Supporting Information

Vacuum evaporation-assisted reaction: Sustainable solution for application of rare earth-based halide solid-state electrolytes

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Table of contents

Experimental section Figs. S1-S28 Tables S1-S6

Experimental section

Materials

HCl (36%, wt.) was purchased from Tianjin Bohua Chemical Reagents Co. Ltd. (China). HBr (48%, wt.), NH₄Cl (99.8%), NH₄Br (99.9%), K₂CO₃ (99.5%), and Li₂CO₃ (99.99%) were purchased from Shanghai Macklin Biochem. Technol. Co. Ltd. (China). Cs₂CO₃ (99.9%) was obtained from 3A AnLan Chem Technol. Co. Ltd. Na₂CO₃ (99.8%) and Li₂S (99.9%) were purchased from Shanghai Aladdin Biochem. Technol. Co. Ltd. Rb₂CO₃ (99.5%) was bought from Shanghai Dibo Chem. Technol. Co. Ltd (China). RE₂O₃ (RE = Sc, Y, Ho, Er, Gd, Dy, Yb, Tm and Lu) (99.99%) and Tb₄O₇ (99.999%) were obtained from Beijing HWRK Chemicals Co. Ltd (China). A Rigaku MiniFlex600 diffractometer (40 kV, 15 mA, Cu K α , $\lambda = 1.5406$ Å) was used to test X-ray diffraction (XRD) patterns of the prepared samples. Scanning electron microscopy (SEM, JEOL JSM-7800F) was used to observe the morphologies of the prepared electrolytes. All the tests were carried out with Ar protection.

Preparation of the samples

Synthesis of Li₃RECl₆ (RE = Sc, Y, Tb, Dy, Ho, Er, Yb, and Tm): The synthesis process of Li₃YCl₆ (LYC) is shown below. First, 6 mmol of Li₂CO₃ (0.443 g) and 2 mmol of Y₂O₃ (0.452 g) were dissolved in a diluted HCl solution in a beaker, and then, excess NH₄Cl (more than 60 mmol) was added. After Li₂CO₃, Y₂O₃ and NH₄Cl were dissolved to forming a clear solution, the H₂O was removed by heating to produce solid precursor. The precursor was ground into power and then transferred to quartz flask in vacuum evaporation-assisted (VEA) reactor. After two-stage heat treatment, the precursor was heated from room temperature (RT) to 350 °C (within 100 min) and kept for 90 min, and then heated to 420 °C (within 30 min) and kept for 120 min with protection by Ar gas under vacuum. The reaction was cooled to RT to obtain the solid LYC in the flask and the by-product NH₄Cl in the condenser tube. Solid LYC was transferred and stored in a glove box. LScC, LTbC, LDyC, LHoC, LErC, LYbC and LTmC were synthesized by the same VEA reaction as LYC.

Synthesis of Li₃REBr₆ (RE = Y, Tb, Dy, Ho, Tm, Yb, and Lu): Li₃REBr₆ was prepared via a similar process as LYC, with Li₃YBr₆ (LYB) used as an example. First, 6 mmol Li₂CO₃ (0.443 g) and 2 mmol Y_2O_3 (0.452 g) were dissolved into diluted HBr solution in a beaker, and then more than 60 mmol NH₄Br was added. All the solid chemicals were dissolved, then the solvent was removed to obtain solid mixed salts. The mixed salts were subsequently ground into powder and put into a quartz flask in the VEA reactor. The reaction was carried out in VEA reactor under Ar gas protection and vacuum. The flask was heated from RT to 400 °C (within 120 min) kept for 90 minutes, then the temperature was increased to 450 °C (within 20 min) and kept for 120 minutes, and then cooled to RT to obtain the solid LYB product from flask and the NH₄Br by-product from the condenser tube. LYB was transferred and stored in a glove box. LTbB, LDyB, LHoB, LTmB, LYbB and LLuB were synthesized in this VEA reactor under the same reaction conditions as LYB.

Synthesis of RE-based halide perovskites: RE-based perovskites of Cs_2NaYCl_6 , Cs_2KYbCl_6 , Na_3TbCl_6 , Rb_3TbCl_6 , Cs_3TbCl_6 , $Cs_3Sc_2Cl_9$, $Cs_3Y_2Cl_9$, Na_6YBr_6 and $Cs_3Y_2Br_9$ can be synthesized by the same method and conditions of LYC or LYB in the VEA reactor.

Notably, the amounts of the raw materials (Cs_2CO_3 , Rb_2CO_3 , K_2CO_3 , Na_2CO_3 , Y_2O_3 , Yb_2O_3 , Tb_4O_7 and Sc_2O_3) used were in accordance with the stoichiometric proportions of those chemical formulas. The molar ratio of halogenated ammonium to RE ions is greater than 15 during the perovskite synthetic process. All the prepared RE-based halide perovskites were transferred into an Ar filled glove box for storage.

Recovered Li_3YX_6 (X = Cl, Br) from degenerate/metamorphous samples: The metamorphous sample (LYC or LYB) was added to deionized water, and appropriate halogenic acid was added to dissolve the RE-based oxyhalides (YOCl or YOBr). Then, excess halogenated ammonium salt (NH₄Cl or NH₄Br) was added. The molar ratio of the ammonium salt to Y³⁺ was greater than 15. The mixture was dried and ground to precursor powder, and then heat treatment was carried out in the VEA reactor with the same process of LYC or LYB preparation.

Massive synthesis of Li₃RECl₆ (RE = Sc, Y): Synthesis of Li₃YCl₆ (LYC), Y₂O₃ (50 mmol, 11.291 g) and Li₂CO₃ (150 mmol, 11.083 g) were dissolved in diluted HCl, then 2.5 mol NH₄Cl (133.64 g) was added and dissolved to obtain mixed salts solution. The solution was dried to obtain solid mixed salts. The mixed salts were subsequently ground to powder. The powder was transferred into a quartz bottle in VEA reactor. After multi-stage continuous heat treatment (first-stage: the powder heated to 280 °C (within 120 min) and kept for 90 min; second-stage, the samples were heated to 320 °C (within 30 min) and kept for 90 min; third-stage: the reaction was heated to 430 °C (within 60 min) and kept for 180 min under Ar gas protection and vacuum. Finally, the reaction system was cooled to obtain approximately 32 g LYC (yield, ~ 99.2%) from the quartz bottle. The solid by-product of NH₄Cl can be collected from the condenser pipe for reuse. The massive LScC and other RE-based chloride SEs can also be synthesized under the same condition as LYC in the VEA reactor.

Massive synthesis of Li₃REBr₆ (RE = Y, Ho): The preparation process of massive Li₃YBr₆ (LYB) is similar to that of LYC. First, the raw materials of Y₂O₃ (50 mmol, 11.291 g), Li₂CO₃ (11.083 g) and NH₄Br (2.5 mmol, 224.85 g) were dissolved in HBr and deionized water to form a clear solution. The solution was subsequently dried to obtain solid mixed salts, and then ground to powder. The powder was transferred into quartz bottle and heat treated in the VEA reactor under Ar gas protection and vacuum. The reaction system was heated to 280 °C (within 120 min) and kept for 90 min. Then heated from 280 °C to 360 °C (within 60 min) and kept for 60 min. Heated up again from 360 °C to 450 °C (within 60 min) and kept for 60 min. Then, the reaction was heated to 500 °C (within 30 min) and kept for 60 min. Finally, the reaction was cooled to obtain approximately 58.5 g LYB (yield, ~ 99.2%) from the quartz bottle. The solid by-product of NH₄Br can be collected from the condenser pipe for reuse. The massive LHoB and other RE-based bromide SEs can be synthesis by using the same condition as LYB.

Solvent-free synthesis of Li_3RECl_6 (RE = Y, Er): Synthesis of Li_3YCl_6 (LYC), Y_2O_3 (2 mmol, 0.452 g), Li_2CO_3 (2 mmol, 0.443 g) and NH₄Cl (20 mmol, 2.143 g) were mixed fully and ground into powder. Then, the powder was heat treated in the VEA reactor under Ar gas protection and vacuum. First, the reaction was heated to 300 °C (within 120 min) and kept for 8 hours. Then, the reaction was heated from 300 °C to 400 °C (within 30 min) and kept

for 30 min. Then the reaction was subsequently heated to 420 °C within 20 min and kept for another 30 min, and then cooled to RT to obtain LYC. The prepared LYC sample was transferred to a glove box for storage and use. LErC or other chloride SEs can be prepared with the same process as LYC.

Solvent-free synthesis of Li₃REBr₆ (RE = Y, Ho): Synthesis of Li₃YBr₆ (LYB), Y₂O₃ (2 mmol, 0.452 g), Li₂CO₃ (2 mmol, 0.443 g) and NH₄Br (20 mmol, 3.842 g) were mixed fully and ground into powder. First, the powder was heated to 330 °C (within 120 min, in the VEA reactor), and kept for 8 hours. Then, the temperature was increased from 330 °C to 430 °C within 60 min and kept at 430 °C for 30 min. The reaction was continuous heated to 450 °C within 20 min and kept for 30 min, and then cooled to RT, and the product of LYB was collected. The reaction was carried out under Ar gas protection and vacuum. LYB product was transferred to glove box for storage and use. LHoB or other bromide SEs can be prepared with the same process as LYB.

Electrochemical characterizations

The alternating current electrochemical impedance spectroscopy (EIS) results of all the synthesized HSEs were measured to obtain the ionic conductivities on an In/HSEs/In (In, indium metal; diameter, 10 mm; thickness, 0.1 mm) cell from an Autolab PGSTAT302N electrochemical workstation (1 MHz – 0.01 Hz; amplitude, 10 mV). Li₃RECl₆ (100 mg) or Li₃REBr₆ (150 mg) powders were cold pressed into pellets (diameter, 10 mm) (500 MPa). Li/LPS/HSEs/HSEs-C cells (LPS, Li₇P₃S₁₁, carbon/HSEs = 10%, mass ratios) were used to evaluate the electrochemical stabilities of the HSEs by testing their cycling voltammetry (CV) curves (-0.5 – 5.0 V, scan rate: 0.5 mV s⁻¹) on a CHI660E instrument at RT. LPS was synthesized according to the literature and used to stabilize the Li anode.¹

The transient current behaviours of blocking SG/LYB/SG (SG, stainless-steel gasket) cell and conductive Li/LYB/Li cell were carried out to study the electron and ion conductivity of LYB. The direct current polarization curves of the SG/LYB/SG and Li/LYB/Li batteries were recorded with applied bias voltages of 1 V and 1 mV on an Autolab PGSTAT302N instrument. Temperature-dependent EIS measurements of In/HSEs/In cells were tested to obtain the activation energy ($E_a = (RT + C)(ln\sigma)$, E_a , kJ/mol = 1/96 eV) of the as-synthesized HSEs from their Arrhenius conductivity plot (-40 – 80 °C). A Li/LYB/Li symmetric cell was used to test the cycling stability of the interface between Li and LYB (0.1 mA cm⁻²).

The Li/LPS/LYB/S solid-state battery was assembled by cold-pressing in an Ar-filled glovebox. S-CNTs (S: 40%, wt.) was synthesized via a previously reported method.² The composite powders of S-CNTs (15%, wt.), LYB (75%, wt.) and Ketjen Black (10%, wt.) were mixed and ball-milled for 20 hours to serve as the cathode. 5 mg cathode material, 100 mg LYB and 8 mg LPS were cold-pressed into pellet (diameter, 10 mm). Then, the Li foil anode, LPS/LYB/S and SG current collector were encapsulated in a 2032-type coin cell. The CV of the Li/LPS/LYB/S solid battery was tested at 0.1 mV s⁻¹ (1.0 ~ 3.0 V, *vs*. Li/Li⁺). The batteries were charged and discharged (1.5 – 2.8 V, 0.1 C) by a LANHE CT2001A battery test system (Rambo, China) at 60 °C.

Fabrication of Li-In/LPS/LYB/LTO battery: The Li and In metal chips were weighed by the molar ratio of 3/7, and then cold pressed repetitiously until the even Li-In alloy anode

plates were obtained. LTO, LYB and KB powders (weight ratio, 21:72:7) were weighed and mixed uniformly by grinding method to obtained the cathode powder. The LYB powder (100 mg) was cold pressed (100 MPa) in a mold (diameter, 10.0 mm) to form LYB pellet, then the LPS powder (10.0 mg) was added on the LYB pellet and cold pressed (200 MPa), forming the LPS/LYB pellet. Subsequently, the Li-In plate and cathode powder (2.0 mg) were placed on the LPS side and LYB side of LPS/LYB pellet respectively, which were pressed together under 500 MPa. The formed Li-In/LYB/LTO battery were cycled at 0.1 C and 10 C (1 C = 175 mA g^{-1}).



Fig. S1 The XRD patterns of the as-synthesized chloride SEs. (a) Li_3ScCl_6 , (b) Li_3YCl_6 , (c) Li_3HoCl_6 , (d) Li_3ErCl_6 , (e) Li_3YbCl_6 , (f) Li_3TbCl_6 , (g) Li_3DyCl_6 , and (h) Li_3TmCl_6 .



Fig. S2 The XRD patterns of the as-synthesized bromide SEs. (a) Li_3YBr_6 , (b) Li_3HoBr_6 , (c) Li_3YbBr_6 , (d) Li_3LuBr_6 , (e) Li_3TbBr_6 , (f) Li_3DyBr_6 and (g) Li_3TmBr_6 .



Fig. S3 The XRD patterns of the as-synthesized RE-based halide perovskites. (a) Cs_2NaYCl_6 , (b) Cs_2KYbCl_6 , (c) Na_3TbCl_6 , (d) Na_3YBr_6 , (e) Rb_3TbCl_6 , (f) Cs_3TbCl_6 , (g) $Cs_3Sc_2Cl_9$, (h) $Cs_3Y_2Cl_9$ and (i) $Cs_3Y_2Br_9$.



Fig. S4 The XRD patterns of the precursors, products and byproducts before and after the VEA reaction. (a) Precursors of 1-LYC-precursor, 2-LYC-precursor and 3-LYC-precursor, the molar ratios of Y to NH₄Cl are 1/20, 1/5 and 1/2.5, respectively. (b) Precursors of 4-LYB-precursor, 5-LYB-precursor and 6-LYB-precursor, the molar ratios of Y to NH₄Br are 1/20, 1/5 and 1/2.5, respectively. (c) The XRD patterns of the products from heating the LYC precursors in (a). (d) The XRD patterns of the products from heating the LYB precursors in (b). (e) The XRD patterns of the byproducts from heating the LYC precursors in (b). The precursors in (a). (f) The XRD patterns of the byproducts from heating the LYB precursors in (b). The precursors in (b). The precursors contain NH₄X and metal halides. The byproducts are NH₄Cl and NH₄Br.



Fig. S5 The morphology and EDS mapping of LScC. (a) SEM image. (b-c) The EDS mapping of Sc and Cl in LScC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Sc and Cl in LScC.



Fig. S6 The morphology and EDS mapping of LYC. (a) SEM image. (b-c) The EDS mapping of Y and Cl in LYC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Y and Cl in LYC.



Fig. S7 The morphology and EDS mapping of LTbC. (a) SEM image. (b-c) The EDS mapping of Tb and Cl in LTbC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Tb and Cl in LTbC.



Fig. S8 The morphology and EDS mapping of LDyC. (a) SEM image. (b-c) The EDS mapping of Dy and Cl in LDyC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Dy and Cl in LDyC.



Fig. S9 The morphology and EDS mapping of LHoC. (a) SEM image. (b-c) The EDS mapping of Ho and Cl in LHoC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Ho and Cl in LHoC.



Fig. S10 The morphology and EDS mapping of LErC. (a) SEM image. (b-c) The EDS mapping of Er and Cl in LErC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Er and Cl in LErC.



Fig. S11 The morphology and EDS mapping of LYbC. (a) SEM image. (b-c) The EDS mapping of Yb and Cl in LYbC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Yb and Cl in LYbC.



Fig. S12 The morphology and EDS mapping of LTmC. (a) SEM image. (b-c) The EDS mapping of Tm and Cl in LTmC from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Tm and Cl in LTmC.



Fig. S13 The morphology and EDS mapping of LYB. (a) SEM image. (b-c) The EDS mapping of Y and Br in LYB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Y and Br in LYB.



Fig. S14 The morphology and EDS mapping of LHoB. (a) SEM image. (b-c) The EDS mapping of Ho and Br in LHoB from (a). (d) The overlay image of (a), (b) and (c). (E) The EDS spectrum of Ho and Br in LHoB.



Fig. S15 The morphology and EDS mapping of LYbB. (a) SEM image. (b-c) The EDS mapping of Yb and Br in LYbB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Yb and Br in LYbB.



Fig. S16 The morphology and EDS mapping of LLuB. (a) SEM image. (b-c) The EDS mapping of Lu and Br in LLuB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Lu and Br in LLuB.



Fig. S17 The morphology and EDS mapping of LTbB. (a) SEM image. (b-c) The EDS mapping of Tb and Br in LTbB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Tb and Br in LTbB.



Fig. S18 The morphology and EDS mapping of LDyB. (a) SEM image. (b-c) The EDS mapping of Dy and Br in LDyB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Dy and Br in LDyB.



Fig. S19 The morphology and EDS mapping of LTmB. (a) SEM image. (b-c) The EDS mapping of Tm and Br in LTmB from (a). (d) The overlay image of (a), (b) and (c). (e) The EDS spectrum of Tm and Br in LTmB.



Fig. S20 The pictures of the process of massive synthesis of Li_3REX_6 . (a) Dissolving the raw materials. (b) Removing the excess solvent. (c) The precursor powder was transferred in quartz bottle. (d) The product (Li_3REX_6) and byproduct (NH_4X) in the bottle and condenser pipe, respectively. (e) Recovery and reuse of NH_4X . (f) Packaged Li_3REX_6 sample in quartz bottle.



Fig. S21 The Nyquist plots of the EIS measurement results of HSEs with metal indium (In) electrodes. (a) LScC. (b) LHoC, LYC, LErC and LYbC. (c) LTbC, LTmC and LDyC. (d) LTbB, LHoB and LYB. (e) LTmB and LDyB. (f) LYbB and LLuB.



Fig. S22 The cyclic voltammograms of Li/LPS/HSEs/HSEs-C cells. (a) LScC, (b) LYC, (c) LTbC, (d) LDyC, (e) LHoC, (f) LErC, (g) LTmC, (h) LTbB, (i) LDyB, (j) LHoB, (k) LTmB and (l) LLuB. Note: LPS, Li₇P₃S₁₁; Carbon, 10%, wt.; Scan rate, 0.5 mV/s; Voltage, -0.5 – 5.0 V, versus Li/Li⁺.



Fig. S23 The Nyquist plots and electrochemical windows of recovered HSEs. (a) The Nyquist plots of recovered LYC. (b) The Nyquist plots of recovered LYB. (c) The cyclic voltammograms of recovered LYB. The Nyquist plots of HSEs tested with indium (In) electrodes. Cyclic voltammograms of Li/LPS/HSEs/HSEs-C cells were tested with the scan rate of 0.5 mV/s from -0.5 to 5.0 V (versus Li/Li⁺), the addition amounts of carbon were 10% wt.



Fig. S24 The Nyquist plots of the EIS measurement results of massive synthesized and solvent-free prepared HSEs. The plots were tested on In/HSEs/In cells. (a) Massive synthesized LScC and LYC. (b) Massive synthesized LHoB and LYB. (c) Solvent-free synthesized LYC and LErC. (d) Solvent-free synthesized LHoB and LYB.



Fig. S25 The cyclic voltammograms of Li/LPS/HSEs/HSEs-C cells. The HSEs were massive synthesized samples. Scan rate, 0.5 mV/s; Voltage, -0.5 - 5.0 V, versus Li/Li⁺; Carbon, 10%, wt.; (a) LScC, (b) LYC, (c) LYB and (d) LHoB.



Fig. S26 The cyclic voltammograms of Li/LPS/HSEs/HSEs-C cells. The HSEs were solvent-free synthesized samples. Scan rate, 0.5 mV/s; Voltage, -0.5 – 5.0 V, versus Li/Li⁺; Carbon, 10%, wt.; (a) LYC, (b) LErC, (c) LYB and (d) LHoB.



Fig. S27 The cyclic voltammograms of Li/LPS/LYB/S battery. The curves obtained with the scan rate of 0.1 mV s⁻¹ from 1.0 - 3.0 V. The reduction and oxidation peaks correspond to the redox of sulfur from $S_8 \rightarrow Li_2S$ and $Li_2S \rightarrow S_8$, respectively.



Fig. S28 The electrochemical performance of the Li-In/LPS/LYB/LTO ($Li_4Ti_5O_{12}$) battery. Galvanostatic charge–discharge curves at various cycles of Li-In/LPS/LYB/LTO at different current density, (a) 0.1 C, (b) 10 C. (c) Cycle stability of the battery at 10 C.

Cation	Chlorides	mp (°C)	bp (°C)	Bromides	mp (°C)	bp (°C)
$\mathrm{NH_4^+}$	NH ₄ Cl	520 (dec.)	338 sp	NH ₄ Br	542 dec.	396 sp
Li ⁺	LiCl	550	1300	LiBr	610	1380
Na	NaCl	802	1465	NaBr	747	1390
K	KCl	771	1420	KBr	734	1435
Rb	RbCl	724	1390	RbBr	692	1340
Cs	CsCl	646	1297	CsBr	636	1300
Sc^{3+}	ScCl ₃	967	/	ScBr ₃	969	/
Y ³⁺	YCl ₃	721	1482	YBr ₃	904	/
Tb^{3+}	TbCl ₃	582	/	TbBr ₃	830	1490
Dy^{3+}	DyCl ₃	718	1530	DyBr ₃	879	/
Ho ³⁺	HoCl ₃	720	1500	HoBr ₃	919	1470
Er ³⁺	ErCl ₃	776	/	ErBr ₃	950	1460
Tm^{3+}	TmCl ₃	845	/	TmBr ₃	954	/
Yb^{3+}	YbCl ₃	854	/	YbBr ₃	956 dec.	/

Table S1 The melting point and boiling point of some halide salts.

Note: dec., decompose; mp, melting point; bp, boiling point; sp, sublimation point; The data was come from *HANDBOOK OF CHEMISTRY and PHYSICS*, 97TH, Edition 2016-2017.

Sample	Li ₃ ScCl ₆ (LScC)	Li ₃ YCl ₆ (LYC)	Li ₃ YBr ₆ (LYB)
Formula sum	Cl6 Li3.00 Sc	Cl18 Li9.00 Y3.00	Br6 Li3.00 Y
Formula weight	278.5 g/mol	967.34 g/mol	589.15 g/mol
Crystal system	monoclinic	trigonal	monoclinic
Space-group	C 1 2/m 1 (12)	P -3 m 1 (164)	C 1 2/m 1 (12)
Cell parameters	a=6.3770(5) Å b=11.1500(11) Å c=6.3474(6) Å β=109.32(0)°	a=11.1959(3) Å c=6.0342(2) Å	a=6.9229(2) Å b=11.9574(3) Å c=6.8587(2) Å β=109.78(0)°
Cell ratio	a/b=0.5719 b/c=1.7566 c/a=0.9954	a/b=1.0000 b/c=1.8554 c/a=0.5390	a/b=0.5790 b/c=1.7434 c/a=0.9907
Cell volume	425.91(48) Å ³	655.04(3) Å ³	534.26(29) Å ³
Ζ	2	1	2
Calc. density	2.17153 g/cm ³	2.45209 g/cm ³	3.66207 g/cm ³
wRp	6.35%	3.62%	2.32%
Rp	3.89%	2.66%	1.64%
CHI	4.487	1.147	0.9143

Table S2 The crystallographic phase data of LScC, LYC and LYB obtained by Rietveld refinement result.

Sample	Atom Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Ų]
Li ₃ ScCl ₆	Sc1	2a	2/m		0	0	0	0.0343(18)
	Li2	4h	2	0.365	0	0.16900	1/2	-0.018(10)
	Li3	2d	2/m	0.27	1/2	0	1/2	-0.090(19)
(LScC)	Li4	4g	2		1/2	0.83470	0	-0.030(4)
	Cl5	8j	1		0.23870	0.83910	0.23710	0.0325(10)
	Cl6	4i	m		0.75790	0	0.23130	0.0313(18)
LizYCle	Cl1	6i	m		0.22150	0.77850	0.26760	0.0100
	Cl2	6i	m		0.55460	0.44540	0.24410	0.0100
	Cl3	6i	m		0.88650	0.11350	0.23190	0.0100
	Li4	6h	2	0.5	0.28840	0	1/2	0.0100
(LYC)	Li5	6g	2		0.33970	0	0	0.0100
	Y6	2d	3m	0.03	1/3	2/3	0.05060	-0.090(4)
	Y7	2d	3m	0.97	1/3	2/3	0.51000	-0.0016(9)
	Y8	1a	-3m		0	0	0	-0.0095(14)
Li ₃ YBr ₆ (LYB)	Br1	8j	1		0.24640	0.16620	0.24380	-0.0069(11)
	Br2	4i	m		0.74920	0	0.24090	-0.0079(17)
	Li3	4h	2	0.5	0	0.15500	1/2	-0.082(12)
	Li4	4g	2		0	0.33490	0	0.8(2)
	Y5	2a	2/m		0	0	0	-0.0280(16)

Table S3 The crystallographic atomic parameters of LScC, LYC and LYB obtained by Rietveld refinement result.

Target product	NH ₄ X	RE and NH ₄ X amount (mmol)	NH ₄ X addition (g)	NH ₄ X collected (g)	NH ₄ X recycle ratio (%)
Li ₃ YCl ₆	NH ₄ Cl	2, 10	0.535	0.500	93.45
Li ₃ YCl ₆	NH ₄ Cl	2,40	2.143	2.036	95.01
Li ₃ YBr ₆	NH ₄ Br	2, 10	0.960	0.908	94.58
Li ₃ YBr ₆	NH ₄ Br	2,40	3.842	3.773	98.20
Li ₃ ScCl ₆	NH ₄ Cl	4, 65.47	3.5	3.45	98.57
Li ₃ ScCl ₆	NH ₄ Cl	6, 98.21	5.25	5.20	99.05
Li ₃ HoCl ₆	NH ₄ Cl	6, 98.21	5.25	5.15	98.09
Li ₃ YBr ₆	NH ₄ Br	6, 91.92	9.0	8.84	98.22
Li ₃ HoBr ₆	NH ₄ Br	6, 91.92	9.0	8.76	97.33
Na ₃ YBr ₆	NH ₄ Br	4, 61.28	6.0	5.93	98.83
Cs ₃ YCl ₉	NH ₄ Cl	4, 65.47	3.5	3.47	99.14
Cs ₂ NaYCl ₆	NH ₄ Cl	4, 65.47	3.5	3.45	98.57

Table S4 The amount changes of the NH_4X during the reaction of VEA method in synthesis of REbased HSEs and halide perovskites.

Compounds	Li-ionic conductivities, (mS cm ⁻¹)	Reduction potential, vs. Li/Li ⁺ (V)	oxidation potential, vs. Li/Li ⁺ (V)
Li ₃ ScCl ₆	0.24	1.4	4.2
Li ₃ YCl ₆	0.049	1.5	4.1
Li ₃ TbCl ₆	0.032	1.4	4.2
Li ₃ DyCl ₆	0.016	1.4	4.2
Li ₃ HoCl ₆	0.057	1.6	4.1
Li ₃ ErCl ₆	0.040	1.4	4.1
Li ₃ TmCl ₆	0.029	1.5	3.9
Li ₃ YbCl ₆	0.027		
Li ₃ YBr ₆	0.80	1.5	3.4
Li ₃ TbBr ₆	1.7	1.5	3.4
Li ₃ DyBr ₆	0.44	1.5	3.4
Li ₃ HoBr ₆	0.93	1.5	3.4
Li ₃ TmBr ₆	0.48	1.4	3.4
Li ₃ YbBr ₆	0.068		
Li ₃ LuBr ₆	0.043	1.4	3.4

Table S5 The Li ion conductivities and electrochemical windows of the VEA synthesized RE HSEs.

Compounds		Li-ionic conductivities, (mS cm ⁻¹)	Reduction potential, vs. Li/Li ⁺ (V)	oxidation potential, vs. Li/Li ⁺ (V)
Recovered	Li ₃ YCl ₆	0.49×10^{-4}	1.5	4.2
	Li ₃ YBr ₆	0.80×10^{-3}	1.5	3.4
	Li ₃ ScCl ₆	0.24×10^{-3}	1.4	4.2
Massive	Li ₃ YCl ₆	0.52×10^{-4}	1.5	4.1
synthesized	Li ₃ YBr ₆	0.80×10^{-3}	1.5	3.4
	Li ₃ HoBr ₆	0.93 × 10 ⁻³	1.5	3.4
	Li ₃ YCl ₆	0.51 × 10 ⁻⁴	1.5	4.1
Solvent-free	Li3ErCl6	$0.39 imes 10^{-4}$	1.4	4.2
synthesized	Li ₃ YBr ₆	0.80×10^{-3}	1.5	3.4
	Li ₃ HoBr ₆	0.93×10^{-3}	1.5	3.4

Table S6 The Li ion conductivities and electrochemical windows of the recovered, massive and solvent-free synthesized RE HSEs.

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- 1. R. Xu, X. Xia, Z. Yao, X. Wang, C. Gu and J. Tu, Preparation of Li₇P₃S₁₁ glassceramic electrolyte by dissolution-evaporation method for all-solid-state lithium ion batteries, *Electrochim. Acta*, 2016, **219**, 235-240.
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