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Supplementary Information

Strain Engineering of Antiperovskite Materials Solid-State Li Batteries: A Computation-Guided Substitution Approach

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1 Ground-state structures

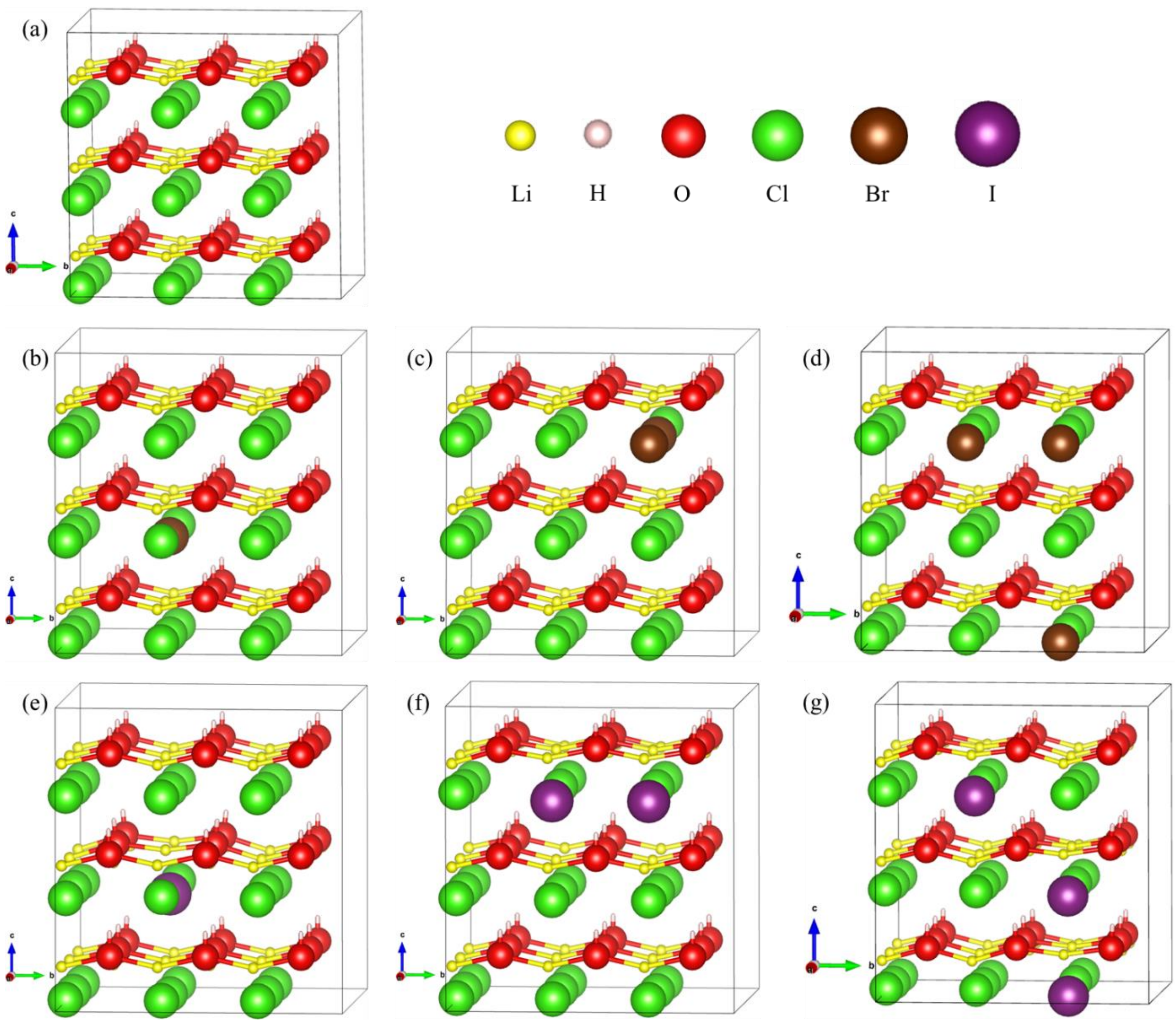

Figure S1. Structure of (a) Li_2OHCl; (b) $Li_2OHCl_{26/27}Br_{1/27}$; (c) $Li_2OHCl_{25/27}Br_{2/27}$; (d) $Li_2OHCl_{8/9}Br_{1/9}$; (e) $Li_2OHCl_{0.963}I_{1/27}$ (f) $Li_2OHCl_{25/27}Br_{2/27}$; and (g) $Li_2OHCl_{8/9}I_{1/9}$.

2 Band gaps and electrochemical stability window

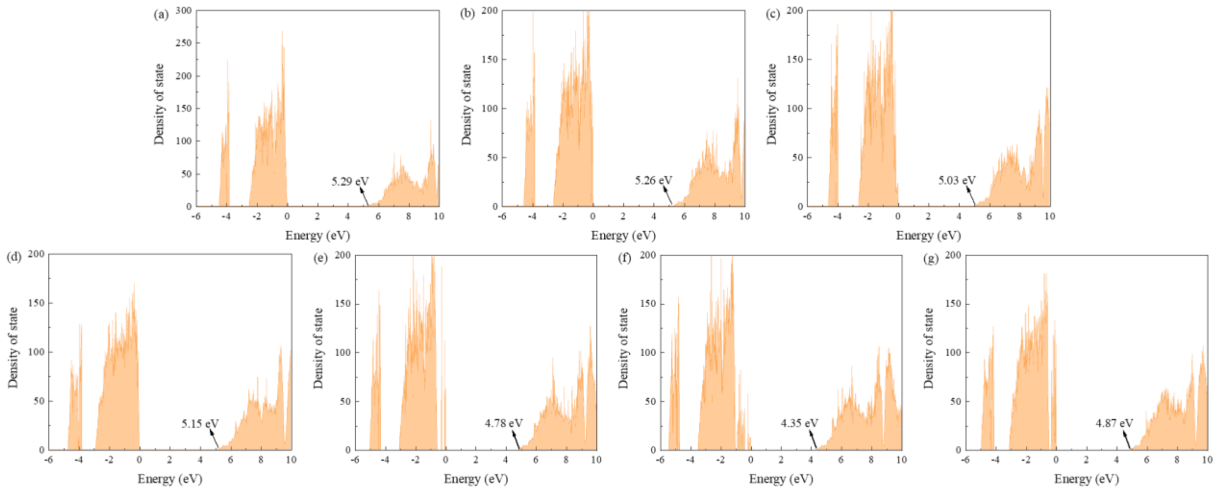

Figure S2. The density of states of (a) Li_2OHCl; (b) $Li_2OHCl_{26/27}Br_{1/27}$; (c) $Li_2OHCl_{25/27}Br_{2/27}$; (d) $Li_2OHCl_{8/9}I_{1/9}$; (e) $Li_2OHCl_{26/27}I_{1/27}$; (f) $Li_2OHCl_{25/27}I_{2/27}$; and (g) $Li_2OHCl_{8/9}I_{1/9}$.

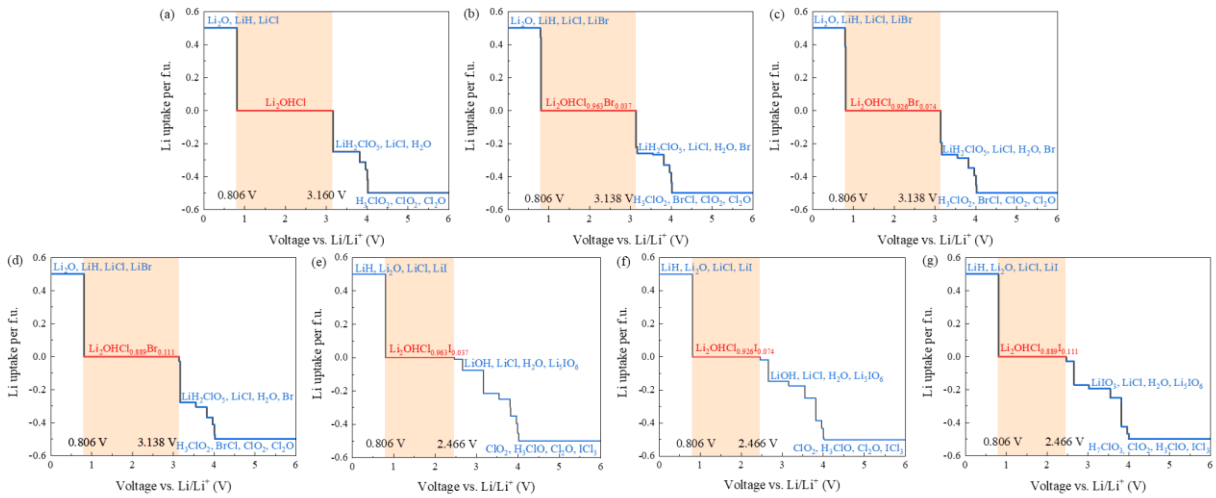

Figure S3. The electrochemical stability window of (a) Li_2OHCl; (b) $Li_2OHCl_{26/27}Br_{1/27}$; (c) $Li_2OHCl_{25/27}Br_{2/27}$; (d) $Li_2OHCl_{8/9}I_{1/9}$; (e) $Li_2OHCl_{26/27}I_{1/27}$; (f) $Li_2OHCl_{25/27}I_{2/27}$; and (g) $Li_2OHCl_{8/9}I_{1/9}$.

Table S1. Decomposition reactions between LiBr and lithium metal.

Decomposition reaction	Voltage (V)
2 LiBr => 2 LiBr	0.0
2 LiBr => Br_2 + 2 Li	3.138

Table S2. Decomposition reactions between LiI and lithium metal.

Decomposition reaction	Voltage (V)
2 LiI => 2 LiI	0.0
2 LiI => I_2 + 2 Li	2.466

Table S3. Decomposition reactions between Li_2OHCl and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl + 2\ Li => LiH + Li_2O + LiCl$	0.0
$Li_2OHCl => LiCl + LiOH$	0.806
$Li_2OHCl => 0.125\ LiH_2ClO_5 + 0.875\ LiCl + 0.375\ H_2O + Li$	3.160
$Li_2OHCl => 0.25\ ClO_2 + 0.75\ LiCl + 0.5\ H_2O + 1.25\ Li$	3.814
$Li_2OHCl => 0.143\ H_7ClO_3 + 0.286\ ClO_2 + 0.571\ LiCl + 1.429\ Li$	3.960
$Li_2OHCl => 0.333\ H_3ClO + 0.333\ ClO_2 + 0.333\ LiCl + 1.667\ Li$	3.996
$Li_2OHCl => 0.333\ H_3ClO + 0.222\ ClO_2 + 0.222\ Cl_2O + 2\ Li$	4.020

Table S4. Decomposition reactions between $Li_2OHCl_{26/27}Br_{1/27}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl_{26/27}Br_{1/27}$ + 2 Li => Li_2O + LiH + 26/27 LiCl + 1/27 LiBr	0.0
$Li_2OHCl_{26/27}Br_{1/27}$ + 1.778 Li => 1/27 $Li_4H_3BrO_3$ + 8/9 Li_2O + 8/9 LiH + 26/27 LiCl	0.796
$Li_2OHCl_{26/27}Br_{1/27}$ => 1/27 $Li_4H_3BrO_3$ + 26/27 LiCl + 8/9 LiHO	0.806
$Li_2OHCl_{26/27}Br_{1/27}$ => 1/27 $Li_4H_3BrO_3$ + 0.85 LiCl + 1/9 LiH_2ClO_5 + 0.333 H_2O + 8/9 Li	3.138
$Li_2OHCl_{26/27}Br_{1/27}$ => 0.838 LiCl + 0.125 LiH_2ClO5 + 0.375 H_2O + 1/27 Br + 1.037 Li	3.169
$Li_2OHCl_{26/27}Br_{1/27}$ => 1/27 BrCl + 0.801 LiCl + 0.125 LiH_2ClO_5 + 0.375 H_2O + 1.074 Li	3.555
$Li_2OHCl_{26/27}Br_{1/27}$ => 1/27 BrCl + 0.676 LiCl + 0.25 ClO_2 + 0.5 H_2O + 1.324 Li	3.814
$Li_2OHCl_{26/27}Br_{1/27}$ => 0.143 H_7ClO_3 + 1/27 BrCl + 0.497 LiCl + 0.286 ClO_2 + 1.503 Li	3.960
$Li_2OHCl_{26/27}Br_{1/27}$ => 0.333 H_3ClO + 1/27 BrCl + 0.259 LiCl + 0.333 ClO_2 + 1.741 Li	3.996
$Li_2OHCl_{26/27}Br_{1/27}$ => 0.333 H_3ClO + 1/27 BrCl + 0.247 ClO_2 + 0.173 Cl_2O + 2 Li	4.020

Table S5. Decomposition reactions between $Li_2OHCl_{25/27}Br_{2/27}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl_{25/27}Br_{2/27}$ + 2 Li => Li_2O + LiH + 25/27 LiCl + 2/27 LiBr	0.0
$Li_2OHCl_{25/27}Br_{2/27}$ + 1.556 Li => 2/27 $Li_4H_3BrO_3$ + 0.778 Li_2O + 0.778 LiH + 25/27 LiCl	0.796
$Li_2OHCl_{25/27}Br_{2/27}$ => 2/27 $Li_4H_3BrO_3$ + 25/27 LiCl + 0.778 LiHO	0.806
$Li_2OHCl_{25/27}Br_{2/27}$ => 2/27 $Li_4H_3BrO_3$ + 0.83 LiCl + 0.1 LiH_2ClO_5 + 0.29 H_2O + 0.78 Li	3.138
$Li_2OHCl_{25/27}Br_{2/27}$ => 0.801 LiCl + 0.125 LiH_2ClO_5 + 0.375 H_2O + 2/27 Br + 1.074 Li	3.169
$Li_2OHCl_{25/27}Br_{2/27}$ => 2/27 BrCl + 0.727 LiCl + 0.125 LiH_2ClO_5 + 0.375 H_2O + 1.148 Li	3.555
$Li_2OHCl_{25/27}Br_{2/27}$ => 2/27 BrCl + 0.602 LiCl + 0.25 ClO_2 + 0.5 H_2O + 1.398 Li	3.814
$Li_2OHCl_{25/27}Br_{2/27}$ => 0.143 H_7ClO_3 + 2/27 BrCl + 0.423 LiCl + 0.286 ClO_2 + 1.577 Li	3.960
$Li_2OHCl_{25/27}Br_{2/27}$ => 0.333 H_3ClO + 2/27 BrCl + 0.186 LiCl + 0.333 ClO_2 + 1.815 Li	3.996
$Li_2OHCl_{25/27}Br_{2/27}$ => 0.333 H_3ClO + 2/27 BrCl + 0.272 ClO_2 + 3.333 Cl_2O + 2 Li	4.020

Table S6. Decomposition reactions between $Li_2OHCl_{8/9}Br_{1/9}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl_{8/9}Br_{1/9}$ + 2 Li => Li_2O + LiH + 8/9 LiCl + 1/9 LiBr	0.0
$Li_2OHCl_{8/9}Br_{1/9}$ + 1.333 Li => 1/9 $Li_4H_3BrO_3$ + 0.667 Li2O + 0.667 LiH + 8/9 LiCl	0.796
$Li_2OHCl_{8/9}Br_{1/9}$ => 8/9 LiCl + 1/9 LiBr + LiOH	0.806
$Li_2OHCl_{8/9}Br_{1/9}$ => 8/9 LiCl + LiOH + 1/9 Br + 1/9 Li	3.138
$Li_2OHCl_{8/9}Br_{1/9}$ => 0.764 LiCl + 0.125 LiH_2ClO_5 + 0.375 H_2O + 1/9 Br + 1.111 Li	3.169
$Li_2OHCl_{8/9}Br_{1/9}$ => 1/9 BrCl + 0.653 LiCl + 0.125 LiH_2ClO_5 + 0.375 H_2O + 1.222 Li	3.555
$Li_2OHCl_{8/9}Br_{1/9}$ => 1/9 BrCl + 0.528 LiCl + 0.25 ClO_2 + 0.5 H_2O + 1.472 Li	3.814
$Li_2OHCl_{8/9}Br_{1/9}$ => 0.143 H_7ClO_3 + 1/9 BrCl + 0.349 LiCl + 0.286 ClO_2 + 1.651 Li	3.960
$Li_2OHCl_{8/9}Br_{1/9}$ => 0.333 H_3ClO + 1/9 BrCl + 1/9 LiCl + 0.333 ClO_2 + 1.889 Li	3.996
$Li_2OHCl_{8/9}Br_{1/9}$ => 0.333 H_3ClO + 1/9 BrCl + 0.296 ClO_2 + 2/27 Cl_2O + 2 Li	4.020

Table S7. Decomposition reactions between $Li_2OHCl_{26/27}I_{1/27}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_{54}O_{27}H_{27}Cl_{26}I$ + 54 Li => 27 LiH + 27 Li_2O + LiI + 26 LiCl	0.0
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 27 LiHO + LiI + 26 LiCl	0.806
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 27 LiHO + 26 LiCl + I + Li	2.466
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 15 LiHO + 26 LiCl + 6 H_2O + Li_5IO_6 + 8 Li	2.660
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 1.875 LiH_2ClO_5 + 24.12 LiCl + 11.62 H_2O + Li_5IO_6 + 23 Li	3.160
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 2.625 LiH_2ClO_5 + $LiIO_3$ + 23.37 LiCl + 10.88 H_2O + 27 Li	3.547
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 5.25 ClO_2 + $LiIO_3$ + 20.75 LiCl + 13.5 H_2O + 32.25 Li	3.814
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 6.75 ClO_2 + ICl_3 + 16.25 LiCl + 13.5 H_2O + 37.75 Li	3.817
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 3.857 H_7ClO_3 + 7.714 ClO_2 + ICl_3 + 11.43 LiCl + 42.57 Li	3.960
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 9 ClO_2 + 9 H_3ClO + ICl_3 + 5 LiCl + 49 Li	3.996
$Li_{54}O_{27}H_{27}Cl_{26}I$ => 7.333 ClO_2 + 9 H_3ClO + 3.333 Cl_2O + ICl_3 + 54 Li	4.020

Table S8. Decomposition reactions between $Li_2OHCl_{25/27}I_{2/27}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl_{25/27}I_{2/27}$ + 2 Li => LiH + Li_2O + 2/27 LiI + 25/27 LiCl	0.0
$Li_2OHCl_{25/27}I_{2/27}$ => LiHO + 2/27 LiI + 25/27 LiCl	0.806
$Li_2OHCl_{25/27}I_{2/27}$ => LiHO + 25/27 LiCl + 2/27 I + 2/27 Li	2.466
$Li_2OHCl_{25/27}I_{2/27}$ => 1/9 LiHO + 25/27 LiCl + 0.444 H_2O + 2/27 Li_5IO_6 + 0.593 Li	2.660
$Li_2OHCl_{25/27}I_{2/27}$ => 0.014 LiH_2ClO_5 + 0.912 LiCl + 0.486 H_2O + 2/27 Li_5IO_6 + 0.704 Li	3.160
$Li_2OHCl_{25/27}I_{2/27}$ => 0.069 LiH_2ClO_5 + 2/27 $LiIO_3$ + 0.856 LiCl + 0.431 H_2O + Li	3.547
$Li_2OHCl_{25/27}I_{2/27}$ => 0.139 ClO_2 + 2/27 $LiIO_3$ + 0.787 LiCl + 0.5 H_2O + 1.139 Li	3.814
$Li_2OHCl_{25/27}I_{2/27}$ => 0.25 ClO_2 + 2/27 ICl_3 + 0.454 LiCl + 0.5 H_2O + 1.546 Li	3.817
$Li_2OHCl_{25/27}I_{2/27}$ => 0.143 H_7ClO_3 + 0.286 ClO_2 + 2/27 ICl_3 + 0.275 LiCl + 1.725 Li	3.960
$Li_2OHCl_{25/27}I_{2/27}$ => 0.333 ClO_2 + 0.333 H_3ClO + 2/27 ICl_3 + 1/27 LiCl + 1.963 Li	3.996
$Li_2OHCl_{25/27}I_{2/27}$ => 0.321 ClO_2 + 0.333 H_3ClO + 0.025 Cl_2O + 2/27 ICl_3 + 2 Li	4.020

Table S9. Decomposition reactions between $Li_2OHCl_{8/9}I_{1/9}$ and lithium metal.

Decomposition reaction	Voltage (V)
$Li_2OHCl_{8/9}I_{1/9}$ + 2 Li => LiH + Li_2O + 1/9 LiI + 8/9 LiCl	0.0
$Li_2OHCl_{8/9}I_{1/9}$ => LiOH + 1/9 LiI + 8/9 LiCl	0.806
$Li_2OHCl_{8/9}I_{1/9}$ => LiOH + 8/9 LiCl + 1/9 I + 1/9 Li	2.466
$Li_2OHCl_{8/9}I_{1/9}$ => 8/9 LiCl + 0.5 H_2O + 0.083 Li_5IO_6 + 0.028 I + 0.694 Li	2.660
$Li_2OHCl_{8/9}I_{1/9}$ => 0.056 $LiIO_3$ + 8/9 LiCl + 0.5 H_2O + 0.056 Li_5IO_6 + 0.778 Li	3.026
$Li_2OHCl_{8/9}I_{1/9}$ => 0.417 LiH_2ClO_5 + 1/9 $LiIO_3$ + 0.847 LiCl + 0.458 H_2O + Li	3.547
$Li_2OHCl_{8/9}I_{1/9}$ => 0.083 ClO_2 + 1/9 $LiIO_3$ + 0.806 LiCl + 0.5 H_2O + 1.083 Li	3.814
$Li_2OHCl_{8/9}I_{1/9}$ => 0.25 ClO_2 + 1/9 ICl_3 + 0.306 LiCl + 0.5 H_2O + 1.694 Li	3.817
$Li_2OHCl_{8/9}I_{1/9}$ => 0.144 H_7ClO_3 + 0.286 ClO_2 + 1/9 ICl_3 + 0.127 LiCl + 1.873 Li	3.960
$Li_2OHCl_{8/9}I_{1/9}$ =>0.067 H_7ClO_3 + 0.311 ClO_2 + 0.178 H_3ClO + 1/9 ICl_3 + 2 Li	3.996

Table S10. Decomposition reactions between LiCl and lithium metal.

Decomposition reaction	Voltage (V)
2 LiCl => 2 LiCl	0.0
2 LiCl => Cl_2 + 2 Li	4.254

3 Migration energy barriers and AIMD simulations

Table S11. Migration energy barriers of 1NN path in $Li_2OHCl_{1-x}Br_x$.

x	Energy barrier (eV)	Weighted Mean migration energy barrier (eV)	Energy (eV)
0	0.2612	0.2612	0, 0.1087, 0.2612, 0.1018, -0.0013
1/27	Near: 0.2339 Far: 0.2149	0.2157	Near: 0, 0.0813, 0.2339, 0.0819, 0.0101 Far: 0, 0.0791, 0.2149, 0.0734, 0.0002
2/27	Near: 0.2429 Far: 0.2262	0.2274	Near: 0, 0.0846, 0.2429, 0.1217, 0.0169 Far: 0, 0.1071, 0.2262, 0.1149, 0.0095
1/9	Near: 0.2754 Far: 0.2338	0.2380	Near: 0, 0.1182, 0.2754, 0.117, 0.0115 Far: 0, 0.1059, 0.2338, 0.104, 0.0111

Table S12. Migration energy barriers of 1NN path in $Li_2OHCl_{1-x}I_x$.

x	Energy barrier (eV)	Weighted Mean migration energy barrier (eV)	Energy (eV)
0	0.2612	0.2612	0, 0.1087, 0.2612, 0.1018, -0.0013
1/27	Near: 0.2214 Far: 0.1816	0.1831	Near: 0, 0.0029, 0.2214, 0.0001, 0.0001 Far: 0, 0.0652, 0.1816, 0.0412, -0.0043
2/27	Near: 0.255 Far: 0.1571	0.1652	Near: 0, 0.0671, 0.255, 0.1712, 0.0563 Far: 0, 0.0587, 0.1571, 0.05, -0.0063
1/9	Near: 0.2671 Far: 0.1906	0.1970	Near: 0, 0.1052, 0.2671, 0.1956, 0.0668 Far: 0, 0.071, 0.1906, 0.1104, 0.0522

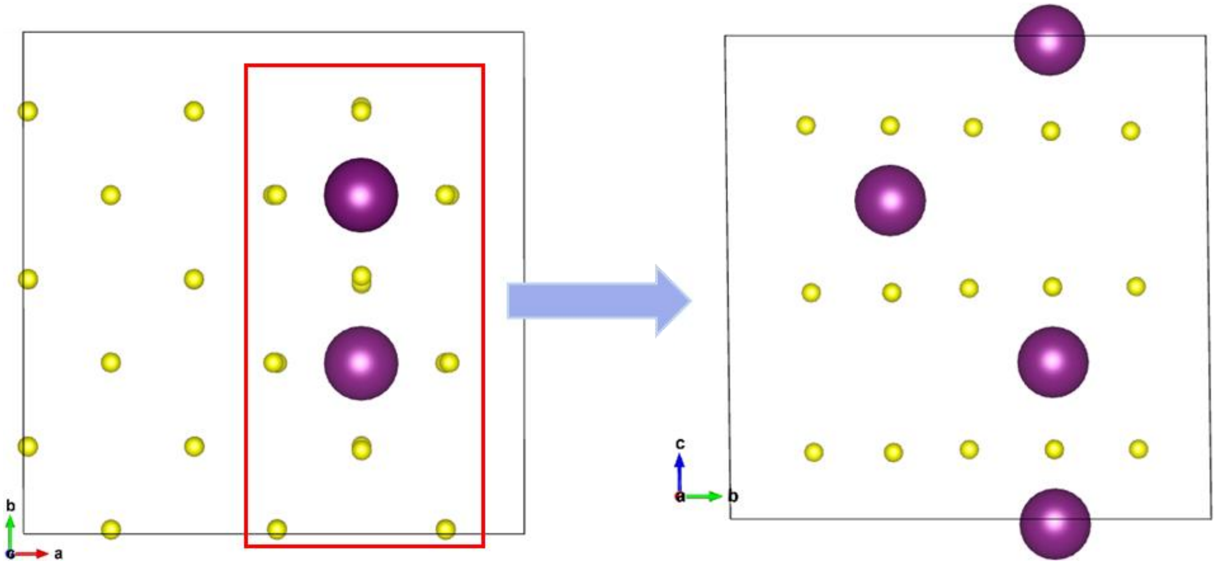

Figure S4. Lithium atom positions from the c-axis in $Li_2OHCl_{8/9}I_{1/9}$.

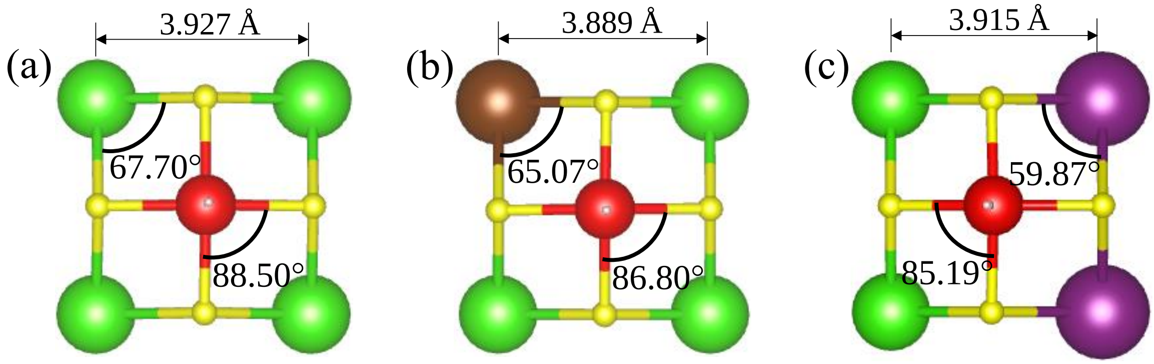

Figure S5. The local bond length and bond angles of (a) Li_2OHCl; (b) $Li_2OHCl_{26/27}Br_{1/27}$; (c) $Li_2OHCl_{25/27}I_{2/27}$.

Table S13. Fractional coordinates of 15 Li atoms on the c-axis.

	Fractional coordinate				
Up	0.81404	0.81380	0.81001	0.80282	0.80272
Middle	0.46850	0.46921	0.47770	0.48102	0.48133
down	0.13862	0.13832	0.14458	0.14520	0.14542

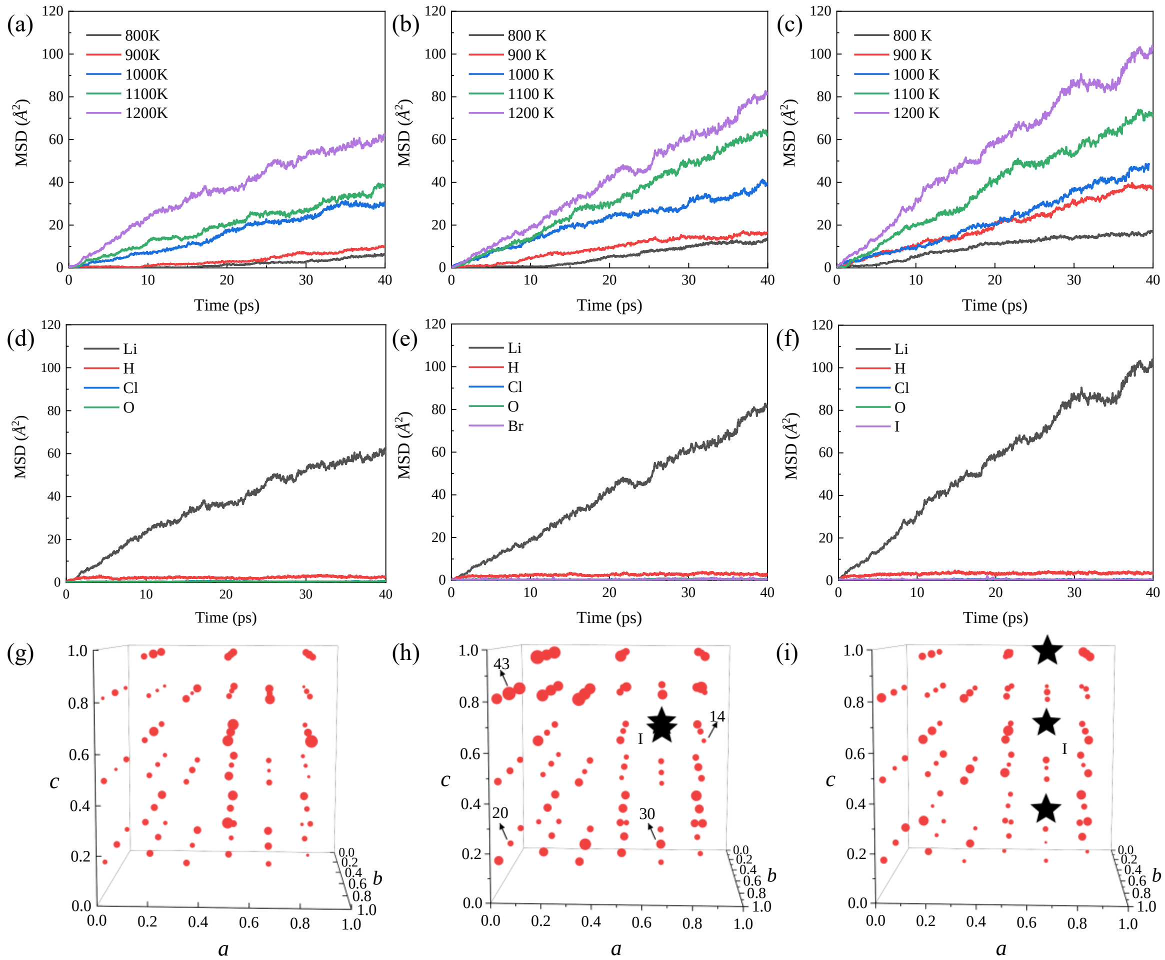

Figure S6. MSD of (a) Li_2OHCl, (b) $Li_2OHCl_{26/27}Br_{1/27}$, and (c) $Li_2OHCl_{25/27}I_{2/27}$ at 800, 900, 1000, 1100, and 1200 K; MSD of Li, H, Cl, O, Br, and I atoms of (d) Li_2OHCl, (e) $Li_2OHCl_{26/27}Br_{1/27}$, and (f) $Li_2OHCl_{25/27}I_{2/27}$ at 1200 K; Li^+ mobility of (g) Li_2OHCl, (h) $Li_2OHCl_{25/27}I_{2/27}$, and (i) $Li_2OHCl_{8/9}I_{1/9}$ at 1200 K. Li and I sites are marked as red circles and black stars, respectively. The size of the circles scales linearly with the number of Li^+ hops.

Table S14. The average number of Li atoms hops from 10 ps to 40 ps as an indication of mobility.

Electrolyte	The average number of Li hops
Li_2OHCl	20.85
$Li_2OHCl_{26/27}Br_{1/27}$	23.40
$Li_2OHCl_{25/27}I_{2/27}$	26.11
$Li_2OHCl_{8/9}I_{1/9}$	21.12

4 Elastic properties

Table S15. Elastic properties and Pugh's ratios of Li_2OHCl, $Li_2OHCl_{1-x}Br_x$, and $Li_2OHCl_{1-x}I_x$.

Electrolyte	*B* / GPa	*G* / GPa	*E* / GPa	*B*/*G*
Li_2OHCl	30.48	17.32	43.68	1.76
$Li_2OHCl_{26/27}Br_{1/27}$	29.34	14.45	37.24	2.03
$Li_2OHCl_{25/27}Br_{2/27}$	25.44	12.35	31.89	2.06
$Li_2OHCl_{8/9}Br_{1/9}$	29.40	16.10	40.85	1.83
$Li_2OHCl_{26/27}I_{1/27}$	24.88	13.89	35.13	1.79
$Li_2OHCl_{25/27}I_{2/27}$	24.93	12.71	32.60	1.96
$Li_2OHCl_{8/9}I_{1/9}$	29.03	16.45	41.50	1.76

5 Experiments

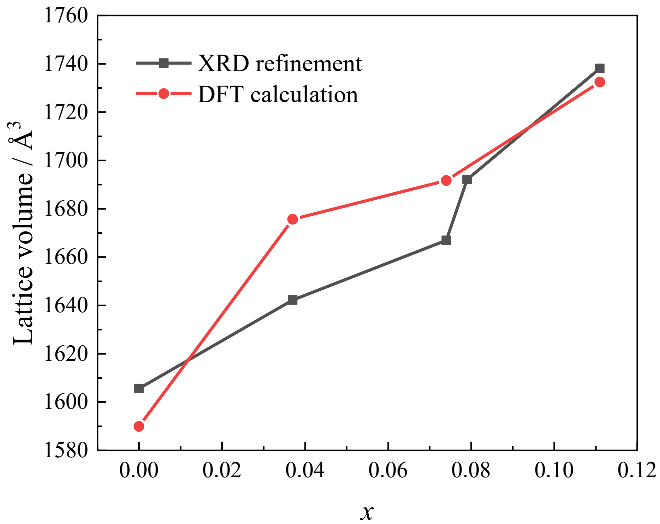

Figure S7. Lattice volumes from XRD refinement and DFT calculation.

Table S16. Calculated lattice constants from XRD refinement and DFT calculation.

	XRD refinement	DFT calculation	Error
Li_2OHCl	a = 3.895 Å b = 3.902 Å c = 3.913 Å	a = 3.942 Å b = 3.942 Å c = 3.827 Å	-1.19% -1.01% 2.25%
$Li_2OHCl_{26/27}I_{1/27}$	a = 11.696 Å b = 11.774 Å c = 11.925 Å	a = 11.664 Å b = 11.664 Å c = 12.316 Å	0.27% 0.94% -3.17%
$Li_2OHCl_{25/27}I_{2/27}$	a = 11.686 Å b = 11.782 Å c = 12.107 Å	a = 11.680 Å b = 11.698 Å c = 12.381 Å	0.05% 0.72% -3.38%
$Li_2OHCl_{0.921}I_{0.079}$	a = 11.713 Å b = 11.791 Å c = 12.252 Å	N/A	N/A
$Li_2OHCl_{8/9}I_{1/9}$	a = 11.780 Å b = 11.690 Å c = 12.622 Å	a = 11.674 Å b = 11.673 Å c = 12.713 Å	0.91% 0.15% -0.72%

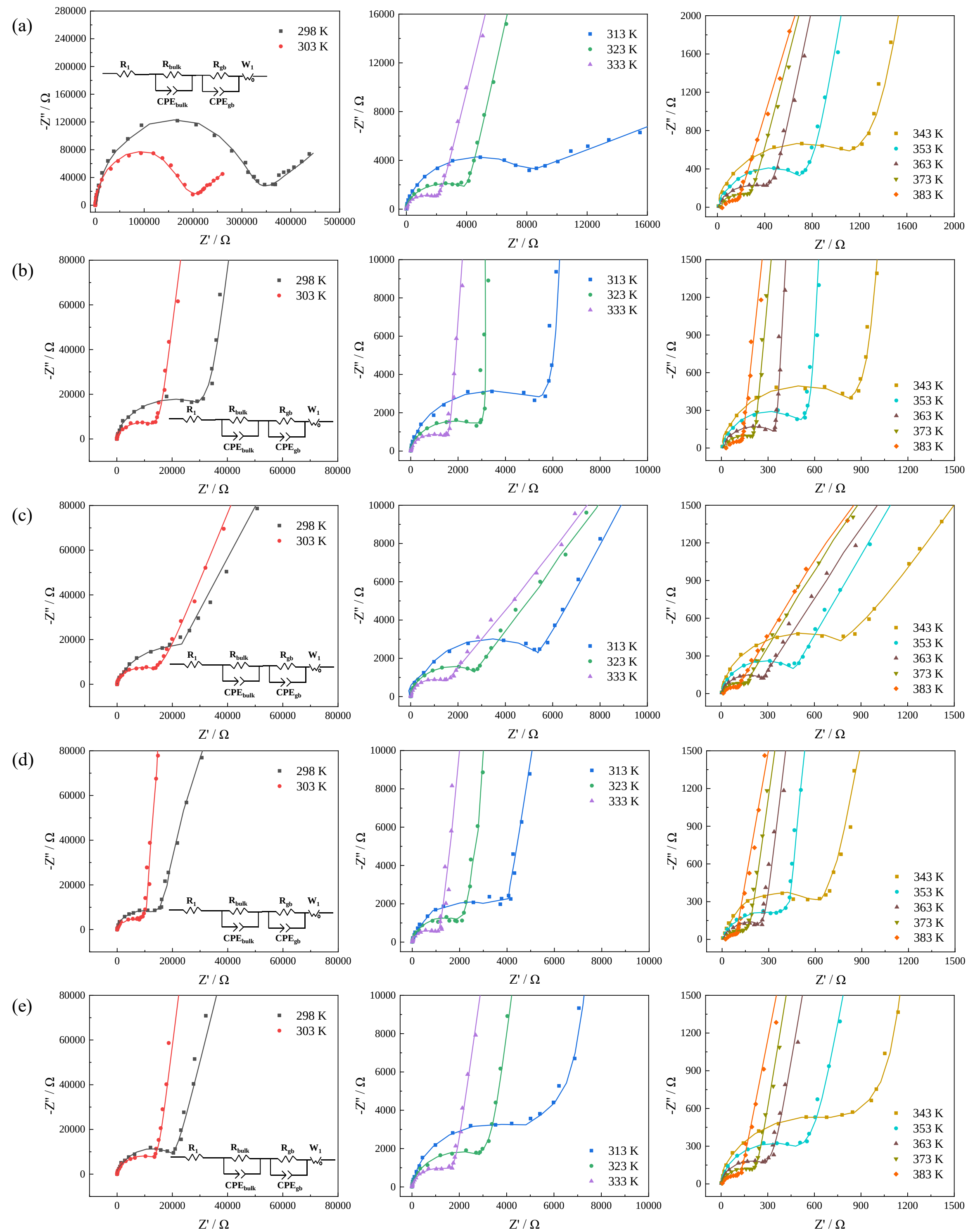

Figure S8. The EIS spectra of (a) Li_2OHCl, (b) $Li_2OHCl_{26/27}I_{1/27}$, (c) $Li_2OHCl_{25/27}I_{2/27}$, (d) $Li_2OHCl_{0.921}I_{0.079}$, and (e) $Li_2OHCl_{8/9}I_{1/9}$.

Table S17. Average thickness and diameter of tested pellets.

	Average thickness / mm	Average diameter / mm
Li_2OHCl	1.153	14.067
$Li_2OHCl_{26/27}I_{1/27}$	1.087	14.143
$Li_2OHCl_{25/27}I_{2/27}$	1.177	14.117
$Li_2OHCl_{0.921}I_{0.079}$	1.107	14.180
$Li_2OHCl_{8/9}I_{1/9}$	1.093	14.233

Table S18. Ionic conductivity and activation energy (T > 313 K) of Li_2OHCl, $Li_2OHCl_{26/27}I_{1/27}$, $Li_2OHCl_{25/27}I_{2/27}$, $Li_2OHCl_{0.921}I_{0.079}$ and $Li_2OHCl_{8/9}I_{1/9}$ from 298 K to 383 K.

	Ionic conductivity (mS/cm)				
T (K)	Li_2OHCl	$Li_2OHCl_{26/27}I_{1/27}$	$Li_2OHCl_{25/27}I_{2/27}$	$Li_2OHCl_{0.921}I_{0.079}$	$Li_2OHCl_{8/9}I_{1/9}$
298	2.49×10^{-4}	2.39×10^{-3}	4.03×10^{-3}	5.28×10^{-3}	3.43×10^{-3}
303	4.28×10^{-4}	5.87×10^{-3}	7.26×10^{-3}	8.37×10^{-3}	5.72×10^{-3}
313	8.39×10^{-3}	1.37×10^{-2}	1.64×10^{-2}	1.91×10^{-2}	1.27×10^{-2}
323	1.93×10^{-2}	2.70×10^{-2}	3.31×10^{-2}	3.33×10^{-2}	2.46×10^{-2}
333	3.73×10^{-2}	4.85×10^{-2}	6.33×10^{-2}	6.57×10^{-2}	4.59×10^{-2}
343	6.90×10^{-2}	8.70×10^{-2}	1.17×10^{-1}	1.11×10^{-1}	7.92×10^{-2}
353	1.10×10^{-1}	1.43×10^{-1}	1.84×10^{-1}	2.01×10^{-1}	1.44×10^{-1}
363	1.79×10^{-1}	2.24×10^{-1}	3.30×10^{-1}	3.08×10^{-1}	2.28×10^{-1}
373	2.86×10^{-1}	3.82×10^{-1}	4.71×10^{-1}	5.04×10^{-1}	3.46×10^{-1}
383	5.11×10^{-1}	5.90×10^{-1}	8.09×10^{-1}	8.32×10^{-1}	5.56×10^{-1}
E_a (eV)	0.6050	0.5804	0.5974	0.5876	0.5862

Table S19. Bulk conductivity and activation energy (T > 313 K) of Li_2OHCl, $Li_2OHCl_{26/27}I_{1/27}$, $Li_2OHCl_{25/27}I_{2/27}$, $Li_2OHCl_{0.921}I_{0.079}$ and $Li_2OHCl_{8/9}I_{1/9}$ from 298 K to 383 K.

	Bulk conductivity (mS/cm)				
T (K)	Li_2OHCl	$Li_2OHCl_{26/27}I_{1/27}$	$Li_2OHCl_{25/27}I_{2/27}$	$Li_2OHCl_{0.921}I_{0.079}$	$Li_2OHCl_{8/9}I_{1/9}$
298	1.14×10^{-3}	8.90×10^{-3}	1.67×10^{-2}	1.74×10^{-2}	1.48×10^{-2}
303	1.65×10^{-3}	2.67×10^{-2}	3.19×10^{-2}	3.36×10^{-2}	2.73×10^{-2}
313	3.09×10^{-2}	5.82×10^{-2}	6.55×10^{-2}	6.60×10^{-2}	4.44×10^{-2}
323	6.25×10^{-2}	1.07×10^{-1}	1.04×10^{-1}	1.04×10^{-1}	8.32×10^{-2}
333	1.04×10^{-1}	2.00×10^{-1}	1.67×10^{-1}	1.72×10^{-1}	1.36×10^{-1}
343	2.07×10^{-1}	3.55×10^{-1}	3.23×10^{-1}	3.96×10^{-1}	2.57×10^{-1}
353	3.37×10^{-1}	5.15×10^{-1}	4.46×10^{-1}	7.06×10^{-1}	4.15×10^{-1}
363	5.20×10^{-1}	6.77×10^{-1}	9.81×10^{-1}	1.15×10^{0}	7.55×10^{-1}
373	7.85×10^{-1}	1.04×10^{0}	2.08×10^{0}	2.31×10^{0}	1.09×10^{0}
383	1.43×10^{0}	1.85×10^{0}	3.69×10^{0}	3.42×10^{0}	1.60×10^{0}
E_a^b (eV)	0.5829	0.5294	0.5477	0.5836	0.5569

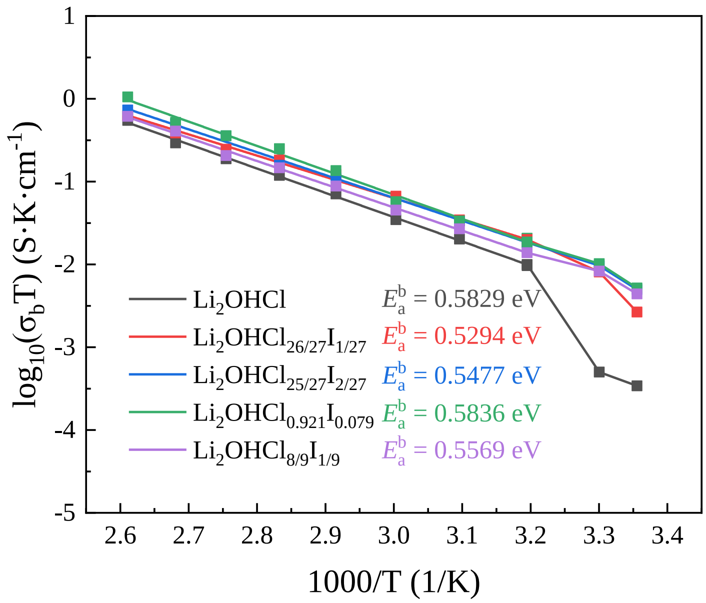

Figure S9. Arrhenius plot of bulk conductivity.

Table S20. Grain boundary conductivity and activation energy (T > 313 K) of Li_2OHCl, $Li_2OHCl_{26/27}I_{1/27}$, $Li_2OHCl_{25/27}I_{2/27}$, $Li_2OHCl_{0.921}I_{0.079}$ and $Li_2OHCl_{8/9}I_{1/9}$ from 298 K to 383 K.

	Grain boundary conductivity (mS/cm)				
T (K)	Li_2OHCl	$Li_2OHCl_{26/27}I_{1/27}$	$Li_2OHCl_{25/27}I_{2/27}$	$Li_2OHCl_{0.921}I_{0.079}$	$Li_2OHCl_{8/9}I_{1/9}$
298	3.50×10^{-4}	2.67×10^{-3}	4.75×10^{-3}	5.52×10^{-3}	3.81×10^{-3}
303	5.00×10^{-4}	6.46×10^{-3}	7.54×10^{-3}	8.78×10^{-3}	6.10×10^{-3}
313	8.64×10^{-3}	1.41×10^{-2}	1.71×10^{-2}	2.00×10^{-2}	1.41×10^{-2}
323	2.29×10^{-2}	2.88×10^{-2}	3.50×10^{-2}	3.58×10^{-2}	2.64×10^{-2}
333	4.51×10^{-2}	5.04×10^{-2}	6.82×10^{-2}	6.89×10^{-2}	4.76×10^{-2}
343	7.36×10^{-2}	9.00×10^{-2}	1.30×10^{-1}	1.21×10^{-1}	8.50×10^{-2}
353	1.15×10^{-1}	1.50×10^{-1}	1.94×10^{-1}	2.23×10^{-1}	1.74×10^{-1}
363	1.88×10^{-1}	2.44×10^{-1}	3.50×10^{-1}	3.25×10^{-1}	2.77×10^{-1}
373	3.10×10^{-1}	4.01×10^{-1}	5.01×10^{-1}	5.43×10^{-1}	3.68×10^{-1}
383	5.65×10^{-1}	6.11×10^{-1}	8.31×10^{-1}	8.66×10^{-1}	6.03×10^{-1}
E_a^{gb} (eV)	0.5927	0.6194	0.6185	0.6111	0.6155

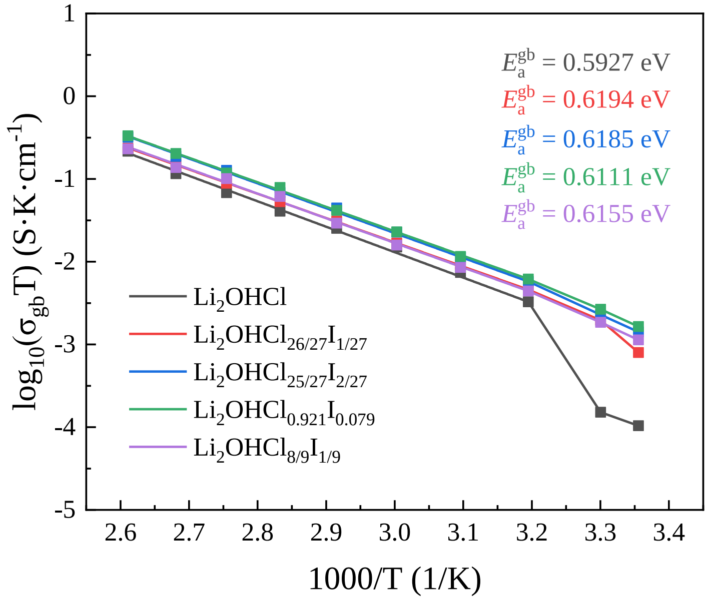

Figure S10. Arrhenius plot of grain boundary conductivity.

Table S21. The predicted highest ionic conductivity and the corresponding volumetric strain from 313 K to 383 K by GPR.

T (K)	Volumetric strain	Predicted ionic conductivity (mS/cm)
313	0.0533	0.0176
323	0.0563	0.0374
333	0.0584	0.0780
343	0.0584	0.1493
353	0.0590	0.2249
363	0.0592	0.4609
373	0.0570	0.5409
383	0.0591	1.0857

Table S22. The predicted highest ionic conductivity and the corresponding composition from 313 K to 383 K by GPR.

T (K)	Composition	Predicted ionic conductivity (mS/cm)
313	$Li_2OHCl_{0.928}I_{0.072}$	0.017
323	$Li_2OHCl_{0.926}I_{0.074}$	0.034
333	$Li_2OHCl_{0.920}I_{0.080}$	0.064
343	$Li_2OHCl_{0.919}I_{0.081}$	0.119
353	$Li_2OHCl_{0.919}I_{0.081}$	0.188
363	$Li_2OHCl_{0.916}I_{0.084}$	0.343
373	$Li_2OHCl_{0.925}I_{0.075}$	0.477
383	$Li_2OHCl_{0.917}I_{0.083}$	0.834

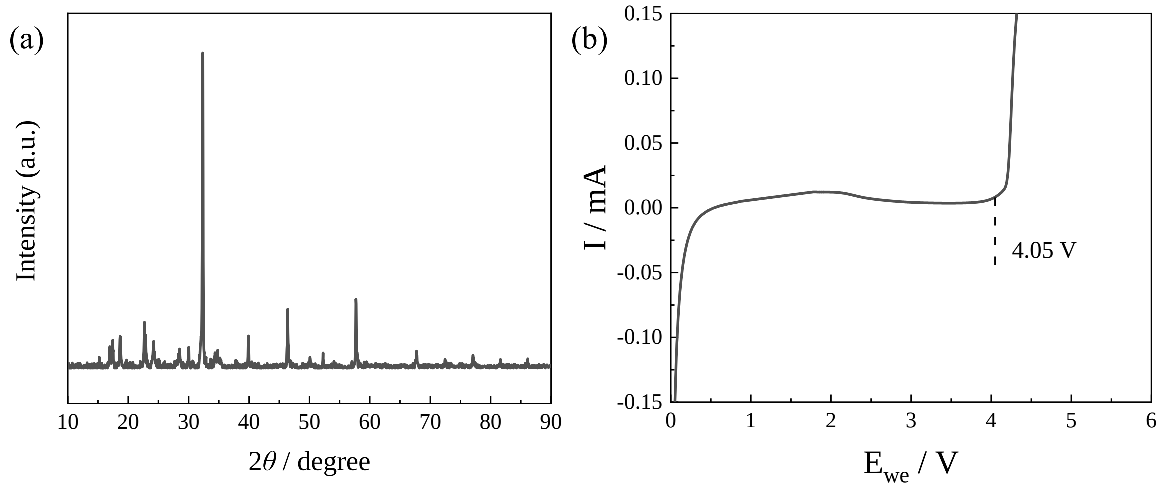

Figure S11 (a) XRD pattern, and (b) LSV curve of $Li_2OHCl_{0.921}I_{0.079}$.