Aqueous Li–ion battery enabled by halogen conversion–intercalation chemistry in graphite

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The use of ‘water-in-salt’ electrolytes has considerably expanded the electrochemical window of aqueous lithium-ion batteries to 3 to 4 volts, making it possible to couple high-voltage cathodes with low-potential graphite anodes1–4. However, the limited lithium intercalation capacities (less than 200 milliamperes-hours per gram) of typical transition-metal oxide cathodes5,6 preclude higher energy densities. Partial5–8 or exclusive9 anionic redox reactions may achieve higher capacity, but at the expense of reversibility. Here we report a halogen conversion–intercalation chemistry in graphite that produces composite electrodes with a capacity of 243 milliamperes-hours per gram (for the total weight of the electrode) at an average potential of 4.2 volts versus Li/Li+. Experimental characterization and modelling attribute this high specific capacity to a densely packed stage-1 graphite intercalation compound, C_{3.5}[Br_{0.5}Cl_{0.5}] (equation (1)), which can form reversibly in water-in-bisalt electrolyte. By coupling this cathode with a passivated graphite anode, we create a 4-volt-class aqueous Li-ion full cell with an energy density of 460 watt-hours per kilogram of total composite electrode and about 100 percent Coulombic efficiency. This anion conversion–intercalation mechanism combines the high energy densities of the conversion reactions, the excellent reversibility of the intercalation mechanism and the improved safety of aqueous batteries.

Using the anionic-redox reaction of halide anions (Br− and Cl−) in graphite, a composite electrode containing equimolar lithium halide salts (LiBr)0.5(LiCl)0.5–graphite (hereafter denoted as LBC-G) was synthesized by mixing anhydrous LiBr and LiCl with graphite at an optimal mass ratio of 2:1:2 (corresponding to a molar ratio of (LiBr)_{0.5}(LiCl)_{0.5} C_{3.5}; see Methods). Herein, the highly concentrated water-in-bisalt (WiBS) electrolyte confined partially hydrated LiBr/LiCl within the solid cathode matrix, and upon oxidation, Br+ and Cl− are stabilized by sequential intercalation into the graphite host as solid graphite intercalation compounds (GICs). This new cathode chemistry inherits the high energy of the conversion reaction and the excellent reversibility of topotactic intercalation, and provides batteries that differ fundamentally from the ‘dual-ion’ batteries that reversibly intercalate complex anions (PF6−, BF4−, TFSI−; TFSI, bis(trifluoromethanesulfonylimide) into graphite at low packing density, where these stable anions experience no redox reactions, resulting in low capacities10,11 below 120 mA h g−1.

Upon exposure to water-in-bisalt (WiBS) electrolyte, the anhydrous LiBr/LiCl extracts approximately 2.4% water from WiBS (Extended Data Fig. 1a, b) forming a hydrated LiBr/LiCl layer on the LBC-G surface (illustrated in Fig. 1a; estimated overall formulations of hydrated salts: LiBr·0.34H2O-LiCl·0.34H2O; electrode-electrolyte = 1:20), which accelerates the halogens’ redox reaction in the form of liquefied anions. Owing to the immiscibility of halide anions in WiBS, this hydrated layer is thermodynamically phase-separated from the bulk electrolyte and builds dynamic water equilibrium (Extended Data Fig. 1c), as previ-ously observed for lithium polysulfides4. Such a liquefied layer allows fast Li+ transport but confines all the halide anions within the cathode, as evidenced by both molecular dynamics (MD) simulations (Extended Data Fig. 1d) and the extremely low Cl/Br content (<32 p.p.m.) detected by chromatographic analysis in WiBS equilibrated with LiCl/ LiBr solution for 500 h (Extended Data Fig. 1e).

The electrochemical behaviours of LBC-G were first evaluated in a three-electrode cell with an aqueous gel polymer electrolyte based on WiBS (see Methods). The cyclic voltammetry (Fig. 1b) and charge/discharge profiles (Fig. 1c, d) indicated two distinct reaction voltage ranges, 4.0–4.2 V for Br− intercalation and 4.2–4.5 V for Cl− intercalation, which deliver a highly reversible discharge capacity of 243 mA h g−1 (for the total mass of LBC-G composite), 82% of which is retained over 230 cycles at a Coulombic efficiency of 100% after the 80th cycle at a current density of 80 mA g−1 (0.2 C). The two-step redox reactions correspond to (Fig. 1a):

LiBr + C_{n} ↔ C_{n}[Br] + Li+ + e− 4.0–4.2 V (1)

LiCl + C_{n}[Br] ↔ C_{n}[BrCl] + Li+ + e− 4.2–4.5 V (2)

where n is the molar ratio of carbon atoms to the intercalated halogens in the GIC. Upon charging, Br− is the first species within the hydration layer to oxidize to a near-zero state (Br0) and to intercalate into graphite, forming C_{n}[Br] (equation (1)). Further charging oxidizes and intercalates Cl− (equation (2)), forming a mixed intercalation compound, C_{n}[BrCl]. The oxidation of each halogen involves a one-electron transfer reaction (theoretical capacity: 309 mA h g−1 for LiBr, 632 mA h g−1 for LiCl12 and the release of one Li+ into the bulk electrolyte. Upon discharging, the reverse process occurs: C[Cl] and Br0 successively de-intercalate from the graphite interlayer, reduce into halides and recombine with Li+ to form both solid LiCl/LiBr crystals and liquefied halides outside of the graphite interlayer (Extended Data Fig. 2a–d). WiBS plays another essential role in this chemistry by pushing the oxidation potential of water to about 4.9 V versus Li/Li+ (refs 13,14), realizing full reversibility of the halide oxidation/reduction without electrolyte decomposition (Extended Data Fig. 3). The galvanostatic intermittent titration technique (GITT) was used to examine the quasi-equilibrium potentials and kinetics of reactions at different stages. The quasi-equilibrium potentials are about 4.05 V for Br− and about 4.35 V for Cl− oxidation/intercalation, respectively (Fig. 1e), whereas the total diffusion coefficients were estimated to be 10−15–10−13 cm2 s−1 (red and blue curves in the inset of Fig. 1e). The diffusion coefficients were also estimated with electrochemical impedance spectroscopy (EIS; Fig. 1f), and fitting with the equivalent circuit in Extended Data Fig. 4a yielded apparent ionic diffusion coefficients of 6.85 × 10−15–2.07 × 10−14 cm2 s−1 (green circles in the inset of Fig. 1e), in excellent agreement with the GITT results. Considering the extremely high diffusion coefficients of halogenides in the graphite interlayer13 (EIS independence of graphite size shown in Extended Data Fig. 4b),
80 mA g−1 charge/discharge profiles of the LBC-G cathode at a current density of stage-I C₃.5 [Br₀.625 Cl₀.375] (E); and stage-I C₃.5 [Br₀.5 Cl₀.5] (F). Although sulfur constitutes the rate-determining step in this chemistry. Further charging introduced a feature between solid salts and the graphite surface constitutes the rate-determining step in this chemistry.

The red curve indicates the quasi-equilibrium potential at different lithiation/de-lithiation stages, which was constructed from the average value of each open-circuit voltage period during charge/discharge. Inset, the finite diffusion coefficients D of the reactants, estimated from GITT and EIS measurements (see Methods). Nyquist plots for the LBC-G cathode, obtained by EIS tests at various SOCs in a three-electrode cell. The dotted lines are fitting curves obtained by using the equivalent circuit shown in Extended Data Fig. 4a. Inset, the same plots in full scale. $Z_{\text{real}}$ and $Z_{\text{imag}}$ are the real and imaginary parts of the impedance, respectively.

Practical gravimetric energy density of the LBC-G cathode compared with that of representative state-of-the-art cathodes, with average discharge voltages referred to Li/Li⁺. Intercalation-type: LiFePO₄ (LFP), LiCoO₂ (LCO), LiNi₀.₅Co₀.₅Al₀.₅O₂ (NCA), LiNi₀.₅Co₀.₅Mn₀.₅O₂ (NCM); conversion-type: FeF₂, C₆₀, Fe₅₀S₃, Li₂S. The values were calculated from the reversible gravimetric capacities using the total mass of the cathode (including active, inactive and polymeric binder) and average discharge voltages. The mass ratios of the active materials are 90% for intercalation-type cathodes, 70% for metal fluorides and 50% for sulfur.

The mass transfer of Br⁻ and Cl⁻ between solid salts and the graphite surface constitutes the rate-determining step in this chemistry.

Figure 1g compares gravimetric energy densities of the LBC-G composite with state-of-the-art cathode materials. LBC-G provides a practical gravimetric capacity of 231 mAh g⁻¹ (for the total weight of the electrode) and volumetric capacity of 450 mAh mL⁻¹ (total volume of the electrode) at an average discharge voltage of 4.2 V, yielding an unprecedented energy density of 970 Wh kg⁻¹, almost twice as high as that of transition-metal intercalation cathodes. Although sulfur conversion chemistry provides comparable gravimetric energy density, LBC-G is much superior per volume because of its more compact storage of halogens in the graphite interlayer (Extended Data Fig. 4c).

In situ Raman spectroscopy (100–550 cm⁻¹) was performed to probe the intercalation mechanism of halogen into graphite (Fig. 2a). With the state of charge (SOC) at 0%–50%, a characteristic peak (at frequency $\omega_0 = 242$ cm⁻¹) was detected, which corresponds to the stretch-mode of intercalated Br₂. Further charging introduced a feature corresponding to the BrCl intercalant ($\omega_0 = 310$ cm⁻¹), verified by a reference prepared by chemical intercalation of BrCl into the graphite (Extended Data Fig. 6g). The peak intensity of the BrCl intercalant is much superior per volume because of its more compact storage of halogens in the graphite interlayer (Extended Data Fig. 4c).

In Fig. 1g, the Nyquist plots for the LBC-G cathode, obtained by EIS tests at various SOCs in a three-electrode cell. The dotted lines are fitting curves obtained by using the equivalent circuit shown in Extended Data Fig. 4a. Inset, the same plots in full scale. $Z_{\text{real}}$ and $Z_{\text{imag}}$ are the real and imaginary parts of the impedance, respectively. g. Practical gravimetric energy density of the LBC-G cathode compared with that of representative state-of-the-art cathodes, with average discharge voltages referred to Li/Li⁺. Intercalation-type: LiFePO₄ (LFP), LiCoO₂ (LCO), LiNi₀.₅Co₀.₅Al₀.₅O₂ (NCA), LiNi₀.₅Co₀.₅Mn₀.₅O₂ (NCM); conversion-type: FeF₂, C₆₀, Fe₅₀S₃, Li₂S. The values were calculated from the reversible gravimetric capacities using the total mass of the cathode (including active, inactive and polymeric binder) and average discharge voltages. The mass ratios of the active materials are 90% for intercalation-type cathodes, 70% for metal fluorides and 50% for sulfur.
increased with charging of LBC-G to 4.5 V. The interaction with the graphene layer weakened the interatomic bonds of halogen intercalants, causing a frequency downshift from 318 cm\(^{-1}\) for free Br\(_2\) (liquid) to 242 cm\(^{-1}\) for the Br\(_2\) intercalant, and from 427 cm\(^{-1}\) for free BrCl (gaseous) to 310 cm\(^{-1}\) for the BrCl intercalant.\(^{15,16}\) We note that during charging/discharging between 3.2 V and 4.5 V, no free Br\(_2\) or BrCl peaks were detected, unless we deliberately destabilized the fully intercalated BrCl-GIC with a high-intensity laser beam (red curve in Fig. 2a); this suggests that all the halogens were intercalated into the graphite structure rather than absorbing on its surface. Upon discharging, the original Raman spectra were restored, demonstrating the reversibility of LCC-G chemistry.

Ex situ X-ray absorption near-edge structure (XANES) spectra reveal how the redox reaction sequence of halogens occurs in the LBC-G cathode (Fig. 2b). For the Br K edge, a distinct and sharp peak at \(13,473 \text{ eV}\), attributed to the Br intra-atomic \(\pi^*\) transition, \(\rightarrow\) appears immediately upon charging. The intensity of this peak, which reflects the hole density of Br \(4p\) orbitals, gradually increased, accompanied by a blue-shifted absorption edge (\(1s \rightarrow \text{ continuum}\))\(^{17}\). This provides clear evidence that Br\(^{-}\) accepts a hole to be oxidized to Br\(^{0}\). For the Cl K edge (Fig. 2c), only a single absorption edge (\(1s \rightarrow \text{ continuum}\)) was observed at the first charge plateau (SOC 0%–50%), indicating that all Cl remained as Cl\(^{-}\). Cl\(^{-}\) oxidation occurred only at the second charge plateau (SOC 50%–100%), as demonstrated by the appearance of the Cl intra-atomic \(1s \rightarrow 3p\) transition peak (about 2,821 eV) due to the removal of a hole by Cl\(^{-}\). By comparing with the reference spectra (dashed lines in Fig. 2b) of chemically intercalated Br\(_2\)-GIC and liquid Br\(_2\), we see that Br was mostly oxidized, but had not entirely reached Br\(^{0}\) at the first charge plateau (SOC 0%–50%). Both density functional theory (DFT) simulations (Fig. 2d) and the literature\(^{1}\) suggest that Br remains at an oxidation state of approximately \(-0.16\) in Br\(_2\)-GICs at 50% SOC. Only after the subsequently intercalated Cl associates with previously intercalated Br does the Br-oxidation state further increase to nearly Br\(^{0}\) (oxidation state \(-0.05\)), owing to the lower electron negativity of Br relative to Cl. The oxidation state of Cl becomes \(-0.25\).

Additional evidence supporting this conversion–intercalation mechanism comes from the charge/dischARGE profiles of LBC-G at different LiBr/LiCl molar ratios (Fig. 2e, f). The capacity ratios of the two charge/discharge plateaus are highly correlated with the LiBr/LiCl molar ratio. The specific capacities calculated by the weights of LiBr and LiCl in the LBC-G cathodes in the high-voltage plateau increases with increasing LiBr/LiCl ratio, \(>4.25\) V (Fig. 2e, Extended Data Fig. 5a) at a low rate of \(\leq 0.2\) C (5-h charge/discharge) is very close to the theoretical redox capacity of LiBr (309 mAh g\(^{-1}\))\(^{20}\), whereas that of the high-potential charging plateaus \(>4.25\) V, when calculated using the weights of LiCl, is close to the theoretical redox capacity of LiCl (632 mAh g\(^{-1}\))\(^{20}\). Interestingly, the Coulombic efficiency of the LBC-G cathodes in the high-voltage plateau increases with increasing LiBr/LiCl ratio, which implies that the single intercalation of Cl\(^0\) in graphite is thermodynamically forbidden at room temperature\(^{20}\), unless it is paired with a Br\(^{0}\). In sharp contrast, neat LiBr\(_{0.5}\)LiCl\(_{0.5}\) in the absence of graphite could deliver a high oxidation capacity during the initial charging, but its discharge capacity is very low owing to the
loss of gaseous halogens (Extended Data Fig. 5b). The carbon host can improve the reversibility of reactions by adsorbing halogens on its surface (Extended Data Fig. 5c), whereas the Coulombic efficiency improves with the graphitization degree of carbon hosts (Extended Data Fig. 5d–h), suggesting that graphitic materials provide a host structure that can reversibly accommodate halogen oxidation products. The structural evolution of the graphite super-lattice was revealed using in situ Raman spectroscopy (1,200–2,850 cm\(^{-1}\)) during halogen intercalation (Fig. 3a)\(^{21}\). Upon halogen intercalation, the graphite G band (1,584 cm\(^{-1}\)) diminishes and gradually evolves into a feature corresponding to a stage-II GIC structure at 50% SOC, whereas at 100% SOC the peak further shifts to 1,631 cm\(^{-1}\), indicating a stage-I GIC.
The in-plane configuration and coordination of halogen intercalants in graphite provide knowledge that is necessary to determine the optimum intercalation concentration of this cathode chemistry. Because such structure is independent of the overall intercalate concentration, the stoichiometry \( n \) of \( C_7^m[Br] \) and \( C_7^m[BrCl] \) always remains the same in each intercalation domain. Ex situ high-energy XRD (perpendicular incidence) for LBC-G at 50% and 100% SOC (Fig. 3d) showed multiple asymmetric and overlapping peaks, revealing mild long-range ordering of intercalant in-plane configurations. At 50% SOC, only three peaks in low diffraction angles can be indexed according to the single-crystal \( Br_2 \)-GIC reference, indicating multi-phase coexistence, localized disorder and structure strain. DFT simulations based on two stoichiometries with \( n \) equal to integer multiples of 7 and 8 (Extended Data Fig. 7) yield zig-zag polymeric-like chains of \(-Br<-Br-\) or \(-Br-Cl-\) with nearest in-plane distance of 2.4–3.2 Å (Fig. 3c, f, insets). All these configurations have similar potentials (within 20 mV), indicating that the real materials might be slightly disordered owing to the coexistence of these idealized model structures, in accordance with ex situ XRD patterns (Fig. 3d). MD simulations (Extended Data Fig. 8) predict that close \(-Br<-Br-\) contacts may serve as hotspots for interconversion between different phases.

By fitting Br spectra acquired by extended X-ray absorption fine structure (EXAFS) measurements of LBC-G at 50% and 100% SOC (Fig. 3e, f), the most compatible models were \( C_{7m}[BrBr] \) and \( C_{7m}[BrCl] \), both with two sets of the nearest in-plane distances (Br-X1 and Br-X2) for the LBC-G cathode. The measured Br-Br distances of 2.4–3.2 Å are in agreement with the EXAFS results. The in-plane and out-of-plane Br-Br distances show characteristic features of \( Br_2 \)-GIC, indicating the coexistence of intercalates with different stoichiometries. The structural model with Br-Br distances of 2.4–3.2 Å is consistent with the experimental data, suggesting that the real materials might be slightly disordered due to the coexistence of these idealized models.
Br·X2, X = Br or Cl) instead of consistent distances for C6Br[BrBr] and C6Cl[BrCl] (Extended Data Fig. 9). Because of the interaction of graphene planes with π electrons, the average nearest-in-plane distances of halogen intercalants were 2.50 Å for Br·Br, 3.15 Å for Br·Br2, 2.43 Å for Br·Cl1 and 3.00 Å for Br·Cl2, somewhat longer than the bond lengths in free Br2 (about 2.30 Å) and BrCl (2.18 Å) molecules. However, these nearest-in-plane distances are much shorter than those of alkali-metal GICs (4.30–4.92 Å) and large-anion GICs (8–10 Å)29, which means that the halogen intercalants possess one of the highest in-plane densities among all GICs reported. This high-density packing is mainly due to the near-zero oxidation valence of halogen intercalates, which generates much lower Coulomb repulsion from average effective charge of about −0.16 per halogen atom (Fig. 2d), compared with about +0.90 for Li-GIC30 and −1 for complex anions.

Aqueous lithium-ion (LIB) full cells were constructed using an aqueous gel electrolyte derived from a WIBS® and LBC-G cathode coupled with a graphite anode protected by a highly fluorinated ether (HFE) polymer gel2, which was developed earlier for 4-V aqueous LIB (cell configuration in Extended Data Fig. 4d, e). A stable discharge capacity of 127 mAh g−1 (total anode/cathode mass) was obtained at an average voltage of 4.1 V at 0.2 C (Fig. 4a), and 74% of this initial capacity was retained over 150 cycles at an average Coulombic efficiency of 99.8% (Fig. 4b). The low self-discharge rate (Extended Data Fig. 2f) demonstrated that the super-concentrated aqueous gel electrolyte effectively suppressed parasitic reactions, especially water decomposition and loss of halogen active material from the cathode.

Because the formation of a hydrated LiBr/LiCl layer via extraction of water from WIBS® is critical for achieving high power density, the WIBS/ cathode mass ratio affects the rate performance. The rate capability was severely compromised when the electrolyte/electrodes mass ratio was reduced from 4:1 to 1.2 (Fig. 4c). However, a high WIBS/cathode ratio is not desired either, because it reduces the energy density. As a simple solution to this dilemma, the anhydrous salts were replaced by their monohydrate forms (LiBr·H2O/LiCl·H2O; Extended Data Fig. 1b), resulting in almost identical charge/discharge profiles (Fig. 4a, b). The rate capability of such full cells is much better, while the impact of the electrolyte/electrodes mass ratio is minimized. Given that battery performances constructed with LiBr/LiCl monohydrates are independent of the electrolyte amount, we estimated the energy density of such aqueous LIBs to be around 460 Wh kg−1 of the electrolyte amount, we estimated the energy density of such aqueous LIBs to be around 460 Wh kg−1 (total anode/cathode mass) was obtained at an average Coulombic efficiency of 99.8% (Fig. 4b).

Aqueous lithium-ion battery that is cost-effective, safe and flexible.

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METHODS

Preparation of electrodes. For the three-electrode cells, LBC-G composite was obtained by homogeneously mixing anhydrous LiBr (99.9%; Sigma-Aldrich), LiCl (99.9%; Sigma-Aldrich) and synthetic graphite powder (TIMCAL TIMREX K54; average particle size of about 4.1 μm) by zirconia ball milling for 15 min. The LiBr:LiCl molar ratio was 1:1, whereas the LiBr:LiCl:graphite mass ratio was about 2:1:2. In the full cells with LiBr/LiCl monohydrates, all the procedures were the same, except that the anhydride and the active material were replaced by LiBr·H2O (99.95%; Sigma-Aldrich) and LBC (99.95%; Sigma-Aldrich). Other control samples were obtained by adjusting the composites to the following mass ratios: LiBr:LiCl:titantium nanopowder, about 2:1:60 for (LiBr)0.05(LiCl)0.95; LiBr:LiCl:active carbon, about 2:1:9 for (LiBr)0.05(LiCl)0.95; LiBr:LiCl:graphitised acetylene black, about 2:1:9 for (LiBr)0.05(LiCl)0.95:CB. Composite LBC-G cathodes were fabricated by compressing LBC-G composite and polytetrafluoroethylene (PTFE; Sigma-Aldrich) at a weight ratio of 95:5 on a titanium metal mesh (Alfa Aesar; 100 mesh). The areal loading of the cathode material was about 38 mg cm⁻². The thickness of the cathode was about 2 μm. The graphite anodes were fabricated by using mesocarbon microbead graphite powder (MTI Corp.) and PTFE at a weight ratio of 9:1 on a stainless steel mesh (200 mesh).

Preparation of electrolytes. The liquid WIBS aqueous electrolytes were first prepared by dissolving 21 mol kg⁻¹ LiTFSI (>98%; TCI Co. Ltd) and 7 mol kg⁻¹ lithium trifluoromethanesulfonate (LiOTf; 99.995%; Sigma-Aldrich) in water (HPLC grade). Aqueous gel electrolytes were prepared by mixing 20 wt% poly(ethylene oxide) (PEO; viscosity-average molecular weight, Mv ≈ 600,000; Sigma-Aldrich) or 10 wt% polyvinyl alcohol (weight-average molecular weight, Mw = 146,000–186,000; >99% hydroxylated; Sigma-Aldrich) with WIBS electrolyte and heated at 80 °C for 1 h in sealed glass moulds. After cooling to room temperature, sticky semi-solid WIBS gel electrolytes were obtained, which could be changed into any shape at 50 °C. The preparation of HFE-PEO gel protection coating has been reported previously. Briefly, the coating gel is prepared by mixing 1,1,2,2-tetrafluoroethethyl-2',2',2'-trifluoroethyl ether (Daikin America or Apollo) with 0.5 M LiTFSI (denoted as LiTFSI-HFE gel) and 10 wt% PEO in HFE- fluoroethylene carbonate (with volume ratio 95:5) and heated at 70 °C for 5 min under vigorous stirring.

Preparation of chemical GICs as reference samples. Reference samples of chemically intercalated Br₂ and BrCl GICs were synthesized following a previously reported procedure. Briefly, Br₂ and BrCl GICs were prepared by exposing the graphite flakes (TIMCAL TIMREX K54) in high-concentration Br₂ vapour (99.99%; Sigma-Aldrich) and BrCl gas in well-sealed flasks for 2 h. BrCl was prepared by mixing Br₂ with an equimolar quantity of Cl₂, which was obtained from the reaction of trichloroisocyanuric acid and hydrochloric acid, at −70 °C. The as-prepared GICs were immediately transferred to the Raman or XRD measurements.

Electrochemical measurements. In the three-electrode cells, the LBC-G electrodes (or other control electrodes) were used as the working electrode, active carbon as the counter-electrode and Ag/AgCl as the reference electrode. The mass ratio of the working electrode versus the electrolyte was 1:20. The three-electrode cells were then galvanostatically charged/discharged using a Land BT2000 battery test system (Wuhan, China) at room temperature. Cyclic voltammetry was carried out using a 5-mV perturbation with frequency in the range 0.01–100,000 Hz at room temperature. The ionic diffusion coefficient was calculated using the following relation of the reactants in the electrode (99.99%; Sigma-Aldrich) and converted to one-dimensional patterns using Fit2D software.

\[ D = \frac{4}{\pi} \left( \frac{V_m}{FS} \right) \left( \frac{dE}{d(t/\sqrt{D})} \right)^2 \]  

where \( F \) is the applied constant current density, \( V_m \) is the molar volume of partially hydrated LiBr/LiCl, \( F \) is the Faraday constant (96,486 C mol⁻¹), \( S \) is the contact area between the electrolyte and the active materials, \( dE/dx \) is the slope of the Coulombic titration curve at composition \( x \), and \( dE/d(t/\sqrt{D}) \) can be obtained from the plot of the transient voltage versus the square root of time during constant current pulses. The four-point EIS measurement was performed with a Gamry 345 interface 1000 using a 5-mV perturbation with frequency in the range 0.01–100,000 Hz at room temperature. The ionic diffusion coefficient was calculated by simulation, using an equivalent circuit including a finite Warburg element.

The full cells were assembled as CR2032-type coin cells using LBC-G as the cathode and HFE-PEO gel-protected graphite electrodes as the anode. The cathode/anode mass ratios were 1.38:1. A titanium metal foil disk was placed between the cathode and the coin cell case to prevent corrosion. As-prepared WIBS gel electrolyte was pressed into films and applied in the coin cells as both electrolyte and separator. The ratio of the total mass of the electrodes to that of the electrolyte was from 1:4 to 2:1. After assembly, the cell was briefly kept at 50 °C for gel polymer electrolyte self-healing. The full cell was then cycled galvanostatically on a Land BT2000 battery test system (Wuhan, China) at room temperature.

The specific (gravimetric or volumetric) energy densities (E) of the full cells were calculated by

\[ E = CU \]  

where \( C \) is the specific (gravimetric or volumetric) cell capacity and \( U \) is the average cell output voltage. The gravimetric capacity \( C_m \) was calculated by

\[ C_m = \frac{E_{cell}}{m_{cathode} + m_{anode}} \]  

where \( C_m \) is the absolute cell capacity; \( m_{cathode} \) is the total mass of the cathode, including LiBr, LiCl graphite and PTFE binder; and \( m_{anode} \) is the total mass of the anode, including graphite, PTFE binder and the polymer passivating coating.

In situ Raman spectroscopy. For the in situ Raman measurements, a LBC-G/G full cell (in a coin cell configuration) was charged and discharged at 40 mA g⁻¹ (0.1 C). A quartz optical window (diameter ≈ 5 mm) was applied on the cathode side. Raman spectra were collected with a Horiba Jobin Yvon Labram Aramis Raman spectrometer using a laser (wavelength of 532 nm) at frequencies between 3,500 cm⁻¹ and 60 cm⁻¹. 16 data points per sample were collected to get a high signal-to-noise ratio.

Ex situ and in situ XRD spectroscopy. For the ex situ XRD measurements, the LBC-G electrodes (working electrodes) were retracted from the three-electrode cell after being charged/discharged to certain SOC levels at 40 mA g⁻¹ (0.1 C). For the in situ XRD study, a full cell (in a coin cell configuration) was charged and discharged at 0.1 C. Kapton windows (d = 3 mm) were used on both sides of the coin cells, where the anode was placed to avoid beam passage through the window. XRD patterns (Fig. 3b) were recorded ex situ on a Bruker D8 Advance XRD system with Cu Kα radiation in grazing-incidence geometry. High-energy synchrotron XRD measurements (Fig. 3c,d) were carried out at the 11-ID-C beamline of the Advanced Photon Source (APS), Argonne National Laboratory. A high-energy X-ray with beam size 0.2 mm × 0.2 mm and wavelength 0.1173 Å was used to obtain two-dimensional diffraction patterns in the transmission geometry. X-ray patterns were recorded with a Perkin-Elmer large-area detector placed at 1,800 mm from the battery cells. The interval between successive diffraction measurements was 5 min. The obtained two-dimensional diffraction patterns were calibrated using a standard CeO₂ sample and converted to one-dimensional patterns using Fit2D software.

The periodic repeat distance (\( d \)) and the intercalant gallery height (\( d_g \)) of the GICs can be calculated using

\[ d_c = d_g + \delta (m - 1) \]  

where \( d \) is the index of the (0 0 l) planes oriented in the stacking direction and \( d_g \) is the observed value of the spacing between two adjacent planes in the XRD patterns, which can be calculated from the diffraction angles by Bragg’s law.

The d spacing of pristine graphite is 3.35 Å. The intensity pattern was usually found for a stage-\( m \) GIC, where the most dominant peak is the (0 0 m+1). The d spacing values of (0 0 m+1) were calculated from the XRD data using Bragg’s law (Extended Data Table 1), and the most dominant stage phase of the observed GIC was assigned.

Ex situ XANES and EXAFS studies. Ex situ X-ray absorption spectroscopy measurements were conducted on the same cell configuration as that used for the in situ XRD measurements. The experiments were carried out in transmission mode at the beamline 20-BM–B of APS. The XANES measurements were performed at the K edge of bromine (about 13,474 eV) and chlorine (about 2,822 eV) to monitor the Cl measurement, the entire X-ray beam, samples and Kapton windows (φ = 3 mm) were used on both sides of the coin cells, where the anode was placed to avoid beam passage through the window. XRD patterns were recorded with a Perkin-Elmer large-area detector placed at 1,800 mm from the battery cells. The interval between successive diffraction measurements was 5 min. The obtained two-dimensional diffraction patterns were calibrated using a standard CeO₂ sample and converted to one-dimensional patterns using Fit2D software.

The periodic repeat distance (\( d \)) and the intercalant gallery height (\( d_g \)) of the GICs can be calculated using

\[ d = \frac{1}{2} m (m - 1) \]  

where \( m \) is the index of the (0 0 l) planes oriented in the stacking direction and \( d_g \) is the observed value of the spacing between two adjacent planes in the XRD patterns, which can be calculated from the diffraction angles by Bragg’s law.

The d spacing of pristine graphite is 3.35 Å. The intensity pattern was usually found for a stage-\( m \) GIC, where the most dominant peak is the (0 0 m+1). The d spacing values of (0 0 m+1) were calculated from the XRD data using Bragg’s law (Extended Data Table 1), and the most dominant stage phase of the observed GIC was assigned.
where \( j \) indicates the \( j \)th atomic shell including the atoms with identical distance to the central atom, \( N_i \) is the coordination number of the \( j \)th shell, \( f_{ij} \) is the backscattering amplitude, \( R_i \) is the average distance between the central atom and backscatters, \( \sigma_j \) is the mean square variation in \( R_j \), \( \delta_i \) is the scattering phase shift, \( \lambda \) is the effective mean free path and \( S_j^2 \) is the amplitude reduction factor. FEFF6 was used to calculate \( f_{ij}, \delta_i \) and \( \lambda \). Fitting of the experimental data was carried out using Artemis to refine the structure parameters \( N_i, R_i, \sigma_j \). The initial crystal structures used in the fitting were DFT-optimized stage-I \( \text{Li}^+ \text{Br}^{-} \) and stage-I \( \text{C}_7[\text{Br}^+ \text{Cl}^-] \); \( S_j^2 \) was fixed at 1.0. Two energy intervals \( \Delta E \) were used in the fitting: one for the \( \text{Br}^{-} \) (or Cl) paths and one for the remaining \( \text{Br}^{-} \)–C paths.

### Phase separation and water equilibrium studies.

For the water uptake estimation, WiBS liquid electrolyte was gradually (in 0.1-g steps) added into 20 mg of anhydrous \( \text{LiBr}/\text{LiCl} \) or \( \text{LiBr}/\text{LiCl} \) monohydrate mixed salts (20 mg; molar ratio, 1:1) during shake mixing for 2 h and 6 h of standing (each time), until no solid residue was observed. For the demonstration of phase separation, an as-prepared aqueous solution of \( \text{LiBr} \cdot 3\text{H}_2\text{O} \) (0.8 g) and \( \text{LiCl} \cdot 3\text{H}_2\text{O} \) (0.4 g) was added into the WiBS liquid electrolyte (3 g), following by 2 h of shake mixing and 1 h of standing. After 500 h of further exposure to \( \text{LiCl}/\text{LiBr} \) solution, a small sample of WiBS was removed and the \( \text{Br}^{-} \) and \( \text{Cl}^{-} \) concentration was tested by anion exchange liquid chromatography (Dionex ICS-1100 Ion Chromatography System).

### Scanning electron microscopy imaging and specific-surface-area measurement.

Scanning electron microscopy of the cyclic cathode was performed using a Hitachi SU-70 microscope equipped with an energy-dispersive X-ray spectroscope system operating at 5 kV. Specific surface areas of the samples were characterized by \( N_2 \) adsorption by means of a Micrometrics ASAP 2020 Porosimeter test station. The samples were degassed (in a vacuum) at 180 °C for 12 h before the test. The specific surface areas were calculated using the Brunauer–Emmett–Teller method from the adsorption branch.

### MD simulations of LiBr in water-in-salt electrolyte.

MD simulations were performed on 18 m (moles salt per kilogram of solvent) \( \text{LiBr} \) in water at 333 K and a mixed salt of 18 m \( \text{LiBr} \) and 21 m \( \text{LiTFSI} \) in water at 363 K. The MD simulations used a previously modified CHARM M \( \text{H}_2\text{O} \) force field in conjunction with the APPL EP many-body polarizable force field for \( \text{LiTFSI} \) in \( \text{H}_2\text{O} \), which predicted liquid electrolyte (3 g), following by 2 h of shake mixing and 1 h of standing. Chromatography (Dionex ICS-1100 Ion Chromatography System).

### Data availability

The data that support the findings of this study are available from the corresponding author on request.

### References

Extended Data Fig. 1 | Immiscibility of LiBr and LiCl in WiBS aqueous electrolyte. a, Hydration of anhydrous LiBr/LiCl mixed salts (20 mg, molar ratio 1:1) in 2 g (left) and 5.1 g (right) of WiBS liquid electrolyte. b, Hydration of LiBr/LiCl monohydrate mixed salts (20 mg, molar ratio 1:1) in 1.5 g (left) and 3.0 g (right) of WiBS liquid electrolyte. The solid residue is indicated by the dashed circle. c, Immiscibility (clear phase separation) of an as-prepared mixture of an aqueous solution (top) of LiBr·3H₂O (0.8 g) and LiCl·3H₂O (0.4 g) in WiBS liquid electrolyte (bottom; 3 g). d, MD simulation cell snapshots, showing the initial configuration (left) and the final configuration (right) after a 9-ns run for a solution of 18 mol kg⁻¹ LiBr and 21 mol kg⁻¹ LiTFSI in H₂O at 363 K; the Br⁻ anions are highlighted in red. e, Only trace concentrations (<35 p.p.m.) of Br⁻ and Cl⁻ are detected in the WiBS liquid electrolyte by anion-exchange liquid chromatography after 500 h of exposure to the LiBr/LiCl solution.
Extended Data Fig. 2 | Solid states of LiBr and LiCl in an LBC-G cathode. a–c, Scanning electron microscope (a) and energy-dispersive X-ray spectroscopy mapping (b, c) images of an LBC-G composite cathode, showing the morphology and elemental distributions of Br (b) and Cl (c) in the cathode layer after 5 full cycles. The distributions of Br and Cl are overlapping, indicating that the two salts are well mixed as a result of their close association during co-intercalation/de-intercalation. d, Ex situ XRD patterns of LBC-G cathodes collected from disassembled cells after the 5th charge and discharge. The disappearance of the LiBr and LiCl peaks and the appearance of the GIC peaks of the LBC-G cathode confirm the BrCl intercalation reaction at the fully charged state, whereas the typical patterns of crystalline LiBr and LiCl at the fully discharged state suggest that solid LiBr and LiCl are reformed after de-intercalation of halogen anions from graphite. The (002) peak of graphite, which has very high intensity, is cut off to show the other peaks. Theta, diffraction angle. e, The potential of the LBC-G cathode during discharge, open-circuit relaxation during a 40-h rest, and charging at 0.2 C. The complete recovery of the charge capacity in the next cycle shows that all of the active LiBr and LiCl material was well confined in the LBC-G cathode and there was no capacity loss during the long rest. f, The open-circuit voltage decays in the 40-h rest of the LBC-G cathode at the fully charged state of 4.5 V at 0.2 C. Self-discharge was evaluated by comparing with the Coulombic efficiency and the capacity loss after resting.
Extended Data Fig. 3 | Absence of corrosion in the current collector and oxidation of graphite and water at the operation potential.

a, Linear sweep voltammetry of a pure graphite electrode (with only PTFE binder) on a Ti-mesh current collector in LiBr·3H₂O, LiCl·3H₂O, and WiBS electrolyte with a Ag/AgCl electrode as reference at 1 mV s⁻¹. The results show absence of side reactions, such as corrosion of the current collector and oxidation of graphite and water, before the onset of the large increase of the current density at about 4.0 V, 4.5 V and 5.0 V versus Li/Li⁺, in accordance with the oxidation of Br⁻, Cl⁻ and water, respectively. b, c, C 1s X-ray photoelectron spectra (b) and overall spectra (c; binding energy of 0–293 eV) of the LBC-G cathode before and after 10 full cycles. LiBr and LiCl were removed to avoid interference. No carbon–oxygen or carbon–halogen bonds were observed. Only traces of Br were detected as intercalation residual.
Extended Data Fig. 4 | Nyquist plot fitting, volumetric energy density and full cell configuration. a, Equivalent circuit used for fitting the Nyquist plots in Fig. 1f, consisting of ohmic resistance $R_1$ and a constant-phase element (CPE1) parallel to a resistor ($R_2$) connected in series with a finite-diffusion Warburg impedance ($W_{s1}$). We note that the open Warburg impedance was not included, whereas the data at low frequencies were truncated accordingly during fitting. b, Comparison of Nyquist plots of LBC-G cathodes containing graphite hosts with different average flake sizes (KS4, about 4 μm; ‘Big graphite’, about 800 μm), showing the independence of the diffusion kinetics from the halogen diffusion length inside the graphite interlayer. c, Practical volumetric energy density of the LBC-G cathode compared with those of other representative state-of-the-art cathodes when paired with Li metal anodes. For a fair comparison, the potential of a unit stack (the smallest cell unit) comprising a 100-μm-thick cathode, a 9-μm separator and a Li metal anode (average discharge voltages referred to Li/Li$^{+}$) was calculated using capacity matching. The volume fraction of the active material in each electrode was considered to be 70 vol% for intercalation materials and 60 vol% for conversion-type cathodes. The material properties in the fully expanded (lithiated) state were used to calculate the volumetric capacity and inactive volume within each electrode. The areal capacities of the anodes and cathodes were matched at 1:1 and no extra capacity was considered for formation losses. d, e, Schematic of the full cell configurations with an LBC-G composite cathode in WiBS aqueous-gel electrolyte during charging (d) and discharging (e).
Extended Data Fig. 5 | Reversible halide redox chemistry enabled by intercalation in graphite. Galvanostatic charge and discharge profiles of different composite cathodes at a current density of 80 mA g\(^{-1}\) in WiBS gel electrolyte. a, LiBr–graphite (mass ratio of about 1:1) cathode in the potential range 3.20–4.62 V. Without the presence of Cl\(^-\), there were no further oxidation reactions of Br\(^0\) until the potential was raised to above 4.55 V versus Li/Li\(^+\), where Br\(^0\) was further irreversibly oxidized into BrO\(^-\). b, Composite of (LiBr)\(_{0.5}\)(LiCl)\(_{0.5}\) and titanium nanopowder (mass ratio 1:20), showing a charge capacity of 85% of the theoretical value for halogen anion redox reactions and negligible discharge capacity. The higher overpotential might be due to the lack of carbon catalysis for the redox reactions. c, (LiBr)\(_{0.5}\)(LiCl)\(_{0.5}\)/graphitized carbon black (mass ratio 1:3). d, (LiBr)\(_{0.5}\)(LiCl)\(_{0.5}\)/active carbon (mass ratio 1:3). e, (LiBr)\(_{0.5}\)(LiCl)\(_{0.5}\)/KS4 (mass ratio 6:4). f, g, N\(_2\) absorption/desorption isotherm of a graphite (KS4) electrode (f) and an active-carbon electrode (g) with 5 wt% PTFE binder. The results indicate that, unlike active carbon, the graphite host cannot provide a large surface area and small size pores to store halogens by adsorption. h, Ex situ XRD intensity of LiBr/LiCl/active-carbon cathodes at fully charged and discharged states. After adsorbing halogen (Br\(_2\) and BrCl) during charging, a relatively strong peak appears in the (002) peak area, and (100) weakens. This might imply the reformation of randomly oriented small graphitic zones with the help of halogen integration, which indicates a minor contribution of intercalation-like behaviour to halogen storage into nano-graphitized grains.
Extended Data Fig. 6 | Reference samples of chemically intercalated halogen GICs. a–f, XRD patterns of chemically intercalated Br₂ (a–c) and BrCl (d–f) GICs used as reference samples. These GICs were prepared by exposing the graphite flakes in high-concentration Br₂ vapour and BrCl gas for 2 h (more synthesis details in Methods). The spontaneous slow de-intercalations of the XRD peaks that appear at 48 h were observed using the θ–2θ scan mode with Cu Kα radiation (1.5418 Å) in reflection geometry. g, Raman spectra (50–500 cm⁻¹) of chemically intercalated Br₂ and BrCl GICs used as reference samples.
Extended Data Fig. 7 | Representative structures of stage-I [Br$_{0.5}$Cl$_{0.5}$] C$_{3.5}$ complex obtained from DFT simulations. All structures have intercalation voltages within 0.02 V per ion of a structure with homogenous Br–Cl–Br–Cl bond lengths of 2.45 Å (top left). The bottom right structure is simulated on the basis of the reported Br$_2$ structure$^{28}$. Quantum chemistry calculations performed on a Cl–Br∙∙∙Cl–Br cluster surrounded by conductive polarized continuum also yielded a zig-zag configuration for the Cl–Br–Cl–Br complex with a Cl–Br–Cl–Br angle of around 110°, which has lower energy than the linear Cl–Br–Cl–Br configuration by 0.1 eV according to MP2/aug-cc-pVTz and PBE/aug-cc-pVTz calculations. The most stable geometry obtained from these cluster calculations is similar to that found in the stage-I complexes shown above.
Extended Data Fig. 8 | Stage-I \([\text{Br}_{0.5}\text{Cl}_{0.5}]\text{C}_{3.5}\) complex structures obtained from ab initio MD simulations. Results from 30 ps of NVT ab initio MD simulations using the CP2K package and starting from a structure with homogenous –Br–Cl– bond lengths, as this structure was the most computationally efficient. 

**a**, Radial distribution function \(g(r)\) of stage-I \([\text{Br}_{0.5}\text{Cl}_{0.5}]\text{C}_{3.5}\) from 30 ps of MD simulations at 333 K (left) and final snapshot of the trajectory (right). 

**b**, DFT results for stage-I \([\text{Br}_{0.5}\text{Cl}_{0.5}]\text{C}_{3.5}\) from 30 ps of simulations at 333 K, following initial annealing at 633 K to accelerate the appearance of disorder (left) and final snapshot of the trajectory (right), with a close Br–Br contact highlighted in red. No close Cl–Cl contacts form at this voltage, as evidenced by the absence of features near the gas-phase Cl–Cl bond length in the radial distribution function. NVT simulations used the Langevin thermostat with an associated time constant of 10 fs and average box dimensions obtained from the equilibration runs performed in the NPT ensemble for 100 ps. A 1 fs timestep was used throughout. No signs of gassing and subsequent graphite exfoliation were observed over 100 ps of additional simulations under constant-pressure conditions, even after brief annealing at 633 K and relaxation back to 333 K.
Extended Data Fig. 9 | Representative in-plane configurations of the cathode structure from DFT calculations. a–d, Stage-II C₇[Br] (a), stage-I C₇[BrCl] (b), stage-II C₈[Br] (c) and stage-I C₈[BrCl] (d) cathodes obtained from DFT simulations. Only a single set of bond lengths can be obtained with this C₄[X] stoichiometry (X, halogen). e–h, Comparison of scattering paths calculated using FEFF6 with different DFT structures to determine the best modes for fitting the experimental XAFS data: stage-II C₇[Br] (e) and C₈[Br] (f), and stage-I C₃.₅[Br₀.₅Cl₀.₅] (g) and C₄[Br₀.₅Cl₀.₅]) (h). The nearest (black), second-nearest (red) and third-nearest (blue) scattering paths around the Br centre are shown. The absence of the second-nearest Br–Br (R \approx 2.6 \text{ Å}) and Br–Cl (R \approx 2.6 \text{ Å}) scattering paths for the C₄[X] stoichiometry suggests that the stoichiometry of C₃.₅[X] would be the dominant one in the real materials.
### Extended Data Table 1 | Calculated d spacing, stage numbers and plane index of Br$_2$ and BrCl GICs

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<th>Plane index</th>
<th>(002)</th>
<th>(003)</th>
<th>(004)</th>
<th>(005)</th>
<th>(006)</th>
<th>(007)</th>
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Values corresponding to the dominant XRD peaks are marked in red. The results were calculated using equation (6).