

Data-mining Fluoride-Based Solid-State Electrolytes for Monovalent Metal Batteries

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Figures

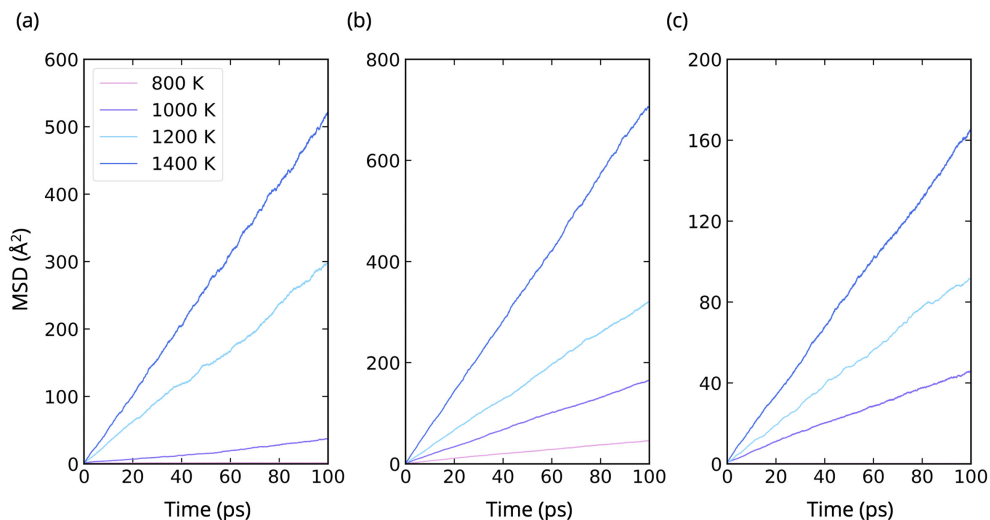


Figure S1: Mean square displacement (MSD) of Li-ion from machine-learned MD simulations over the last 100 ps for Na-based fluorides at various temperatures (800, 1,000, 1,200, and 1,400 K): (a) KLiBeF_4 , (b) Li_3ScF_6 and (c) $\text{NaLiHo}_2\text{F}_8$.

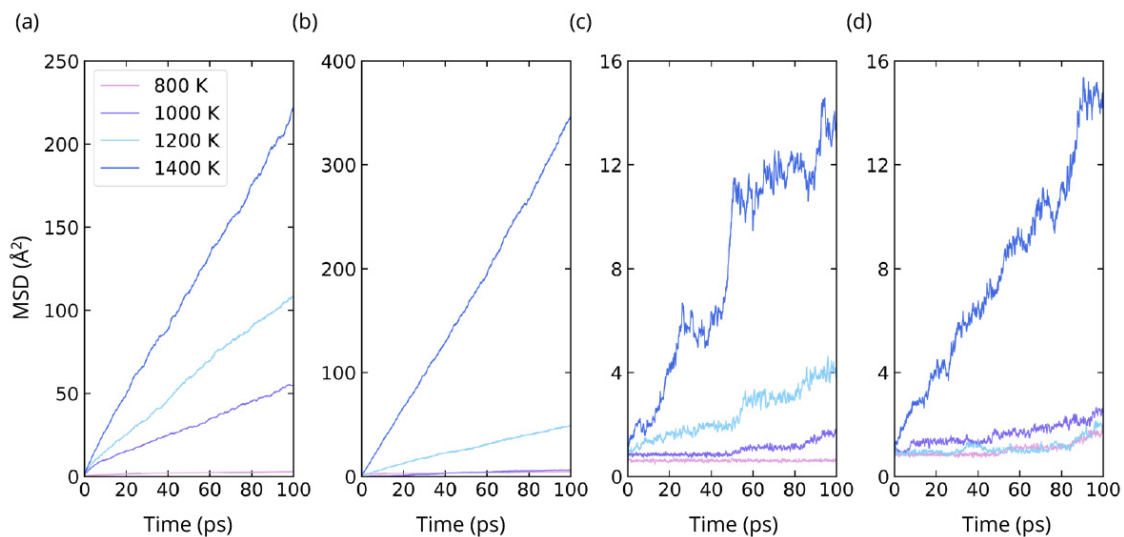


Figure S2: Mean square displacement (MSD) of Na-ion from machine-learned MD simulations over the last 100 ps for Na-based fluorides at various temperatures (800, 1,000, 1,200, and 1,400 K): (a) Na_2BeF_4 , (b) Na_3HfF_7 , (c) NaGdF_4 , and (d) NaPrF_4 .

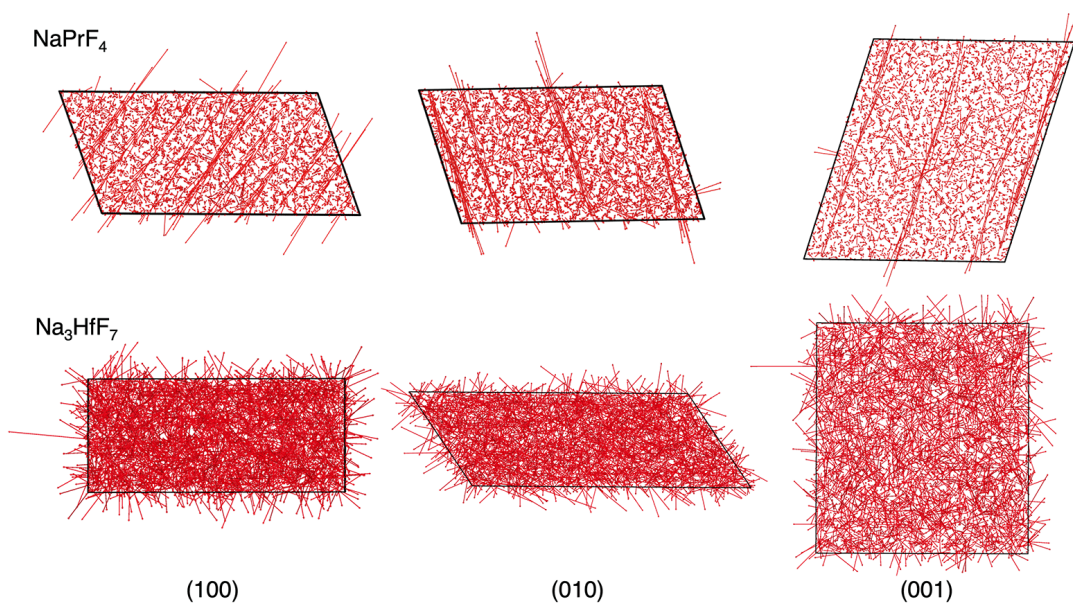


Figure S3: Na-ion diffusion topologies in the supercells of NaPrF₄ and Na₃HfF₆ obtained from the MD trajectory at 1,000 K. The displacement vectors of Na ions are projected with red solid lines within specific crystallographic planes.

Tables

Table S1: Physiochemical information of Li-based fluoride as the final SSE candidates for LMB obtained through the screening process and MD calculations: compositions, Materials Project-ID (MP-ID), electrochemical stability windows (reduction limit (V_{red}) and oxidation limit (V_{ox})), Pugh ratios (P) with their corresponding elastic bulk (K) and shear moduli (G), and activation barriers (E_a) for Li-ion diffusivity for selected candidates which show appreciable ionic diffusion at 1,000 K.

Material	MP-ID	$V_{\text{red}} - V_{\text{ox}}$ (V)	P	K (GPa)	G (G Pa)	E_a (eV)
KLiBeF ₄	mp-6253	0.9 – 6.1	1.76	32.45	57.02	1.58
Li ₃ ScF ₆	mp-560890	0.4 – 6.2	1.75	39.26	68.75	0.43
NaLiHo ₂ F ₈	mp-1210008	0.5 – 6.0	2.46	49.87	122.79	1.51
K ₂ LiScF ₆	mp-1111110	0.4 – 6.1	1.91	35.07	67.02	-
LiYF ₄	mp-556472	0.4 – 6.5	1.91	52.22	99.99	-
Rb ₂ LiYF ₆	mp-1114432	0.6 – 5.7	2.23	27.97	62.40	-
Rb ₂ LiScF ₆	mp-1114702	0.5 – 5.8	2.12	31.60	66.91	-
NaLiEr ₂ F ₈	mp-1209986	0.4 – 6.5	2.48	48.80	120.79	-
LiLuF ₄	mp-561430	0.3 – 6.8	2.41	57.34	137.98	-
NaLiLu ₂ F ₈	mp-1209991	0.5 – 7.3	2.47	51.63	127.70	-
NaLiTm ₂ F ₈	mp-1210006	0.4 – 8.0	2.46	51.14	125.95	-

Table S2: Physiochemical information of Na-based fluoride as the final SSE candidates for NMB obtained through the screening process and MD calculations: compositions, Materials Project-ID (MP-ID), electrochemical stability windows (reduction limit (V_{red}) and oxidation limit (V_{ox})), Pugh ratios (P) with their corresponding elastic bulk (K) and shear moduli (G), and activation barriers (E_a) for Na-ion diffusivity for selected candidates which show appreciable ionic diffusion at 1,000 K.

Material	MP-ID	$V_{\text{red}} - V_{\text{ox}}$ (V)	P	K (GPa)	G (GPa)	E_a (eV)
NaGdF ₄	mp-1221034	0.1 – 7.1	2.55	46.18	117.94	0.62
Na ₂ BeF ₄	mp-3318	0.4 – 6.2	1.81	36.12	65.39	0.77
Na ₃ HfF ₇	mp-34579	0.1 – 6.3	2.02	37.21	75.27	0.74
NaPrF ₄	mp-1220948	0.1 – 6.2	2.50	42.78	106.85	0.04
Na ₃ ScF ₆	mp-1113433	0.1 – 6.0	1.93	36.29	70.30	-
K ₂ NaAlF ₆	mp-6586	0.3 – 6.2	1.98	32.90	65.43	-
Na ₂ MgScF ₇	mp-1210466	0.3 – 6.0	1.98	38.48	76.44	-
K ₃ NaBe ₂ F ₈	mp-1211627	0.4 – 5.8	1.92	30.61	58.95	-
Na ₂ ThF ₆	mp-4829	0.2 – 6.0	2.33	38.77	90.64	-
NaYF ₄	mp-1220682	0.1 – 6.1	2.01	44.42	89.39	-
NaHoF ₄	mp-1220708	0.1 – 6.1	2.51	46.00	115.60	-
NaSmF ₄	mp-1220915	0.1 – 6.0	2.48	46.69	116.18	-
NaErF ₄	mp-1221036	0.1 – 6.1	2.51	47.69	119.72	-
NaMgF ₃	mp-2955	0.1 – 6.0	2.02	38.09	77.01	-
Rb ₂ NaAlF ₆	mp-1079583	0.3 – 5.8	2.20	29.38	64.77	-
Rb ₃ NaBe ₂ F ₈	mp-13630	0.3 – 5.5	2.15	26.62	57.37	-
Rb ₂ NaErF ₆	mp-13815	0.1 – 5.6	2.63	24.88	65.62	-
K ₂ NaScF ₆	mp-6058	0.1 – 5.8	2.01	29.31	59.09	-
Rb ₂ NaHoF ₆	mp-15318	0.1 – 5.8	2.63	24.64	65.04	-
NaPaO ₃	mp-865120	0.1 – 4.9	2.03	62.15	126.69	-
NaLiLu ₂ F ₈	mp-1209991	0.1 – 6.4	2.47	51.63	127.69	-
NaNd ₉ (Si ₃ O ₁₃) ₂	mp-1221031	0.2 – 4.0	2.08	80.52	167.82	-
NaLiTm ₂ F ₈	mp-1210006	0.1 – 8.0	2.46	51.14	125.94	-

Table S3: Calculated Li and Na-ion diffusivity (D) in (10^{-7} cm² S⁻¹) of selected candidates for LMB and NMB for each temperature (1,400 K, 1,200 K, 1,000 K, and 800 K).

System	Material	D_{1400}	D_{1200}	D_{1000}	D_{800}
LMB	KLiBeF ₄	835.6	505.8	222.3	1.4
LMB	Li ₃ ScF ₆	1192.8	535.4	272.0	73.9
LMB	NaLiHo ₂ F ₈	346.4	5.46	2.2	1.8
NMB	NaGdF ₄	9.2	5.8	1.2	0.1
NMB	Na ₂ BeF ₄	348.7	177.4	83.8	3.5
NMB	Na ₃ HfF ₇	575.1	76.0	6.1	5.3
NMB	NaPrF ₄	22.2	4.27	2.73	2.57

Table S4: Physiochemical information of Li-based archetype and prepared Li-based chlorides (abbreviated as “prepared”) SSE materials for LMB: compositions, Materials Project-ID (MP-ID), electrochemical stability windows (reduction limit (V_{red}) and oxidation limit (V_{ox})), Pugh ratios (P) with their corresponding elastic bulk (K) and shear moduli (G), and activation barriers (E_a). The values of E_a are taken from previous theoretical studies.

Type	Material	MP-ID	$V_{\text{red}} - V_{\text{ox}}$ (V)	P	K (GPa)	G (GPa)	E_a (eV)
<i>Archetype</i>	LLZO	mp-6253	0.1 – 3.1	1.57	80.91	127.36	0.61 [1]
<i>Archetype</i>	Li_3PO_4	mp-560890	0.7 – 4.1	1.22	72.78	88.80	0.60 [2]
<i>Prepared</i>	LiAlCl_4	mp-22983	1.6 – 4.4	2.49	12.70	31.66	0.47 [3]
<i>Prepared</i>	Li_3ErCl_6	mp-676361	0.8 – 4.2	2.46	19.22	47.19	0.47 [4]
<i>Prepared</i>	Li_3InCl_6	mp-676109	2.3 – 4.4	2.45	14.80	36.30	0.34 [5]

Table S5: Physiochemical information of Na-based archetype and prepared Na-based chlorides (abbreviated as “prepared”) SSE materials for LMB: compositions, Materials Project-ID (MP-ID), electrochemical stability windows (reduction limit (V_{red}) and oxidation limit (V_{ox})), Pugh ratios (P) with their corresponding elastic bulk (K) and shear moduli (G), and activation barriers (E_a). The values of E_a are taken from previous theoretical studies.

Type	Material	MP-ID	$V_{\text{red}} - V_{\text{ox}}$ (V)	P	K (GPa)	G (GPa)	E_a (eV)
<i>Archetype</i>	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$	mp-1221034	1.2 – 3.3	1.50	63.04	94.78	0.28 [6]
<i>Archetype</i>	Na_3PS_4	mp-3318	1.3 – 2.1	1.62	22.65	36.70	0.54 [7]
<i>Prepared</i>	NaAlCl_4	mp-23363	1.6 – 4.2	2.76	11.33	31.30	0.42 [8]
<i>Prepared</i>	Na_3ErCl_6	mp-28542	0.6 – 3.7	2.84	14.17	40.27	0.65 [9]
<i>Prepared</i>	Na_3InCl_6	mp-23503	2.2 – 4.0	2.82	10.98	30.96	0.70 [10]

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