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# Insights into the halogen-induced p-band center regulation promising high-performance lithium–sulfur batteries†

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Sn-based halide perovskites are expected to solve the problems of the shuttle effect and sluggish redox kinetics of lithium polysulfides (LiPSs) in lithium–sulfur batteries (LSBs) due to their high conductivity and electrocatalytic activity, but their intrinsic catalytic mechanism for LiPSs remains to be explored. Herein, halide perovskites with varying halide anions, Cs<sub>2</sub>SnX<sub>6</sub> (X = Cl, Br, I), are purposefully designed to unveil the halogen-induced regulatory mechanism. Theoretical calculations demonstrate that increasing the halogen atomic number induces the shift of the p-band center closer to the Fermi level, which results in the localized charge distribution around halide anions and rapid charge separation/transfer at Sn sites, enhancing the adsorptive and catalytic activity and redox kinetics of LiPSs. Experimental investigations exhibit that LSBs assembled with the Cs<sub>2</sub>SnI<sub>6</sub> modified separator deliver a high initial capacity of 1000 mA h g<sup>-1</sup> at 2C, with a minimum decay rate of 0.068% per cycle after 500 cycles. More impressively, the Cs<sub>2</sub>SnI<sub>6</sub> battery with a high sulfur loading (6.1 mg cm<sup>-2</sup>) and a low electrolyte/sulfur ratio (5.5 μL mg<sup>-1</sup>) achieves a remarkable reversible capacity of 768.8 mA h g<sup>-1</sup>, along with robust wide-temperature-tolerant cycling performance from –20 to 50 °C. These findings underscore the critical role of p-band center regulation in rationally designing advanced LSBs.

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## 1. Introduction

Lithium–sulfur batteries (LSBs) have been developed for next-generation energy storage because of their high theoretical capacity (1675 mA h g<sup>-1</sup>), high energy density (2600 W h kg<sup>-1</sup>), low cost and environmental friendliness when compared to lithium-ion batteries.<sup>1–3</sup> However, the industrial application of LSBs has been hindered seriously by several challenging bottlenecks. For example, due to the low conductivity of sulfur species and Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub>, the “shuttle effect”, which is caused by the dissolution of lithium polysulfides (LiPSs) in the electrolyte, leads to unsatisfactory actual capacity and cycling stability of LSBs. In addition, the sluggish conversion kinetics of LiPS also lead to a rapid decrease in the cycling capability of LSBs.<sup>4–6</sup> The shuttle effect and sluggish conversion kinetics of LiPSs in LSBs can be mitigated by constructing cathode materials,<sup>7</sup> designing multifunctional composite separators,<sup>8</sup> and optimizing electrolytes and lithium anodes.<sup>9</sup> Among them, the most critical aspect of separator design has been identified as the

introduction of electrocatalytic materials that have both adsorption and catalytic properties toward LiPSs, which can effectively address the challenges mentioned above faced by LSBs.<sup>10,11</sup>

In previous research studies, various polar and non-polar electrocatalytic materials have been explored to adsorb LiPSs and catalyze their redox reactions,<sup>12–21</sup> including metal oxides,<sup>22</sup> metal phosphides,<sup>23</sup> and metal sulfides.<sup>24</sup> Among them, oxide perovskites demonstrate good adsorptive and catalytic effects on LiPSs through their ferroelectric effect.<sup>25</sup> For instance, oxide perovskites such as LaNiO<sub>3</sub>,<sup>26</sup> SrTiO<sub>3</sub>,<sup>27</sup> and the layered double perovskite PrBaCo<sub>2</sub>O<sub>6</sub><sup>28</sup> have been utilized to fabricate separators for LSBs. These oxide perovskites inhibit the shuttle effect and promote the conversion of LiPSs. However, oxide perovskites still face challenges related to a lack of active sites and poor conductivity.<sup>29</sup> In practical applications, the conductivity and electrocatalytic activity of electrocatalytic materials can be enhanced by adjusting their surface electronic state and the rate of charge transfer. Halide perovskites are known for their superior charge transport properties, tunable band structure, and high defect tolerance, which endow them with excellent electrocatalytic activity.<sup>30–34</sup> Halide perovskites can also regulate structural characteristics by altering the material composition. However, the presence of toxic lead in the chemical composition of most halide perovskites and their structural instability remain the two main

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limiting factors hindering their application.<sup>35</sup> Compared to other halide perovskites, halide double perovskites possess a greater number of halogen active sites and exhibit enhanced chemical stability in air and polar solutions. In contrast, halide perovskites are prone to oxidation in air and react with water and polar solutions.<sup>36</sup> Traditional lead-based halide perovskites have restricted applications due to the toxicity of lead. Sn-based halide double perovskites are environmentally friendly and have a narrower band gap than other metal-based halide perovskites, which render better conductivity to them.<sup>37</sup> Moreover, by regulating the p-band center, higher ion/electron conductivity can be achieved, which helps to improve the adsorption and catalytic performance toward LiPSs. To date, the exploration of p-band center regulation of Sn-based halide double perovskites and their application in LSBs has been limited, particularly lacking in-depth investigations into the intrinsic mechanism of halide anions catalyzing LiPS conversion at the atomic scale.

With these comprehensive considerations in mind, in this contribution, we have purposefully constructed a series of Sn-based halide double perovskites with different halide anions,  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ), to explore the regulatory mechanism of halide anions on the electronic structure. Both theoretical calculations and experimental results coherently confirmed that the p-band center of halogen anions shifted positively toward the Fermi level with the increase in the halogen atomic number. Such a unique electronic structural change endowed the material with remarkable electrocatalytic performance due to several advantages it possesses. Specifically, the I atoms in  $\text{Cs}_2\text{SnI}_6$  first promoted the p-band center to be closer to the Fermi level, resulting in a higher charge transfer rate, which was more beneficial for catalyzing the conversion of LiPSs. Second,  $\text{Cs}_2\text{SnI}_6$  achieved more localized charge distribution around the I atom, rendering a weaker charge distribution at the Sn center and promoting charge separation and transfer, which benefited the adsorptive and catalytic reactions of LiPSs on its surface. Third, the binding energy between  $\text{Cs}_2\text{SnI}_6$  and LiPSs was higher than the other two counterparts, while  $\text{Cs}_2\text{SnI}_6$  had the lowest energy barriers for LiPSs and  $\text{Li}_2\text{S}$  decomposition reactions. As a result,  $\text{Cs}_2\text{SnI}_6$  exhibited excellent adsorption and catalytic conversion capability for LiPSs. The initial specific capacity of LSBs assembled with  $\text{Cs}_2\text{SnI}_6$  modified separators was as high as  $1000 \text{ mA h g}^{-1}$  at 2C, along with a decay rate of only 0.068% after 500 cycles. Notably, the  $\text{Cs}_2\text{SnI}_6$  battery with a high-S loading ( $6.1 \text{ mg cm}^{-2}$ ) and a low electrolyte/sulfur (E/S) ratio ( $5.5 \mu\text{l mg}^{-1}$ ) still exhibited an extremely high capacity of  $768.8 \text{ mA h g}^{-1}$ . Additionally, the  $\text{Cs}_2\text{SnI}_6$  battery exhibited initial capacities of  $912.7 \text{ mA h g}^{-1}$  at  $-20^\circ\text{C}$  at 0.1C and  $1350.7 \text{ mA h g}^{-1}$  at  $50^\circ\text{C}$  at 0.5C, respectively. Encouragingly, the reversible capacities of  $772.6$  and  $892.3 \text{ mA h g}^{-1}$  could still be retained after 100 cycles at  $-20$  at  $50^\circ\text{C}$ , respectively. All in all, LSBs assembled with the  $\text{Cs}_2\text{SnI}_6$  modified separator presented high reversible capacity and stable cycling performance, even under harsh operation conditions, including high sulfur loading, low E/S ratios, and extremely high/low working temperatures.

## 2. Experimental section

### 2.1. Preparation of materials

Sn-based halide double perovskites  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) were synthesized by a hydrothermal method. First, 0.947 g of tin acetate and 0.384 g of cesium acetate were dissolved in 10 mL of HX ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and stirred for 1 h. The mixed solution was transferred to a 25 mL autoclave and heated at  $150^\circ\text{C}$  for 3 h. After being cooled to room temperature, the precipitate was collected by centrifugation, washed several times with isopropanol, and dried in a vacuum at  $60^\circ\text{C}$  for 24 h. Then, the perovskite was ball-milled for 36 h to reduce the size of the perovskite particles.

### 2.2. Material characterization

The crystal structure of the original sample powder was characterized using a Rigaku Ultima IV XRD instrument produced by Rigaku Corporation (Cu-K $\alpha$  radiation source; voltage, 40 kV; current, 20 mA; sweep speed,  $1^\circ$  or  $10^\circ \text{ min}^{-1}$ ). To obtain more detailed crystal structure data, the XRD data were refined using the Rietveld-refinement method and the General Structure Analysis System software. The microscopic morphology was analyzed using an FEI-Quanta FEG 250 field emission scanning electron microscope. The high-resolution microscopic morphology and structure of the material were observed using a JEM-2010F transmission electron microscope from JEOL Japan, and selected area electron diffraction (SAED) was conducted to observe the crystal plane composition. The element valence states were studied using XPS (Physical Electronics 5400 ESCA). The sulfur content in the cathode material was analyzed by thermogravimetry (TG, SDT 650).

### 2.3. Visualized adsorption of $\text{Li}_2\text{S}_6$

$\text{Li}_2\text{S}_6$  solution was prepared to characterize the adsorption properties of the material. S powder and  $\text{Li}_2\text{S}$  were mixed according to the stoichiometric ratio, dissolved in dimethyl ether, and stirred until transparent. The concentration of  $\text{Li}_2\text{S}_6$  was  $2.5 \text{ mmol L}^{-1}$ . 0.1 mol of  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) was added to 4.0 mL of  $\text{Li}_2\text{S}_6/\text{DME}$  solution. After shaking for 1.0 min, the adsorption of  $\text{Li}_2\text{S}_6$  on different adsorbents was observed after 6 h. The adsorption supernatant was diluted with dimethyl ether (1 : 8) and analyzed by ultraviolet spectroscopy. After adsorbing  $\text{Li}_2\text{S}_6$ , the material was dried in a glove box filled with Ar gas and subjected to XPS analysis.

### 2.4. Nucleation of $\text{Li}_2\text{S}$

S and  $\text{Li}_2\text{S}$  were mixed stoichiometrically and dissolved in a mixed solution of 1, 3-dioxopentane/dimethyl ether ( $v/v = 1/1$ ) containing 1.0 mol per L lithium bis(trifluoromethanesulfonyl) imide (LiTFSI).  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) particles were ultrasonically dispersed in isopropyl alcohol and dropped on carbon paper to prepare  $\text{Li}_2\text{S}$  nucleation plates. The battery was assembled and discharged at a constant current of 0.112 mA to 2.10 V and then discharged at a constant voltage of 2.09 V until the current was lower than  $10^{-5} \text{ A}$  for  $\text{Li}_2\text{S}$  nucleation and



growth. According to Faraday's law, the charge of the whole process was calculated to evaluate the nucleation/growth rate of  $\text{Li}_2\text{S}$ .

### 2.5. Assembly and tests of $\text{Li}_2\text{S}_6$ symmetric cells

The carbon paper was cut into 12 mm discs, and ethanol dispersions of  $\text{Cs}_2\text{SnX}_6$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) particles were dropped onto the discs to fabricate symmetrical battery electrodes with a loading of  $0.5 \text{ mg cm}^{-2}$ . Two identical electrodes were assembled into a standard 2025 button cell containing  $20.0 \mu\text{L}$  of  $\text{Li}_2\text{S}_6$  ( $0.5 \text{ mol L}^{-1}$  in  $[\text{S}]$ ) and DOL/dimethyl ether ( $v/v = 1/1$ ) electrolyte. The preparation method of the  $\text{Li}_2\text{S}_6$  electrolyte was identical to that of the  $\text{Li}_2\text{S}_8$  solution. Cyclic voltammetry (CV) curves of the above symmetrical cells were recorded between  $-0.8$  and  $0.8 \text{ V}$  (Shanghai Chenhua CHI660e Electrochemical Workstation). The implemented scanning rate was  $100 \text{ mV s}^{-1}$ .

### 2.6. Cell assembly and electrochemical measurements

$\text{Cs}_2\text{SnI}_6$ , carbon nanotubes (CNTs), and polyvinylpyrrolidone (PVP, K30) binder were uniformly mixed in isopropanol at a mass ratio of  $6:3:1$ , and the resulting mixture was ultrasonically treated for 2 h, stirred for 3 h, and vacuum filtered onto the commercial Celgard 2500. The modified separator was prepared by drying at  $60 \text{ }^\circ\text{C}$  and heating in an oven for 12 h. Control samples,  $\text{Cs}_2\text{SnBr}_6$  modified separators, and  $\text{Cs}_2\text{SnCl}_6$  modified separators (with the same mass ratio as the above samples) were prepared using the same procedure. Sulfur powder and Ketjen black (KB) were ground and mixed at a mass ratio of  $3:1$ . The resulting mixture was transferred to a stainless steel high pressure vessel ( $50 \text{ mL}$ ) lined with polytetrafluoroethylene and heated at  $155 \text{ }^\circ\text{C}$  for 12 h to obtain the KB and sulfur composite (KB/S). The cathode was prepared by uniformly mixing 80 wt% KB/S composite, 10 wt% Super P, and 10 wt% polyvinylidene difluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP). Then, the mixed slurry was scraped onto aluminum foil and dried at  $60 \text{ }^\circ\text{C}$  for 12 h to obtain the S cathode. The S load was maintained at approximately  $1.0 \text{ mg cm}^{-2}$  (LA133 binder was used for the high sulfur loading tests). Next, the prepared S cathode, modified separator, and lithium anode were assembled into a CR2025 battery filled with Ar in a glove box. A  $30 \mu\text{L}$  electrolyte containing  $1 \text{ M LiTFSI}$  was added to the battery, where LiTFSI was present in a mixed solvent of 1,2-dimethoxyethane and 1,3-dioxocyclopentene ( $1:1$  in volume), containing 2%  $\text{LiNO}_3$ . The assembled battery was tested at room temperature using the LAND CT2001A battery test system. Cyclic voltammetry (CV) was performed on a CHI660E electrochemical workstation at a scan rate of  $0.1 \text{ mV s}^{-1}$ . Additionally, electrochemical impedance spectroscopy (EIS) tests were performed on the same instrument with an amplitude of  $5 \text{ mV}$  in a frequency range of  $10 \text{ mHz}$  to  $100 \text{ kHz}$ .

### 2.7. Computational details

The Perdew–Burke–Ernzerhof exchange–correlation generalized gradient approximation (GGA) was used for all computational structural relaxation processes in the study. Partial occupancies of the Kohn–Sham orbitals were allowed using the

Gaussian smearing method with a width of  $0.05 \text{ eV}$ . The electronic energy was considered self-consistent when the energy change was smaller than  $10^{-5} \text{ eV}$ . Geometry optimization was considered convergent when the energy change was smaller than  $0.05 \text{ eV } \text{Å}^{-1}$ . The Brillouin zone integration used  $2 \times 2 \times 1$  Monkhorst–Pack *k*-point sampling for the structure. The adsorption energy ( $E_{\text{ads}}$ ) was calculated as follows:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{ad}} - E_{\text{sub}} \quad (1)$$

where  $E_{\text{total}}$ ,  $E_{\text{ad}}$ , and  $E_{\text{sub}}$  represent the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The free energy was calculated using the following equation:

$$\Delta G = \Delta E_{\text{ads}} + \Delta E_{\text{zpe}} - T\Delta S \quad (2)$$

where  $\Delta G$ ,  $\Delta E_{\text{ads}}$ ,  $\Delta E_{\text{zpe}}$ , and  $T\Delta S$  represent the free energy and total energy from DFT calculations, zero point energy, and entropic contributions, respectively, where  $T$  was set to  $300 \text{ K}$ .

## 3. Results and discussion

### 3.1. Theoretical calculation and electronic structure analysis

As is well established,  $\text{Cs}_2\text{SnX}_6$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) exhibit a highly symmetrical cubic structure and possess excellent stability both in air and water, rendering them ideal candidates for exploring the regulatory mechanisms of halide anions.<sup>33</sup> Based on density functional theory (DFT), the electronic structure of  $\text{Cs}_2\text{SnX}_6$  was investigated through density of states (DOS) and band structure calculations prior to the experiment. Halogen substitutions alter the bulk-phase configuration of Sn-based halide double perovskites. To demonstrate the intrinsic semiconducting properties through band structure and bandgap calculations, bulk-phase models were employed for DOS analysis.<sup>38</sup> Conversely, surface structural models were adopted for PDOS calculations to assess the p-band center of surface halogens, given that polysulfide adsorption and catalytic mechanisms in LSBs primarily operate at material surfaces.<sup>39</sup> The band gap and DOS for bulk  $\text{Cs}_2\text{SnI}_6$  are presented in Fig. 1a. The simulated band gap value is  $0.15 \text{ eV}$ , corresponding to the DOS distribution, which is significantly smaller than those of bulk  $\text{Cs}_2\text{SnBr}_6$  ( $1.36 \text{ eV}$ , Fig. 1b) and  $\text{Cs}_2\text{SnCl}_6$  ( $2.53 \text{ eV}$ , Fig. 1c). The electrical conductivity of bulk  $\text{Cs}_2\text{SnX}_6$  increases as the band gap decreases, which is intimately linked to the electrochemical performance of LSBs. Notably,  $\text{Cs}_2\text{SnI}_6$  exhibits the narrowest band gap, corresponding to the highest electrical conductivity. This structural feature significantly enhances the electron transport efficiency and is extremely advantageous for electrochemical reactions in LSBs. Given that the electrocatalytic reaction is essentially an electron transfer process, the valence electrons of elements, serving as electron donors or acceptors, exert a direct influence on the efficiency of electron transfer and play a pivotal role in electrocatalytic reactions.<sup>40</sup> For metal elements, their valence electrons are primarily electrons of d bands, while for nonmetal elements, their valence electrons are the p band electrons. The projected density of states (PDOS)



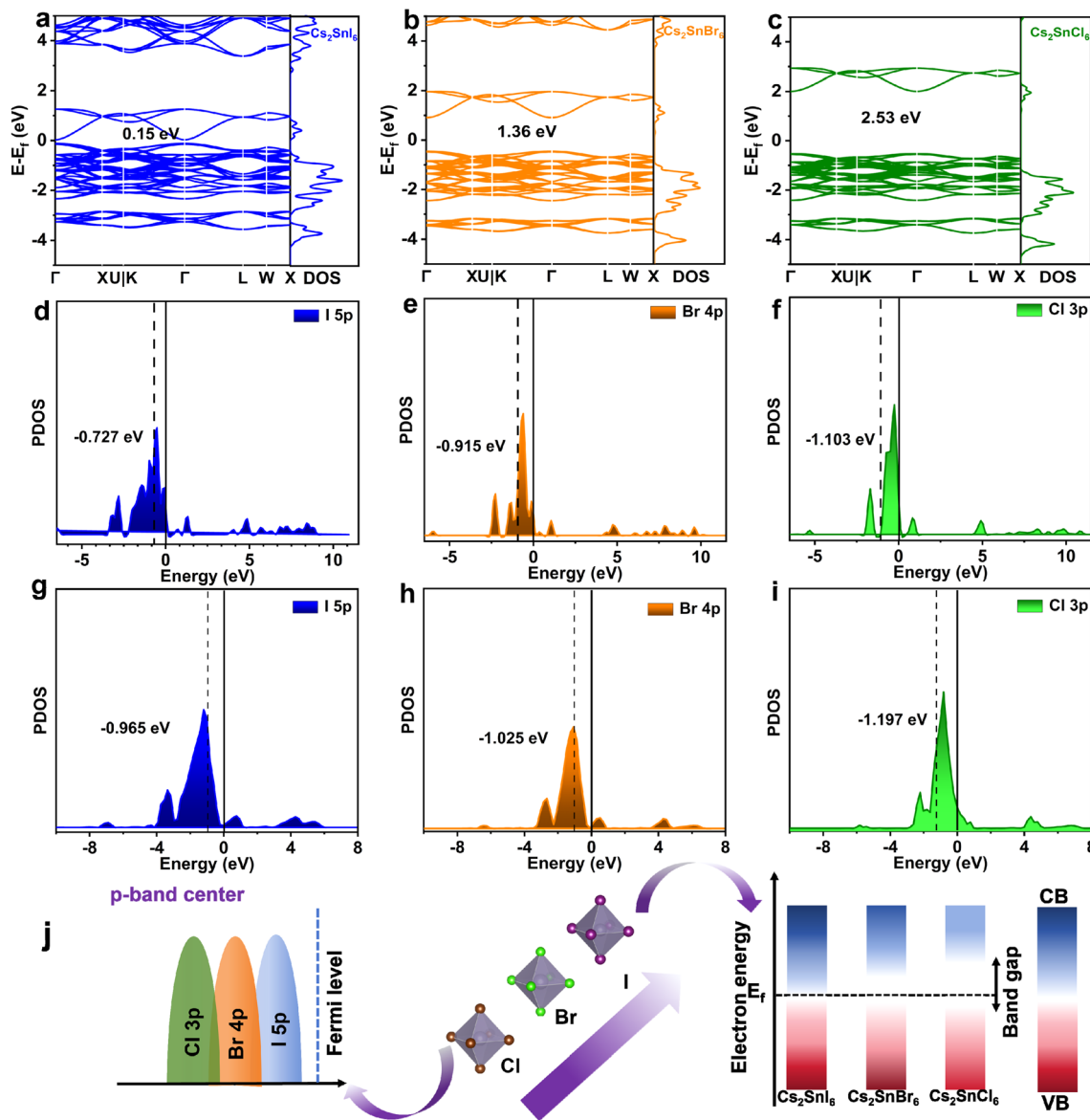


Fig. 1 DFT calculations of  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ): electronic band structures of (a)  $\text{Cs}_2\text{SnI}_6$ , (b)  $\text{Cs}_2\text{SnBr}_6$ , and (c)  $\text{Cs}_2\text{SnCl}_6$ . (d–i) PDOS files of (d and g) I 5p, (e and h) Br 4p, and (f and i) Cl 3p for (d–f) fresh  $\text{Cs}_2\text{SnX}_6$  and (g–i) after adsorbing  $\text{Li}_2\text{S}_6$ . (j) Schematic illustration of the p-band center regulation and electronic band structure of halide anions in  $\text{Cs}_2\text{SnX}_6$ .

of the p-band centers for nonmetal elements (Cl, Br, and I) was calculated to investigate the role of valence electrons in electrocatalytic reactions. The PDOS plots of I in  $\text{Cs}_2\text{SnI}_6$  reveal that the calculated p-band center is located at  $-0.727$  eV (Fig. 1d). By contrast, the p-band center of Br is centered at  $0.915$  eV for the case of  $\text{Cs}_2\text{SnBr}_6$  (Fig. 1e). As for  $\text{Cs}_2\text{SnCl}_6$ , the calculated p-band center of Cl is  $-1.103$  eV (Fig. 1f), positioned farthest from the Fermi level among the three. Clearly, as the halogen atomic number increases, the p-band centers move even closer to the Fermi level, which can potentially accelerate electron transfer.<sup>41</sup> The change in valence electrons of halogen elements facilitates the formation and cleavage of bonds during the redox process of LiPSs, ultimately enhancing the efficiency of the electrocatalytic process.<sup>42</sup>

During the charge–discharge cycles of LSBs, LiPSs are always adsorbed onto the surface of electrocatalysts  $\text{Cs}_2\text{SnX}_6$ . This process is accompanied by the redistribution of electrons between the electrocatalysts and LiPSs. The PDOS plot reveals that the p-band center of I in the  $\text{Cs}_2\text{SnI}_6\text{-Li}_2\text{S}_6$  system is located at  $-0.727$  eV (Fig. 1g), which is the closest to the Fermi level among the three systems. This electronic structural feature enhances the interaction between  $\text{Cs}_2\text{SnI}_6$  and  $\text{Li}_2\text{S}_6$ , thereby facilitating the adsorption and activation of  $\text{Li}_2\text{S}_6$ . In the  $\text{Cs}_2\text{SnBr}_6\text{-Li}_2\text{S}_6$  system, the p-band center of Br is located at  $-1.025$  eV (Fig. 1h). In contrast, in the  $\text{Cs}_2\text{SnCl}_6\text{-Li}_2\text{S}_6$  system, the p-band center of Cl is located at  $-1.197$  eV (Fig. 1i), representing the most negative value among the three systems. The results here suggest that as the element changes from I to Cl, its p-band



center gradually shifts upwards and away from the Fermi level, which will weaken the interaction strength between the electrocatalyst and  $\text{Li}_2\text{S}_6$ , thereby resulting in decreased electrocatalytic performance. By investigating the interaction between  $\text{Li}_2\text{S}_6$  and  $\text{Cs}_2\text{SnX}_6$ , the underlying mechanisms through which these electronic structure changes influence the electrocatalytic performance have been elucidated further. The schematic diagram (Fig. 1j) explicitly illustrates the regulatory mechanism of the p-band center and electronic structure induced by the halogen change in  $\text{Cs}_2\text{SnX}_6$ , where  $\text{Cs}_2\text{SnCl}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnI}_6$  all exhibit octahedral structures. The transition of halide anions from Cl to I first causes a shift in the position of the p-band center relative to the Fermi level. As the atomic number of the halogen increases, the p-band center of the halide anion shifts toward the Fermi level, indicating an enhanced electron transfer rate, and consequently improves the electrocatalytic performance. Besides, the band gap also changes accordingly. The band gaps of the conduction band (CB) and valence band (VB) of  $\text{Cs}_2\text{SnCl}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnI}_6$  gradually decrease, which leads to an increase in their conductivity. Overall, a series of theoretical calculations for  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) demonstrate that by contrapuntally adjusting the halogen composition in halide perovskites, the p-band center and electronic structure of halide anions can be effectively regulated, thereby improving the conductivity and electrocatalytic activity of the materials.

### 3.2. Physicochemical and structural characterization studies

To verify the theoretical calculation results mentioned above, a series of Sn-based halide double perovskites  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) with different halide anions were synthesized by a hydrothermal method.<sup>43</sup> Typical X-ray diffraction (XRD) patterns reveal that the diffraction peaks near  $2\theta = 13^\circ, 26^\circ,$  and  $52^\circ$  correspond to the (111), (222), and (622) crystal planes of  $\text{Cs}_2\text{SnI}_6$  (JCPDS no. 73-0330), respectively (Fig. S1, ESI<sup>†</sup>). Additionally, the distinct and sharp peaks indicate a high degree of crystallinity in  $\text{Cs}_2\text{SnI}_6$ . Similar reflections are also observed for  $\text{Cs}_2\text{SnBr}_6$  (JCPDS no. 97-8957, Fig. S1b, ESI<sup>†</sup>) and  $\text{Cs}_2\text{SnCl}_6$  (JCPDS no. 75-0376, Fig. S1c, ESI<sup>†</sup>). It is noteworthy that after comparing XRD patterns of the three samples, the characteristic peak position shifts to even smaller angles with increasing halogen atomic number, featuring an increase in the unit cell volume of the samples. To determine their detailed crystal structures, the Rietveld method was employed to fit the experimental XRD data using GSAS/EXPGUI software. The low  $R_p$  and  $R_{wp}$  factors consistent with experimental data were obtained, demonstrating a high degree of fitting accuracy.  $\text{Cs}_2\text{SnI}_6$  (Fig. 2a),  $\text{Cs}_2\text{SnBr}_6$  (Fig. 2b), and  $\text{Cs}_2\text{SnCl}_6$  (Fig. 2c) exhibit the same perovskite structure ( $Fm\bar{3}m$ ) with lattice volumes of 1117, 1273, and  $1577 \text{ \AA}^3$ , respectively (Fig. S2, ESI<sup>†</sup>). It is observed that as the halogen atomic number increases, the lattice parameters  $a, b,$  and  $c$  also increase accordingly, leading to an expansion of the unit cell volume, which directly influences the structural

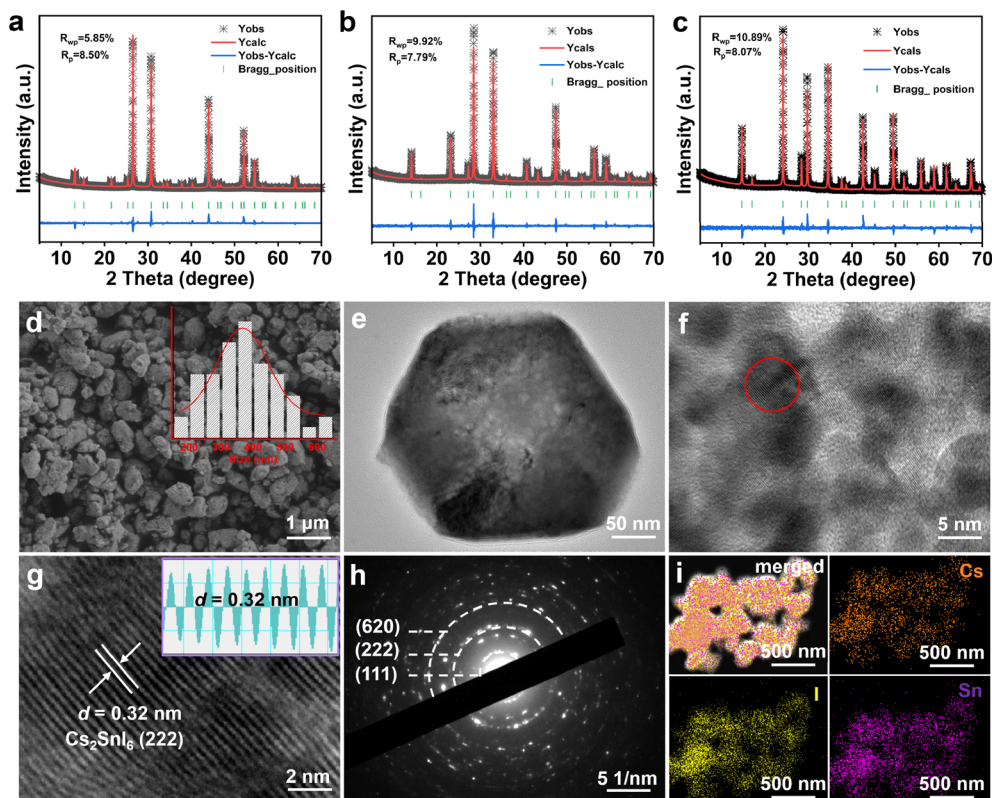


Fig. 2 XRD Rietveld refinement of (a)  $\text{Cs}_2\text{SnI}_6$ , (b)  $\text{Cs}_2\text{SnBr}_6$ , and (c)  $\text{Cs}_2\text{SnCl}_6$ . (d) FESEM, (e and f) TEM and (g) HRTEM images, (h) SAED pattern, and (i) EDS mapping images of Cs, Sn, and I elements for  $\text{Cs}_2\text{SnI}_6$ . The inset in panel (d) shows the particle size distribution diagram.



framework of the material. The expanded unit cell volume will boost ion diffusion and electron transport,<sup>44</sup> contributing to the improved electrochemical performance of LSBs.

Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) were conducted to elaborately investigate the morphological and structural evolution of the samples. FESEM observations (Fig. S3, ESI<sup>†</sup>) reveal that the as-prepared Cs<sub>2</sub>SnCl<sub>6</sub>, Cs<sub>2</sub>SnBr<sub>6</sub>, and Cs<sub>2</sub>SnI<sub>6</sub> exhibit well-defined octahedral structures with particle size ranging approximately from 1 to 10 μm, and Cs<sub>2</sub>SnI<sub>6</sub> presents the most uniform size distribution among them. Due to their micro-scale size, the subsequent ball-milling is highly necessary to obtain the nano-dimensional Cs<sub>2</sub>SnX<sub>6</sub> samples before their application in LSBs. As noted, Cs<sub>2</sub>SnI<sub>6</sub> forms uniform block shaped particles with sizes of approximately 200–500 nm after ball-milling (Fig. 2d). In contrast, the size of Cs<sub>2</sub>SnBr<sub>6</sub> significantly decreases to ~200 nm (Fig. S4a, ESI<sup>†</sup>), along with the smaller size of ~100 nm for Cs<sub>2</sub>SnCl<sub>6</sub> (Fig. S4b, ESI<sup>†</sup>), indicating that ball milling effectively reduces the particle size, which will contribute to its uniform distribution in the modified separator. The clear lattice fringes with a well-defined spacing of 0.32 nm, as presented in Fig. 2g,

correspond to the (222) crystal plane of Cs<sub>2</sub>SnI<sub>6</sub>, indicating its good crystallinity. Similarly, the well-discerned lattice fringes with spacings of 0.31 and 0.30 nm are easily identified and ascribed to the (222) crystal planes of Cs<sub>2</sub>SnBr<sub>6</sub> (Fig. S5a, ESI<sup>†</sup>) and Cs<sub>2</sub>SnCl<sub>6</sub> (Fig. S5b, ESI<sup>†</sup>), respectively. The variation trend in spacing follows the order of Cs<sub>2</sub>SnI<sub>6</sub> > Cs<sub>2</sub>SnBr<sub>6</sub> > Cs<sub>2</sub>SnCl<sub>6</sub>, which is in good agreement with the XRD refinement results presented above. Furthermore, the clear diffraction rings of the selected area electron diffraction (SAED) pattern (Fig. 2h) indicate the polycrystalline nature of Cs<sub>2</sub>SnI<sub>6</sub>, along with the well-indexed (111), (222), and (620) crystal planes. Similarly, both Cs<sub>2</sub>SnBr<sub>6</sub> (Fig. S5c, ESI<sup>†</sup>) and Cs<sub>2</sub>SnCl<sub>6</sub> (Fig. S5d, ESI<sup>†</sup>) exhibit polycrystalline features as well, owing to their multiple clear diffraction rings. Further elemental energy dispersive spectroscopy (EDS) mappings visualize the homogeneous distribution of Cs, Sn, and I throughout the Cs<sub>2</sub>SnI<sub>6</sub> particles, as depicted in Fig. 2i. Correspondingly, EDS mappings (Fig. S6, ESI<sup>†</sup>) also authenticate the uniform distribution of Cs, Sn, and halogen elements (Br or Cl) in Cs<sub>2</sub>SnBr<sub>6</sub> and Cs<sub>2</sub>SnCl<sub>6</sub> particles. The uniform morphology, high crystallinity, and homogeneous elemental distribution of nanosized Cs<sub>2</sub>SnX<sub>6</sub> particles jointly promote their excellent electrochemical performance in LSBs.

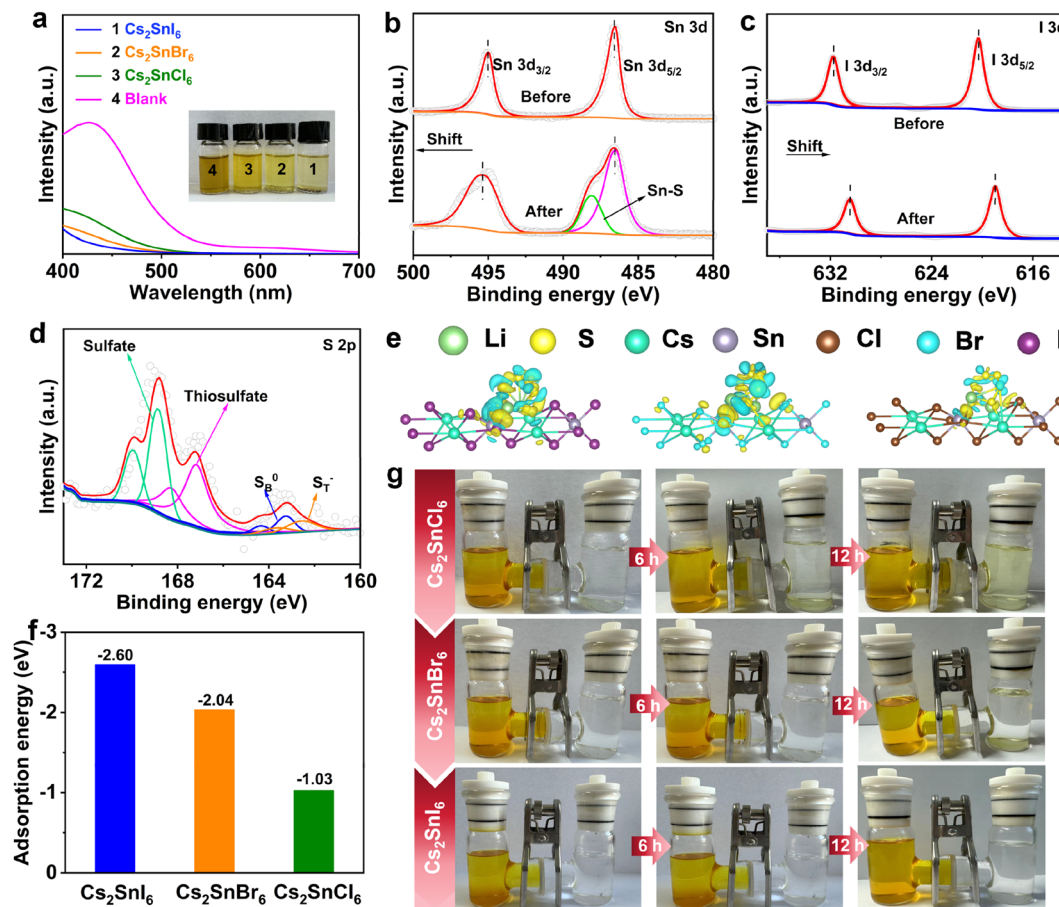


Fig. 3 (a) UV-vis spectra and the corresponding digital photos (inset) of Cs<sub>2</sub>SnX<sub>6</sub> adsorbed Li<sub>2</sub>S<sub>6</sub> after 12 h. High-resolution (b) Sn 3d and (c) I 3d spectra of Cs<sub>2</sub>SnI<sub>6</sub> before and after adsorbing Li<sub>2</sub>S<sub>6</sub>, and (d) S 2p spectra of Cs<sub>2</sub>SnI<sub>6</sub> adsorbed with Li<sub>2</sub>S<sub>6</sub>. (e) Charge density difference analysis of Li<sub>2</sub>S<sub>6</sub>-Cs<sub>2</sub>SnX<sub>6</sub>. (f) Adsorption energy of Li<sub>2</sub>S<sub>6</sub>-Cs<sub>2</sub>SnX<sub>6</sub>. (g) Permeation tests of LiPSs in H-type electrolytic cells with Cs<sub>2</sub>SnX<sub>6</sub> modified separators as indicated.



The adsorption capability of the four materials for LiPSs was compared through adsorption experiments in the  $\text{Li}_2\text{S}_6$  solution (Fig. 3a). After 6 h, the yellow  $\text{Li}_2\text{S}_6$  solution with  $\text{Cs}_2\text{SnI}_6$  shows a nearly colorless appearance, highlighting its strongest absorbability to LiPSs among the three samples. The underlying reasons for this lie in the fact that  $\text{Cs}_2\text{SnI}_6$  provides a certain adsorption capacity for  $\text{Li}_2\text{S}_6$ , as evidenced by the yellowish color of the  $\text{Li}_2\text{S}_6$  solution containing  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$ . These intuitive results were further verified by UV-vis spectra, as the solution containing  $\text{Cs}_2\text{SnI}_6$  exhibits the weakest signal of  $\text{S}_6^{2-}$  in the range of 400–500 nm.<sup>45</sup> The interactions between  $\text{Cs}_2\text{SnX}_6$  and  $\text{Li}_2\text{S}_6$  were further explored by high-resolution XPS before and after adsorption. Among them, the peaks at 486.8 eV and 495.2 eV are attributed to  $\text{Sn}^{4+}$ . After adsorption, the Sn 3d peaks shift to higher binding energies, from 486.8/495.2 eV to 486.9/495.4 eV, respectively. And a new pair of signals attributed to Sn–S bonds at 487.5 eV emerge, suggesting the facile anchoring of  $\text{Li}_2\text{S}_6$  on  $\text{Cs}_2\text{SnI}_6$ .<sup>46</sup> The peak of the Sn–S bond appears in the Sn 3d XPS spectra of both  $\text{Cs}_2\text{SnBr}_6$  (Fig. S7a, ESI†) and  $\text{Cs}_2\text{SnCl}_6$  (Fig. S7b, ESI†). Notably, the Sn–S bond in  $\text{Cs}_2\text{SnI}_6$  is the strongest among the three, indicating its strongest adsorption ability for  $\text{Li}_2\text{S}_6$ . Besides this, as shown in Fig. 3c, the peaks at 620.3 eV and 631.8 eV are attributed to  $\text{I}^-$ . After adsorbing  $\text{Li}_2\text{S}_6$ , the I 3d peaks shift toward lower binding energy, from 620.3/631.8 eV to 619.0/630.5 eV, revealing an interaction between I and  $\text{Li}_2\text{S}_6$ . The noticeable interactions between  $\text{Li}_2\text{S}_6$  and Br/Cl are also detected, as such shifts are still found both in Br 3d (Fig. S7c, ESI†) and Cl 2p spectra (Fig. S7d, ESI†). It is especially mentioned that the shift in I 3d is the most pronounced, which means that the interaction between I and  $\text{Li}_2\text{S}_6$  is the strongest among the halogens and explicitly confirms the superior adsorption capability of  $\text{Cs}_2\text{SnI}_6$  toward LiPSs. Such characteristic interactions between the materials and LiPSs are further embodied in S 2p spectra of  $\text{Cs}_2\text{SnX}_6$  absorbed with  $\text{Li}_2\text{S}_6$  (Fig. 3c and S8, ESI†). Specifically, the two pairs of peaks in the high-binding-energy region (167.3–169.5 eV) correspond to sulfates and thiosulfates formed on the material surfaces through chemical interactions with LiPSs, and the other two pairs of peaks in the low-binding-energy region (161.8–163.7 eV) are related to the bridging sulfur ( $\text{S}_\text{B}^\ominus$ ) and terminal sulfur ( $\text{S}_\text{T}^-$ ).<sup>47</sup> Compared with  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  (Fig. S8, ESI†), LiPSs captured on  $\text{Cs}_2\text{SnI}_6$  (Fig. 3d) exhibit even higher peak intensities in the high-binding-energy region, further confirming the stronger chemical adsorption of  $\text{Cs}_2\text{SnI}_6$  toward LiPSs from another point of view.<sup>48</sup>

To further analyze the regulatory mechanism of  $\text{Cs}_2\text{SnX}_6$  (X = Cl, Br, I) on the adsorption of  $\text{Li}_2\text{S}_6$ , adsorptive models were constructed through DFT calculations (Fig. S9, ESI†). According to the DFT results, I and Sn atoms preferentially bond to Li and S atoms on LiPSs surface, which is consistent with the XPS analysis results presented above. Fig. 3e provides the charge density difference diagrams of  $\text{Li}_2\text{S}_6$  adsorbed on different catalysts, where cyan and yellow correspond to charge depletion and accumulation, respectively. Apparently, the electron cloud density of the I center in  $\text{Cs}_2\text{SnI}_6$  is higher than those of the Br center and Cl center, indicating that the contribution of halide anions to local charge distribution increases with the increase

of atomic number. Consequently, I anions in  $\text{Cs}_2\text{SnX}_6$  act as a more active site.  $\text{Cs}_2\text{SnI}_6$  achieves more local charge distribution at the I center, resulting in weaker charge distribution at the Sn center, thereby promoting charge separation and transfer and improving the conversion reaction kinetics of LiPSs. While the local charge distributions at the Br center and Cl center in  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  become weak, leading to the relatively slower conversion reaction kinetics of LiPSs. Additionally,  $\text{Li}_2\text{S}_6$  has the adsorption energy of  $-2.60$  eV on the  $\text{Cs}_2\text{SnI}_6$  surface, which is higher than those of  $\text{Cs}_2\text{SnBr}_6$  ( $-2.04$  eV) and  $\text{Cs}_2\text{SnCl}_6$  ( $-1.03$  eV), as manifested in Fig. 3f. The results above indicate that the regulation of the halogen anion p-band center indeed enhances the electron transfer ability of  $\text{Cs}_2\text{SnI}_6$  and strengthens its binding energy with LiPSs. Therefore,  $\text{Cs}_2\text{SnI}_6$  can better capture LiPSs and suppress the shuttle effect more effectively.

The modified separators for LSBs were prepared by simply coating polypropylene (PP) with the nanosized  $\text{Cs}_2\text{SnX}_6$  (X = Cl, Br, I). The  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  modified separators were attached closely to PP with the thicknesses of 16.0, 14.3, and 15.0  $\mu\text{m}$ , respectively (Fig. S10, ESI†).<sup>49</sup> Evidently,  $\text{Cs}_2\text{SnX}_6$  (X = Cl, Br, I) and the conductive agent carbon nanotubes (CNTs) were observed to be uniformly distributed across the surface of the separator (Fig. S11, ESI†). The visible permeation experiment was carried out with H-type electrolyzers (Fig. 3g). Visually, LiPSs partially pass through the separator modified with  $\text{Cs}_2\text{SnCl}_6$  just after 6 h, as evidenced by the initially colorless right chamber turning pale yellow. While the colorless transparent solutions are still observed in the right chambers for the cases of  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnI}_6$  after 6 h, indicating that the inhibiting ability of the  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnI}_6$  separators is indeed better than that of the  $\text{Cs}_2\text{SnCl}_6$  separator. After 12 h, the electrolyte color turns out to be deepened in the right chamber of the  $\text{Cs}_2\text{SnCl}_6$  separator, and a light yellow solution appears for the case of  $\text{Cs}_2\text{SnBr}_6$ . In sharp contrast, the electrolyte in the right chamber of the  $\text{Cs}_2\text{SnI}_6$  separator always remains almost colorless even after the uninterrupted penetration/diffusion for 12 h, convincingly corroborating that the migration of LiPSs is effectively inhibited even at high LiPS concentrations, which is undoubtedly ascribed to the robust chemical adsorption capability of  $\text{Cs}_2\text{SnI}_6$ .<sup>50</sup>

### 3.3. Electrochemical evaluation

A symmetrical battery was assembled with  $\text{Li}_2\text{S}_6$  electrolyte to measure the redox kinetics during the liquid–liquid conversion process. Notably,  $\text{Cs}_2\text{SnI}_6$  exhibits the highest redox current response among the three samples (Fig. 4a), indicating that  $\text{Cs}_2\text{SnI}_6$  significantly enhances the kinetics of the liquid–liquid conversion reaction. To further understand the superb function of our modified separators, electrochemical performance of LSBs assembled with KB/S (S content: 73.6 wt%) (Fig. S12, ESI†) as the cathode and metallic Li as the anode was systematically investigated. Cyclic voltammetry (CV) measurements were first carried out at a scanning rate of  $0.1 \text{ mV s}^{-1}$  in the voltage window from 1.7 to 2.8 V (vs.  $\text{Li/Li}^+$ ), as plotted in Fig. 4b. The CV curve displays two distinct cathodic peaks at 2.33 V (peak 1)



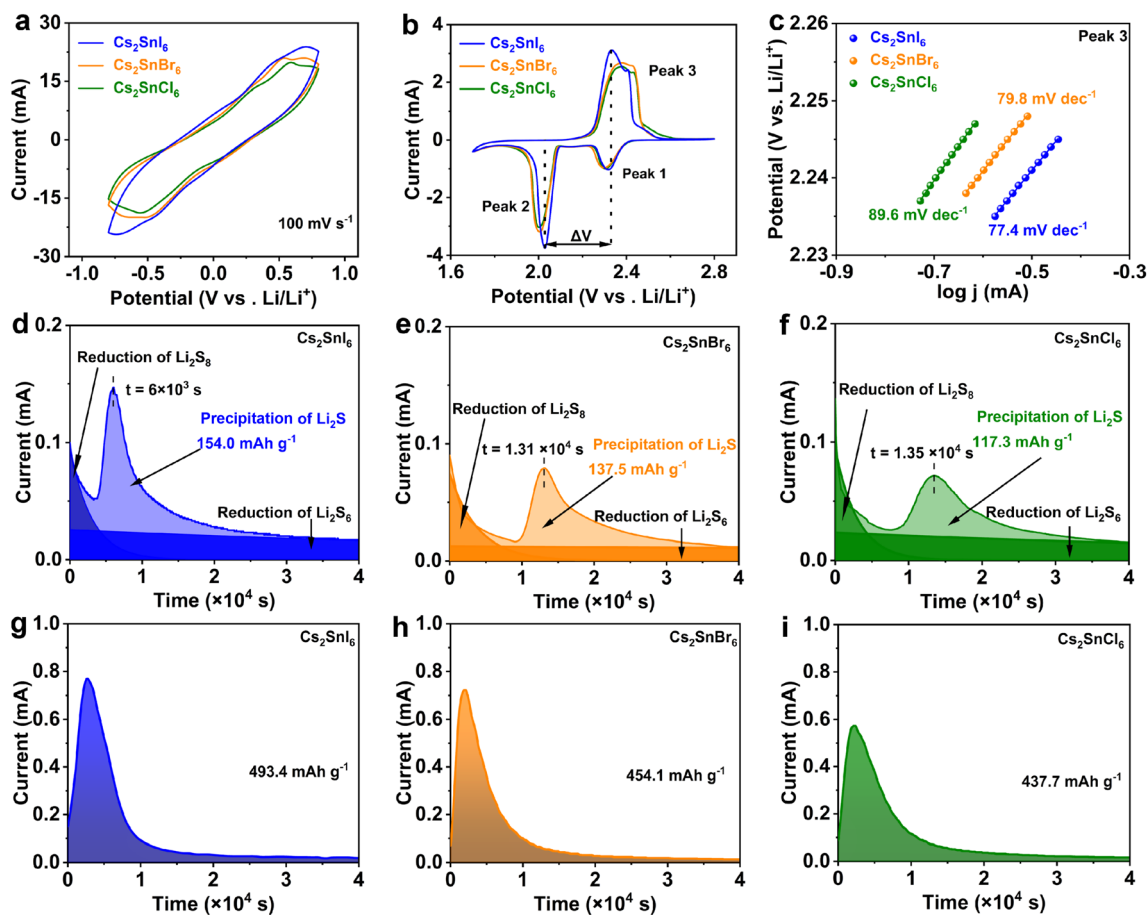


Fig. 4 CV curves of (a)  $\text{Li}_2\text{S}_6$ -symmetric batteries ( $100 \text{ mV s}^{-1}$ ) and (b) LSBs ( $0.1 \text{ mV s}^{-1}$ ) with  $\text{Cs}_2\text{SnX}_6$  modified separators as indicated. (c) Tafel plots and slopes of peak 3 derived from the CV profiles. Fitted chronoamperometry curves of  $\text{Li}_2\text{S}$  (d–f) nucleation and (g–i) dissolution with different separators as indicated.

and 2.03 V (peak 2), corresponding to the reduction of the  $\text{S}_8$  ring into soluble  $\text{Li}_2\text{S}_n$  ( $\text{Li}_2\text{S}_n$ ,  $4 \leq n \leq 8$ ) and further conversion into  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ .<sup>51</sup> Besides, the anodic peak appears at 2.34 V (peak 3), which is attributed to the desulfurization of  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  and  $\text{Li}_2\text{S}_n$ . Compared to reference samples of  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$ , the CV curve with the configured  $\text{Cs}_2\text{SnI}_6$  battery shows the sharpest redox peak and the smallest overpotential (Fig. 4b). The local magnification of the oxidation and reduction peaks in the CV curve evidences that the  $\text{Cs}_2\text{SnI}_6$  battery exhibits the highest peak current value, indicating that  $\text{Cs}_2\text{SnI}_6$  has the best catalytic performance for both oxidation and reduction reactions in LSBs (Fig. S13, ESI<sup>†</sup>).<sup>52</sup> Moreover, the anodic peak of  $\text{Cs}_2\text{SnI}_6$  exhibits an obvious negative shift, further depicting its efficient catalytic activity in accelerating the electrochemical activity of  $\text{LiPs}$ .<sup>53</sup> To verify the reaction kinetics of different batteries, Tafel slopes were calculated by fitting the oxidation and reduction peak curves of  $\text{Cs}_2\text{SnX}_6$  batteries. Specifically, the fitted Tafel slopes of the oxidation peaks for  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  batteries are 77.4, 79.8, and 89.6  $\text{mV dec}^{-1}$ , respectively (Fig. 4c). Additionally, the fitted Tafel slopes of the first reduction peaks for  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  batteries are 49.0, 55.7, and 60.4  $\text{mV dec}^{-1}$ , respectively

(Fig. S14a, ESI<sup>†</sup>). As for the second reduction peak, the fitted Tafel slopes for  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  batteries are 28.3, 30.2, and 31.1  $\text{mV dec}^{-1}$ , respectively (Fig. S14b, ESI<sup>†</sup>). Therefore, the smallest Tafel slopes for both oxidation and reduction reactions are observed in the  $\text{Cs}_2\text{SnI}_6$  battery, highlighting the excellent catalytic performance of  $\text{Cs}_2\text{SnI}_6$  for both oxidation and reduction reactions. This is attributed to the p-band center of I in  $\text{Cs}_2\text{SnI}_6$ , which is closer to the Fermi level; therefore, superior catalytic activities towards the redox reactions of sulfur species are obtained.

The electrochemical process in the discharge process involves both liquid–liquid and liquid–solid conversion reactions. To figure out the catalytic ability of  $\text{Cs}_2\text{SnI}_6$  in the liquid–solid conversion process, the nucleation and decomposition behaviors of  $\text{Li}_2\text{S}$  on different  $\text{Cs}_2\text{SnX}_6$  substrates were investigated by chronoamperometry. The response time of  $\text{Li}_2\text{S}$  nucleation (6000 s) in  $\text{Cs}_2\text{SnI}_6$  (Fig. 4d) is significantly shorter than those of  $\text{Cs}_2\text{SnBr}_6$  (13 100 s, Fig. 4e) and  $\text{Cs}_2\text{SnCl}_6$  (13 500 s, Fig. 4f), revealing its faster nucleation rate. Moreover,  $\text{Cs}_2\text{SnI}_6$  exhibits a higher nucleation capacity of 154.0  $\text{mA h g}^{-1}$ , surpassing those of  $\text{Cs}_2\text{SnBr}_6$  (137.5  $\text{mA h g}^{-1}$ ) and  $\text{Cs}_2\text{SnCl}_6$  (117.3  $\text{mA h g}^{-1}$ ). The high nucleation ability of  $\text{Li}_2\text{S}$  authenticates that  $\text{Cs}_2\text{SnI}_6$  effectively



catalyzes the liquid–solid conversion kinetics from  $\text{Li}_2\text{S}_4$  to  $\text{Li}_2\text{S}$ . For the decomposition curve of  $\text{Li}_2\text{S}$ ,  $\text{Cs}_2\text{SnI}_6$  has the highest specific capacity of  $493.4 \text{ mA h g}^{-1}$  (Fig. 4g). By comparison, the lower  $\text{Li}_2\text{S}$  dissolution specific capacities are delivered by  $\text{Cs}_2\text{SnBr}_6$  ( $454.1 \text{ mA h g}^{-1}$ , Fig. 4h) and  $\text{Cs}_2\text{SnCl}_6$  ( $437.7 \text{ mA h g}^{-1}$ , Fig. 4i). These observations corroborate the superb ability of  $\text{Cs}_2\text{SnI}_6$  to decompose  $\text{Li}_2\text{S}$  during the charging process, which is reasonably attributed to the more charge distribution at the I site in  $\text{Cs}_2\text{SnI}_6$  after adsorbing LiPSs, thus exhibiting better catalytic activity.

The rate performance of the assembled LSBs was tested within the current rate range of 0.2–5C ( $1\text{C} = 1675 \text{ mA h g}^{-1}$ ). The capacities of LSBs using  $\text{Cs}_2\text{SnI}_6$  modified separators at

rates of 0.2, 0.5, 1, 2, 3, 4, and 5C were estimated as 1271, 1106, 997, 906, 876, 830, and  $771 \text{ mA h g}^{-1}$ , respectively (Fig. 5a). Upon switching back to 0.2C, a capacity as large as  $1138 \text{ mA h g}^{-1}$  can still be recovered, manifesting its admirable stability and high reversibility. The charge–discharge plots of the  $\text{Cs}_2\text{SnI}_6$  battery present two clear plateaus evident even at a higher current rate of 5C, with a high-capacity response and a low polarization potential (Fig. 5b). Nevertheless, LSBs using  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  modified separators exhibited low capacities at the same rates (Fig. S15, ESI†). The excellent rate performance of the  $\text{Cs}_2\text{SnI}_6$  battery is attributed to its outstanding adsorption and catalytic performance, which verifies the crucial role of halogen-induced p-band center

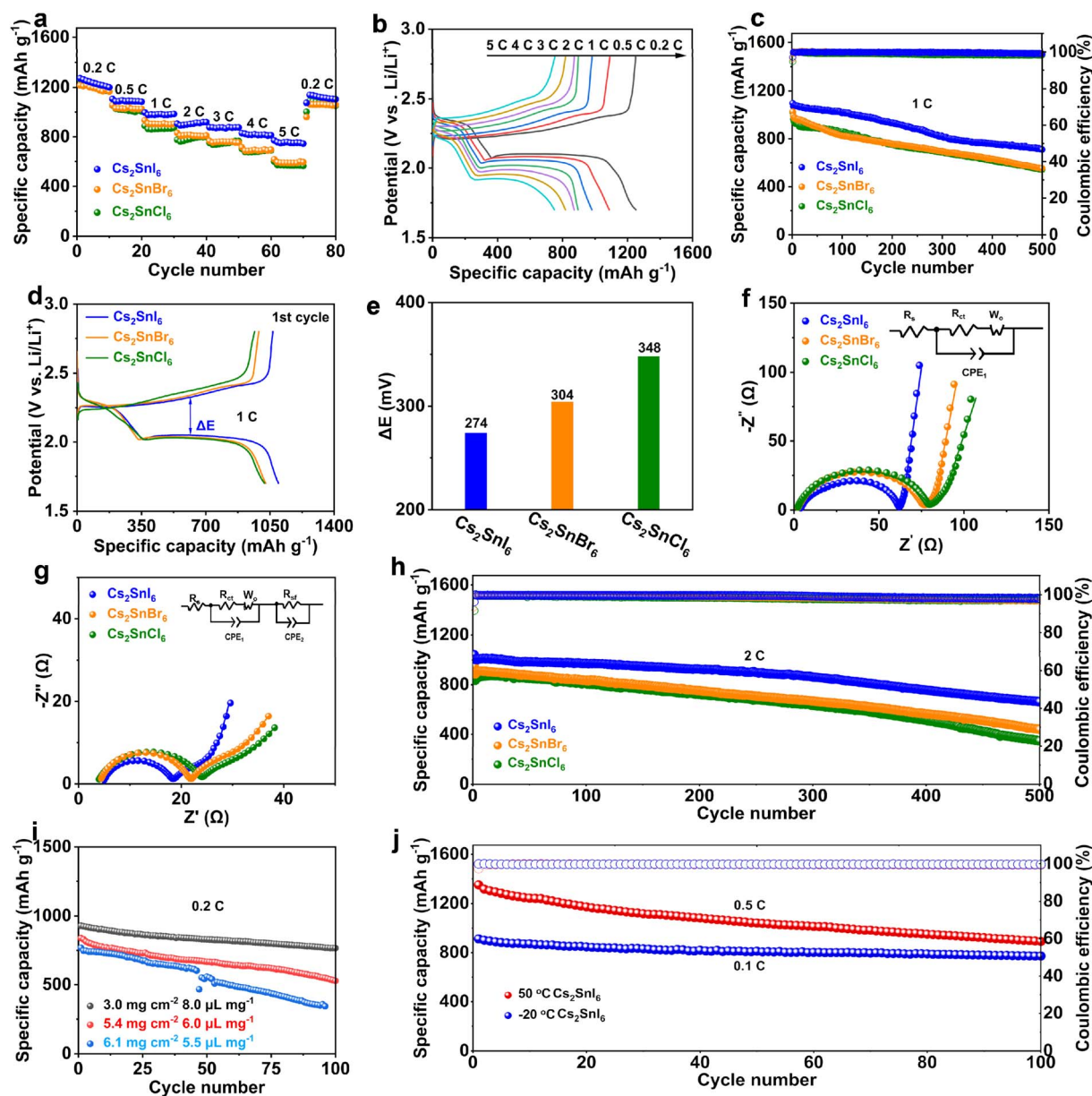


Fig. 5 (a) Rate performance and (b) charge–discharge curves of  $\text{Cs}_2\text{SnX}_6$  batteries at different current densities. (c) Cycle stability, (d) the first charge–discharge plots, and (e) polarization overpotentials of  $\text{Cs}_2\text{SnX}_6$  batteries at 1C. EIS data of  $\text{Cs}_2\text{SnX}_6$  batteries (f) before and (g) after cycling at 1C. (h) Cycling stability of  $\text{Cs}_2\text{SnX}_6$  batteries at 2C. Cycle stability of  $\text{Cs}_2\text{SnI}_6$  batteries (i) under high loading and low E/S ratio conditions and (j) at different operating temperatures of  $50 \text{ }^\circ\text{C}$  (0.5C) and  $-20 \text{ }^\circ\text{C}$  (0.1C).



regulation in  $\text{Cs}_2\text{SnI}_6$ . The cycling properties of LSBs with different separators at 1C are comparatively collected in Fig. 5c. An initial discharge capacity of  $1097 \text{ mA h g}^{-1}$  is achieved by LSBs using the  $\text{Cs}_2\text{SnI}_6$  modified separator at 1C, and a retention capacity of  $713 \text{ mA h g}^{-1}$  is retained after 500 cycles, higher than those of LSBs with  $\text{Cs}_2\text{SnBr}_6$  ( $1027$  and  $554 \text{ mA h g}^{-1}$ ) and  $\text{Cs}_2\text{SnCl}_6$  separators ( $1021$  and  $543 \text{ mA h g}^{-1}$ ) under the same conditions. The fast capacity degradation of  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  batteries is ascribed to their poor adsorption and catalytic abilities toward LiPSs.

To investigate the influence of the mechanism of  $\text{Cs}_2\text{SnX}_6$  with different anions on the battery performance, the charge-discharge plots of  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  batteries at 1C rate were analyzed in detail. All the LSBs with different modified separators at 1C illustrate two distinct discharge platforms at 2.30 V and 2.05 V (Fig. 5d), which correspond to the electrochemical conversion of elemental sulfur to soluble polysulfides ( $\text{Li}_2\text{S}_n$ ,  $4 \leq n \leq 8$ ) based on the cathodic peaks observed in the CV curve (Fig. 4b), followed by reduction to insoluble  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ . Among them, the almost overlapping voltage platforms at different cycles are observed for the  $\text{Cs}_2\text{SnI}_6$  battery (Fig. S16, ESI<sup>†</sup>), suggesting that the  $\text{Cs}_2\text{SnI}_6$  modified separator has high sulfur redox chemical reversibility and cycling stability. The polarization overpotential of the  $\text{Cs}_2\text{SnI}_6$  battery is 274 mV (Fig. 5e), even lower than those of  $\text{Cs}_2\text{SnBr}_6$  (304 mV) and  $\text{Cs}_2\text{SnCl}_6$  (348 mV). The observed smallest charge-discharge voltage hysteresis further suggests that  $\text{Cs}_2\text{SnI}_6$  significantly enhances the catalytic activity for the conversion reaction of LiPSs, thereby improving the utilization of sulfur species.<sup>54</sup> As the atomic number of halogen increases, the adsorption and catalytic ability of  $\text{Cs}_2\text{SnX}_6$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) for LiPSs in the cathode region also increases. Consequently, the  $\text{Cs}_2\text{SnI}_6$  modified separator achieves high-performance LSBs.

The resistance characteristics of  $\text{Cs}_2\text{SnX}_6$  were further explored through electrochemical impedance spectroscopy (EIS) analysis. The Nyquist curves of batteries equipped with different separators were obtained before (Fig. 5f) and after cycling (Fig. 5g). All the EIS plots of LSBs consist of the intersections with the  $Z'$  axis, a semicircle in the middle frequency region and a tail line in the low-frequency region, corresponding to the solution resistance ( $R_s$ ), charge-transfer resistance ( $R_{ct}$ ) and Warburg impedance, respectively. Using the equivalent circuit diagrams (the insets), the fitted plots are found to be in good agreement with the experimental data, along with the fitting results (Table S1, ESI<sup>†</sup>). Clearly, all the  $\text{Cs}_2\text{SnX}_6$  batteries display low  $R_s$  values ranging from 1.6 to 2.9  $\Omega$ . These low  $R_s$  values are attributed to the excellent conductivity of the modified separator, which effectively promotes electron and ion transport, thereby enhancing the performance of LSBs. Additionally, the  $R_{ct}$  of  $\text{Cs}_2\text{SnI}_6$  battery is estimated as  $\sim 62.0 \Omega$ , significantly lower than those of  $\text{Cs}_2\text{SnBr}_6$  (76.0  $\Omega$ ) and  $\text{Cs}_2\text{SnCl}_6$  (78.6  $\Omega$ ), indicating its superior charge transfer kinetics. As a result, the  $\text{Cs}_2\text{SnI}_6$  modified separator will render the faster redox reactions of LiPSs and reduce the electrochemical reaction resistance.<sup>55</sup> More particularly, one additional semicircle appears in the high-medium frequency region of EIS plots for all batteries after cycling (Fig. 5g), which probably stems from the

extra surface film resistance ( $R_{sf}$ ) caused by the formation of an insoluble  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  passivation layer on the electrode surface.<sup>56,57</sup> Despite this, the  $\text{Cs}_2\text{SnI}_6$  battery still consistently exhibits the lowest  $R_{sf}$  and  $R_{ct}$  after cycling, suggesting the uniform deposition of  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  induced by  $\text{Cs}_2\text{SnI}_6$ , thanks to the superb adsorption and catalytic ability of  $\text{Cs}_2\text{SnI}_6$  towards LiPSs.<sup>58,59</sup>

The shuttle effect in LSBs inevitably leads to adverse side reactions between lithium metal anodes and migrated LiPSs. To investigate the inhibitory effects of  $\text{Cs}_2\text{SnI}_6$ ,  $\text{Cs}_2\text{SnBr}_6$ , and  $\text{Cs}_2\text{SnCl}_6$  on LiPSs shuttle, LSBs were disassembled after 500 cycles at 1C. Noticeably, the distribution of sulfur species on the cathode surface of the  $\text{Cs}_2\text{SnI}_6$  battery is relatively uniform, whereas the cathode surfaces of  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  batteries exhibited varying degrees of uneven sulfur deposition after cycling (Fig. S17, ESI<sup>†</sup>). Moreover, FESEM observations and the corresponding digital photographs indicate that the lithium anode in the  $\text{Cs}_2\text{SnI}_6$  battery exhibits a smooth and dense surface after cycling (Fig. S18, ESI<sup>†</sup>).<sup>60</sup> In contrast, the lithium anode surfaces of  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  batteries show an undesirable loose structure, uneven lithium deposition, and numerous cracks, primarily caused by the migration of soluble LiPSs to the anode side.<sup>61</sup> In addition, the morphology of the cycled  $\text{Cs}_2\text{SnI}_6$  modified separator (cathode side) remains largely unchanged, strongly confirming the good stability of the  $\text{Cs}_2\text{SnI}_6$  separator during cycling (Fig. S19, ESI<sup>†</sup>). In summary, the  $\text{Cs}_2\text{SnI}_6$  modified separator effectively suppresses the shuttle effect, which is mainly related to its excellent adsorption and catalytic properties for LiPSs. Subsequently, a long-cycle test was conducted at a high current rate to evaluate the long-cycle stability of the battery. At 2C, the initial capacity of the  $\text{Cs}_2\text{SnI}_6$  battery remains as high as  $1000 \text{ mA h g}^{-1}$  (Fig. 5h), which is still kept at  $660 \text{ mA h g}^{-1}$  after 500 cycles, corresponding to a small capacity decay rate of only 0.068% per cycle. In sharp contrast, the  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  batteries display significant capacity degradation just after about 300 cycles. The higher cycling stability of the  $\text{Cs}_2\text{SnI}_6$  battery is attributed to the modulation of the p-band center induced by halogen ions, which enhances LiPSs adsorption and catalytic ability of  $\text{Cs}_2\text{SnI}_6$ , thus effectively suppressing the shuttle effect of LiPSs.

The performance of LSBs assembled with the  $\text{Cs}_2\text{SnI}_6$  modified separator under high sulfur load was further evaluated to check their potential application in high-energy-density devices. The gained initial capacities of  $\text{Cs}_2\text{SnI}_6$  batteries with sulfur loadings of 3.0, 5.4, and 6.1  $\text{mg cm}^{-2}$  at 0.2C are 928.6, 838.5, and 768.8  $\text{mA h g}^{-1}$ , respectively. Typically, the charge-discharge curve of the  $\text{Cs}_2\text{SnI}_6$  battery reveals two distinct plateaus even at a high sulfur loading of 6.1  $\text{mg cm}^{-2}$  (Fig. S20a, ESI<sup>†</sup>). Under the conditions of sulfur loading of 3.0, 5.4, and 6.1  $\text{mg cm}^{-2}$  and corresponding E/S ratio of 8.0, 6.0, and 5.5  $\mu\text{L mg}^{-1}$ , the recorded charge-discharge plots of the  $\text{Cs}_2\text{SnI}_6$  battery show almost overlapping voltage plateaus (Fig. S20b-d, ESI<sup>†</sup>), identifying that the separator modified by  $\text{Cs}_2\text{SnI}_6$  has high sulfur redox chemical reversibility. Considering the multi-scenario application of LSBs, their battery performance in extremely high and low temperature environments is also of



great significance. To evaluate this, cyclic performance tests were conducted on the  $\text{Cs}_2\text{SnI}_6$  battery over a wide temperature range of  $-20$  to  $50$  °C. The initial capacities of the  $\text{Cs}_2\text{SnI}_6$  battery at  $-20$  °C (0.1C) and  $50$  °C (0.5C) are  $912.7$  and  $1350.7$   $\text{mA h g}^{-1}$ , respectively, coupled with the reversible capacities of  $772.6$  and  $892.3$   $\text{mA h g}^{-1}$  after 100 cycles, respectively (Fig. 5j). Although the polarization overpotential of the  $\text{Cs}_2\text{SnI}_6$  battery over the wide temperature range increases with decreasing temperatures (Fig. S21, ESI†), it still maintains a modest overpotential, which proves that the  $\text{Cs}_2\text{SnI}_6$  battery can undergo rapid LiPS conversion over such a wide temperature range, guaranteeing its high initial specific capacity and excellent cycling stability even at extreme low and high temperatures. Compared with other electrocatalytic materials under the same testing conditions, the  $\text{Cs}_2\text{SnI}_6$  battery exhibits excellent performance under long cycling (Table S2, ESI†), high sulfur loading, low E/S ratio (Table S3, ESI†), and extreme temperature conditions (Table S4, ESI†). The above electrochemical

performance tests established the regulatory relationship between different halide anions of  $\text{Cs}_2\text{SnX}_6$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and electrochemical properties of LSBs. As the atomic number of the halogen increases, the rate performance, high-loading discharge capability, and cycling stability of LSBs are progressively enhanced. Among them, the  $\text{Cs}_2\text{SnI}_6$  battery emanates superior electrochemical performance. Such distinctive improvement is primarily attributed to the effective adsorption of LiPSs by  $\text{Cs}_2\text{SnI}_6$ , which significantly suppresses the shuttle effect of LiPSs. Additionally, the inherent catalytic ability of  $\text{Cs}_2\text{SnI}_6$  substantially accelerates the conversion reactions of LiPSs, further enhancing the overall electrochemical performance.

To thoroughly elucidate the specific catalytic mechanisms of  $\text{Cs}_2\text{SnX}_6$  for the redox reactions of LiPSs, an atomic-level analysis was further carried out. Accordingly, the adsorption models of  $\text{Cs}_2\text{SnX}_6$  with different LiPSs generated at various charge-discharge stages were constructed through DFT calculations.

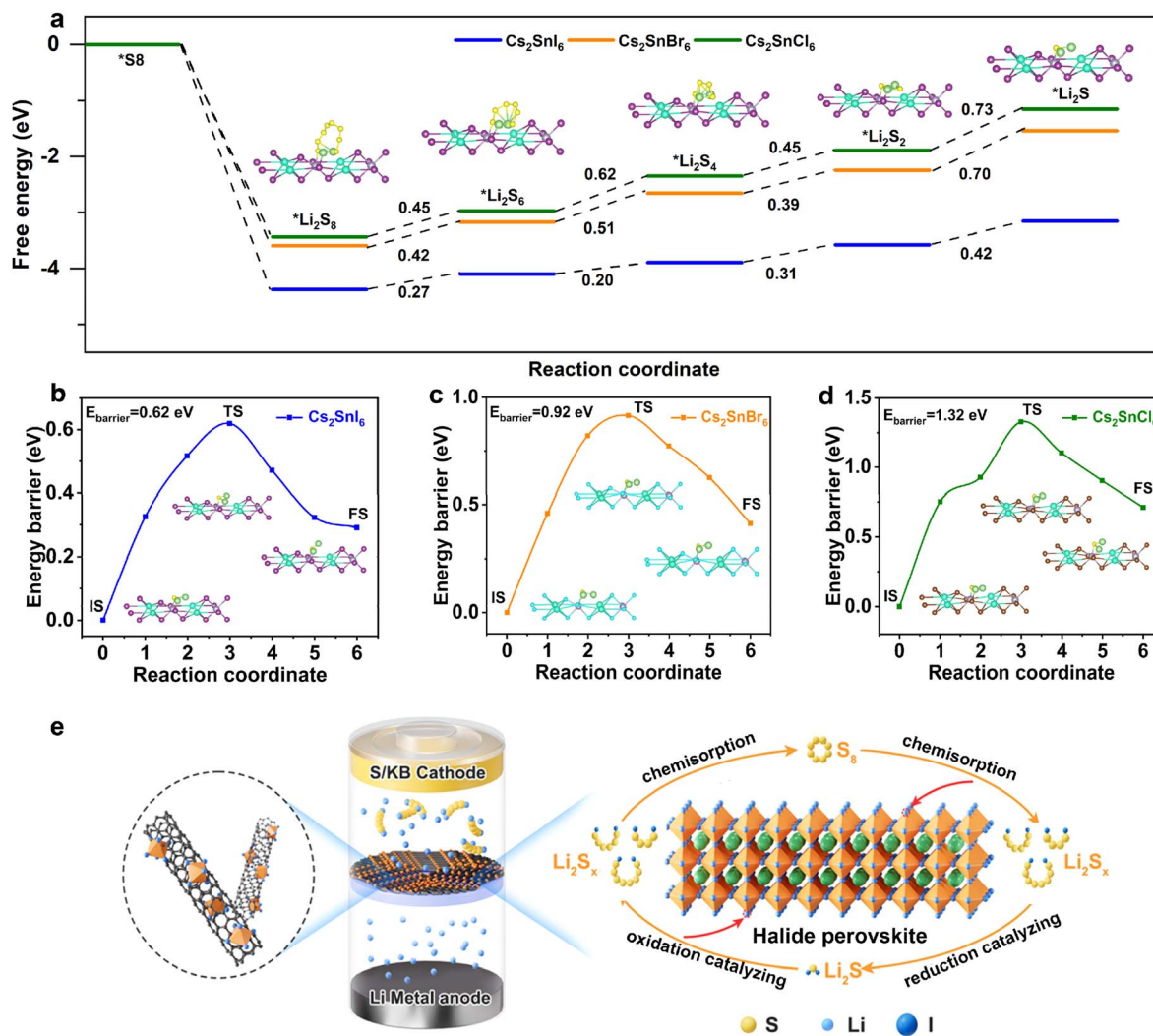


Fig. 6 (a) Relative free energy for reduction of sulfur species (a) on the surfaces of  $\text{Cs}_2\text{SnX}_6$ . Energy barriers of  $\text{Li}_2\text{S}$  decomposition on the surfaces of (b)  $\text{Cs}_2\text{SnI}_6$ , (c)  $\text{Cs}_2\text{SnBr}_6$ , and (d)  $\text{Cs}_2\text{SnCl}_6$ . (e) Schematic illustration of the merits of the  $\text{Cs}_2\text{SnI}_6$  modified separator inhibiting the "shuttle effect" in LSBs.



The Gibbs free energy distribution of  $\text{Cs}_2\text{SnX}_6$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) surfaces from  $\text{S}_8$  to  $\text{Li}_2\text{S}$  is shown in Fig. 6a. The thermodynamic analysis of the continuous reduction pathway reveals that all transformation steps from  $\text{Li}_2\text{S}_8$  to  $\text{Li}_2\text{S}$  exhibit positive Gibbs free energy changes, indicating the thermodynamically non-spontaneous characteristics, which necessitate the use of catalysts to facilitate LiPS conversion. Overall, the  $\Delta G$  value of electrochemical reactions from  $\text{Li}_2\text{S}_8$  to  $\text{Li}_2\text{S}$  in the  $\text{Cs}_2\text{SnI}_6$  system is smaller than those in  $\text{Cs}_2\text{SnBr}_6$  and  $\text{Cs}_2\text{SnCl}_6$  systems, indicating that the electrochemical conversions of LiPSs are more favorable on the surface of  $\text{Cs}_2\text{SnI}_6$ . In particular, in the rate-limiting processes of liquid–solid conversion from  $\text{Li}_2\text{S}_4$  to  $\text{Li}_2\text{S}_2$  and solid–solid conversion from  $\text{Li}_2\text{S}_2$  to  $\text{Li}_2\text{S}$ , the  $\Delta G$  values of  $\text{Cs}_2\text{SnI}_6$  are 0.31 and 0.42 eV, respectively, which are lower than those of  $\text{Cs}_2\text{SnBr}_6$  (0.39 and 0.70 eV) and  $\text{Cs}_2\text{SnCl}_6$  (0.45 and 0.84 eV), suggesting that the sulfur reduction reaction of  $\text{Cs}_2\text{SnI}_6$  is thermodynamically more favorable. The decomposition of  $\text{Li}_2\text{S}$  is the first step in the charging process of LSBs and involves a solid–liquid phase transition, which results in relatively slow reaction kinetics. Consequently, the decomposition rate of  $\text{Li}_2\text{S}$  is critical to the charging process of LSBs. The calculated energy barriers for the decomposition of  $\text{Li}_2\text{S}$  on the surfaces of  $\text{Cs}_2\text{SnX}_6$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) reveal that  $\text{Cs}_2\text{SnI}_6$  has a decomposition barrier of 0.62 eV (Fig. 6b), which is lower than those of  $\text{Cs}_2\text{SnBr}_6$  (0.92 eV) (Fig. 6c) and  $\text{Cs}_2\text{SnCl}_6$  (1.32 eV) (Fig. 6d). Such a finding fully substantiates that, during the charging process of LSBs,  $\text{Li}_2\text{S}$  undergoes accelerated dissociation on the surface of  $\text{Cs}_2\text{SnI}_6$ , which is in good agreement with the aforementioned electrochemical results. The calculation results show that the thermodynamic and kinetic processes can be improved by changing the halogen in the Sn-based halide double perovskite, which can simultaneously catalyze both the reduction of LiPSs and the oxidation of  $\text{Li}_2\text{S}$ . Specifically, as the atomic number of the halogen increases, the p-band center gradually approaches the Fermi level and the band gap decreases. These changes promote electron transfer, which is beneficial for the transformation of S species, thereby weakening the energy barriers in LiPSs reduction process and  $\text{Li}_2\text{S}$  oxidation process.

The action mechanism of the  $\text{Cs}_2\text{SnI}_6$  modified separator in LSBs is schematically illustrated in Fig. 6e. Clearly, during the discharge process, a large amount of soluble LiPSs is present in the cathode region, while the anode region only contains  $\text{Li}^+$ . This demonstrates the effective inhibition of LiPSs shuttle by the  $\text{Cs}_2\text{SnI}_6$  modified separator. The  $\text{Cs}_2\text{SnI}_6$  modified separator effectively inhibits LiPSs shuttle due to its capability to chemically adsorb soluble LiPSs and the catalytic activity of surface I sites in promoting LiPSs conversion. The generated  $\text{Li}_2\text{S}$  can be uniformly distributed around the active sites. Additionally, the I sites on the surface of  $\text{Cs}_2\text{SnI}_6$  also catalyze the oxidative reaction and decomposition of  $\text{Li}_2\text{S}$ , re-exposing the active sites for subsequent adsorption and catalysis. These structural characteristics of  $\text{Cs}_2\text{SnI}_6$  modified separators ensure excellent catalytic effects on both oxidation and reduction reactions in LSBs, thereby effectively inhibiting LiPSs shuttle and enhancing the electrochemical performance of LSBs.

## 4. Conclusion

In summary, the regulatory mechanism of halogen-induced p-band centers and their effects on the adsorption and catalytic performance of LSBs were successfully explored through the research model of Sn-based halide perovskites. By combining DFT calculations with electrochemical characterization, a quantitative relationship was established between the electronic structure characteristics of halide anions and the adsorption and catalytic performance of LiPSs. DFT calculations revealed the regulatory mechanism of the p-band center of halide anions and the catalytic mechanism of LiPSs conversion reaction. As the atomic number of the halogen increases, the p-band center of the halogen anion shifted positively toward the Fermi level, resulting in a higher charge transfer rate and promoting the kinetics of the conversion reaction of LiPSs. Meanwhile,  $\text{Cs}_2\text{SnI}_6$  achieved a greater local charge distribution on the I center, leading to a weaker charge distribution at the Sn center and further promoting charge separation and transfer. Therefore, the binding energy between halide perovskites and LiPSs increased, the potential barrier for LiPSs decomposition decreased accordingly, and the phase transition speed of LiPSs increased. LSBs assembled with the  $\text{Cs}_2\text{SnI}_6$  modified separator exhibited a high discharge capacity ( $1000 \text{ mA h g}^{-1}$  at 2C), excellent rate performance ( $771.0 \text{ mA h g}^{-1}$  at 5C), and long-term cycle stability (0.068% decay rate per cycle after 500 cycles at 2C). Even under extreme temperature conditions, the  $\text{Cs}_2\text{SnI}_6$  battery maintained a high discharge capacity ( $912.7 \text{ mA h g}^{-1}$  at 0.1C at  $-20^\circ\text{C}$  and  $1350.7 \text{ mA h g}^{-1}$  at 0.5C at  $50^\circ\text{C}$ ). In this contribution, the adsorption and catalytic performance of LiPSs were regulated by adjusting the p-band center in halide perovskites, providing a new approach for developing advanced LSBs through halogen-induced p-band center regulation engineering.

## Data availability

The data supporting this article can be available from the authors upon request.

## Author contributions

Hanzhang Fang: formal analysis, investigation, writing – original draft, writing – review & editing. Wenshuo Hou: formal analysis, writing – original draft, writing – review & editing, conceptualization, funding acquisition. Chuanlong Li: formal analysis, investigation. Shuo Li: formal analysis, investigation. Fulu Chu: validation, software, funding acquisition. Xuting Li: validation, writing – review & editing. Xianping Zhang: formal analysis, writing – review & editing, conceptualization. Linrui Hou: validation, software, funding acquisition. Changzhou Yuan: formal analysis, investigation, conceptualization, writing – review & editing, funding acquisition. Yanwei Ma: formal analysis.



## Conflicts of interest

There are no conflicts to declare.

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