Supporting Information

All-climate all-solid-state batteries enabled by high-entropy amorphous oxyhalide solid electrolytes

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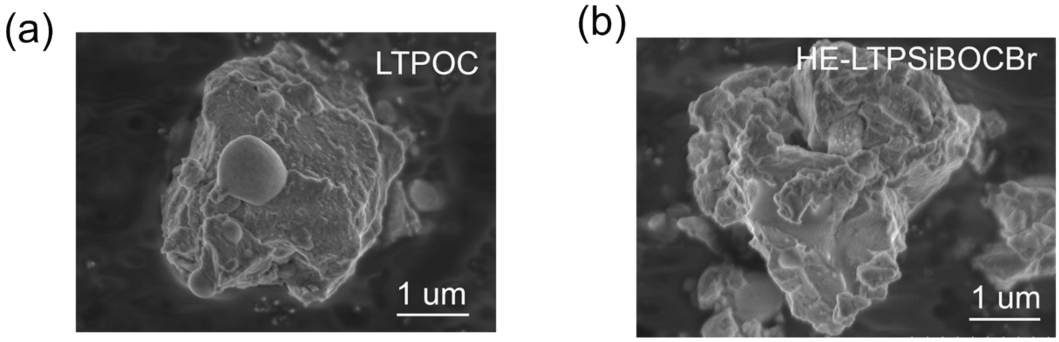

Fig. S1. (a) SEM image of $Li_{1.35}TaP_{0.45}O_{1.8}Cl_5$. (**b**) SEM image of $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$.

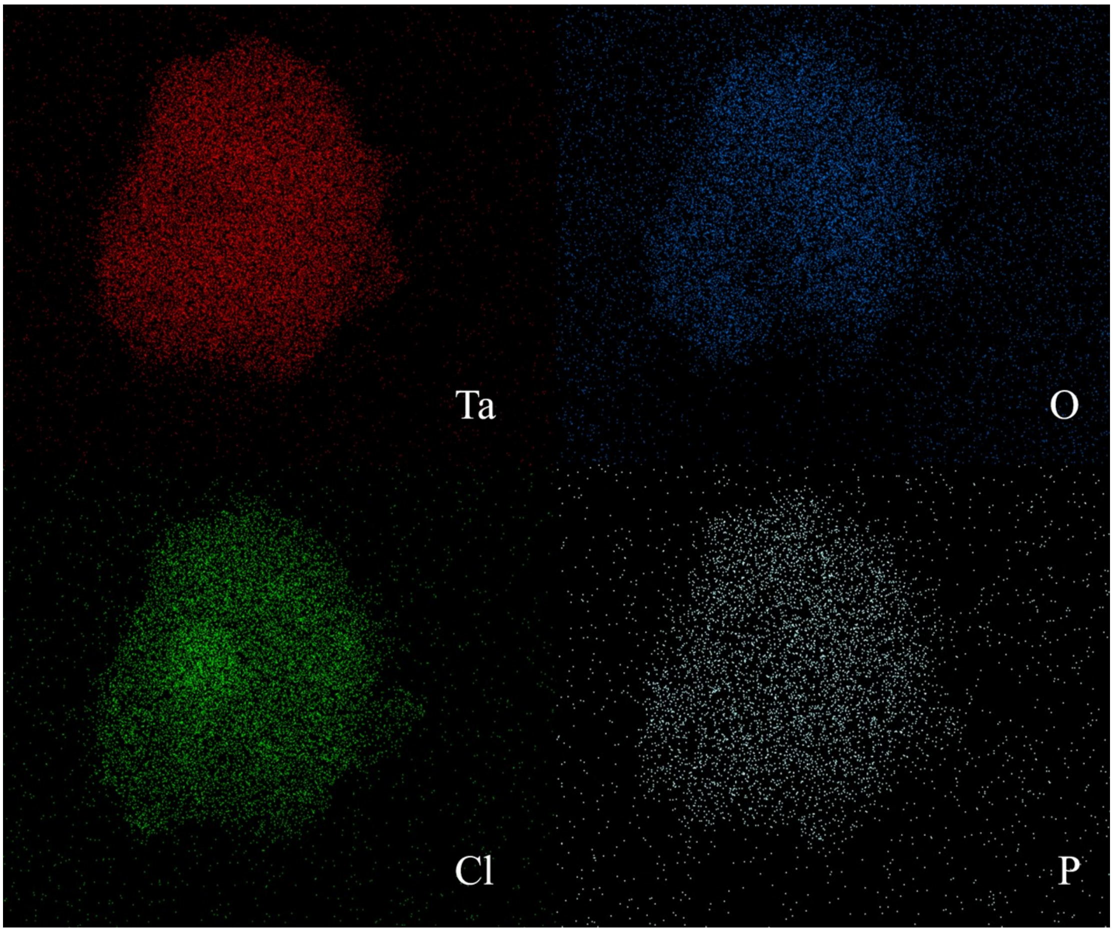

Fig. S2. EDS mapping for $Li_{1.35}TaP_{0.45}O_{1.8}Cl_5$.

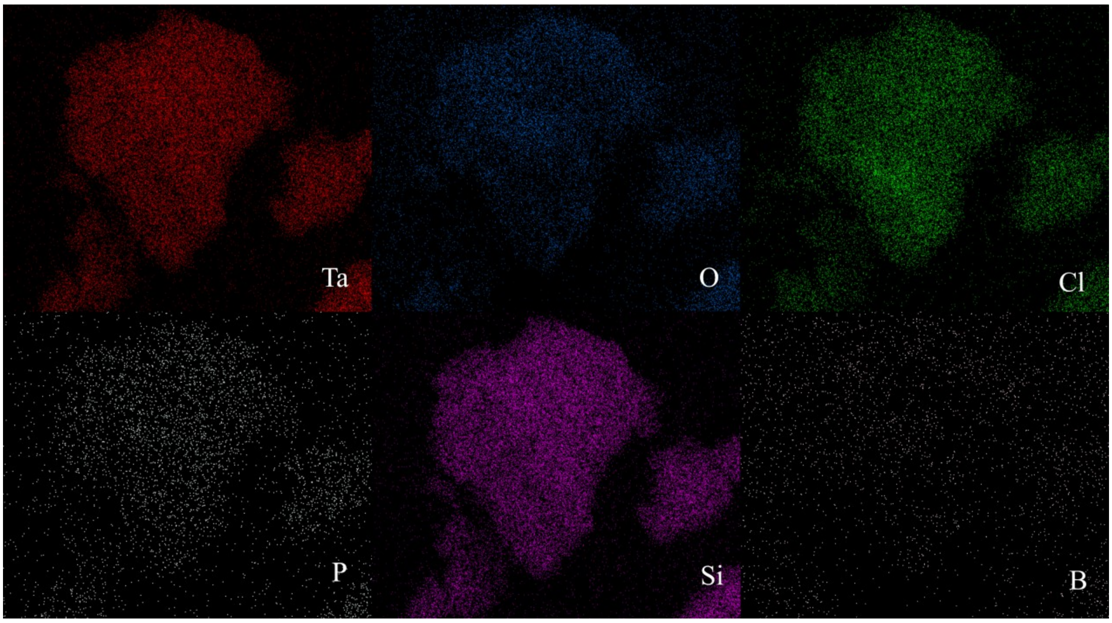

Fig. S3. EDS mapping for $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$.

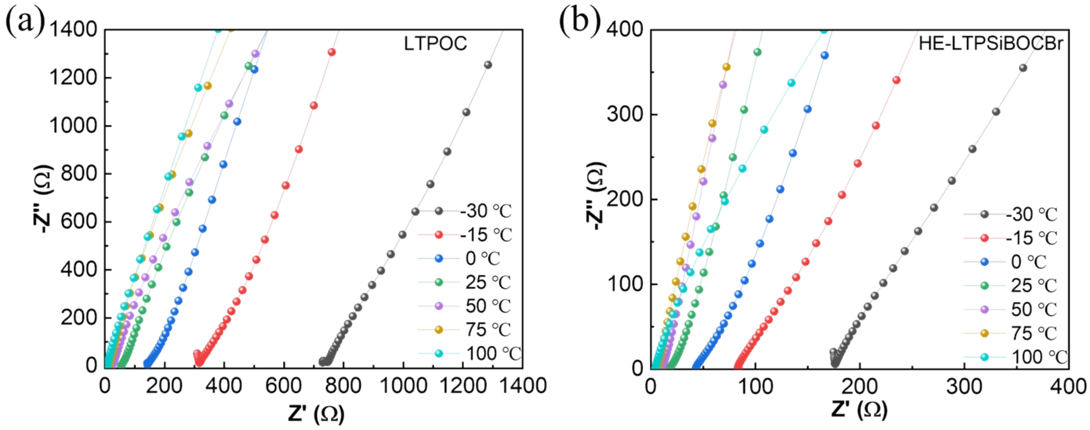

Fig. S4. Nyquist profiles of (a) $Li_{1.35}TaP_{0.45}O_{1.8}Cl_5$ and (b) $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$ in temperature range of −30 and 100 ^{o}C.

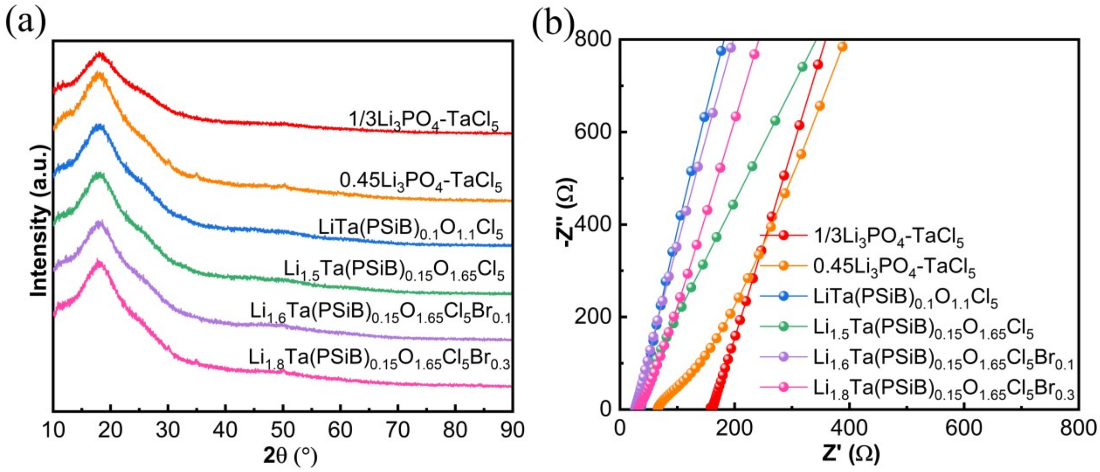

Fig. S5. (a) XRD patterns and (b) Nyquist profiles of 1/3Li_3PO_4-$TaCl_5$, 0.45 Li_3PO_4-$TaCl_5$, $LiTa(PSiB)_{0.1}O_{1.1}Cl_5$, $Li_{1.5}Ta(PSiB)_{0.15}O_{1.65}Cl_5$, $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$, and $Li_{1.8}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.3}$.

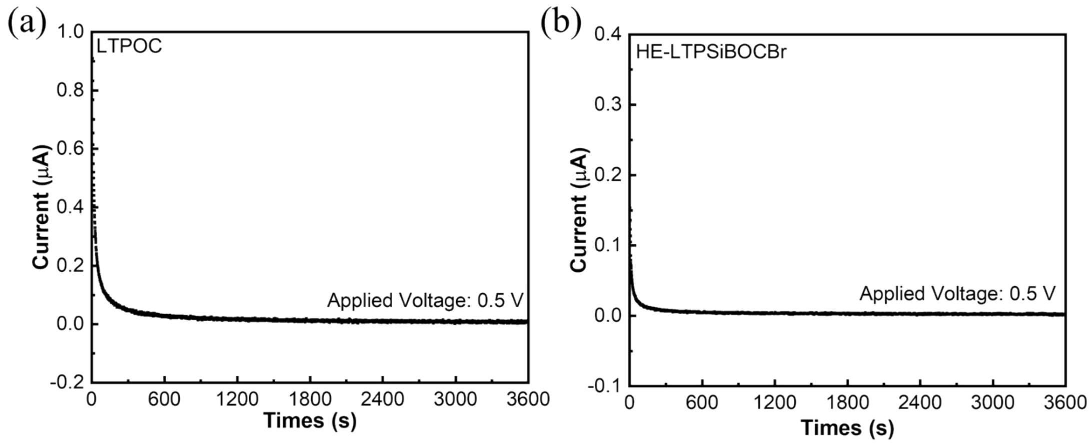

Fig. S6. Direct-current polarization current–time curves for (a) $Li_{1.35}TaP_{0.45}O_{1.8}Cl_5$ and (b) $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$.

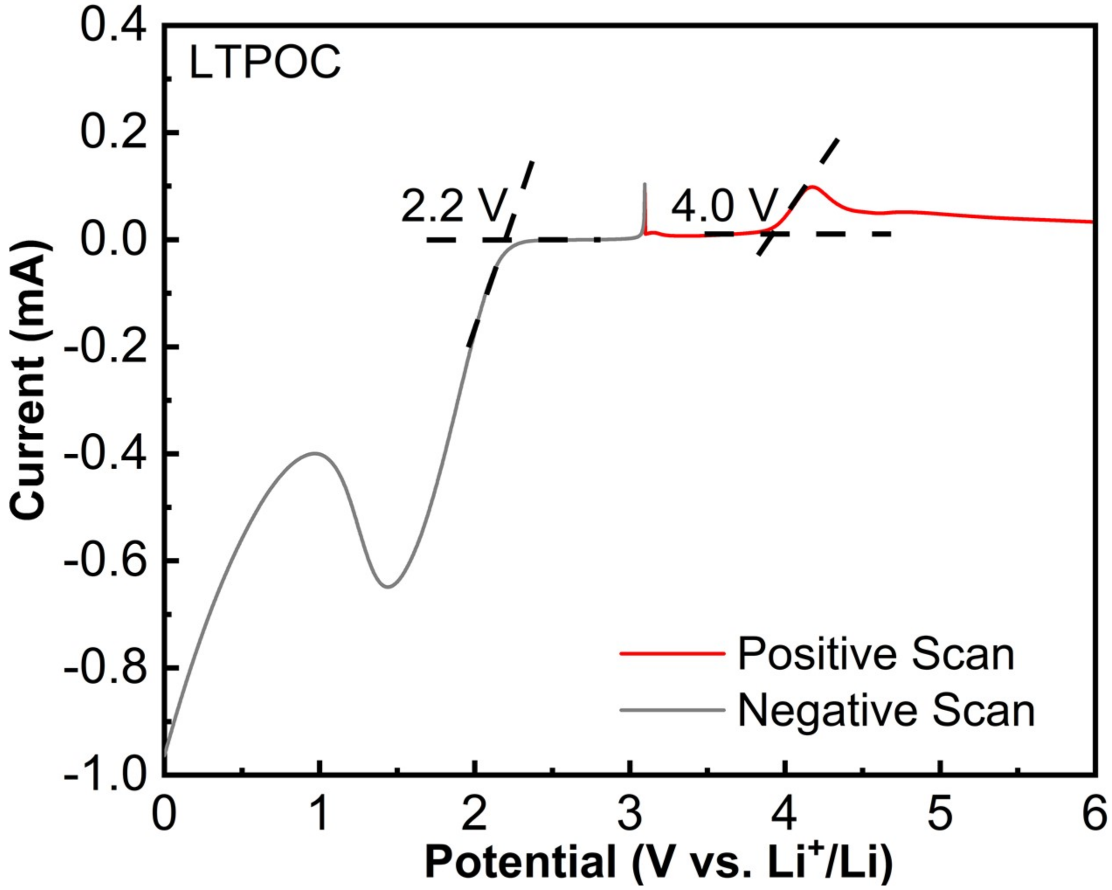

Fig. S7. Linear sweep voltammetry curves for $Li_{1.35}TaP_{0.45}O_{1.8}Cl_5$.

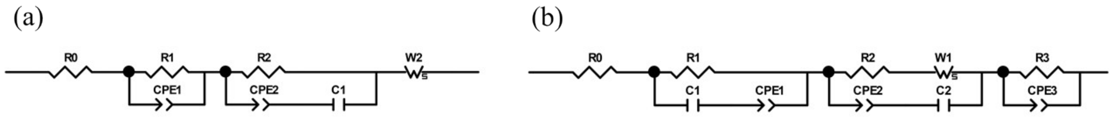

Fig. S8. Equivalent circuit of ASSBs using $Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$ at (a) room temperature and (b) −30 °C.

Table S1. Comparison of ionic conductivity and ASSB performance with the representative halide-based SEs

	Materials	**Conductivity (mS cm^{-1})**	**ASSB Performance: cathodes and cycling**	**Ref.**
Rare-earth halides	Li_3YCl_6	0.51	$LiCoO_2$, 98% retention after 100 cycles at 0.1 C.	[1]
	$Li_2Sc_{2/3}Cl_4$	1.5	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, 100 cycles at 0.1 C.	[2]
	$Li_{2.633}Er_{0.633}Zr_{0.367}Cl_6$	1.1	$LiCoO_2$, 200 cycles at 0.5 C.	[3]
	$Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$	3.02	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, 81.6% retention after 100 cycles at 0.44 C.	[4]
	$Li_3YCl_3Br_3$	7.2	$LiCoO_2$, 70 cycles at 0.1 C.	[5]
	$Li_{2.6}Yb_{0.4}Hf_{0.4}Cl_6$	1.5	$LiNi_{0.88}Co_{0.09}Al_{0.03}O_2$, 83.6% retention after 1,000 cycles at 0.5 C.	[6]
	$Li_{2.9}In_{0.75}Zr_{0.1}Sc_{0.05}Er_{0.05}Y_{0.05}Cl_6$	2.18	$LiNi_{0.5}Co_{0.3}Al_{0.2}O_2$, 81.7% retention after 1,000 cycles at 1 C.	[7]
Oxyhalides	nLi_2O-$TaCl_5$-10%TaF_5	2.3	$LiCoO_2$, 81% retention after	[8]

			300 cycles at 1 mA cm^{-2}.	
	$LiAlOCl_4$	1.04	$LiNi_{0.88}Co_{0.09}Mn_{0.03}O_2$, 84.86% retention after 1,500 cycles at 0.5 C.	[9]
	$LiNbOCl_4$	10.4	$LiCoO_2$, 97% retention after 100 cycles at 0.3 C.	[10]
	$1.6Li_2O\text{-}TaCl_5$	6.6	$LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$, 90.7% retention after 2,400 cycles at 2 C.	[11]
Extreme-condition on ASSBs using halide-based SEs	$1.25/3Li_3N\text{-}TaCl_5$	5.91	$LiCoO_2$, 83.5% retention after 100 cycles at 18 mA g^{-1} (-30 ^oC).	[12]
	$Li_{1.5}(LaCeZrHfTa)_{0.2}Cl_{5.3}$	1.8	$LiNi_{0.88}Co_{0.09}Mn_{0.03}O_2$, 390 cycles at 0.2 C (-30 ^oC).	[13]
	Li_2OHCl/Li_3InCl_6	1.29	$LiFePO_4$, 86.7% retention after 100 cycles at 0. 2 C (80 ^oC).	[14]
	Li_3InCl_6	2	$LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$, 65% retention after 50 cycles at 1 mA cm^{-2} (80 ^oC).	[15]
High-entropy	$Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5$	7.1	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, 82%	This

amorphous oxyhalide	$Br_{0.1}$		retention after 2,400 cycles at 2 C (25 ^{o}C), zero capacity fade over 100 cycles at −30 ^{o}C, and 80% retention following 1,300 cycles at 10 C (60 ^{o}C).	work

Table S2. Ionic conductivity as a function of composition.

Composition	**Conductivity ($mS\ cm^{-1}$)**
$1/3Li_3PO_4$-$TaCl_5$	0.79
$0.45Li_3PO_4$-$TaCl_5$	1.93
$LiTa(PSiB)_{0.1}O_{1.1}Cl_5$	3.49
$Li_{1.5}Ta(PSiB)_{0.15}O_{1.65}Cl_5$	4.55
$Li_{1.6}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.1}$	4.90
$Li_{1.8}Ta(PSiB)_{0.15}O_{1.65}Cl_5Br_{0.3}$	3.98

Table S3. Fitting results of ASSB resistances

ASSB	Type	Fitting result (Ω cm^2)
25 °C	Electrolyte resistance	36.7
	Charge transfer resistance	14
	Interfacial resistance	157
-30 °C	Electrolyte resistance	250.4
	Charge transfer resistance	53.3
	Interfacial resistance	572.3

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