

Salting-in electrolyte enables reversible heavy p-block electrochemistry in water

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Abstract

Heavy p-block elements (HPEs; Sn, Pb, Sb, Bi, Se and Te)^{1,2}, with flexible electronic structures and rich multielectron redox chemistry, hold promise for electrochemically driven technologies in functional coatings, electronics, and energy conversion and storage^{3–15}. However, their aqueous electrochemistry remains challenging because direct exposure of HPE cations to water readily triggers parasitic reactions, including hydrolysis, corrosion, precipitation, gas evolution, and passivation^{16–21}. Here we challenge the prevailing assumption in electrolyte design that dissolving HPE cations necessitates hydration, and propose a counterintuitive principle of “dissolved but not hydrated” to unlock aqueous HPE electrochemistry. We implement this concept through a dual-salt salting-in electrolyte strategy, distilled into a two-parameter design principle. The auxiliary cation should be strongly hydrated yet weakly ion-pairing to suppress water activity, while the auxiliary anion should preferentially coordinate HPE cations to expel water from their solvation shells. First-principles descriptor screening, corroborated by spectroscopic analyses, interrogates a curated library of hundreds of cation–anion combinations and identifies $\text{Ca}^{2+}\text{--Cl}^-$ as the uniquely optimal auxiliary-ion pair that most effectively suppresses water activity and drives anion coordination to HPE cations, thereby forming water-shielded chlorocomplexes that stabilize HPE cations in water. This electrolyte design enables reversible plating and stripping across the HPE family (Sn, Pb, Sb, Bi, Se and Te), yielding uniform electrodeposits and rendering HPEs viable multielectron electrodes in aqueous batteries. The proposed HPE-based aqueous batteries enabled by this salting-in electrolyte exhibit stable rechargeability with high capacity retention. By rendering an intrinsically unstable class of elements redox-active in water, this work overcomes long-standing barriers to heavy p-block electrochemistry and establishes a general framework for multielectron aqueous electrochemical systems.

Introduction

Heavy p-block elements (HPEs), commonly defined as p-block congeners from groups 13 to 17 in periods 4 to 6 (Fig. 1a), encompass a key subset comprising Pb, Sn, Sb, Bi, Se and Te that is central to modern technologies^{1,2}, with applications spanning conventional packaging, advanced electronics and emerging electrochemical energy-storage systems driven by rapid electrification. Their technological value is most often realized as coatings and deposited layers on diverse substrates, tailored to the application, including Pb for radiation shielding, corrosion protection, solar cells and lead–acid batteries^{3–5}; Sn for tinplate packaging, electronic solders, Sn-metal batteries, and Sn-based Na-ion and Li-ion batteries^{6–8}; Sb and Bi as essential components in thermoelectrics, alloy-type negative electrodes of Na-ion batteries and electrocatalysts for CO_2 reduction^{8–11}; and Se and Te as semiconducting chalcogenides for optoelectronic and thermoelectric devices, as well as high-capacity electrodes increasingly explored in alkali-metal batteries^{9,12–15}. However, how to translate the materials promise of HPEs into manufacturable coatings and layers on target substrates that deliver conformal growth and precise compositional control, while remaining low cost, environmentally benign and practical, remains challenging. Established physical vapor deposition (PVD) relies on vacuum-assisted vaporization of solid

precursors followed by gas-phase transport and condensation²², whereas chemical vapor deposition (CVD) employs volatile species and thermally activated surface reactions but remains dependent on tailored precursors, elevated temperatures and vacuum infrastructure²³. By contrast, electrochemical deposition provides a solution-based, low-temperature, and inherently scalable route for fabricating metallic and semiconducting layers²⁴. It proceeds through mass transport, interfacial desolvation, electron transfer, and surface nucleation and growth, enabling the direct cathodic reduction of dissolved ions on conductive substrates²⁵. In contrast to vapor-phase routes (PVD and CVD), electrochemical methods offer precise control over composition, morphology, and thickness without requiring vacuum infrastructure or high-temperature processing. Collectively, these attributes position electrochemical deposition as a compelling platform for scalable and sustainable manufacturing of HPE materials.

Realizing such electrochemistry requires the corresponding HPE cations to be both chemically stable and sufficiently soluble in solvent (Fig. 1b, left). However, aqueous HPE electrochemistry remains fundamentally constrained (Fig. 1b, right), because multivalent HPE cations are intrinsically incompatible with water. These cations typically suffer from low solubility (e.g., Pb^{2+} , Te^{4+} , and Se^{4+}), pronounced hydrolytic instability (e.g., Sn^{2+} , Sb^{3+} , Bi^{3+} , Se^{4+} , and Te^{4+}), and complicated parasitic side reactions (e.g., Sn^{2+} , Se^{4+} and Te^{4+}), which collectively undermine electrochemical reversibility and impede controlled deposition^{16–21}. Previous attempts to overcome these challenges have typically resorted to toxic acids such as fluoroboric acid (HBF_4) and hexafluorosilicic acid (H_2SiF_6) in aqueous solutions, or to expensive high-concentration salt electrolytes, high-temperature molten salts, ionic liquids, and organic solvents^{26–31}. Beyond the significant increases in cost and safety risks, these approaches often suffer from poor electrochemical reversibility and sluggish kinetics.^{21,26,28,32–38} These long-standing limitations have fundamentally impeded the development and broader application of aqueous electrochemical deposition of HPEs. In this work, we recast the fundamental solvation-design problem, recognizing that reversible aqueous HPE electrochemistry is unattainable within current electrolyte-design principles.

First-principles descriptor-guided auxiliary ion screening

The instability of HPE cations in water stems primarily from the strong electrostatic attraction between the highly positive electrostatic potential (ESP) of HPE cations and the electron-rich O atoms of H_2O (Fig. 1c, left). Although anions with highly negative ESP could, in principle, outcompete H_2O for coordination at HPE cation centers through electrostatic attraction (Fig. 1c and Supplementary Fig. 1), current aqueous electrolyte design assumes that dissolving HPE cations necessitates hydration, leading to predominantly H_2O -rich solvation shells in which ion pairing occurs mainly in solvent-separated or contact forms. Within this framework, dissolution becomes effectively inseparable from hydration, and hydration in turn initiates the failure pathways of aqueous HPE electrochemistry. Here we challenge this hydration-based assumption and propose a counterintuitive electrolyte-design principle of “dissolved but not hydrated” HPE cations to unlock aqueous HPE electrochemistry. To implement this principle, we devised a salting-in electrolyte strategy based on a dual-salt design comprising an HPE salt and an

auxiliary salt, in which the auxiliary salt is selected to suppress H₂O activity and drive HPE cation coordination from hydration to anion coordination. Guided by first-principles interaction descriptors that quantify cation hydration and cation–anion pairing, we screened a curated library of hundreds of cation–anion combinations to pinpoint auxiliary ions that satisfy these coupled requirements (Supplementary Note 1).

Accordingly, the auxiliary cation should be strongly hydrated to most effectively suppress bulk water activity, thereby minimizing direct H₂O coordination to HPE cations. On this basis, we evaluated a library of monovalent (Li⁺, Na⁺ and K⁺), divalent (Be²⁺, Mg²⁺ and Ca²⁺), trivalent (Al³⁺), and first-row transition-metal (TM) ions (Cr²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) using ab initio molecular dynamics (AIMD) to resolve their hydration structures and density functional theory (DFT) to quantify hydration strength (Fig. 1d,e and Supplementary Figs. 2–5). Higher coordination numbers (CNs) and more negative binding energies correspond to stronger hydration. Among these candidates in their hydrated forms (Fig. 1d,e), Li⁺ and Na⁺ combine weak binding with low CNs; Be²⁺ and Al³⁺ show distinctly strong binding yet low CNs, whereas K⁺ reaches higher CNs but with much weaker binding; and TM ions and Mg²⁺ display strong binding but only modest CNs. By contrast, Ca²⁺ stands out by stabilizing seven- and eight-coordinate hydration shells with substantial binding energies, matching our hydration-driven design goal. We next screened auxiliary anions using a single design rule: they should preferentially coordinate to HPE cations over auxiliary cations to form anion-protective HPE complexes. We evaluated a panel of anions, including Cl[−], Br[−], I[−], perchlorate (ClO₄[−]), nitrate (NO₃[−]), acetate (OAc[−]), tetrafluoroborate (BF₄[−]), methanesulfonate (MSA[−]), hexafluorophosphate (PF₆[−]), triflate (OTf[−]), and bis(trifluoromethanesulfonyl)imide (TFSI[−]). To quantify this preference, we used Pb²⁺ as the benchmark HPE cation, as it has the lowest positive ESP among the HPE cations and thus the weakest electrostatic interaction with the negatively charged anions (Fig. 1c and Supplementary Fig. 1). Mapping ESP distributions on anion surfaces clearly differentiates these candidates (Fig. 1f). Smaller anions with more concentrated negative charge, such as Cl[−], exhibit more negative ESP values than larger, charge-delocalized species, such as TFSI[−], whereas OAc[−] is strongly anisotropic, with very negative carboxylate oxygen sites and a much less negative methyl group. We then used the lowest-ESP site on each anion as the coordination locus to construct Ca²⁺ and Pb²⁺ complexes with one to four ligands.

Across the anion coordination series, three-coordinate complexes consistently exhibit the most negative binding energies and are therefore the most stable species (Supplementary Figs. 6–8). For Ca²⁺ within these three-coordinate series, binding strength increases nearly linearly as the anionic ESP minimum becomes more negative, from weak TFSI[−] to strong OAc[−] binding (Fig. 1g). However, this trend becomes less definitive for Pb²⁺: [Pb(TFSI)₃][−] remains weakly bound, whereas [PbCl₃][−] and [Pb(OAc)₃][−] display nearly identical binding energies (Fig. 1h). Moreover, Pb²⁺–Cl[−] and Pb²⁺–OAc[−] interactions are substantially stronger than Pb²⁺–H₂O coordination, indicating that both anions act as plausible ligands in water (Supplementary Figs. 6a,b and 8a). A closer comparison reveals that [Ca(OAc)₃][−] binds more

strongly than $[\text{Pb}(\text{OAc})_3]^-$, whereas $[\text{CaCl}_3]^-$ is less strongly bound than $[\text{PbCl}_3]^-$ (Fig. 1g,h). Thus, when Ca^{2+} and Pb^{2+} coexist in aqueous solutions, the relative binding strengths dictate that OAc^- is driven to associate with Ca^{2+} , whereas Cl^- is preferentially bound to Pb^{2+} . Electron localization function (ELF) mapping of three-coordinate Pb^{2+} complexes reveals a stereochemically active lone pair ($6s^2$) occupying a basin opposite the ligands, which drives pyramidalization into trigonal-pyramidal geometries (Fig. 1h, insets; Supplementary Figs. 9–11). In contrast, Ca^{2+} lacks a lone pair and adopts more open trigonal-planar configurations (Fig. 1g, insets). Independent gradient model based on Hirshfeld (IGMH) analysis shows how the lone-pair-induced steric field alters anion binding (Fig. 1i; Supplementary Figs. 12–14). In trigonal-planar $[\text{Ca}(\text{OAc})_3]^-$, each OAc^- binds Ca^{2+} strongly in a bidentate fashion through both carboxylate oxygens, whereas in trigonal-pyramidal $[\text{Pb}(\text{OAc})_3]^-$ the lone pair occupies one coordination site, forcing OAc^- to bind mainly through a single oxygen and weakening its overall interaction (Fig. 1i, top). By comparison, compact Cl^- ligands in $[\text{PbCl}_3]^-$ are barely affected by this steric crowding and retain $\text{Pb}-\text{Cl}$ bonds stronger than those in planar $[\text{CaCl}_3]^-$ (Fig. 1i, bottom). Supplementary binding-energy analyses confirm that $\text{Cl}^--\text{H}_2\text{O}$ interactions are much weaker than $\text{Pb}^{2+}-\text{Cl}^-$ bonding and only slightly stronger than $\text{H}_2\text{O}-\text{H}_2\text{O}$ hydrogen bonding (Supplementary Figs. 15 and 16), thereby excluding hydrated Cl^- as the limiting factor for HPE cation- Cl^- coordination. Among the auxiliary cations examined, Ca^{2+} , aside from weakly hydrated monovalent ions, displays the weakest binding for Cl^- (Supplementary Figs. 17 and 18), whereas higher-ESP HPE cations (Sn^{2+} , Sb^{3+} , Bi^{3+} , Se^{4+} , and Te^{4+}) bind Cl^- more strongly than H_2O (Supplementary Figs. 19–23). First-principles screening thus establishes Ca^{2+} as the optimal auxiliary cation, strongly hydrated yet only weakly binding to anions, and identifies Cl^- as the preferred auxiliary anion, binding strongly to HPE cations but only weakly to Ca^{2+} within the dual-salt design framework.

A general salting-in strategy for HPE cations

To map the solvation landscape of candidate auxiliary chlorides that suppress H_2O activity while maintaining readily releasable Cl^- , we used DFT to enumerate all plausible Cl^- -bearing solvation structures, assessed their stability from binding energies, and quantified cation- Cl^- interactions using IGMH analysis (Supplementary Note 2). Each structure is placed on a two-dimensional map of binding energy vs. an IGMH-derived interaction index (Fig. 2a, constructed from Supplementary Figs. 24–34), where more negative $\text{sign}(\lambda_2)\rho$ values indicate stronger cation- Cl^- attraction. On this IGMH-energy map, Li^+ , Na^+ , and K^+ form loosely bound Cl^- -bearing hydrated structures with low overall binding energies and only weakly vdW-level cation- Cl^- binding. Ca^{2+} , in contrast, maintains strong overall hydration yet still exhibits a predominantly vdW-level $\text{Ca}^{2+}-\text{Cl}^-$ binding. Mg^{2+} strengthens into a weakly attractive regime, whereas first-row transition-metal ions together with Be^{2+} and Al^{3+} show pronounced direct cation- Cl^- attraction. Notably, among the representative complexes, $[\text{CaCl}(\text{H}_2\text{O})_7]^+$ exemplifies the desired balance. It couples extensive hydration with a weak $\text{Ca}^{2+}-\text{Cl}^-$ association (insets of Fig. 2a),

placing aqueous CaCl_2 in an optimal regime that suppresses H_2O activity while preserving high availability of free Cl^- . To translate the descriptor-guided conclusions into practice, we implemented a salting-in strategy using representative auxiliary chlorides (NaCl , KCl , MgCl_2 , CaCl_2 , MnCl_2 , and ZnCl_2). Taking Pb^{2+} as a model HPE cation, we examined whether these salts could release enough coordinatively available Cl^- to convert sparingly soluble PbCl_2 into soluble chlorocomplexes. PbCl_2 solubility was quantified by increasing the chloride concentration from 1 m to the highest practical integer molalities for each salt, namely 6 m NaCl , 4 m KCl , 5 m MgCl_2 , 6 m CaCl_2 , 6 m MnCl_2 , and, for comparison, 6 m ZnCl_2 . As shown in Fig. 2b, NaCl and KCl , despite weak cation– Cl^- interactions, afford only modest salting-in effect because each contributes a single Cl^- and weakly suppresses H_2O activity. Among the divalent chlorides, MnCl_2 gives limited gains (~ 0.07 m PbCl_2 at 5 m MnCl_2) and ZnCl_2 gives none; both fall in the strong cation– Cl^- attraction regime of Fig. 2a ($\text{sign}(\lambda_2)\rho < -0.05$ a.u.), with Zn^{2+} in particular favoring first-shell Cl^- over H_2O and thus retaining chloride (Supplementary Fig. 29a). By contrast, MgCl_2 produces a measurable but smaller salting-in effect than CaCl_2 , consistent with Mg^{2+} – Cl^- interactions in the attractive-weak regime, whereas Ca^{2+} combines strong hydration with a weak vdW-level Ca^{2+} – Cl^- contact. Consequently, CaCl_2 furnishes the largest pool of coordinatively available Cl^- and yields the highest PbCl_2 solubility (~ 0.40 m) via formation of soluble chlorocomplexes (Fig. 2b), in agreement with the two-parameter map (Fig. 2a).

Pb L_3 -edge X-ray absorption fine structure (EXAFS) analysis identifies the soluble Pb^{2+} species in 6 m CaCl_2 containing 0.4 m PbCl_2 (Fig. 2c, Supplementary Fig 35, and Supplementary Tables 1 and 2). The Fourier-transformed spectrum exhibits a dominant first-shell peak at ~ 2.4 Å (uncorrected for phase shift), which fits Pb – Cl scattering with an optimal fitted coordination number of three and shows no detectable Pb – O contribution from H_2O (Supplementary Note 3), supporting its assignment to $[\text{PbCl}_3]^-$ (Fig. 2c). This assignment is consistent with the DFT-optimized structure of a trigonal-pyramidal geometry (Fig. 1h, inset). In CaCl_2 solutions up to 6 m, Raman spectra reveal a strongly disrupted hydrogen-bond network of bulk water (Fig. 2d; Supplementary Figs. 36 and 37) and ^{17}O NMR spectra exhibit pronounced upfield shifts (Fig. 2e; Supplementary Fig. 38), together confirming that Ca^{2+} most effectively lowers H_2O activity through strong hydration (Supplementary Note 4). Ca K-edge EXAFS analysis further elucidates the high-coordination hydration structure of Ca^{2+} (Fig. 2f, Supplementary Fig. 39, Supplementary Tables 3 and 4, and Supplementary Note 5). In the dilute 1 m CaCl_2 solution, Fourier-transformed EXAFS and first-shell fitting suggest that Ca^{2+} is reasonably modeled as being coordinated by eight H_2O molecules to form $[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$ (Fig. 2f, top). In 6 m CaCl_2 solution, one H_2O molecule is readily replaced by Cl^- , yielding a stable $[\text{CaCl}(\text{H}_2\text{O})_7]^+$ configuration (Fig. 2f, middle), which remains essentially unchanged upon addition of 0.4 m PbCl_2 (Fig. 2f, bottom). Consistently, ^{35}Cl NMR spectra exhibit progressive upfield shifts from 1 m to 6 m CaCl_2 solutions (Supplementary Fig. 40), tracking the transformation from $[\text{Ca}(\text{H}_2\text{O})_8]^{2+}$ to $[\text{CaCl}(\text{H}_2\text{O})_7]^+$. IGMH analysis further reveals that $[\text{PbCl}_3]^-$ exhibits a

pronounced blue attractive region along the Pb–Cl contacts ($\text{sign}(\lambda_2)\rho = -0.057$ a.u.), consistent with strong halogen-bond-like binding, in sharp contrast to the weak, vdW-level Ca^{2+} – Cl^- contact in $[\text{CaCl}(\text{H}_2\text{O})_7]^+$ (Fig. 2g). Overall, CaCl_2 -based SICEs solubilize Pb^{2+} as $[\text{PbCl}_3]^-$, consistent with strong Ca^{2+} hydration and weak Ca^{2+} – Cl^- pairing (Fig. 2h).

Building on these insights, we extended the CaCl_2 -based SICE to a broader family of hydrolysis-prone HPE cations, including Sn^{2+} , Sb^{3+} , Bi^{3+} , Te^{4+} , and Se^{4+} (Supplementary Note 6). Notably, 6 m CaCl_2 effectively suppresses hydrolysis and stabilizes these HPE cations in water as dissolved but not hydrated chlorocomplexes, in sharp contrast to CaCl_2 -free solutions (Supplementary Figs. 41–46). Raman bands attributable to HPE–Cl stretching, together with DFT-optimized structures, confirm that HPE cations remain as trigonal-pyramidal $[\text{SnCl}_3]^-$, tetrahedral $[\text{SbCl}_4]^-$, and octahedral $[\text{BiCl}_6]^{3-}$ and $[\text{TeCl}_6]^{2-}$ chlorocomplexes^{39–44}, even when solubilized to high concentrations of up to 6 m SnCl_2 , 4 m SbCl_3 , 2.5 m BiCl_3 , and 3 m TeCl_4 in 6 m CaCl_2 (Fig. 2i–l). IGMH analyses place these HPE–Cl interactions within the stable, halogen-bond-like regime (insets of Fig. 2 i–l; Supplementary Fig. 47). Together with binding-energy analyses (Supplementary Figs. 19–22), these results show that in CaCl_2 -based SICEs, Cl^- outcompetes H_2O in the first coordination shell of HPE cations, thereby suppressing their intrinsic tendency toward hydrolysis by stabilizing them as Cl^- -protected soluble chlorocomplexes. However, Se^{4+} represents an exception. Despite its appreciable Se^{4+} – Cl^- affinity (Supplementary Fig. 23), no fully Cl^- -coordinate complex is detected. Instead, CaCl_2 diverts the hydrolysis pathway. In 1 m SeCl_4 , the dominant product is trigonal-pyramidal H_2SeO_3 ($3\text{H}_2\text{O} + \text{Se}^{4+} \rightarrow \text{H}_2\text{SeO}_3 + 4\text{H}^+$), whereas in 6 m CaCl_2 + 1 m SeCl_4 the product shifts to trigonal-pyramidal SeOCl_2 ($\text{H}_2\text{O} + 2\text{Cl}^- + \text{Se}^{4+} \rightarrow \text{SeOCl}_2 + 2\text{H}^+$), as confirmed by Raman spectra and DFT-optimized structures (Fig. 2m and Supplementary Fig. 48)^{45,46}. IGMH analyses reveal strong Se–O (aqua/hydroxo/oxo) interactions together with appreciable Se–Cl attraction (insets of Fig. 2m; Supplementary Fig. 49), rationalizing the coexistence and persistence of H_2SeO_3 and SeOCl_2 . This behavior reflects an intrinsic Se^{4+} preference for O donors: Cl^- cannot fully displace aqua/hydroxo/oxo ligands, thereby stabilizing the mixed oxo–chloride SeOCl_2 in the CaCl_2 -based SICE.

Reversible heavy p-block electrochemistry in SICEs

Having established that CaCl_2 -based SICEs stabilize HPE cations as dissolved chlorocomplexes in water, we next evaluated their redox reversibility against the corresponding HPEs. Electrochemical tests were carried out in a three-electrode configuration using 6 m CaCl_2 containing 1 m of the target chlorides, except PbCl_2 , which was limited to 0.4 m by solubility (Fig. 3a–c, Supplementary Figs. 50 and 51, and Supplementary Note 7). Cyclic voltammetry (CV) reveals well-defined and reversible redox couples for $[\text{PbCl}_3]^-/\text{Pb}$, $[\text{SnCl}_3]^-/\text{Sn}$, $[\text{SbCl}_4]^-/\text{Sb}$, $[\text{BiCl}_6]^{3-}/\text{Bi}$, and $[\text{TeCl}_6]^{2-}/\text{Te}$ at -0.32 V, -0.30 V, 0.05 V, 0.06 V, and 0.57 V vs. SHE, respectively (Fig. 3a). The low-polarization responses reflect fast charge-transfer kinetics enabled by soluble chlorocomplexes. In parallel, the SeOCl_2/Se couple delivers highly reversible redox

peaks at 0.90 V vs. SHE in CaCl_2 -based SICE, in stark contrast to the sluggish kinetics and cathodic shift to 0.63 V observed in 1 M SeCl_4 electrolyte, where hydrolyzed oxyanions prevail (Fig. 3b). SeOCl_2 reduces markedly faster than H_2SeO_3 owing to the facile cleavage of relatively weak, halogen-bond-like Se-Cl bonds, whereas H_2SeO_3 and its derivatives (HSeO_3^- and SeO_3^{2-}) undergo slow, multistep proton-coupled electron-transfer pathways that require breaking stronger Se-O/Se-OH linkages (Supplementary Fig. 49). Galvanostatic electrochemical deposition further confirms the high electrochemical stability of all chlorocomplexes studied, yielding flat potential plateaus and consistent deposition of the target HPEs without discernible polarization buildup over time (Fig. 3c).

To assess structural and morphological features, the galvanostatic electrodeposits were systematically examined by scanning electron microscopy (SEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and X-ray diffraction (XRD), as detailed in Supplementary Note 8.1 (Supplementary Figs. 52–58). SEM images show that electrochemical reduction of soluble chlorocomplexes— $[\text{PbCl}_3]^-$, $[\text{SnCl}_3]^-$, $[\text{SbCl}_4]^-$, $[\text{BiCl}_6]^{3-}$, $[\text{TeCl}_6]^{2-}$, and SeOCl_2 —yields compact deposits with distinct morphologies and compositions, demonstrating the broad applicability of SICEs for HPE electrodeposition (Fig. 3d–i and Supplementary Fig. 52). Pb deposits form large, faceted grains with uniform spatial distribution (Fig. 3d); Sn deposits yield well-defined faceted grains of uniform size (Fig. 3e); Sb deposits form densely packed spherical grains (Fig. 3f); Bi deposits exhibit a lamellar morphology composed of micron-sized stacked plates (Fig. 3g); and Te deposits develop smooth hemispherical grains with a broad size distribution (Fig. 3h). In contrast, Se deposits as a continuous amorphous-like film lacking discernible crystalline features (Fig. 3i). HAADF-STEM imaging resolves clear lattice fringes for Pb, Sn, Sb, Bi, and Te, with interplanar spacings of ~ 0.29 nm for Pb (111) plane, ~ 0.29 nm for Sn (200) plane, ~ 0.31 nm for Sb (012) plane, ~ 0.23 nm for Bi (110) plane, and ~ 0.22 nm for Te (110) plane (Fig. 3j–n and Supplementary Figs. 53–57), in agreement with XRD patterns (Fig. 3p). By contrast, Se shows neither lattice fringes in HAADF-STEM nor Bragg peaks in XRD, confirming its amorphous nature (Fig. 3o,p and Supplementary Fig. 58). Energy-dispersive spectroscopy (EDS) elemental mapping reveals that Se accounts for 99.1 at% among Se, O, and Cl, verifying the high purity and compositional uniformity of the deposited film (inset of Fig. 3i). The CaCl_2 -based SICEs further enable one-step electrodeposition of representative heavy p-block alloys (e.g. PbSn and BiSb) through controlled tuning of chlorocomplex precursor ratios (Supplementary Figs. 59–61 and Supplementary Note 8.2). Collectively, these results show that SICEs overcome the intrinsic instabilities of aqueous heavy p-block electrochemistry, establishing a generalizable platform for reliable electrodeposition of high-quality HPEs and their alloys.

We further confirmed the high reversibility of heavy p-block electrochemistry through repeated HPE plating and stripping behaviors in symmetric and asymmetric cells. Using Pb as a representative case, the Pb||Pb symmetric cell maintains low polarization (< 20 mV) for nearly 3,000 h (Fig. 3q), while the Pb||Cu asymmetric cell delivers stable plating/stripping behavior with a high average CE of 99.9% over 500 cycles (Fig. 3r,s). More importantly, the electrochemical reversibility enabled by CaCl_2 -based SICEs is universally applicable across a wide spectrum of HPEs. Symmetric cells employing Sn, Sb, Bi, Se, and Te

electrodes all exhibit low polarization (typically <80 mV) and long-term stability with cycling lifetimes from 1,000 to 3,600 h (Fig. 3t). Corresponding asymmetric cells achieve high average CEs (99.6–100.0%; Fig. 3u), further confirming the universality of the salting-in chlorocomplex strategy across diverse heavy p-block systems. Detailed electrochemical data are provided in Supplementary Figs. 62–66. Post-cycling morphological and structural analyses of both HPE electrodes and their electrodeposits on current collectors reveal dense, dendrite-free morphologies without detectable byproducts (Supplementary Figs. 67–75), underscoring the highly reversible HPE plating/stripping behavior and rationalizing the durable cycling lifetimes (Supplementary Note 9). This high electrochemical reversibility persists in concentrated chlorocomplex electrolytes based on SICEs with 6 m SnCl_2 , 4 m SbCl_3 , 2.5 m BiCl_3 , or 3 m TeCl_4 (Supplementary Fig. 76).

Rechargeable aqueous HPE-electrode batteries

Here we focus on aqueous batteries as a representative system, given their inherently high-power density, safety, and low-cost characteristics. We recognize that technology-ready aqueous electrode chemistries with stable multielectron redox pathways remain scarce. However, when HPE cations are stabilized as chlorocomplexes in SICEs, these elements can operate as either negative or positive electrodes via reversible plating and stripping, enabling rational full-cell pairing with suitable counter electrodes and greatly expanding the design space of aqueous batteries. Enabled by reversible plating and stripping in CaCl_2 -based SICEs (Fig. 3t,u), HPEs as electrodes fulfill the essential criterion for stable and reversible multielectron redox in water. They span a wide redox window from -0.32 V vs. SHE for $[\text{PbCl}_3]^-/\text{Pb}$ to 0.90 V vs. SHE for SeOCl_2/Se , and deliver high theoretical specific capacities (258.7 – 1358.2 mAh g^{-1}), along with long-term reversibility, dendrite-free deposition, corrosion resistance, and tunable redox potentials (Fig. 4a and Supplementary Fig. 77a)^{7,14,15,21,31,47,48}. Within this landscape, Sn and Pb, with low redox potentials and moderate specific capacities, are ideal negative electrode candidates; Sb and Bi, with intermediate potentials and higher specific capacities, can function as either negative or positive electrodes; and Se and Te electrodes, featuring high redox potentials and four-electron pathways, emerge as promising high-energy positive electrodes.

To exemplify this concept, we first constructed aqueous Pb-metal batteries using metallic Pb foil as the negative electrode, paired with conventional I^-/I_2 , Br^-/Br_2 , and Cl^-/Cl_2 conversion positive electrodes (Supplementary Fig. 77b). These configurations deliver theoretical specific energies of 100, 182, and 278 Wh kg^{-1} for $\text{Pb}||\text{PbI}_2$, $\text{Pb}||\text{PbBr}_2$, and $\text{Pb}||\text{PbCl}_2$ full batteries, respectively. Unlike century-old lead–acid batteries that rely on concentrated, corrosive H_2SO_4 electrolyte and suffer from limited rechargeability and low specific energy (~ 40 Wh kg^{-1})³, the proposed architecture exploits the soluble $[\text{PbCl}_3]^-$ chlorocomplex to establish a distinct aqueous chemistry where Pb^{2+} shuttles reversibly between the negative and positive electrodes. As shown in Fig. 4b, the $\text{Pb}||\text{PbI}_2$ full battery delivers a discharge capacity of 110 mAh g^{-1} at 0.5 C (1 C = 116 mA g^{-1}) and retains 94 mAh g^{-1} at 10 C, demonstrating rapid charge-transfer kinetics and excellent rate capability. The discharge capacity fully recovers to 110

mAh g⁻¹ after rate cycling and remains at 92 mAh g⁻¹ after 500 cycles at 0.5 C (Fig. 4c), effectively suppressing the capacity degradation typically observed for iodide-based positive electrodes. Long-term cycling confirms excellent durability, with >90% capacity retention over 800 and 1,000 cycles at 1 C and 5 C, respectively, corresponding to discharge capacities of 100 and 90 mAh g⁻¹ (Supplementary Fig. 78). Furthermore, the Pb/PbBr₂ full battery exhibits higher discharge capacities (>125 mAh g⁻¹) and elevated operating voltages (>1.2 V) at 2 C and 5 C (1 C = 146 mA g⁻¹), retaining ~80% of its initial discharge capacity after 1,000 cycles (Fig. 4d–f). Notably, the more energetic Pb/PbCl₂ full battery delivers a discharge capacity of 165 mAh g⁻¹ (theoretical capacity of 192 mAh g⁻¹ for PbCl₂) and maintains a stable output voltage above 1.4 V for over 200 cycles (Supplementary Fig. 79).

We further expanded the design space of HPE-based batteries by constructing a new class of aqueous Sn-metal batteries, in which the [SnCl₃]⁻/Sn couple features a favorable redox potential of -0.30 V vs. SHE and a high specific capacity of 451.7 mAh g⁻¹, establishing Sn as a promising high-energy negative electrode. However, as in lead–acid systems, most reported aqueous Sn-metal batteries employ strongly acidic electrolytes, where the intrinsic challenges of Sn²⁺—including limited solubility, oxidative instability, hydrolysis, and acid-induced corrosion—remain unresolved^{7,49}. In contrast, SICEs address these issues by stabilizing Sn²⁺ as highly soluble [SnCl₃]⁻ chlorocomplexes, thereby eliminating solubility and stability constraints and suppressing corrosive degradation of the metallic negative electrode. This stabilization allows the Sn negative electrode to be paired flexibly with both I₂ and KBr positive electrodes (Supplementary Fig. 77c). The Sn/I₂ full battery, employing a four-electron 2I⁻/I₂/2I⁺ conversion positive electrodes with two discharge plateaus, delivers a high discharge capacity of 380 mAh g⁻¹ at 2 C (1 C = 400 mA g⁻¹) and maintains stable cycling for over 500 cycles (Fig. 4g,h). In parallel, the Sn/KBr full battery operates at an average voltage above 1.2 V and retains a capacity of ~150 mAh g⁻¹ after 200 cycles (Supplementary Fig. 80a,b). To extend this HPE-based design paradigm, we investigated four-electron Te and Se positive electrodes, which offer high theoretical specific capacities (840.2 and 1358.2 mAh g⁻¹) and favorable redox potentials of 0.57 V and 0.90 V vs. SHE, respectively. Motivated by these properties, we constructed high-energy aqueous hybrid batteries by pairing the two-electron [SnCl₃]⁻/Sn negative electrode with either the [TeCl₆]²⁻/Te or SeOCl₂/Se positive electrode, employing decoupled SICEs to ensure electrochemical compatibility between the anodic and cathodic species (Supplementary Fig. 77d). Both Sn/Te and Sn/Se full batteries exhibit stable four-electron conversion reactions sustained for over 100 h of continuous cycling (Fig. 4i). The Sn/Te full battery displays highly overlapping charge/discharge curves, indicative of efficient redox reversibility (Fig. 4j), while the Sn/Se full battery operates at a higher voltage of ~1.1 V (Fig. 4k), consistent with the intrinsically higher redox potential of the SeOCl₂/Se couple relative to [TeCl₆]²⁻/Te. This proof-of-concept demonstrates the electrochemical compatibility of soluble HPE cations and establishes a battery architecture that enables dual reversible plating/stripping behavior within a single device. Together with additional rechargeable Sb- and Bi-based batteries (Supplementary Figs. 77e,f and 80c–f, and Supplementary Note 10), these results confirm the generality of SICE-enabled HPE-based

electrochemical systems. To underscore their translational potential, we assembled a larger-format Pb/PbBr_2 full battery that delivers performance comparable to its small-scale counterpart and successfully powers a commercial LED (Fig. 4l,m). This demonstration highlights the practical viability, versatility, and scalability of the SICE strategy for next-generation aqueous energy storage.

Conclusion

In summary, heavy p-block electrochemistry in water, long regarded as intrinsically unstable under conventional electrolyte design, is reframed here as a problem of solvation design, motivating a counterintuitive “dissolved but not hydrated” concept to overcome this instability. Rather than tolerating direct HPE cation– H_2O contact, we re-engineer the solvation shells of HPE cations into anion-coordination-dominated environments that shield them from hydrolysis and other parasitic reactions. Building on this principle, first-principles-based descriptors of cation hydration and cation–anion binding, corroborated by spectroscopic analyses, enabled the screening of hundreds of cation–anion pairs, pinpointing auxiliary salts that pair a strongly hydrated yet weakly coordinating cation with an anion that preferentially coordinates HPE cations. The resulting CaCl_2 -based SICE establishes a chlorocomplex-dominated solvation regime in which anion-protective HPE cations, rather than hydrated species, govern multielectron redox and render an otherwise unstable family of elements reversibly redox-active in water. From a technological standpoint, CaCl_2 -based SICES shift heavy p-block electrochemistry from toxic, corrosive, high-temperature, or nonaqueous baths to benign aqueous electrolytes that support compositionally precise HPE electrodeposition and rechargeable multielectron aqueous batteries with HPE electrodes. These demonstrations likely represent only a small subset of what is possible: by making heavy p-block electrochemistry viable in water, the same solvation-design framework could unlock aqueous routes to thermoelectric and optoelectronic devices, electrocatalysis, electronic metallization and protective coatings, and electrochemical recycling of heavy p-block materials.

Methods

Materials and electrolytes

Sodium chloride (NaCl , 99%), potassium chloride (KCl , 99%), magnesium chloride (MgCl_2 , 99%), calcium chloride (CaCl_2 , 99%), manganese chloride (MnCl_2 , 99%), zinc chloride (ZnCl_2 , 98%), lead chloride (PbCl_2 , 99%), tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), antimony chloride (SbCl_3 , 99%), bismuth chloride (BiCl_3 , 98%), selenium chloride (SeCl_4 , 98%) and tellurium chloride (TeCl_4 , 99%) were purchased from Sigma-Aldrich. The electrolytes were prepared by dissolving the calculated amounts of chlorides in deionized water according to the molality (m , mol kg^{-1}). Unless otherwise specified, electrochemical investigations of Pb, Sn, Sb, Bi, Te, and Se systems were conducted in aqueous electrolytes of 0.4 m PbCl_2 , 1 m SnCl_2 , 1 m SbCl_3 , 1 m BiCl_3 , 1 m TeCl_4 , and 1 m SeCl_4 , each dissolved in 6 m CaCl_2 . For Sn-based electrolytes, 1 vol% Polyethylene glycol (PEG 400) was additionally added during electrochemical measurements.

Preparation of current collectors

Copper (Cu) foil ($\sim 9\ \mu\text{m}$ thickness), titanium (Ti) foil ($\sim 20\ \mu\text{m}$ thickness), Ti mesh with 100 mesh, polytetrafluoroethylene (PTFE) aqueous dispersion solution, and conductive carbon (Ketjen black; KB) were purchased from Crand New Energy Technology. Cu and Ti foils were directly used as the current collectors for Pb/Cu and Sn/Cu cells, and Sb/Ti and Bi/Ti cells, respectively, without additional treatments. KB electrode was prepared by thoroughly grinding KB and PTFE in a mass ratio of 9:1 in isopropanol (99%, Sigma-Aldrich) until forming a homogeneous and dough-like mass. The resulting mixture was then pressed onto Ti mesh and dried in a vacuum oven at $80\ ^\circ\text{C}$ overnight, yielding a KB loading of $\sim 3\ \text{mg cm}^{-2}$. The KB electrode was used as current collectors for Se/KB and Te/KB cells and three-electrode measurements. The current collectors of Cu foil, Ti foil and KB-coated electrode were cut into 12 mm diameter discs.

Preparation of HPE electrodes

Lead (Pb, >99%), tin (Sn, >99%), and bismuth (Bi, >99%) foils (purchased from SCI Materials Hub) were rolled using a roll press (MSK-2150-H5) to a final thickness of $100\ \mu\text{m}$ for use as electrode materials. Antimony (Sb, >99.99%) beads with ($\leq 5\ \text{mm}$), tellurium (Te, >99.99%) powder of ~ 30 mesh, and selenium (Se, >99.99%) powder (~ 50 mesh) were purchased from Sigma-Aldrich. Prior to electrode fabrication, they were ball-milled at 500 rpm for 24 h under a 50-min milling 10-min resting condition, yielding uniformly dispersed powders with average sizes in the micrometer range. Sb or Se electrodes were fabricated by thoroughly grinding Sb or Se powder, KB, and PTFE in a mass ratio of 8:1:1 in isopropanol. Te electrode was similarly prepared by grinding Te powder, graphite (purchased from Crand New Energy Technology), KB, and PTFE in a mass ratio of 6:2:1:1 in isopropanol. The mixtures were ground until forming plasticine-like masses, which were then pressed onto Ti mesh and dried in a vacuum oven at $80\ ^\circ\text{C}$ overnight, yielding active material loadings of $\sim 20\ \text{mg cm}^{-2}$. The electrodes, including Sn, Pb, Sb, Bi, Se, and Te, were cut into circular discs with a diameter of 10 mm.

Preparation of haloid electrodes

Lead iodide (PbI_2 , 99%), lead bromide (PbBr_2 , 98%), iodine (I_2 , 99%), potassium bromine (KBr, 99%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][TFSI], 98%) and tetrapropylammonium bromide (TPABr, 98%) were purchased from Sigma-Aldrich. Active carbon (AC, YP80F) was purchased from Crand New Energy Technology. PbI_2 , PbBr_2 , PbCl_2 , BiCl_3 , SbCl_3 , I_2 , and KBr electrodes were prepared by mixing the active materials with additives in specific mass ratios. The detailed compositions and mass ratios were as follows: PbI_2 (6:2:1:1 for PbI_2 : AC: KB: PTFE), PbBr_2 (6:1:2:0.5:0.5 for PbBr_2 : TPABr: AC: KB: PTFE), PbCl_2 (6: 3: 2: 1: 0.5 for PbCl_2 : [BMIM][TFSI]: AC: KB: PTFE), BiCl_3 (6:3.5:2:1:0.5 for BiCl_3 : [BMIM][TFSI]: AC: KB: PTFE), SbCl_3 (5:3:2:0.5:0.5 for SbCl_3 : [BMIM][TFSI]: AC: KB: PTFE), I_2 (4:4:1:1 for I_2 : AC: KB: PTFE), and KBr (6:1:2:0.5:0.5 for KBr: TPABr: AC: KB: PTFE). All materials were ground thoroughly in isopropanol until forming a uniform and dough-like paste. The resulting slurries were then pressed onto Ti mesh and dried at $70\ ^\circ\text{C}$ in an oven for 8 h. The active

material loadings were $\sim 3.0 \text{ mg cm}^{-2}$ for PbI_2 , $\sim 4.5 \text{ mg cm}^{-2}$ for PbBr_2 , $\sim 3.1 \text{ mg cm}^{-2}$ for PbCl_2 , $\sim 3.3 \text{ mg cm}^{-2}$ for BiCl_3 , $\sim 3.8 \text{ mg cm}^{-2}$ for SbCl_3 , $\sim 2.5 \text{ mg cm}^{-2}$ for I_2 , and $\sim 3.5 \text{ mg cm}^{-2}$ for KBr . The electrodes, including PbI_2 , PbBr_2 , PbCl_2 , BiCl_3 and SbCl_3 , I_2 and KBr , were cut into circular discs with a diameter of 10 mm.

Swagelok cell assembly

The custom-made Swagelok-type cell was used for cell cycling. Two-electrode configurations, including symmetric ($\text{Pb} \parallel \text{Pb}$, $\text{Sn} \parallel \text{Sn}$, $\text{Sb} \parallel \text{Sb}$, $\text{Bi} \parallel \text{Bi}$, $\text{Se} \parallel \text{Se}$ and $\text{Te} \parallel \text{Te}$), asymmetric ($\text{Pb} \parallel \text{Cu}$, $\text{Sn} \parallel \text{Cu}$, $\text{Sb} \parallel \text{Ti}$, $\text{Bi} \parallel \text{Ti}$, $\text{Se} \parallel \text{KB}$ and $\text{Te} \parallel \text{KB}$), and full ($\text{Pb} \parallel \text{PbI}_2$, $\text{Pb} \parallel \text{PbBr}_2$, $\text{Pb} \parallel \text{PbCl}_2$, $\text{Bi} \parallel \text{BiCl}_3$, and $\text{Sb} \parallel \text{SbCl}_3$) cells, were assembled with electrodes placed face-to-face in Swagelok-type cells. The electrodes were separated by a glass fiber separator (GF/A, Whatman) soaked with $\sim 100 \mu\text{L}$ of electrolyte. Unless otherwise specified, the electrolytes used for electrochemical tests were $0.4 \text{ m PbCl}_2 + 6 \text{ m CaCl}_2$ for Pb-based systems, $1 \text{ m SnCl}_2 + 6 \text{ m CaCl}_2$ for Sn-based systems, $1 \text{ m SbCl}_3 + 6 \text{ m CaCl}_2$ for Sb-based systems, $1 \text{ m BiCl}_3 + 6 \text{ m CaCl}_2$ for Bi-based systems, $1 \text{ m SeCl}_4 + 6 \text{ m CaCl}_2$ for Se-based systems, and $1 \text{ m TeCl}_4 + 6 \text{ m CaCl}_2$ for Te-based systems.

Membrane-separated dual-chamber cell assembly

The home-built two-electrode membrane-separated dual-chamber cell was used for hybrid cell cycling. The hybrid $\text{Sn} \parallel \text{I}_2$ battery was assembled using a Sn anode, a glass fiber separator soaked with $\sim 100 \mu\text{L}$ of $1 \text{ m SnCl}_2 + 5 \text{ m CaCl}_2$ electrolyte (anolyte side), a Nafion 117 ion-exchange membrane, a second separator soaked with $\sim 100 \mu\text{L}$ of 5 m CaCl_2 electrolyte (catholyte side), and an I_2 cathode. The $\text{Sn} \parallel \text{KBr}$ cell followed the same configuration, using 6 m CaCl_2 electrolyte as the catholyte and a KBr cathode. For $\text{Sn} \parallel \text{Se}$ and $\text{Sn} \parallel \text{Te}$ cells, the catholyte comprised 1 m SeCl_4 or TeCl_4 in 6 m CaCl_2 , with Se or Te as the cathode, respectively. The Nafion membrane enabled Ca^{2+} conduction to balance charge between compartments and was pretreated by soaking in 1 m CaCl_2 for 24 h and rinsing thoroughly with deionized water before use.

Electrochemical measurements

Three-electrode cyclic voltammetry (CV) and galvanostatic electrodeposition experiments were carried out in beaker cells containing 10 mL of electrolyte per test, using a Biologic VMP3 workstation. The three-electrode setup consisted of a KB-coated working electrode, a KCl-saturated Ag/AgCl reference electrode, and a Pb, Sn, Sb, Bi, Se, or Te counter electrode. Two-electrode galvanostatic cycling tests were conducted using a multichannel Neware battery testing system. All electrochemical measurements were carried out at room temperature.

Materials characterizations

^{17}O and ^{35}Cl nuclear magnetic resonance (NMR) spectra were collected using a Bruker (*AVANCE III, HD* 500 MHz) NMR spectrometer. Chemical shifts for ^{17}O NMR were referenced to an internal capillary tube containing D_2O , while ^{35}Cl NMR was referenced to a saturated NaCl in D_2O sealed within a capillary tube placed inside the NMR tube. Scanning electron microscopy (SEM) was performed using a JEOL JSM-7600F microscope to examine surface morphologies. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra, including both high- and low-frequency regions, were obtained using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm laser. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out on a JEOL JEM-ARM200F NeoARM microscope operating at 200 kV with a spherical aberration corrector. HAADF-STEM samples were prepared using a focused ion beam (FIB) system (ZEISS Crossbeam 540). X-ray absorption spectroscopy was used to characterize the coordination of Ca^{2+} and Pb^{2+} in aqueous medium. The measurements were conducted at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS). All data acquisition was performed in transmission mode employing a $\text{Si}(111)$ double-crystal monochromator except for sample of 1 m CaCl_2 solution at Ca K-edge which is performed in SDD mode. Data are collected at Ca K-edge and Pb L_3 -edge. All data were processed with Athena and Artemis (version 0.9.26)⁵⁰. The value of E_0 was determined by the first peak position of the first derivative of the XANES curve. WT-EXAFS analysis was conducted using HAMA Fortran software⁵¹, employing the Morlet wavelet as the mother wavelet function. The kappaMorlet and sigmaMorlet parameters were adjusted to optimize k-resolution for different R regions.

Geometric structure optimization prior to AIMD Simulation

All simulations were carried out using spin-polarized methods as implemented in the QUICKSTEP code of the CP2K 2025 package^{52,53} based on DFT. The general gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE)⁵⁴ was used as the exchange-correlation functional. The Kohn-Sham (KS) equations were solved according to the Gaussian and plane wave (GPW) formalism. Grimme's DFT-D3 correction⁵⁵ was adopted to describe the weak van der Waals interaction. The GPW used Goedecker-Teter-Hutter pseudo potentials⁵⁶ to describe the interactions between core and valence electrons, while the valence electron density was represented in terms of Gaussian type orbital (GTO) basis set functions. In particular, we used DZVP-MOLOPT-SR-GTH basis sets for geometry optimization and TZVP-MOLOPT-SR-GTH basis sets for static calculations, and the Brillouin zone integration was sampled using a Monkhorst-Pack⁵⁷ special k-point mesh with a resolution of $2\pi \times 0.04$ was applied. The convergence criterion for the maximum force was set as 5×10^{-4} atomic units. The auxiliary PW basis set, which is needed for the efficient solution of the Poisson's equation in reciprocal space, was truncated at 500 Ry. All Electronic structure and wave function analysis were conducted using Multiwfn software⁵⁸.

AIMD simulations

All AIMD simulations reported here were performed using DFT with the Gaussian and Plane Wave combined approach as implemented in CP2K/Quickstep. The electrons were treated using the exchange correlation PBE functional with a Grimme D3 correction. Core electrons were described using the Goedecker-Teter-Hutter (GTH) pseudo-potentials, and the valence density was developed on a double-zeta DZVP basis set along with an auxiliary plane wave basis set with cutoff energy of 500 Ry. The temperature of the simulation was maintained at 300 K using the Canonical sampling through velocity rescaling (CSVR) thermostat coupled to the system. The AIMD simulations were performed with a time step of 1 fs to investigate the hydration structures of auxiliary cations in water. Each system contained one cation and 60 H₂O molecules, with additional Cl[−] placed in a distant corner of the simulation box to maintain charge neutrality without perturbing hydrated interactions. For all the MD trajectories, the initial ~3 ps was regarded as the equilibration period, and then followed by production periods of 10 ps. Note that due to the large size of the supercells, only Γ point was used in all calculations. For AIMD simulations involving transition metal cations, we considered spin polarization, while other cations were not considered.

Geometric optimization and property analysis of solvation structures

All the structures used in density functional theory calculation were optimized by Gaussian 16 at B3LYP hybrid function with def2-TZVP basis. Then a single point calculation was carried at same level. DFT-D3(BJ) method was used to describe weak interaction between molecules. The electrostatic potential, IGMH⁵⁹, molecular vdW volume⁶⁰ and ELF⁶¹ were analyzed by Multiwfn and was drawn by VMD package⁶². The total binding energy (DE) was calculated using the $[\text{Ca}(\text{H}_2\text{O})_n]^{2+}$ ($n = 1-8$) complex as an example, according to $DE = E_{\text{Ca}(\text{H}_2\text{O})_n} - E_{\text{Ca}^{2+}} - nE_{\text{H}_2\text{O}}$, where $E_{\text{Ca}(\text{H}_2\text{O})_n}$, $E_{\text{Ca}^{2+}}$ and $E_{\text{H}_2\text{O}}$ are the energies of $[\text{Ca}(\text{H}_2\text{O})_n]^{2+}$, Ca^{2+} , and H_2O , respectively.

Declarations

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or Supplementary Information

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Author contributions

All authors approved the final version of the manuscript. Y.S.M. and H.Y.Y supervised the project. Y.-F.C. proposed the research direction and conceived the idea of the work. Y.-F.C. designed and performed the experiments. Y.-F.C., M.Z., H.S., Y.L., N.Z. and W.L. performed the materials characterizations and data analysis. Y.-F.C. and M.Z. performed the theoretical studies. Y.-F.C., Y.H.Z., Y.S.M. and H.Y.Y wrote the manuscript. All authors contributed to the discussion and the manuscript preparation.

Competing interests

The authors declare no competing interests.

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Figures

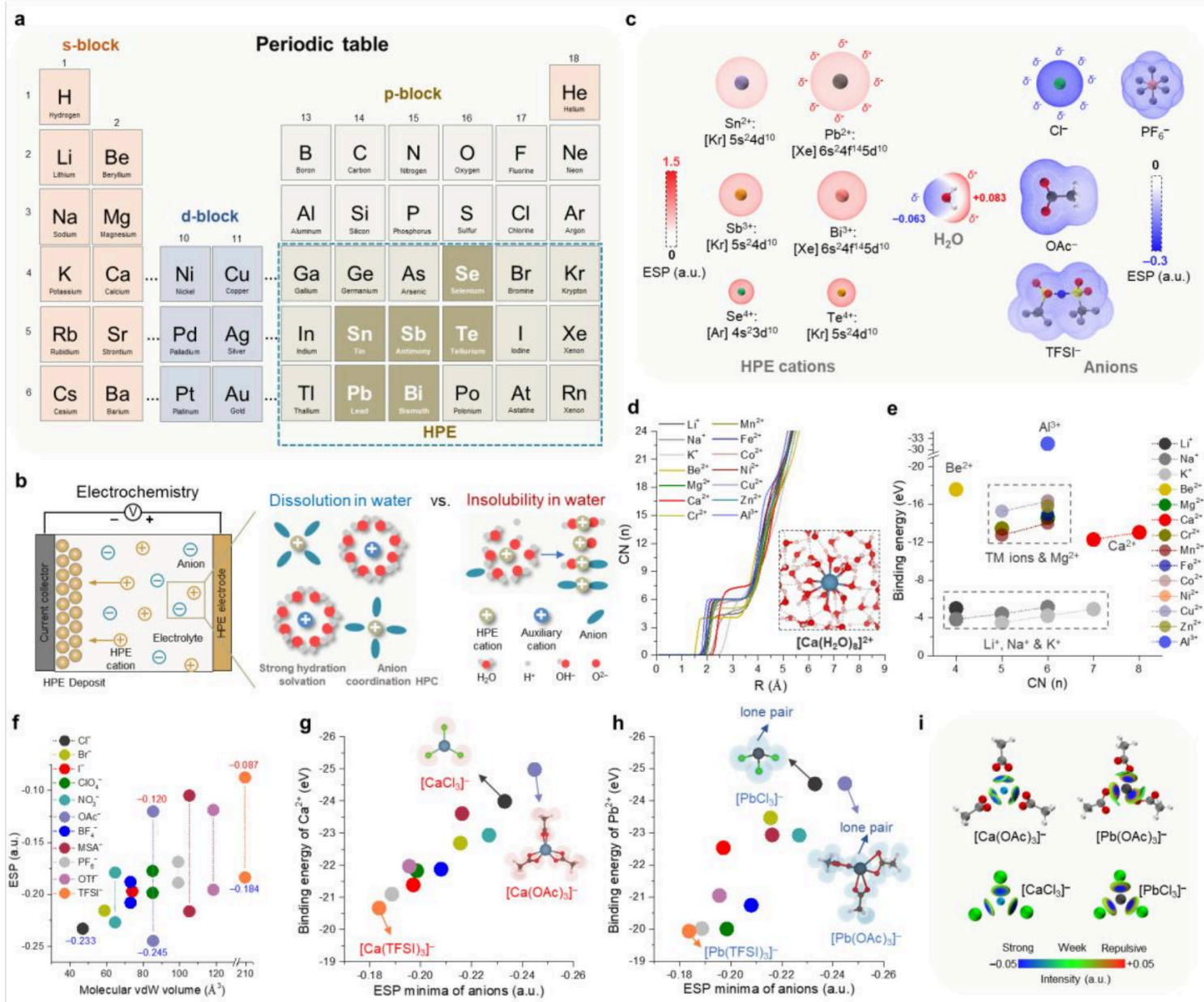


Figure 1

Design principles for stabilizing HPE cations in water. **a**, Position of representative HPEs in the periodic table. **b**, Schematic illustration of heavy p-block electrochemistry, showing soluble HPE cations formed through anion-coordinate solvation with strongly hydrated auxiliary cations, in contrast to insoluble HPE cations in water. **c**, Surface ESP distributions of HPE cations, H_2O , and anions. **d**, CNs of auxiliary cations in water obtained from AIMD simulations (derived from Supplementary Figs. 2, 3). **e**, Binding energies of hydrated auxiliary cations with varying CNs of H_2O molecules. **f**, Surface ESP distributions of various anions mapped as a function of their molecular van der Waals (vdW) volumes. **g**, Correlation between Ca^{2+} -anion binding energy for trianionic coordination structures and the anionic ESP minima. Insets: ELF maps (isosurface = 0.5) of DFT-optimized $[\text{CaCl}_3]^-$ and $[\text{Ca}(\text{OAc})_3]^-$ structures. **h**, Correlation between Pb^{2+} -anion binding energy for trianionic coordination structures and the anionic ESP minima.

Insets: ELF maps (isosurface = 0.5) of DFT-optimized $[\text{PbCl}_3]^-$ and $[\text{Pb}(\text{OAc})_3]^-$ structures. **i**, $\text{Sign}(\lambda_2)\rho$ colored isosurfaces of $\delta g_{\text{inter}} = 0.01$ a.u. from IGMH analyses of DFT-optimized $[\text{Ca}(\text{OAc})_3]^-$, $[\text{Pb}(\text{OAc})_3]^-$, $[\text{CaCl}_3]^-$, and $[\text{PbCl}_3]^-$ structures.

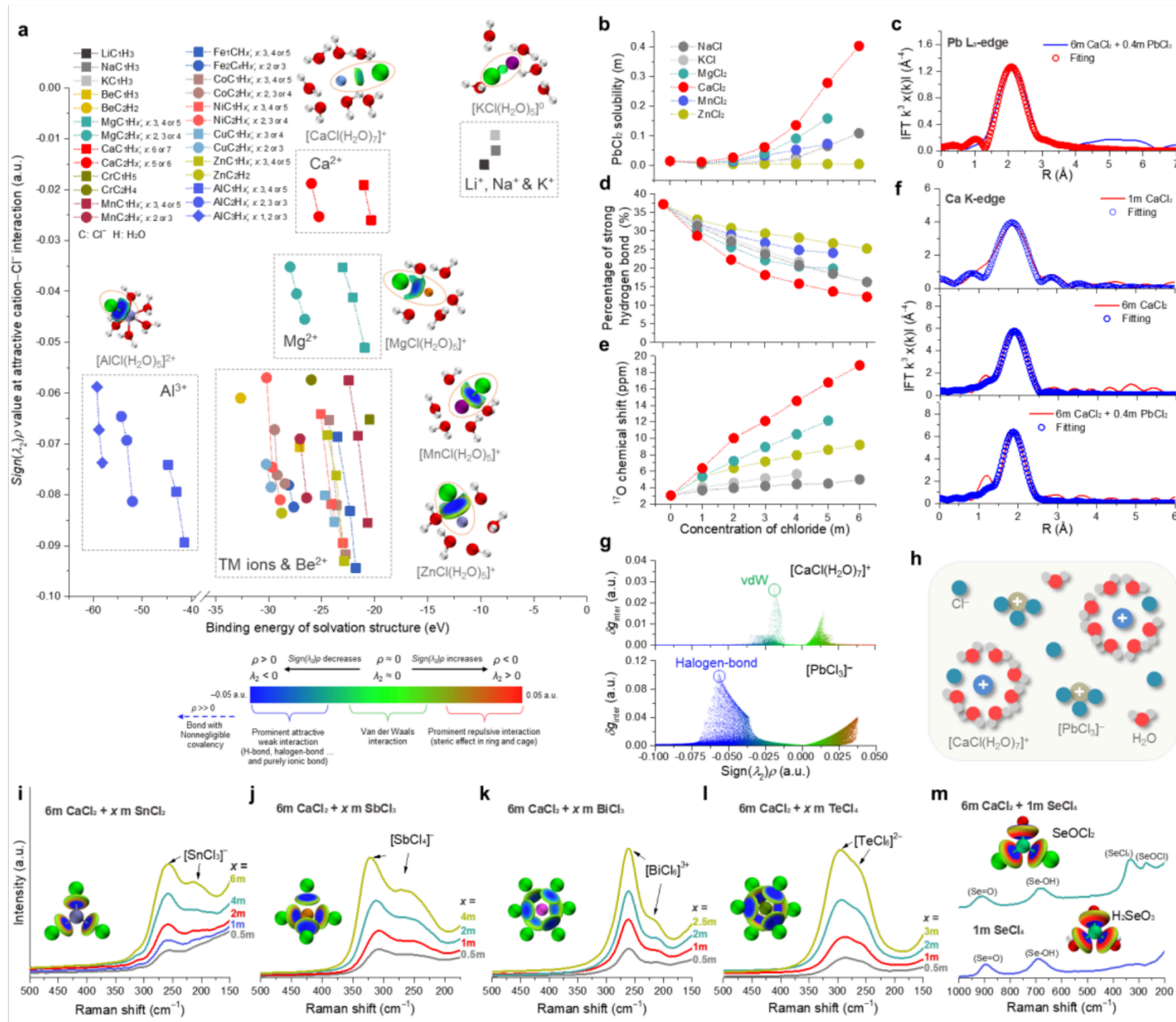


Figure 2

Proposed SICEs. **a**, Relationship between binding energy and $\text{sign}(\lambda_2)\rho$ value at the attractive cation-Cl⁻ interaction where δg_{inter} reaches its maximum. Insets: $\text{sign}(\lambda_2)\rho$ -colored isosurfaces at $\delta g_{\text{inter}} = 0.01$ a.u. from IGMH analyses of representative solvation structures. **b**, Solubility of PbCl_2 in various chloride-based solutions. **c**, Fourier transform magnitudes of Pb L₃-edge EXAFS spectrum (solid line) and fit (hollow circles) for 0.4 m PbCl_2 + 6 m CaCl_2 solution. **d**, **e**, Percentage of strong hydrogen-bonds obtained from Raman spectra (**d**) and ^{17}O NMR chemical shifts (**e**) in aqueous NaCl, KCl, MgCl₂, CaCl₂,

MnCl₂ and ZnCl₂ solutions with increasing concentrations. **f**, Fourier transform magnitudes of the Ca K-edge EXAFS spectra (solid line) and fits (hollow circles) for 1 m CaCl₂, 6 m CaCl₂ and 0.4 m PbCl₂ + 6 m CaCl₂ solutions. **g**, Scatter plots of δg_{inter} against $\text{sign}(\lambda_2)\rho$ for Ca²⁺–Cl[–] interactions in [CaCl(H₂O)₇]⁺ and Pb²⁺–Cl[–] interactions in [PbCl₃][–]. **h**, Schematic of soluble Pb²⁺ formation in water via strongly hydrated [CaCl(H₂O)₇]⁺ and Cl[–]-coordinated [PbCl₃][–]. **i–l**, Raman spectra of SnCl₂ (**i**), SbCl₃ (**j**), BiCl₃ (**k**) and TeCl₄ (**l**) in 6 m CaCl₂ solutions with increasing concentrations. **m**, Raman spectra of 1 m SeCl₄ and 1 m SeCl₄ + 6 m CaCl₂ solutions. Insets: $\text{sign}(\lambda_2)\rho$ -colored isosurfaces at $\delta g_{\text{inter}} = 0.01$ a.u. from IGMH analysis of DFT-optimized [SnCl₃][–] (**i**), [SbCl₄][–] (**j**), [BiCl₆]^{3–} (**k**), [TeCl₆]^{2–} (**l**), and H₂SeO₃ and SeOCl₂ (**m**) structures.

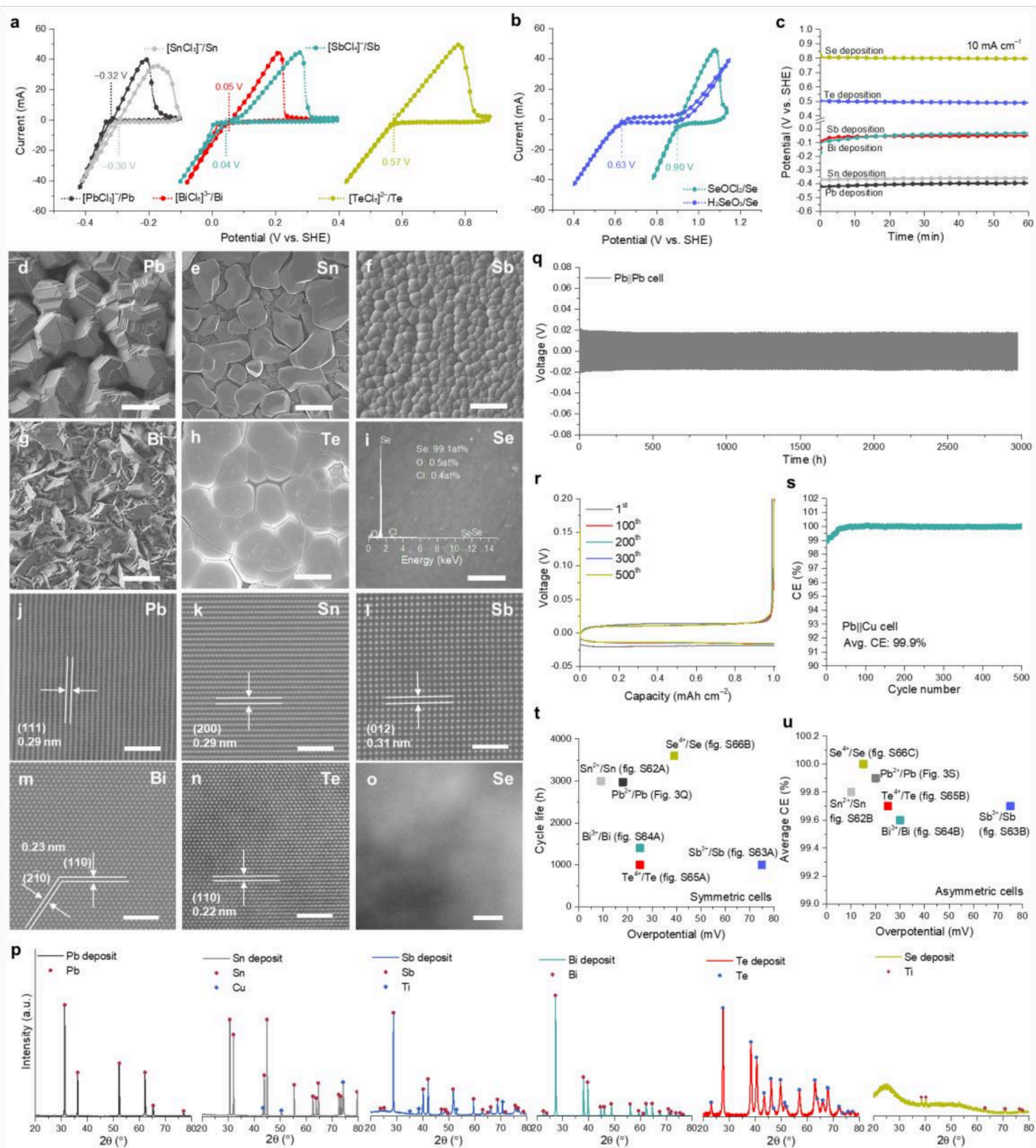


Figure 3

Reversible heavy p-block electrochemistry. **a, b,** CV curves of $[\text{PbCl}_3]^-/\text{Pb}$, $[\text{SnCl}_3]^-/\text{Sn}$, $[\text{SbCl}_4]^-/\text{Sb}$, and $[\text{BiCl}_6]^{3-}/\text{Bi}$ (a), and $\text{H}_2\text{SeO}_3/\text{Se}$ and SeOCl_2/Se (b) in SICEs at a scan rate of 1 mV s^{-1} . **c,** Galvanostatic electrodeposition of HPEs in SICEs at 10 mA cm^{-2} for 1 h. **d–i,** SEM images of Pb (d), Sn (e), Sb (f), Bi (g), Te (h), and Se (i) electrodeposits. Scale bars: 20 μm . Inset in (i): EDS mapping of Se electrodeposits.

j–o, Atomic-resolution HAADF-STEM images of Pb (**j**), Sn (**k**), Sb (**l**), Bi (**m**), Te (**n**), and Se (**o**) electrodeposits. Scale bars: 2 nm. **p**, Corresponding XRD patterns of HPE electrodeposits with standard reference codes. **q**, Cycling performance of Pb||Pb symmetric cell at 1 mA cm⁻² and 1 mAh cm⁻². **r, s**, Voltage profiles (**r**) and CE (**s**) of Pb||Cu asymmetric cell at 1 mA cm⁻² with a fixed plated capacity of 1 mAh cm⁻². **t, u**, Summary of cycle life (**t**) and average CEs (**u**) of symmetric and asymmetric HPE cells during repeated plating/stripping behaviors.

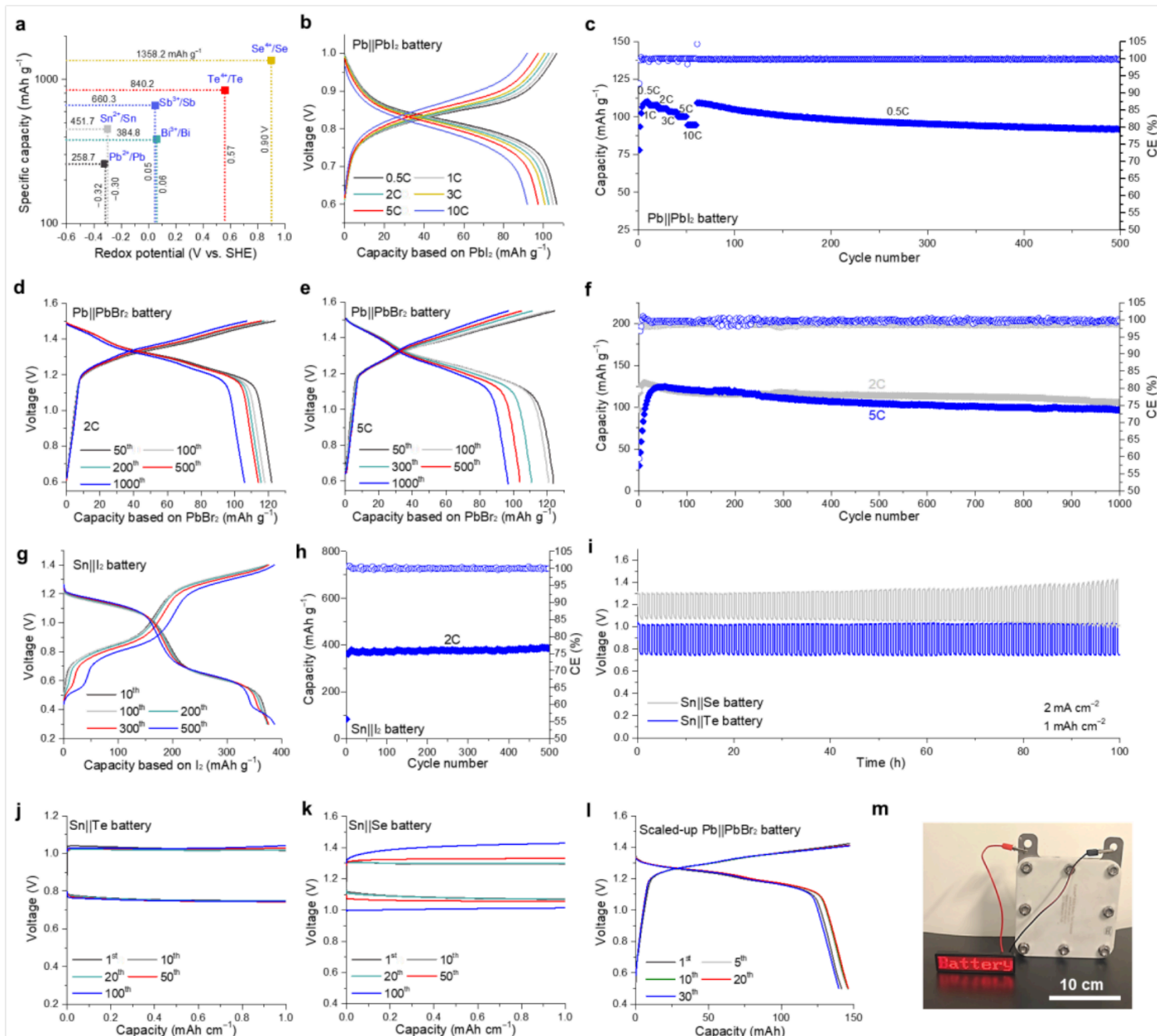


Figure 4

Proposed aqueous HPE-based batteries. **a**, Redox potentials and theoretical specific capacities of HPE electrodes. **b, c**, Rate-dependent charge/discharge profiles (**b**) and cycling performance (**c**) of Pb||PbI₂ full battery at different rates. **d–f**, Charge/discharge profiles of Pb||PbBr₂ full batteries at 2 C (**d**) and 5 C (**e**).

(**e**), and corresponding cycling performance (**f**). **g, h**, Charge/discharge profiles (**g**) and cycling performance (**h**) of SnSeI_2 full battery at 2 C. **i–k**, Voltage polarization curves of SnSe and SnTe full batteries at 2 mA cm^{-2} and 1 mAh cm^{-2} (**i**), and corresponding charge/discharge profiles of SnTe (**j**) and SnSe (**k**) full batteries. **l, M**, Charge/discharge profiles of scaled-up PbSePbBr_2 full battery at 40 mA (**l**), and its photograph powering an LED display (**m**).

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