

Electronic Supporting Materials

Fig. S1 Fully-relaxed structures for (a) Na_3SI , (b) $\text{Na}_3\text{SBF}_4_2$, and (c) $\text{Na}_9\text{S}_2\text{OI}_3$.

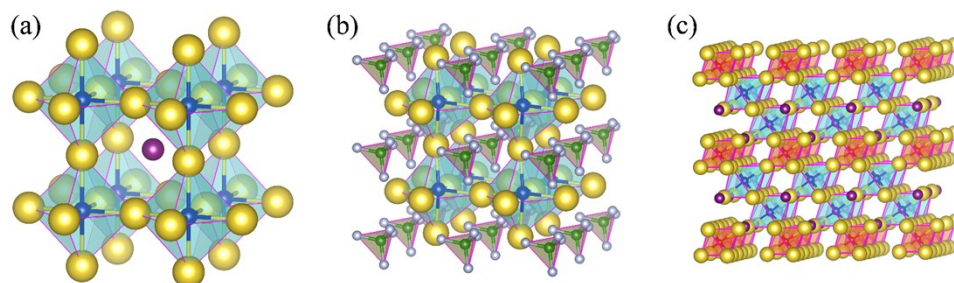


Fig. S2 Calculated phonon band structures for the dynamical unstable structures of (a) Na_3SI , (b) Na_3BF_4_2 , (c) $\text{Na}_9\text{S}_2\text{OI}_3$.

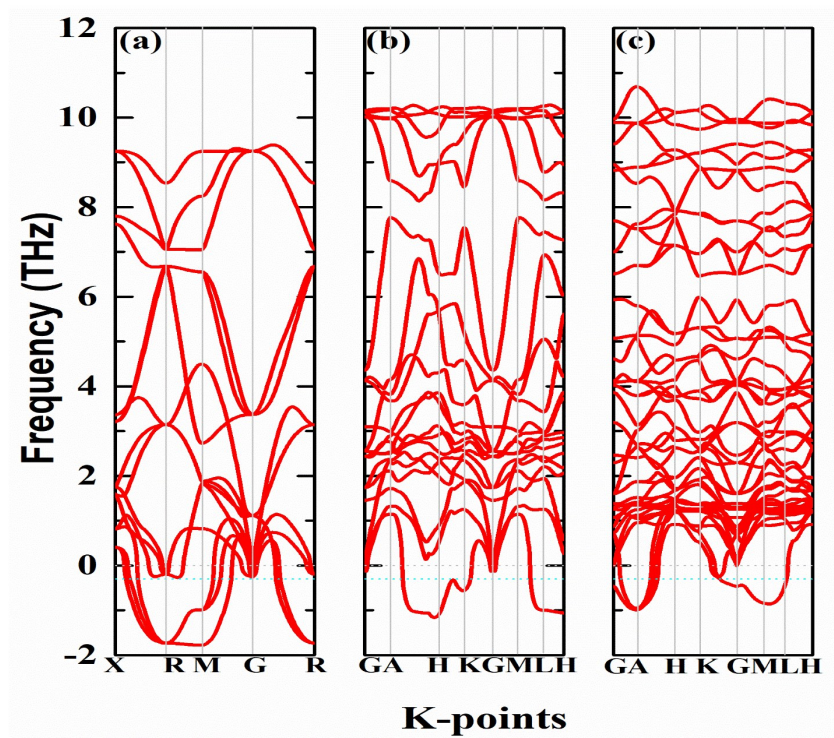


Fig. S3 Free energy of formation per unit cell (uc.) for the compounds of (a) Na_6SOICl , (b) $\text{Na}_9\text{S}_2\text{OI}_2\text{Cl}$, (c) $\text{Na}_9\text{S}_2\text{OI}_2\text{Cl}_2$, (d) Na_3SBF_4 .

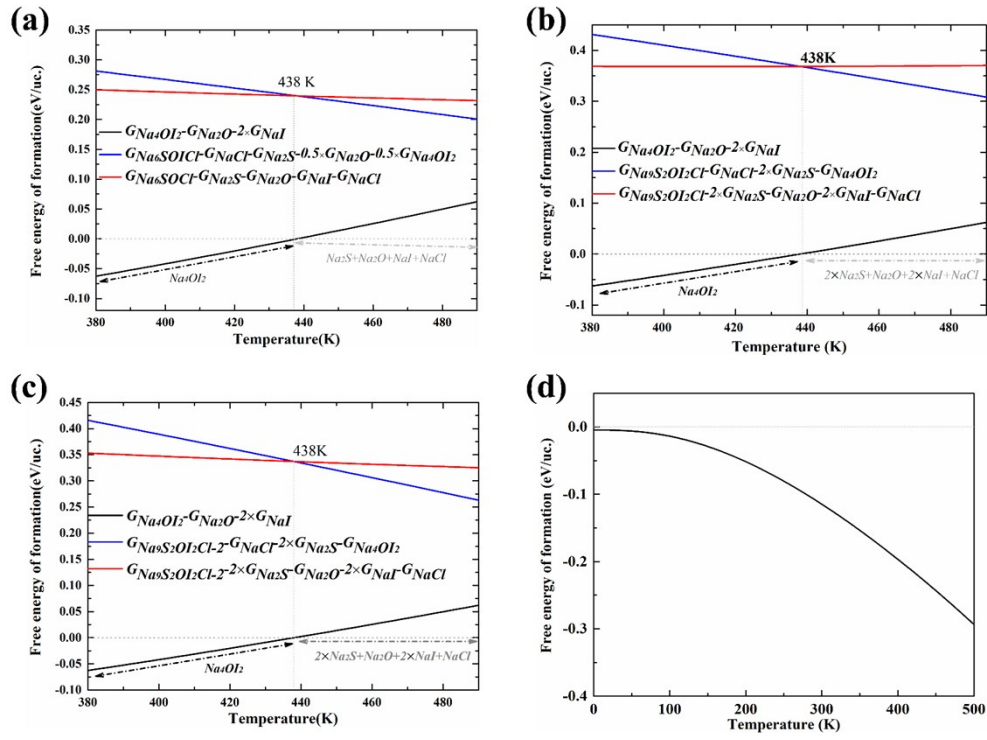


Fig. S4 Diffusion coefficients of Na_3SBF_4 for sodium ions from AIMD simulation. The D values at room temperature and $-50\text{ }^\circ\text{C}$ are presented by open patterns on the right side of the figure panel.

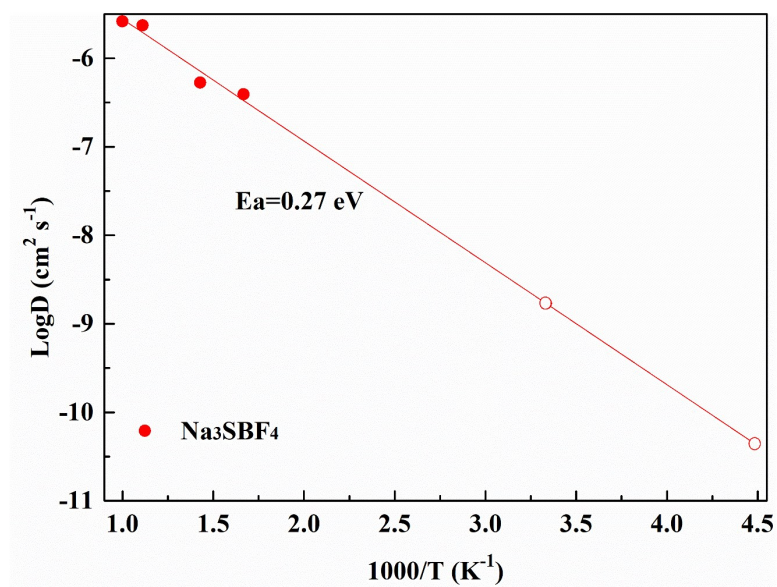


Fig. S5 Diffusion paths for a single sodium ion in (a) $\text{Na}_{25}\text{O}_9\text{Cl}_7$ and (d) $\text{Na}_{25}\text{S}_5\text{O}_4\text{I}_7$ in a time length of 90 ps.

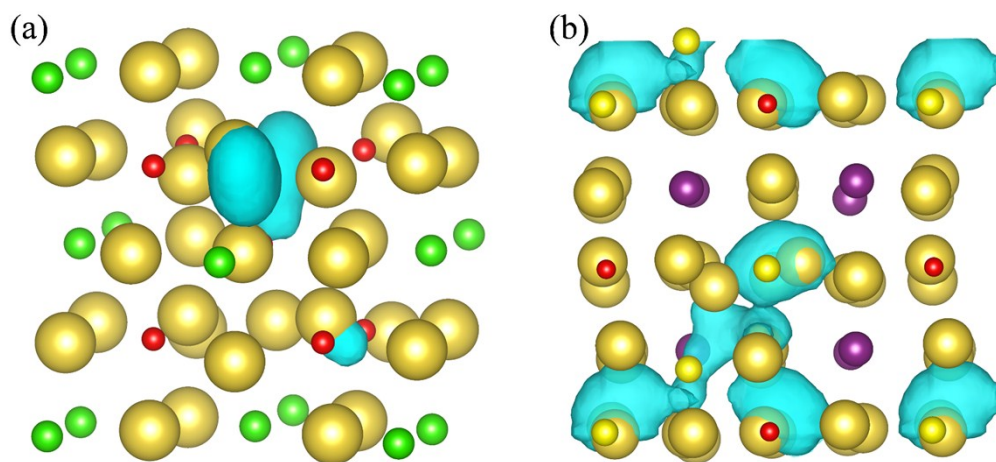


Table S1 Summary of data for the reduction and oxidation potential from the literatures, with associated phase equilibria compositions on the interface are listed (RP: reduction potential; PE at RP: phase equilibria at the reduction potential; OP: oxidation potential; PE at OP: phase equilibria at the oxidation potential; OPFD: oxidation potential of fully de-sodium).

System	RP (V)	PE at RP	OP (V)	PE at OP	OPFD (V)
Na ₃ SbS ₄	1.36	Na ₂ S+Sb	2.53	NaS+Na ₂ SbS ₂	2.57
Na ₁₀ GeP ₂ S ₁₂ ¹⁴	1.25	GeS+Na ₃ PS ₄ +Na ₂ S	1.70	Na ₃ PS ₄ + Na ₄ GeS ₄	2.16
Na ₁₀ SnP ₂ S ₁₂ ¹⁴	1.25	SnS+Na ₃ PS ₄ +Na ₂ S	1.82	Na ₃ PS ₄ + Na ₄ SnS ₄	2.16
Na ₁₁ Sn ₂ PS ₁₂ ¹⁴	1.25	SnS+Na ₃ PS ₄ +Na ₂ S	1.82	Na ₃ PS ₄ + Na ₄ SnS ₄	2.16
Na ₃ PSe ₄	1.39	Na ₂ Se+P	1.61	Na ₂ PSe ₃ +NaSe	2.05
Na ₃ PS ₄	1.49	Na ₂ S+P	1.55	Na ₂ S+P ₂ S ₅	1.76
Na ₆ SOI ₂	0	Stable v.s.Na	1.5	Na ₂ O+Na ₂ S+Na ₂ I	2.55

Attachment: The configuration file for (a) Na₆SOI₂ and (b) Na₂₅S₅O₄I₇ in the VASP format (POSCAR).

(a)

POSCAR for Na₆SOI₂

1.0

7.0461001396	0.0000000000	0.0000000000	
3.5230500698	6.1021017185	0.0000000000	
3.5230500698	2.0340339062	5.7531166729	
Na	S	O	I
6	1	1	2

Direct

0.268849999	0.731150031	0.268849999
0.731150031	0.268849999	0.731149971
0.268849999	0.268849999	0.731150031
0.731149971	0.731150031	0.268849999
0.731150031	0.268849999	0.268849999
0.268849999	0.731149971	0.731150031
0.000000000	0.000000000	0.000000000
0.500000000	0.500000000	0.500000000
0.250000000	0.250000000	0.250000000
0.750000000	0.750000000	0.750000000

(b)

POSCAR for Na₂₅S₅O₄I₇

1.0

9.9646997452000008	0.0000000000000000	0.0000000000000000	
0.0000000000000000	9.9646997452000008	0.0000000000000000	
0.0000000000000000	0.0000000000000000	9.9646997452000008	
Na	S	O	I
25	5	4	7

Direct

0.5149068721192082	0.2578501984415217	0.4915717393973192
0.4772058518271877	0.7242501365520739	0.4073232920821145
0.5239079513929182	0.4736797569159594	0.2615610211635180
0.4822234672418594	0.4588325796177342	0.7283750607543784
0.2702704836340799	0.4941254346858462	0.4907776573481102
0.7377239285178325	0.5251115667613164	0.5230541474966833
0.4743924297494441	0.7733036771072933	0.0107689737379964
0.5278397133335917	0.2329104063571569	0.0079117474419414
0.4739190068385395	0.0314116069567532	0.7734579709713501
0.5280284403223263	0.0102814245738468	0.2288914938631558
0.2671008607249699	0.0213456157600259	0.0193888959739317
0.7330457419413419	-0.0403267728298538	-0.0436111079714611
-0.0315916753266939	0.2789725580631424	-0.0095988717137195
-0.0007464681636038	0.7411607165364640	-0.0227516336737502

-0.0067018409030668	0.5228953362089347	0.7592842783227705
-0.0186016920829984	0.5098130004502649	0.2208789943910112
0.7651527569542230	0.5490191136215268	-0.0418381439839896
0.2245190613707332	0.4932997860583663	-0.0007765218980644
-0.0063056949281810	0.7623360939748177	0.5208029401332757
-0.0093918669492142	0.2248585966195970	0.5026535655430860
-0.0199696542281073	-0.0079593682741158	0.2731549951881700
0.0009727404752219	-0.0187784453068735	0.7365251240558151
0.7724366915702432	-0.0303399361613810	0.5370036504114847
0.2279573397812681	-0.0030077607931453	0.4916788332523798
0.5521269228077481	0.7432722628427854	0.6702497403154185
-0.0016999138374897	0.0140541359854675	0.0053696917483158
0.0035825829520318	0.4934928515895114	0.4890336370591358
0.5017200560074589	-0.0258887247077375	0.5074456728328589
0.4987850261268999	0.5044389386722720	-0.0081665956946372
0.8027584953112574	0.7528043950287812	0.7502474859504951
0.5042815314324905	0.5148738979307820	0.5020215767236091
0.5010670702074558	0.0019401497882493	-0.0021319649304367
-0.0057650926568253	0.5055311225636520	-0.0084109045820088
-0.0004927504282459	-0.0050196081236678	0.5025833048797118
0.7373713767828349	0.2487809748524353	0.7407146831931702
0.2322542370791147	0.7528526732316829	0.2339137711763648
0.2507805145807057	0.7503113124488763	0.7533823913193146
0.7462280006748299	0.2478769772179475	0.2590792689830533
0.2762567603846255	0.2487655801338410	0.2585157279218397
0.7445587504725735	0.7490127009483639	0.2399889095318683
0.2478919868894099	0.2490050686994840	0.7396755012844196