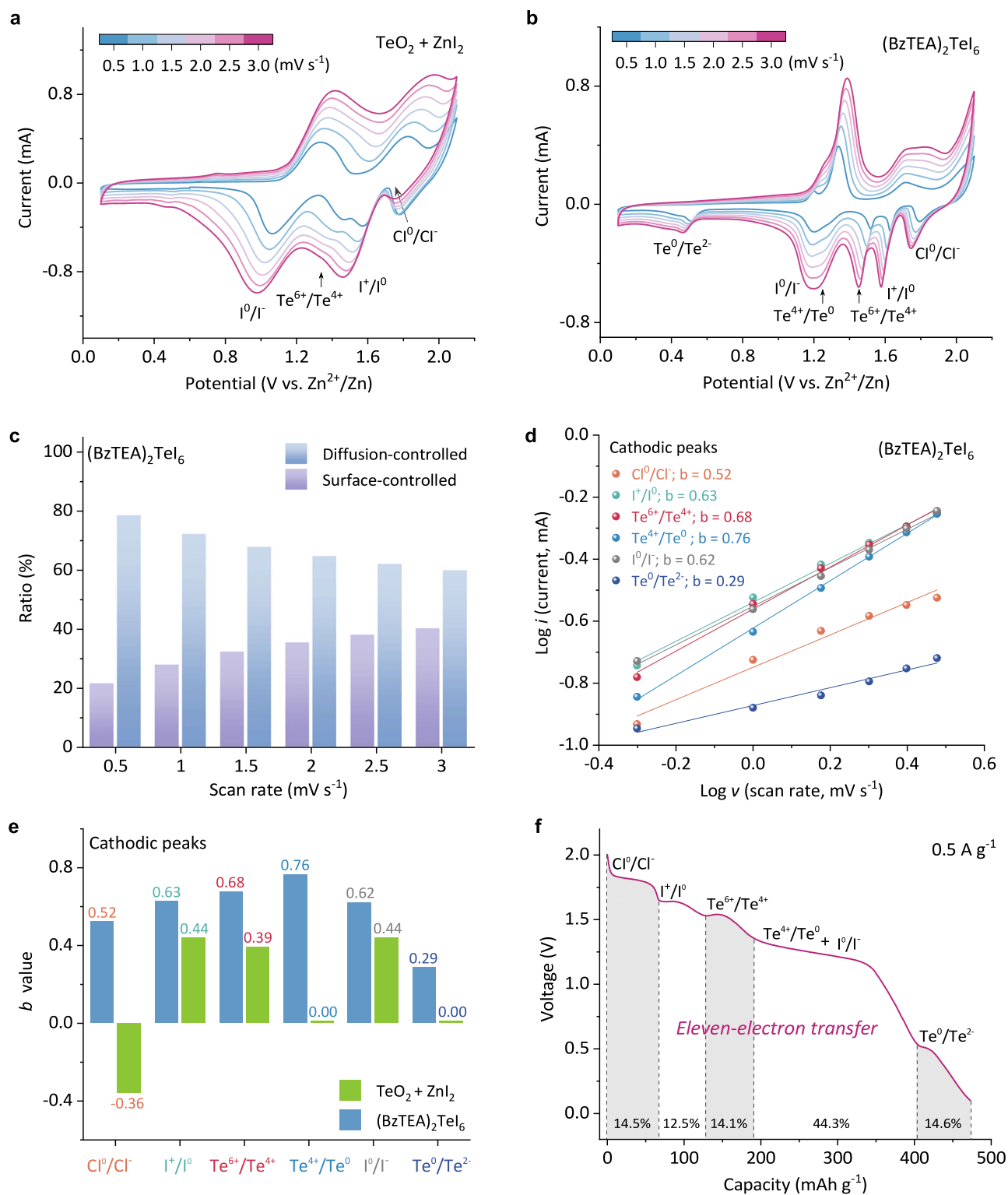


Fig. 2 | Electrochemical properties of the $\text{Zn}||(\text{BzTEA})_2\text{TeI}_6$ battery. CV curves of batteries coupled with **a** “ $\text{TeO}_2 + \text{ZnI}_2$ ” cathode and **b** “ $(\text{BzTEA})_2\text{TeI}_6$ ” cathode in $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ electrolyte. **c** Diffusion-/surface-controlled contribution at different scan rates and **d** the fitting plots between $\log(i)$ and $\log(v)$ of the cathodic

peaks, and **e** the derived b value a summary diagram. **f** Discharge curve at a current density of 0.5 A g^{-1} demonstrates the redox reactions of tellurium and halogen elements.

the coordinated water molecules surrounding Zn^{2+} increased in the form of $[\text{ZnCl}_3(\text{H}_2\text{O})_3]$ and octahedral $[\text{ZnCl}_2(\text{H}_2\text{O})_4]$ cluster, giving rise to the free Cl^- radicals that sat in the electrolyte voids (Supplementary Fig. 21). The mean squared displacement (MSD) study in Fig. 4b proved a much higher mobility of Cl^- ion in $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ (4.30×10^8

$\text{cm}^2 \text{ s}^{-1}$) while that for $\text{ZnCl}_2 \cdot 1.4\text{H}_2\text{O}$ was $8.64 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. The radial distribution function (RDF) result in Fig. 4c confirmed that the coordination number of Cl^- decreased from 3.6 to 3.3 after introducing ChCl . Moreover, the amorphous features of $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ and the absence of undissolved solutes emphasized that the designed

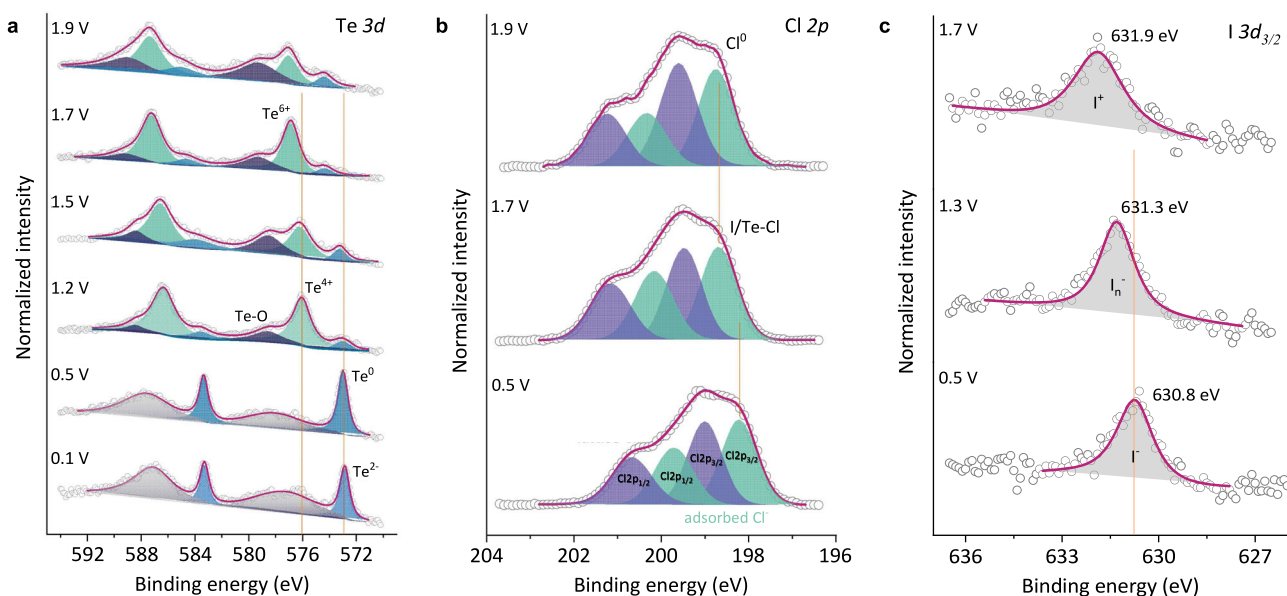


Fig. 3 | Characterization of cyclized (BzTEA)₂TeI₆ perovskite cathode. XPS spectra of **a** Te 3d, **b** Cl 2p, and **c** I 3d_{3/2} core levels.

electrolyte was a homogeneous solution (Supplementary Figs. 22, 23), which offered high Cl⁻ mobility to compensate and stabilize high-valent tellurium ions.

Of note, the (BzTEA)₂TeI₆ perovskite surface synergistically provided a fast channel for transporting Cl⁻ ions, favoring the stabilization of high-valent tellurium ions. As shown in Fig. 4d, the migration energy of Cl⁻ along the (10-1) lattice plane of perovskite oscillated from -9.5 to 9.6 eV. In contrast, the amplitude of the migration barrier on TeO₂ soared to over 156 eV. In addition to kinetic influences, the conversion reactions on the (BzTEA)₂TeI₆ surface were thermodynamically preferred. Specifically, as demonstrated in Fig. 4e, the formation energy of critical chalcogen- and halogen-related redox reactions all decreased, especially for TeCl₃⁺ and TeCl₅⁺, which reduced from 7.7 eV to 5.8 eV and 3.0 eV to 0.8 eV, respectively. Besides, the presence of perovskite surface ended up enhancing the confinement ability toward chalcogen and halogen elements by virtue of halogen bonds (such as Te-I...Cl-Te and Te-I...I) and positive dangling bonds, as summarized in Fig. 4f. The effective coordination among perovskite surface, high-valent cations, and passivating Cl ligand jointly favored their stabilization and associated redox reactions (Supplementary Figs. 24, 25). The more significant adsorption energy of I₅⁻ (-1.97 eV) than I₃⁻ (-1.30 eV) helped explain the proliferation of I₅⁻ during the charging process, pointing out improved reaction kinetics and suppressed shuttle effects (Supplementary Fig. 26).

Electrochemical performance of Zn||(BzTEA)₂TeI₆ battery

We subsequently assembled batteries to examine the practical performance of the perovskite cathode in the Ch_{0.4}Zn_{0.6}Cl_{1.6}·1.5H₂O electrolyte. As presented in Fig. 5a, the Zn||(BzTEA)₂TeI₆ battery delivered a steady capacity of 473 mAh g⁻¹_{Te/I} at 0.5 A g⁻¹ and 258 mAh g⁻¹_{Te/I} at 3 A g⁻¹, which reverted to 411 mAh g⁻¹_{Te/I} after current reset, showing a high capacity retention of 87%. The relatively lower coulombic efficiency (CE) at lower C-rates could be attributed to the loss of chlorine gas during the slow charge/discharge process (Supplementary Fig. 27). This loss was suppressed at higher C-rates due to the shorter cycle time and saturated Cl₂ dissolution in the electrolytes. The corresponding galvanostatic charge-discharge (GCD) curves in Fig. 5b show five stable discharge plateaus at 1.81 V (for Cl⁰/Cl⁻), 1.64 V (for I⁺/I⁰), 1.53 V (for Te⁶⁺/Te⁴⁺), 1.26 V (for overlapped Te⁴⁺/Te⁰ and I⁰/I⁻), and 0.51 V (for Te⁰/Te²⁻), outperforming the Zn||Ch_{0.4}Zn_{0.6}Cl_{1.6}·1.5H₂O||TeO₂ + ZnI₂ and Zn||30 M ZnCl₂||(BzTEA)₂TeI₆

batteries (Supplementary Fig. 28). The highly reversible chalcogen- and halogen-related redox reactions jointly contributed to an eleven-electron transfer mode and verified the feasibility of the organic-inorganic hybrid tellurium iodide perovskite cathode. Figure 5c highlights the advantages of the (BzTEA)₂TeI₆ perovskite cathode that offered a record capacity compared with related references⁵⁵⁻⁶³. Long-term cycling performance was provided in Fig. 5d, e and Supplementary Fig. 29. The Zn||(BzTEA)₂TeI₆ battery successfully cycled 500 times at 1 A g⁻¹ and 3 A g⁻¹ with a high CE of approaching 98% and capacity retention of over 77% and 82%, respectively, superior to the reported counterparts (Supplementary Fig. 30). Moreover, the Zn||(BzTEA)₂TeI₆ battery retained 79.4% of its initial capacity after a storage period of 5 h due to the suppressed shuttle effect, while that for the Zn||“TeO₂ + I₂” battery was down to 16.7% (Fig. 5f and Supplementary Fig. 31). The viability of the Zn||(BzTEA)₂TeI₆ battery was additionally confirmed using a DC-DC converter, which maintained a consistent voltage output of 3.29 V for more than 250 min (Supplementary Fig. 32). As a summary, Fig. 5g emphasizes the importance of the special eleven-electron transfer mode actualized by the perovskite cathode and proper electrolyte design^{39,61-68}. The structural advance endowed the zinc ion batteries with a high average voltage of 1.3 V and a large energy density of over 577 Wh kg⁻¹_{Te/I}. The pouch cell based on the (BzTEA)₂TeI₆ perovskite cathode further gave a high capacity of 113 mAh (at 10 mA cm⁻²) with a capacity retention of over 66% after 100 cycles (Fig. 5h). The pouch cell also presented good storage stability with a capacity loss of less than 24% after a resting time of 12 h (Supplementary Fig. 33).

Discussion

In conclusion, the designed (BzTEA)₂TeI₆ perovskite, as a proven methodology to actualize both B-site chalcogen and X-site halogen redox reactions, were examined upfront as the conversion-type cathode materials. The (BzTEA)₂TeI₆ cathode effectively confined active chalcogen and halogen elements and allowed fast transfer of chloride ions, stabilizing high-valent tellurium cations in the form of tellurium chloride ions. After coupling with the adaptive Ch_{0.4}Zn_{0.6}Cl_{1.6}·1.5H₂O electrolyte, an eleven-electron transfer was successfully realized in the Zn||(BzTEA)₂TeI₆ batteries as the emerging redox pairs including Cl⁰/Cl⁻ (1.81 V), I⁺/I⁰/I⁻ (1.64 and 1.26 V), Te⁶⁺/Te⁴⁺ (1.53 V), Te⁴⁺/Te⁰ (1.26 V), and Te⁰/Te²⁻ (0.51 V), all of which benefited a high energy density of over 577 Wh kg⁻¹_{Te/I}. As a result, the Zn||(BzTEA)₂TeI₆ battery

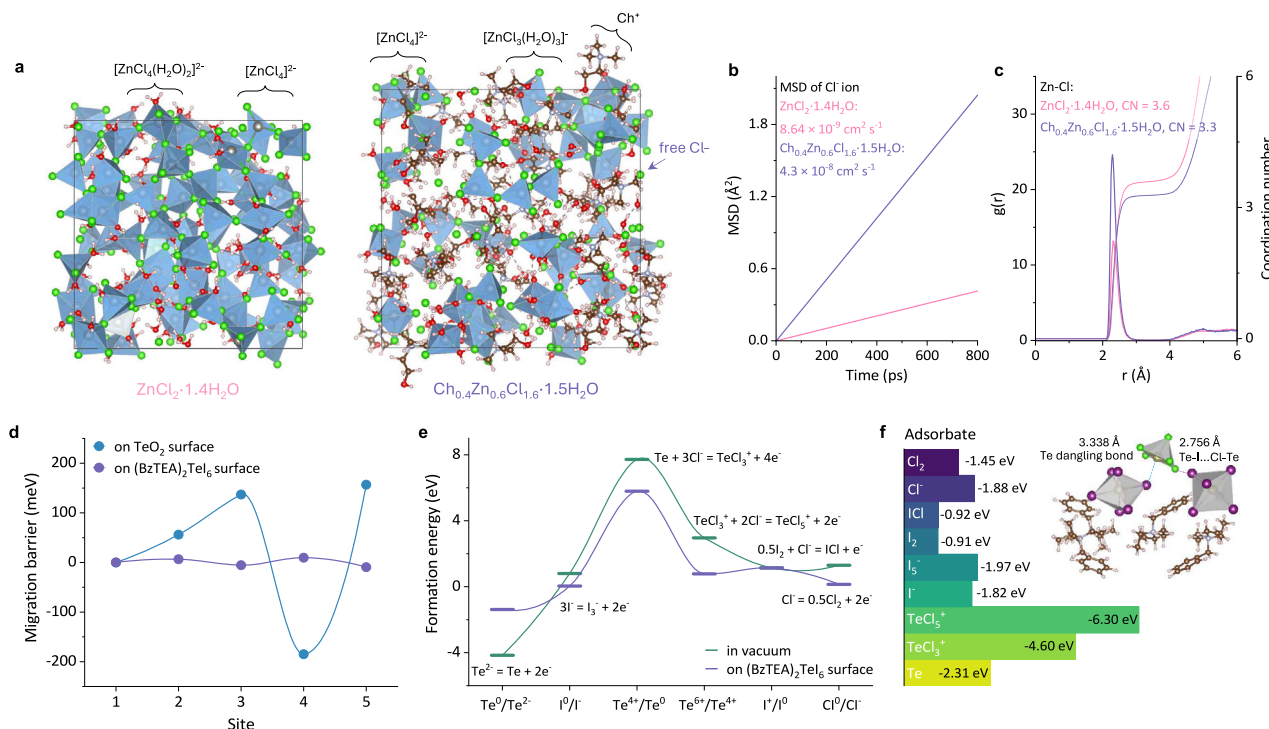


Fig. 4 | Theoretical studies of the eleven-electron transfer. **a** Visualization of $\text{ZnCl}_2 \cdot 1.4\text{H}_2\text{O}$ (left) and $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ (right) electrolytes. **b** MSD and **c** RDF spectra derived from MD simulations. **d** Migration energy of chloride ions on TeO_2 and perovskite surface. **e** Formation energy of associated redox pairs in vacuum

and on perovskite surface. **f** Surface adsorption energy of $(\text{BzTEA})_2\text{Te}_6$ toward intermediate tellurium and halogen elements. Inset in **f** denotes the coordination between perovskite and TeCl_5^+ ions.

demonstrated a high capacity of $473 \text{ mAh g}^{-1}_{\text{Te}/1}$ at 0.5 A g^{-1} and experienced 500 cycles at 1 A g^{-1} with a capacity of over 77%. The corresponding pouch cell delivered a high capacity of 113 mAh, showcasing promising storage stability.

Methods

Chemicals and reagents

Tellurium oxide ($\geq 99\%$), benzyltriethylammonium chloride (BzTEACl or TEACl, 98%), hydrogen iodide (HI, 48%), isopropanol (99%), zinc chloride (98%), choline chloride (ChCl, 98%), zinc sulfate (ZnSO_4 , AR), zinc acetate ($\text{Zn}(\text{OAc})_2$, 99%), zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$, 98%) and 1-methyl-2-pyrrolidinone (NMP, 98%) were purchased from Aladdin. Polyvinylidene difluoride (PVDF) was purchased from SOLVAY (Solef 1008). The conductive agent, Ketjenblack EC-300J, was purchased from Nouryon. All chemicals were used as received without further treatment.

Preparation of $(\text{BzTEA})_2\text{Te}_6$ microcrystal cathode and battery assembly

The perovskite microcrystals were obtained by a saturated recrystallization method. Specifically, 0.1 mmol of TeO_2 and 0.2 mmol of BzTEACl were added into 1 ml HI solution. The mixture was heated to 110°C and held for over 1 h with vigorous stirring, subsequently cooling to room temperature. The obtained black residue was washed with isopropanol and dried under a vacuum. The $(\text{BzTEA})_2\text{Te}_6$ perovskite microcrystals were mixed and ground with Ketjenblack and PVDF binder in NMP with a mass ratio of 7:2:1 for 1 h. The obtained liquid slurry was evenly covered on the carbon cloth substrate, followed by a vacuum bakeout process at around 80°C overnight. The mass loading of the perovskite cathode was estimated to be $1\text{--}1.2 \text{ mg cm}^{-2}$. 39 mmol ZnCl_2 was dissolved in 1 ml H_2O at 100°C and slowly cooling to 30°C , and the clear supernatant was used as the $\text{ZnCl}_2 \cdot 1.4\text{H}_2\text{O}$ electrolyte. 0.4 mol ChCl and 0.6 mol ZnCl_2 were

dissolved in 1.5 mol H_2O to form the $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ electrolyte. Specifically, 1 g of $\text{Ch}_{0.4}\text{Zn}_{0.6}\text{Cl}_{1.6} \cdot 1.5\text{H}_2\text{O}$ contains 0.16 g H_2O , 0.51 g ChCl, and 0.33 g ZnCl_2 . The cathode, zinc metal anode ($100 \mu\text{m}$, 1 cm^2), and a glass fiber ($420 \mu\text{m}$, 1.1 cm^2) sat in between were packed in a Swagelok cell for further evaluation (at room temperature without the need for a chamber).

Material and electrochemical characterizations

Absorption spectra were collected using a Shimadzu UV 3600 UV/visible/IR spectrophotometer, while Fourier-transform infrared (FTIR) measurements were conducted with a Perkin Elmer FT-IR spectrophotometer. Raman measurements were performed on a WITec Alpha300 R confocal Raman imaging system with a 532 nm laser. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Smartlab X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was carried out on a PHI model 5802, with the carbon spectrum serving as a calibration reference. The FEI Quanta 250 scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were utilized to examine the morphology and elemental composition of the samples. Cyclic voltammograms (CVs) and related electrochemical data were collected on a CHI 660E electrochemical workstation. The long-term stability and rate performance of the batteries were evaluated using the LAND battery testing system at room temperature (with a cut-off potential of 2.04 V).

Calculation and theoretical simulations

The b value was derived from the equation $i = av^b$ where i is the response current, v is the sweep rate. The b value of 0.5 signifies a purely faradaic (diffusion-controlled) process while a b value of 1 indicates a purely capacitive (surface-controlled) process, as outlined in the initial report by Lindquist et al. in 1997⁶⁹. The quantitative contribution of the charge storage process was evaluated by the equation $i = k_1v + k_2v^{0.5}$ where k_1v is the surface-controlled process and $k_2v^{0.5}$ is

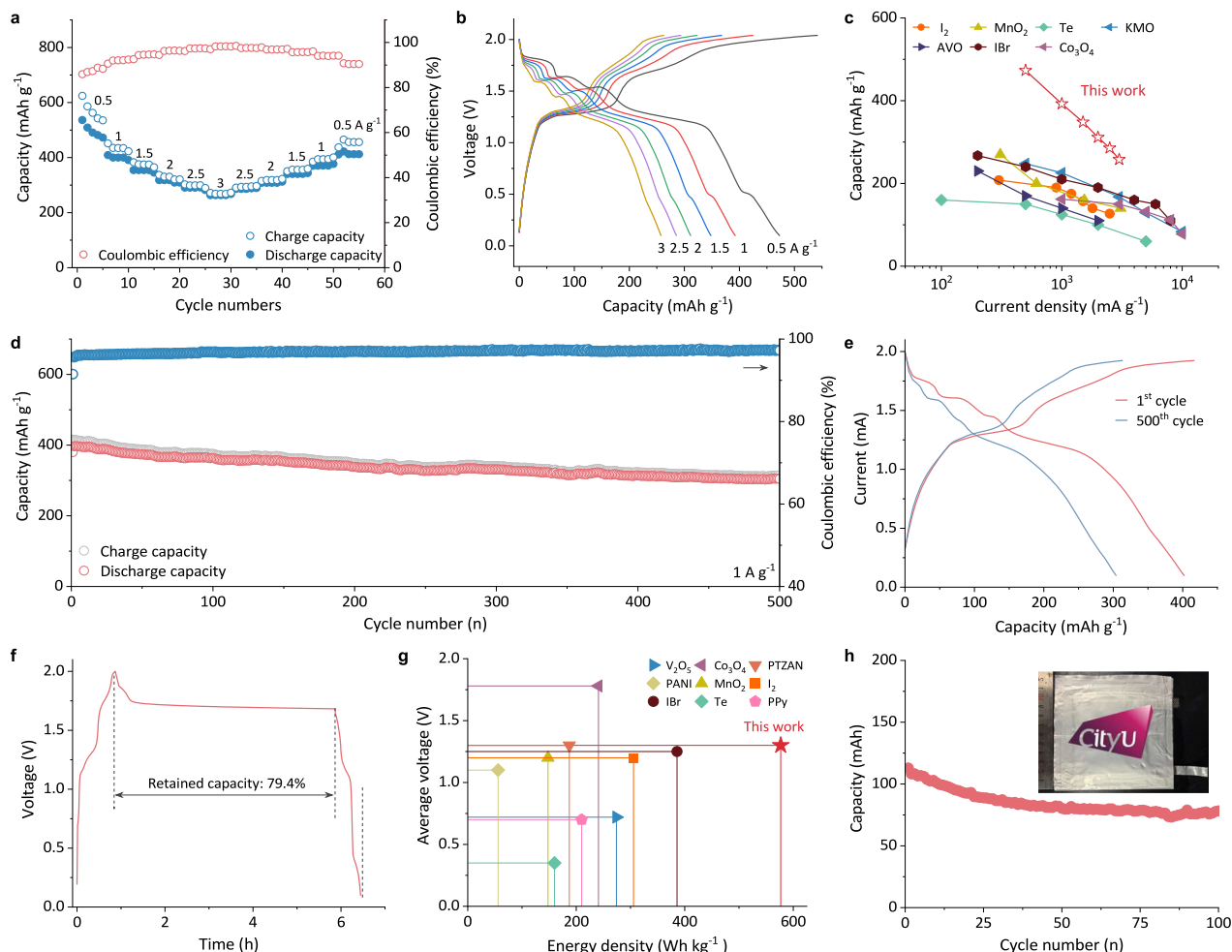


Fig. 5 | Cycling performance of the Zn||(BzTEA)₂TeI₆ battery. **a Rate performance, **b** the corresponding GCD curves, and **c** comparison with typical cathode of zinc ion batteries. **d** Long-term cycling property of zinc battery at 1 A g⁻¹, **e** selected GCD curves, and **f** the self-discharge profile. **g** comparison of relative aqueous zinc ion batteries regarding average voltage and energy density. **h** Cycling performance of the pouch cell with a high loading mass of 12 mg cm⁻². The sources of referential**

samples in **c** and **g** are cited as ref. 55 for I₂, ref. 56 for MnO₂, ref. 58 for Te, ref. 59 for KMO (K_{0.27}MnO₂·0.54H₂O), ref. 60 for AVO (Ag_{0.3}V₂O₅), ref. 61 for IBr, ref. 63 for V₂O₅, ref. 62 for Co₃O₄, ref. 64 for PTZAN [4,4'-(10H-phenothiazine-3,7-diyl)bis(N,N-diphenylaniline)], ref. 65 for PANI (Polyaniline), ref. 66 for MnO₂, ref. 67 for I₂, ref. 61 for IBr, ref. 39 for Te, ref. 68 for PPy (Polypyrrole).

the diffusion-controlled part³³. The energy density was calculated by integrating the battery voltage over the specific capacity which was determined based on the mass of active elements (tellurium and iodine). The density functional theory (DFT) was employed for first-principles calculations using the Dmol3 mode within a numerical atom-centered basis function framework. The Perdew-Burke-Ernzerhof (PBE) method was used for electronic exchange-correlation interactions, while the Generalized Gradient Approximation (GGA) method with PBE formulation was applied for structural optimization⁷⁰. DFT semi-core pseudopotentials were chosen for the core treatment of relativistic effects, replacing core electrons with a single effective potential⁷¹. The adsorption energy, E_{ads} , was calculated using the formula $E_{ads} = E_{ensemble} - E_{absorbent} - E_{adsorbate}$, where the subscript represents the energy of the absorbent, adsorbate, or the entire system post adsorption⁷². The Raman spectrum of I₅⁻ was simulated under the excitation of 532 nm laser at 273 K, with Lorentzian smearing of 20 cm⁻¹.

Data availability

All data that support the findings of this study are presented in the manuscript and Supplementary Information or are available from the

corresponding author upon request. Source data are provided with this paper.

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Author contributions

S.W., X.Y. and C.Z. designed the study. C.Z. supervised the experiments. S.W., Z.W., H.H., X.G., Y.W., Z.C., D.Z. and X.Z. conducted structural, electrochemical, and spectroscopic characterizations and analyzed the data. S.W. performed the theoretical calculations. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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