Supporting Information

Al-Substituted Na_5FeS_4 as Earth-Abundant Positive Electrode Active Materials for All-Solid-State Sodium Batteries

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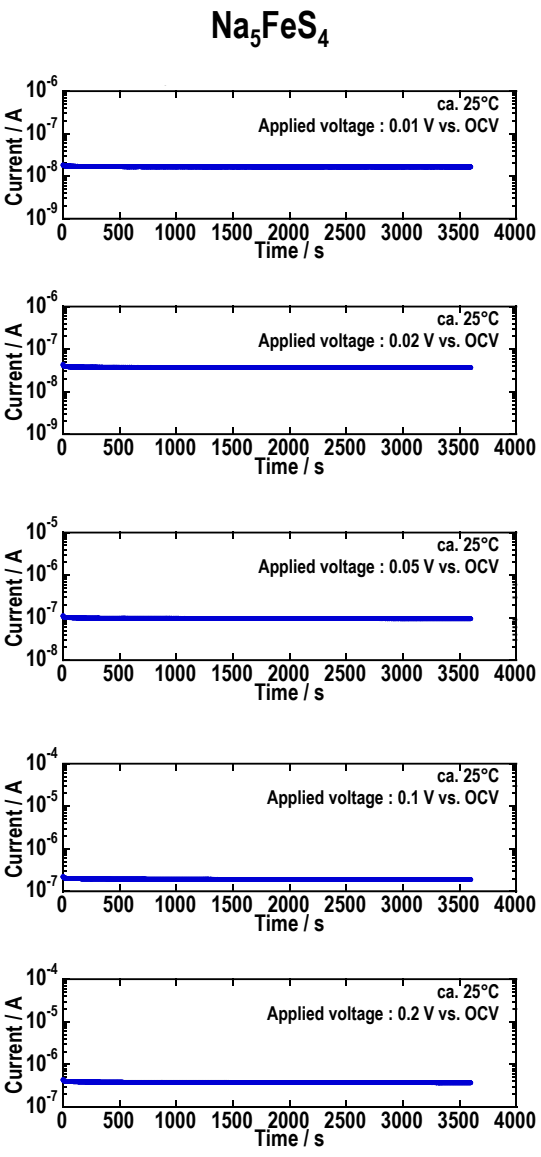

Figure S1 Representative current−time profiles obtained from the DC polarization measurement of the electron-blocking cell containing Na_5FeS_4. The applied voltages were held for 1 h at *ca.* 25 ºC.

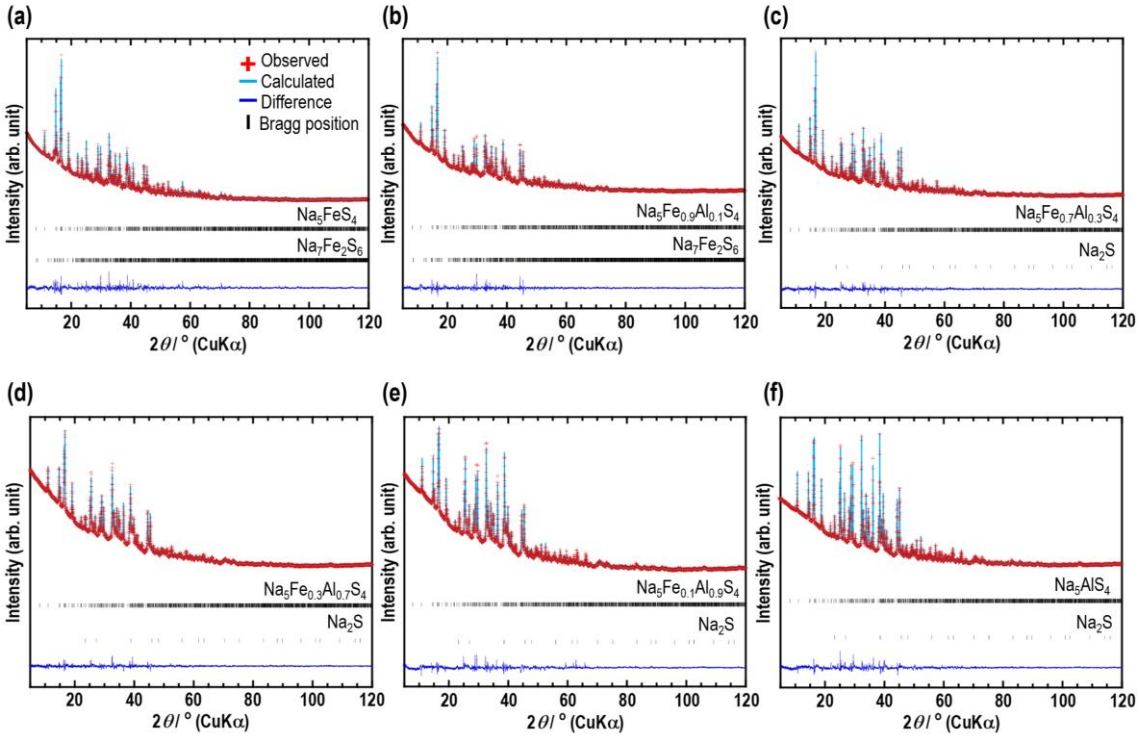

Figure S2 Refined XRD patterns of (a) Na_5FeS_4, (b) $Na_5Fe_{0.9}Al_{0.1}S_4$, (c) $Na_5Fe_{0.7}Al_{0.3}S_4$, (d) $Na_5Fe_{0.3}Al_{0.7}S_4$, (e) $Na_5Fe_{0.1}Al_{0.9}S_4$, and (f) Na_5AlS_4.

Table S1 Crystallographic data for the prepared Na_5FeS_4.

Primary phase	Na_5FeS_4					
Crystal System	Orthorhombic		**Lattice Parameter**			a = 11.9631(5) Å b = 7.0986(3) Å c = 21.5760(9) Å
Space Group	*Pbca* (No. 61)					
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.1611(7)	0.1141(14)	0.8289(4)	0.021(4)
Na2	8c	1.0	0.0629(10)	0.0646(14)	0.4272(4)	0.052(5)
Na3	8c	1.0	0.4206(10)	0.1305(19)	0.7442(6)	0.082(6)
Na4	8c	1.0	0.3678(8)	0.1073(15)	0.4903(5)	0.045(5)
Na5	8c	1.0	0.3009(6)	0.0413(13)	0.1339(6)	0.029(4)
S1	8c	1.0	0.3570(5)	0.2573(11)	0.3776(7)	0.041(2)
S2	8c	1.0	0.1334(6)	0.2537(10)	0.2128(5)	0.035(4)
S3	8c	1.0	0.1215(6)	0.2140(10)	0.5410(5)	0.027(3)
S4	8c	1.0	0.4459(5)	0.1590(8)	0.6223(4)	0.026(2)
Fe	8c	1.0	0.0398(3)	0.1655(5)	0.1279(3)	0.0298(16)

*R_{wp} = 3.02, S = 2.3449

Table S2 Crystallographic data for the prepared $Na_5Fe_{0.95}Al_{0.05}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**		a = 11.9672(4) Å	
Space Group	*Pbca* (No. 61)			b = 7.0981(2) Å c = 21.5763(7) Å	
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.1095(9)	0.1095(9)	0.8311(3)	0.015(2)
Na2	8c	1.0	0.0616(10)	0.0616(10)	0.4336(3)	0.057(3)
Na3	8c	1.0	0.1370(12)	0.1370(12)	0.7505(4)	0.046(3)
Na4	8c	1.0	0.0916(10)	0.0916(10)	0.4980(3)	0.050(3)
Na5	8c	1.0	0.0412(10)	0.0412(10)	0.1341(4)	0.049(3)
S1	8c	1.0	0.2495(7)	0.2495(7)	0.3752(4)	0.0318(16)
S2	8c	1.0	0.2596(7)	0.2596(7)	0.2155(3)	0.024(2)
S3	8c	1.0	0.2090(6)	0.2090(6)	0.5423(3)	0.027(2)
S4	8c	1.0	0.1518(6)	0.1518(6)	0.6185(3)	0.0286(18)
Fe	8c	0.95	0.1668(3)	0.1668(3)	0.12535(19)	0.0211(11)
Al	8c	0.05	0.1668(3)	0.1668(3)	0.12535(19)	0.0211(11)

*R_{wp} = 2.54, S = 1.9649

Table S3 Crystallographic data for the prepared $Na_5Fe_{0.9}Al_{0.1}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**		a = 11.9698(6) Å b = 7.0951(3) Å c = 21.5743(10) Å	
Space Group	*Pbca* (No. 61)				
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å²
Na1	8c	1.0	0.1602(5)	0.1042(10)	0.8334(3)	0.017(3)
Na2	8c	1.0	0.0686(7)	0.0570(12)	0.4328(3)	0.070(4)
Na3	8c	1.0	0.4046(6)	0.1225(12)	0.7491(4)	0.047(4)
Na4	8c	1.0	0.3678(6)	0.0937(9)	0.4972(4)	0.023(3)
Na5	8c	1.0	0.2946(5)	0.0388(11)	0.1325(5)	0.042(3)
S1	8c	1.0	0.3564(3)	0.2494(7)	0.3757(5)	0.0090(12)
S2	8c	1.0	0.1281(5)	0.2577(7)	0.2162(3)	0.022(3)
S3	8c	1.0	0.1267(5)	0.2040(7)	0.5436(4)	0.036(3)
S4	8c	1.0	0.4420(4)	0.1605(6)	0.6233(4)	0.0352(19)
Fe	8c	0.9	0.0416(2)	0.1652(4)	0.1239(3)	0.0244(12)
Al	8c	0.1	0.0416(2)	0.1652(4)	0.1239(3)	0.0244(12)

*R_{wp} = 2.57, S = 1.9590

Table S4 Crystallographic data for the prepared $Na_5Fe_{0.7}Al_{0.3}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**		a = 11.9784(3) Å	
Space Group	*Pbca* (No. 61)			b = 7.08674(17) Å	
				c = 21.5680(5) Å	
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å²
Na1	8c	1.0	0.1617(4)	0.1099(7)	0.8288(2)	0.029(2)
Na2	8c	1.0	0.0626(5)	0.0587(7)	0.4322(2)	0.052(2)
Na3	8c	1.0	0.4093(4)	0.1281(8)	0.7498(3)	0.044(3)
Na4	8c	1.0	0.3566(4)	0.0959(7)	0.4965(3)	0.043(2)
Na5	8c	1.0	0.2911(3)	0.0461(7)	0.1340(3)	0.024(2)
S1	8c	1.0	0.3579(2)	0.2527(5)	0.3752(4)	0.0266(10)
S2	8c	1.0	0.1295(3)	0.2589(5)	0.2128(3)	0.0257(16)
S3	8c	1.0	0.1281(3)	0.2084(5)	0.5418(3)	0.0265(16)
S4	8c	1.0	0.4438(2)	0.1528(4)	0.6211(3)	0.0265(11)
Fe	8c	0.7	0.04045(17)	0.1669(3)	0.12535(19)	0.0157(8)
Al	8c	0.3	0.04045(17)	0.1669(3)	0.12535(19)	0.0157(8)

*R_p = 1.53, R_{wp} = 2.37, S = 1.8246

Table S5 Crystallographic data for the prepared $Na_5Fe_{0.5}Al_{0.5}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**			a = 11.9906(3) Å b = 7.07732(18) Å c = 21.5645(5) Å
Space Group	*Pbca* (No. 61)				
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.1630(4)	0.1046(8)	0.8296(2)	0.025(2)
Na2	8c	1.0	0.0603(5)	0.0595(8)	0.4327(2)	0.052(2)
Na3	8c	1.0	0.4091(4)	0.1291(9)	0.7489(3)	0.039(3)
Na4	8c	1.0	0.3566(5)	0.0967(8)	0.4989(3)	0.041(2)
Na5	8c	1.0	0.2894(4)	0.0481(8)	0.1328(3)	0.039(2)
S1	8c	1.0	0.3565(3)	0.2552(5)	0.3756(4)	0.0231(11)
S2	8c	1.0	0.1277(4)	0.2610(5)	0.2128(3)	0.028(2)
S3	8c	1.0	0.1302(3)	0.2076(5)	0.5421(3)	0.0255(19)
S4	8c	1.0	0.4464(3)	0.1514(4)	0.6214(3)	0.0248(13)
Fe	8c	0.5	0.04001(19)	0.1692(3)	0.1249(2)	0.0182(10)
Al	8c	0.5	0.04001(19)	0.1692(3)	0.1249(2)	= B(Fe)

*R_{wp} = 2.53, S = 1.9506

Table S6 Crystallographic data for the prepared $Na_5Fe_{0.3}Al_{0.7}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**		a = 12.0066(6) Å b = 7.0691(4) Å c = 21.5693(12) Å	
Space Group	*Pbca* (No. 61)				
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.1593(5)	0.1009(12)	0.8329(3)	0.061(3)
Na2	8c	1.0	0.0606(6)	0.0644(10)	0.4291(3)	0.066(3)
Na3	8c	1.0	0.4116(5)	0.1272(9)	0.7477(3)	0.028(2)
Na4	8c	1.0	0.3539(5)	0.0813(9)	0.4996(3)	0.049(3)
Na5	8c	1.0	0.2905(4)	0.0505(9)	0.1314(4)	0.040(2)
S1	8c	1.0	0.3572(3)	0.2553(6)	0.3754(4)	0.0176(12)
S2	8c	1.0	0.1268(4)	0.2621(6)	0.2136(3)	0.027(2)
S3	8c	1.0	0.1290(4)	0.2009(6)	0.5443(3)	0.032(2)
S4	8c	1.0	0.4473(3)	0.1501(4)	0.6224(3)	0.0157(11)
Fe	8c	0.3	0.0407(2)	0.1691(4)	0.1259(3)	0.0310(13)
Al	8c	0.7	0.0407(2)	0.1691(4)	0.1259(3)	= B(Fe)

*R_{wp} = 2.07, S = 1.5946

Table S7 Crystallographic data for the prepared $Na_5Fe_{0.1}Al_{0.9}S_4$.

Crystal System	Orthorhombic	**Lattice Parameter**			a = 12.0165(6) Å b = 7.0582(4) Å c = 21.5598(11) Å
Space Group	*Pbca* (No. 61)				
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.1596(5)	0.1095(9)	0.8319(3)	0.042(3)
Na2	8c	1.0	0.0642(6)	0.0712(10)	0.4336(3)	0.062(4)
Na3	8c	1.0	0.4111(5)	0.1296(10)	0.7499(3)	0.030(2)
Na4	8c	1.0	0.3582(5)	0.0859(10)	0.4986(3)	0.052(3)
Na5	8c	1.0	0.2967(4)	0.0507(9)	0.1359(3)	0.048(3)
S1	8c	1.0	0.3600(3)	0.2597(6)	0.3769(4)	0.0238(13)
S2	8c	1.0	0.1265(4)	0.2610(6)	0.2133(3)	0.031(2)
S3	8c	1.0	0.1287(4)	0.1992(6)	0.5441(3)	0.0294(18)
S4	8c	1.0	0.4465(3)	0.1457(5)	0.6239(3)	0.0230(12)
Fe	8c	1.0	0.0431(3)	0.1686(5)	0.1229(3)	0.0289(15)
Al	8c	1.0	0.0431(3)	0.1686(5)	0.1229(3)	= B(Fe)

*R_{wp} = 2.72, S = 2.1125

Table S8 Crystallographic data for the prepared Na_5AlS_4.

Crystal System	Orthorhombic	**Lattice Parameter**		a = 12.0214(3) Å b = 7.05641(16) Å c = 21.5697(5) Å	
Space Group	*Pbca* (No. 61)				
Atom	**Wyckoff**	**Occ.**	***x***	***y***	***z***	U_{iso} / Å^2
Na1	8c	1.0	0.3555(4)	0.9126(6)	0.4998(2)	0.0552(18)
Na2	8c	1.0	0.2894(3)	0.5561(6)	0.3648(2)	0.0394(16)
Na3	8c	1.0	0.5624(4)	0.5650(6)	0.4343(17)	0.0440(17)
Na4	8c	1.0	0.5878(4)	0.3711(7)	0.2493(2)	0.0477(19)
Na5	8c	1.0	0.8411(3)	0.1047(6)	0.8317(16)	0.0305(17)
S1	8c	1.0	0.3706(2)	0.2043(4)	0.9566(17)	0.0214(11)
S2	8c	1.0	0.4476(19)	0.8510(3)	0.3792(17)	0.0211(8)
S3	8c	1.0	0.1411(2)	0.2437(4)	0.6241(2)	0.0235(9)
S4	8c	1.0	0.6274(3)	0.7624(4)	0.2124(17)	0.0247(12)
Al	8c	1.0	0.0426(2)	0.8279(4)	0.8769(2)	0.0258(11)

*R_{wp} = 2.57, S = 2.0297

Table S9 Mass fractions of the primary and secondary phases determined by multiphase Rietveld refinement of the synthesized $Na_5Fe_{1-x}Al_xS_4$ samples.

	Mass fraction / wt%		
	Main phase	Secondary phase	
	$Na_5Fe_{1-x}Al_xS_4$	$Na_7Fe_2S_6$	Na_2S
Na_5FeS_4	81.40	18.60	
$Na_5Fe_{0.95}Al_{0.05}S_4$	80.80	19.20	
$Na_5Fe_{0.9}Al_{0.1}S_4$	79.80	20.20	
$Na_5Fe_{0.7}Al_{0.3}S_4$	98.35		1.65
$Na_5Fe_{0.5}Al_{0.5}S_4$	98.00		2.00
$Na_5Fe_{0.3}Al_{0.7}S_4$	95.63	4.37	
$Na_5Fe_{0.1}Al_{0.9}S_4$	96.27	3.73	
Na_5AlS_4	97.17		2.83

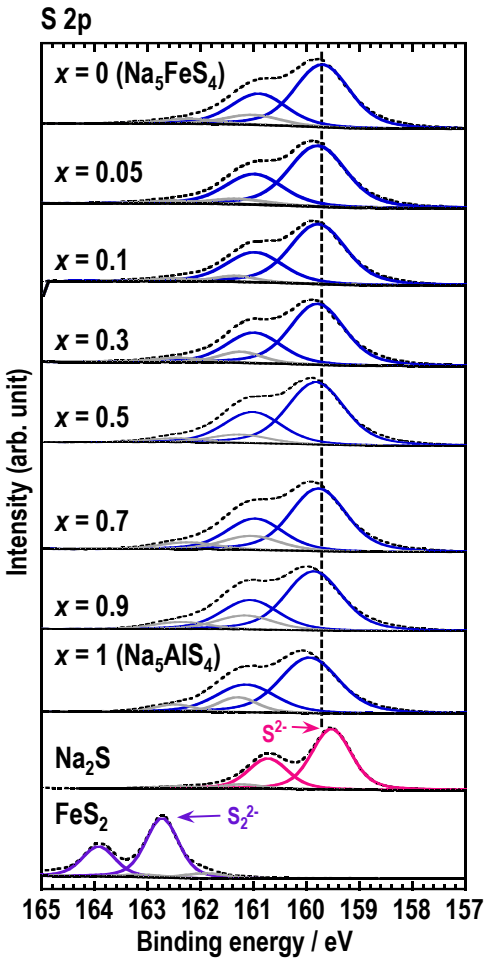

Figure S3 XPS S 2p spectra of $Na_5Fe_{1-x}Al_xS_4$.

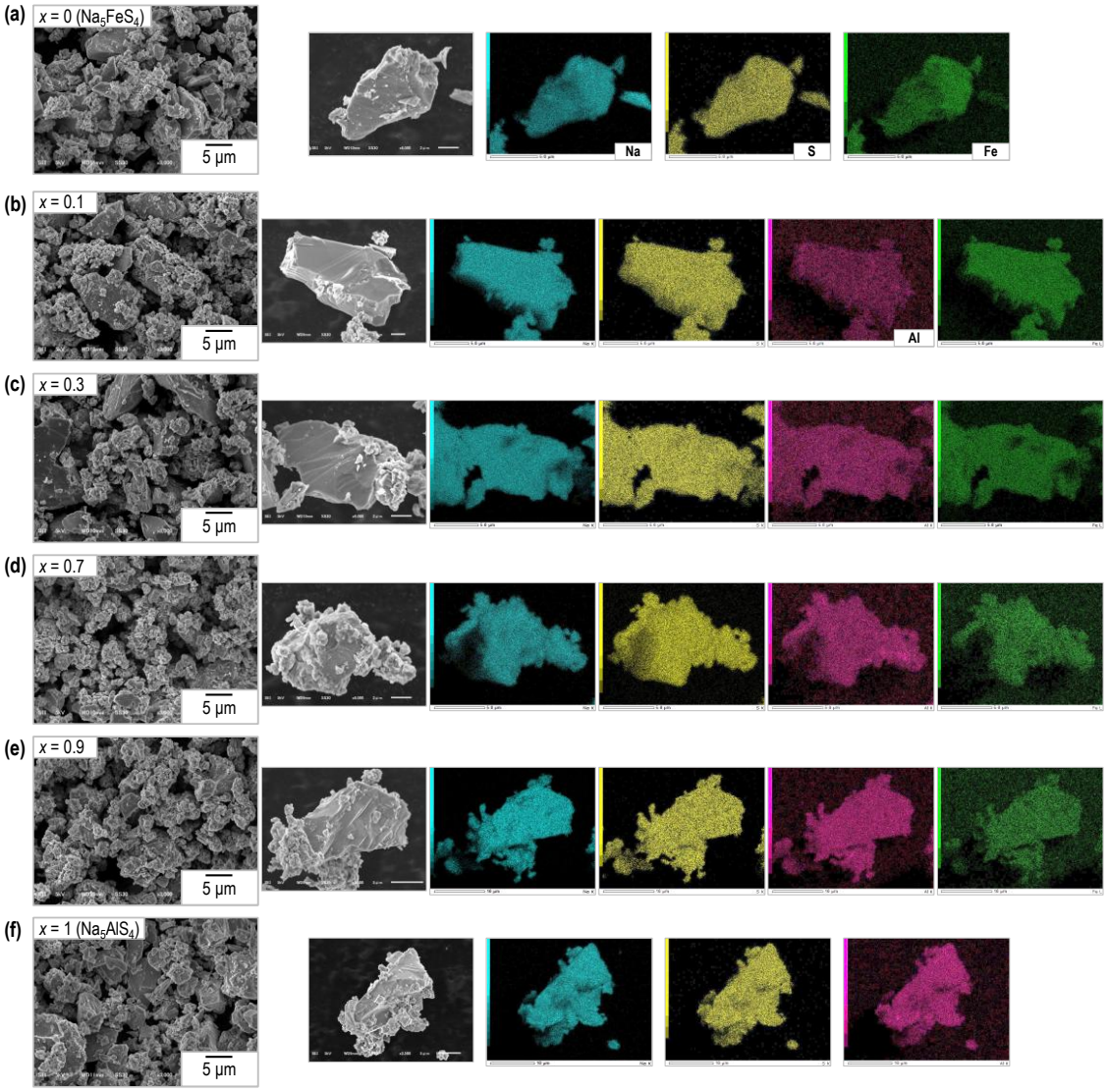

Figure S4 SEM images and EDX elemental mappings for Na, S, Al, and Fe of $Na_5Fe_{1-x}Al_xS_4$ for x = (a) 0, (b) 0.1, (c) 0.3, (d) 0.7, (e) 0.9, and (f) 1.

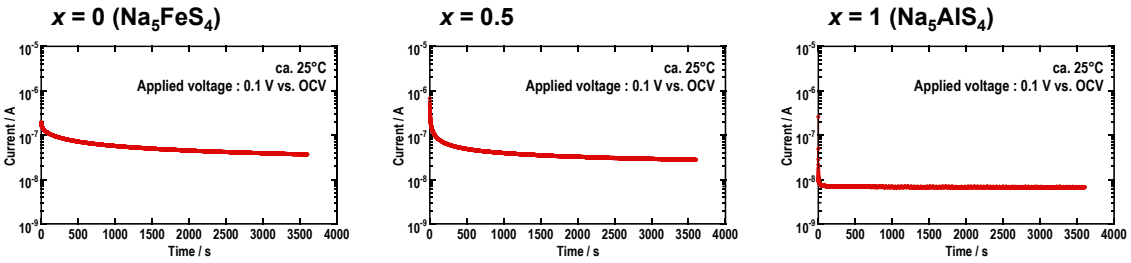

Figure S5 Representative current−time profiles obtained from the DC polarization measurement of the ion-blocking cells using Na_5FeS_4 (x=0), $Na_5Fe_{0.5}Al_{0.5}S_4$ (x=0.5), and Na_5AlS_4 (x=1).

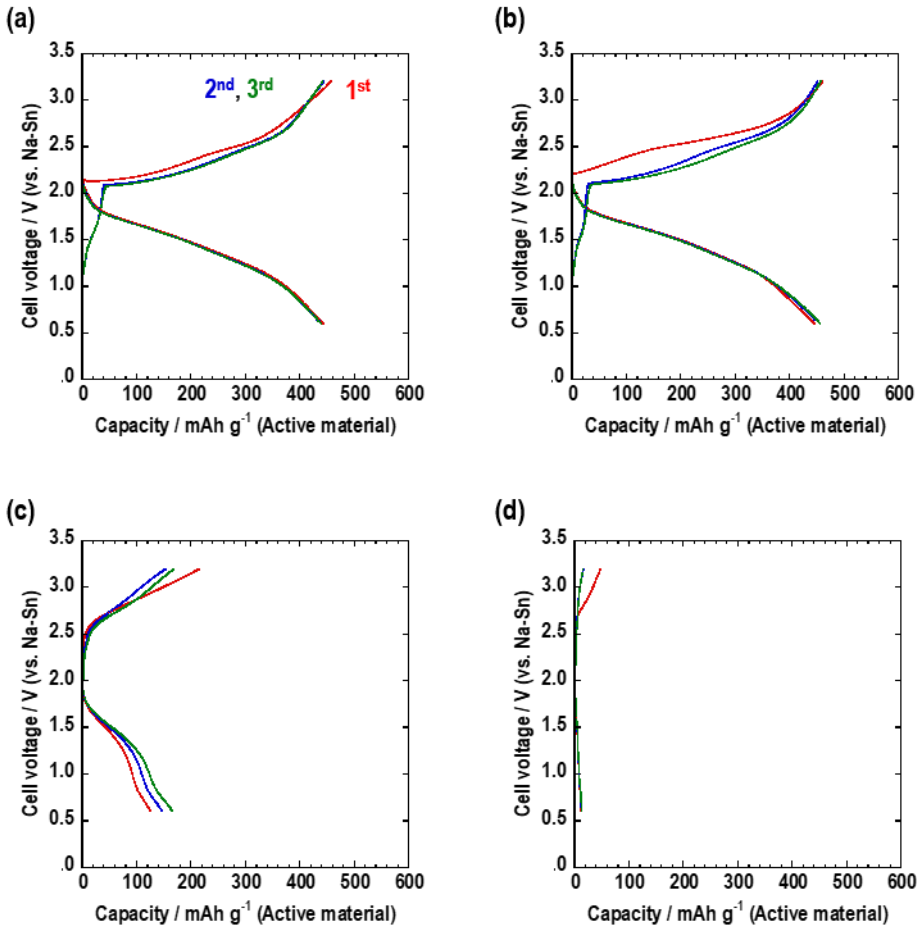

Figure S6 Charge–discharge curves for 3 cycles of all-solid-state cells with Na–Sn / Na_3PS_4 / Na_3PS_4-AB-(a) $Na_5Fe_{0.9}Al_{0.1}S_4$, (b) $Na_5Fe_{0.7}Al_{0.3}S_4$, (c) $Na_5Fe_{0.3}Al_{0.7}S_4$, and (d) $Na_5Fe_{0.1}Al_{0.9}S_4$.

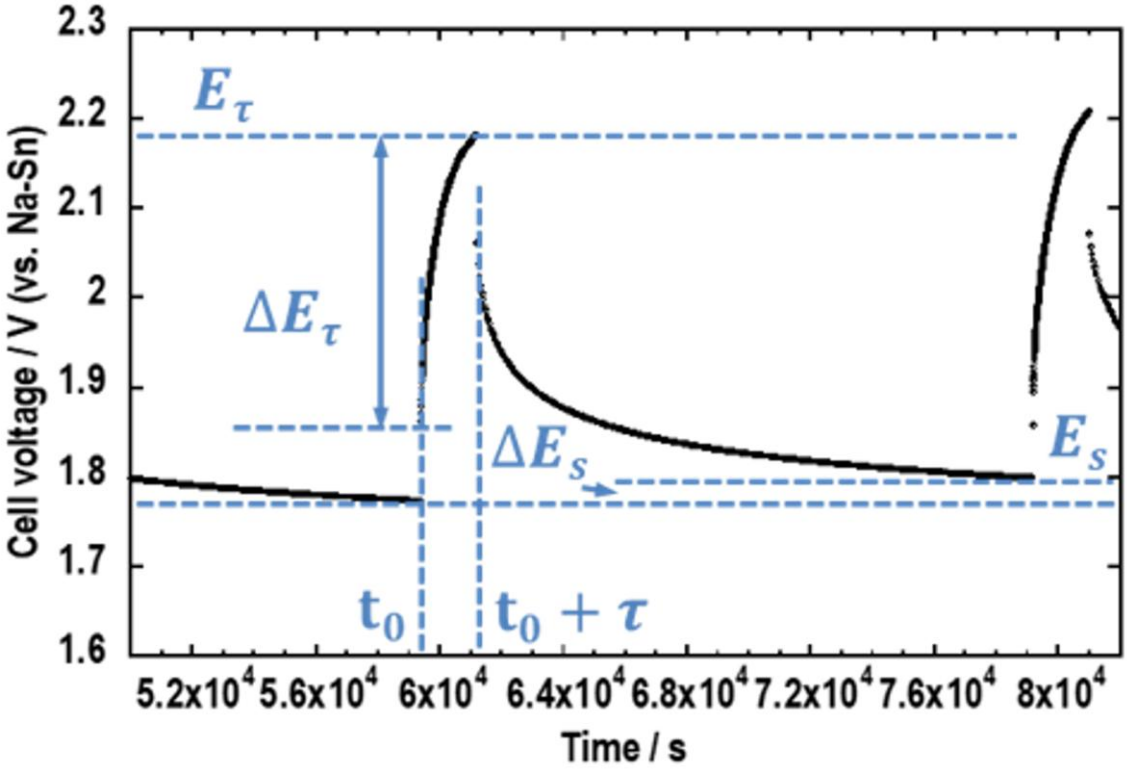

Figure S7 Schematic illustration of the determination of ΔE_τ and ΔE_s from the intermittent charge-relaxation profile. E_τ is the voltage at the end of the galvanostatic pulse of duration τ, and E_s is the stabilized voltage during the subsequent relaxation period. The voltage was regarded as stabilized when the absolute voltage-change rate became less than 1.0 mV h^{-1}.