Supplementary Materials

Regulating Na^+ vacancies and stabilizing lattice structure via Al^{3+}/O^{2-} doping for low-cost dry-air-stable NaCl-based solid electrolytes

Chengyu Fu[1], Chenjie Lou[3], Liming Zhang[1], Longfei Li[1], Baozhang Li[4], Yi Sun[1], Mingxue Tang[3], Pengcheng Shi[2,*], Xuyong Feng[1,*], Hongfa Xiang[1,*]

[1]School of Materials Science and Engineering, Engineering Research Center of High-Performance Copper Alloy Materials and Processing, Ministry of Education, Hefei University of Technology, Hefei 230009, Anhui, China.
[2]School of Energy Materials and Chemical Engineering, Hefei University, Hefei 230601, Anhui, China.
[3]Center for High Pressure Science and Technology Advanced Research, Beijing 100193, China.
[4]Huacai New Energy Technology Co., Ltd., Hefei 230088, Anhui, China.

Correspondence to: Prof. Hongfa Xiang, Prof. Xuyong Feng, School of Materials Science and Engineering, Engineering Research Center of High-Performance Copper Alloy Materials and Processing, Ministry of Education, Hefei University of Technology, Hefei, 230009, Anhui, China. E-mail: 2021800026@hfut.edu.cn or hfxiang@hfut.edu.cn; 2021800026@hfut.edu.cn; Prof. Pengcheng Shi, School of Energy Materials and Chemical Engineering, Hefei University, Hefei 230601, Anhui, China. E-mail: shipc@hfuu.edu.cn

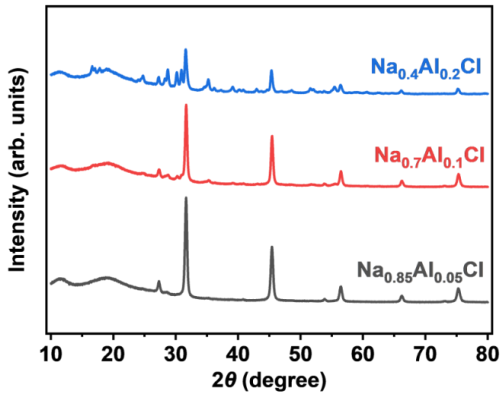

Figure S1. XRD patterns of $Na_{1-3y}Al_yCl$.

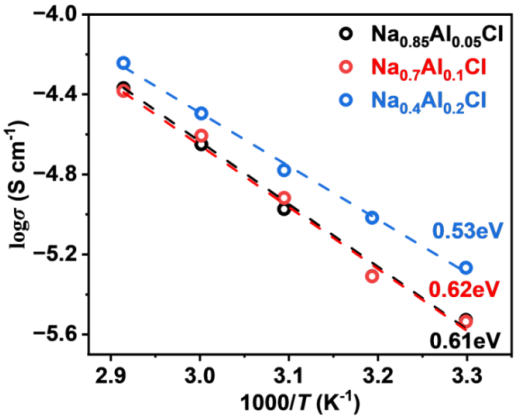

Figure S2. Arrhenius conductivity plots of $Na_{1-3y}Al_yCl$.

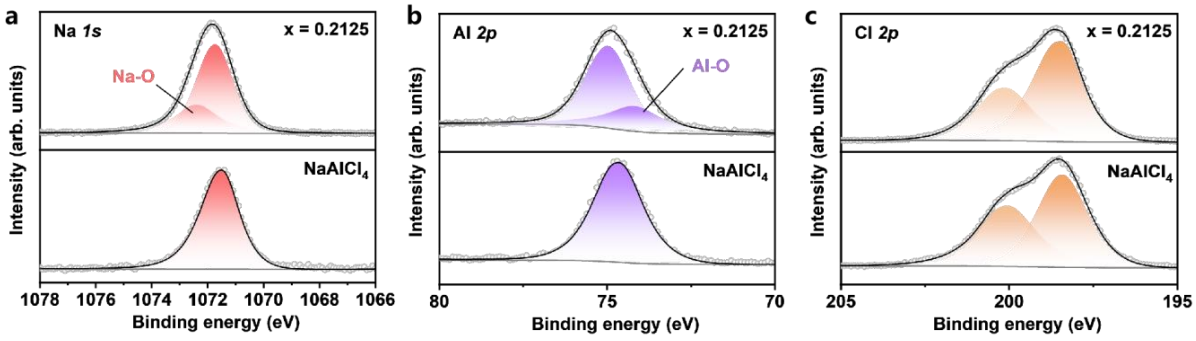

Figure S3. (a) Na *1s*, (b) Al *2p* X-ray and (c) Cl *2p* photoelectron spectroscopy (XPS) spectra of NACO0.2125 and $NaAlCl_4$.

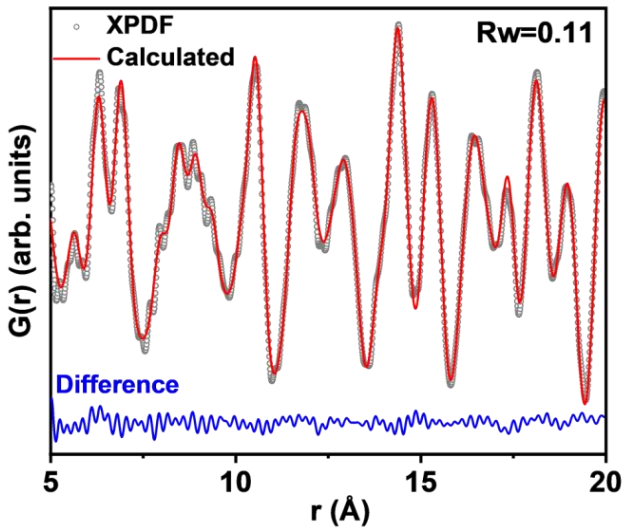

Figure S4. PDF fitting results of NACO0.2125.

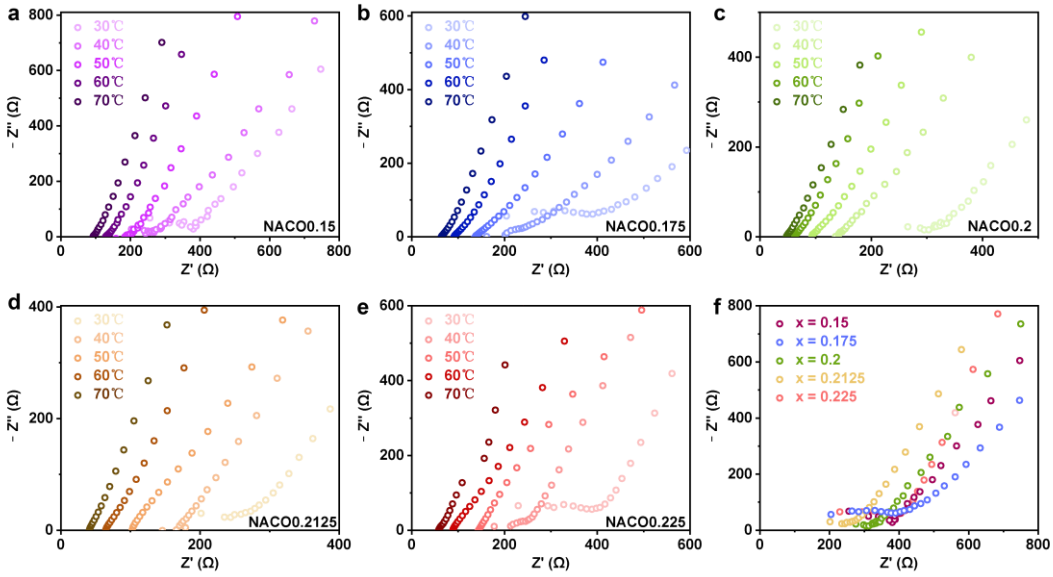

Figure S5. Nyquist plots of NACOx. a) NACO0.15, b) NACO0.175, c) NACO0.2, d) NACO0.2125. e) NACO0.225. f) NACOx at room temperature.

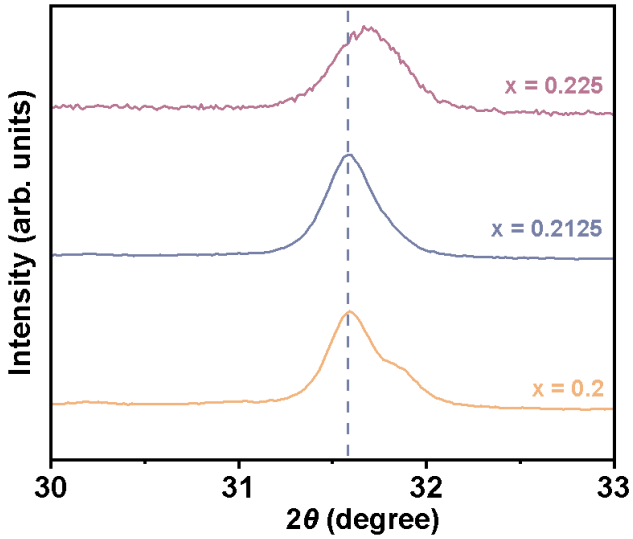

Figure S6. Enlarged XRD patterns of NACOx

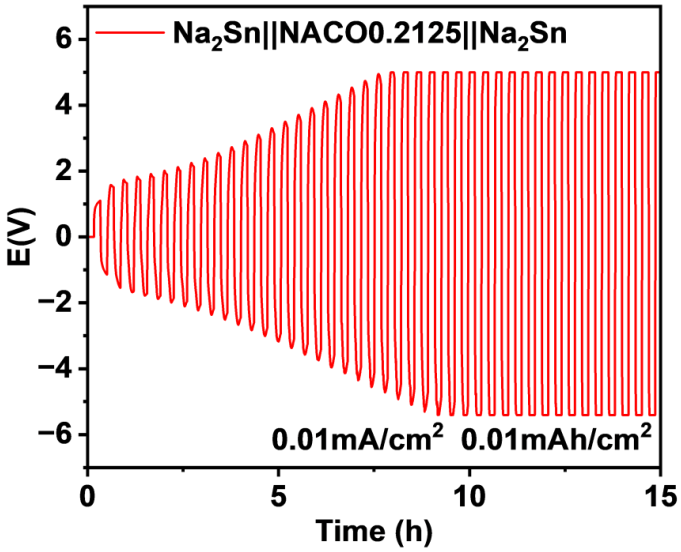

Figure S7. Galvanostatic cycling of the $Na_2Sn||NACO0.2125||Na_2Sn$ symmetric cells at 30 °C

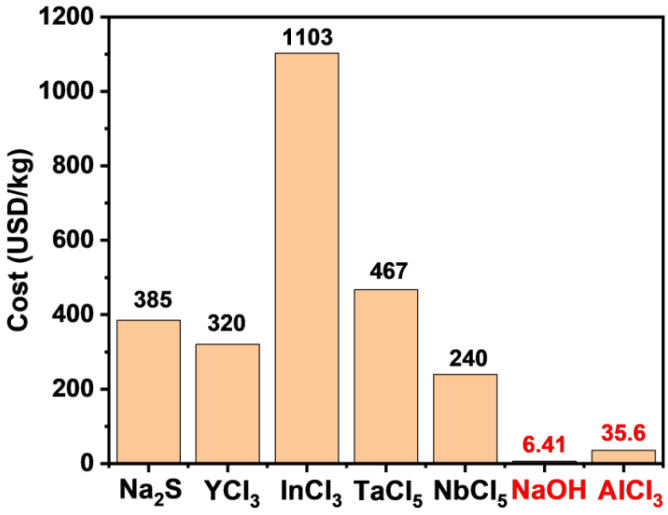

Figure S8. The comparison of cost of raw materials.

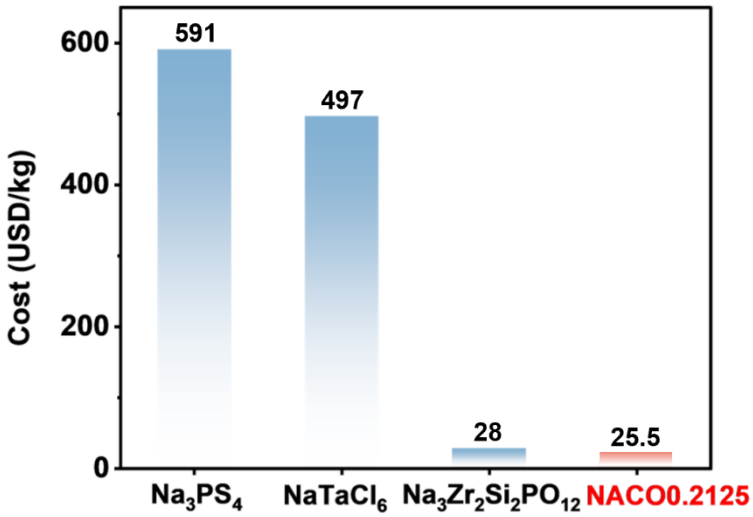

Figure S9. The comparison of cost of SSEs.

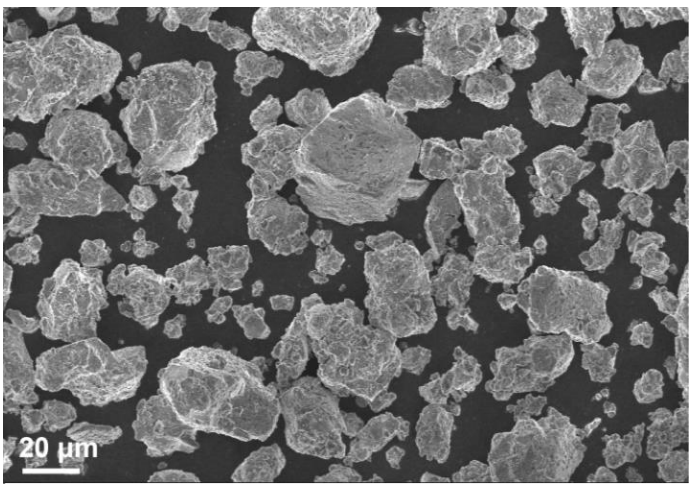

Figure S10. SEM image of NACO0.2125.

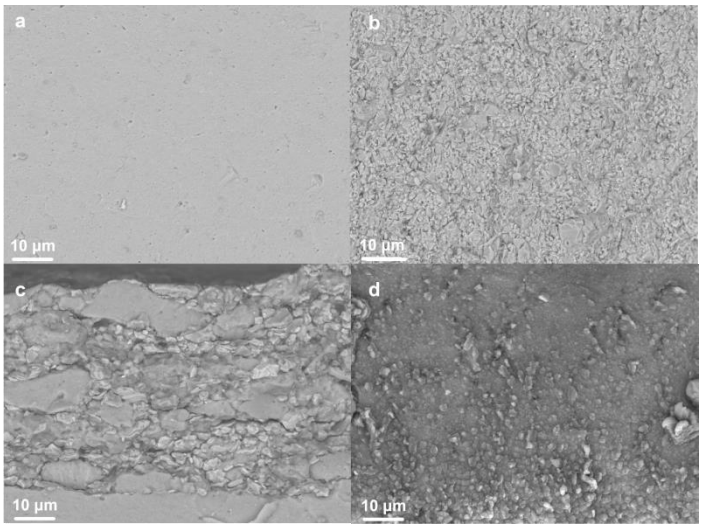

Figure S11 Cross-sectional SEM image of (a) NACO0.2125, (b) Na_3PS_4, (c) composite cathode and (d) Na_2Sn.

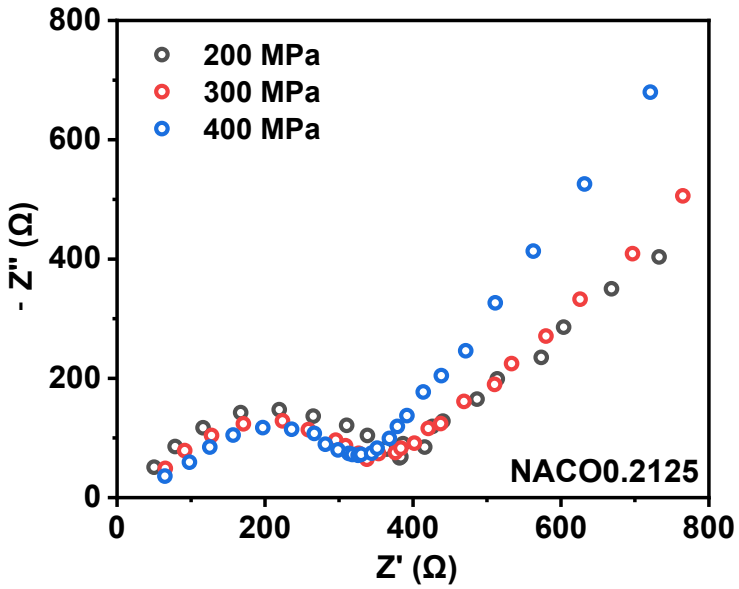

Figure S12. Nyquist plots of NACOx on different pressure

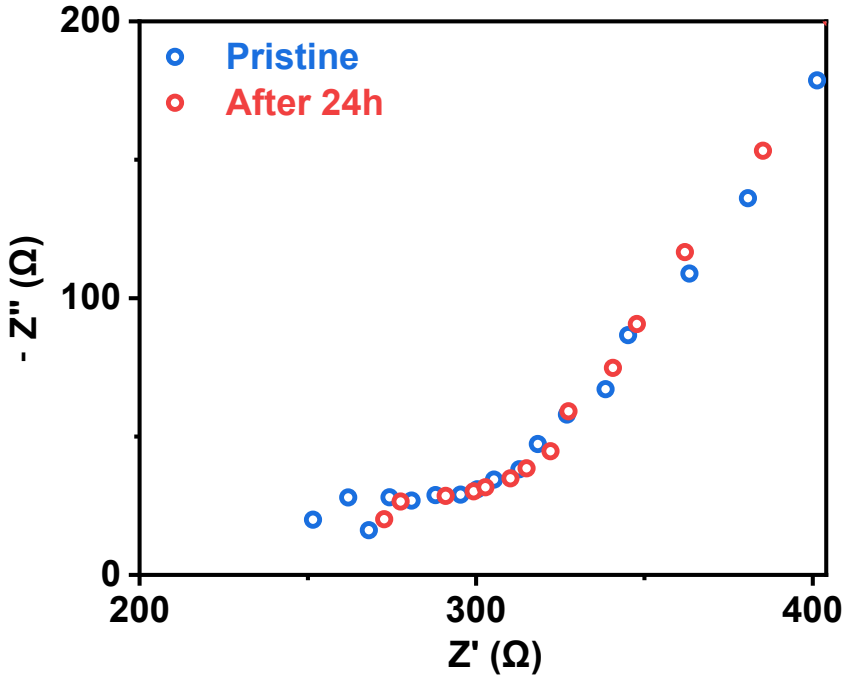

Figure S13. Enlarged Nyquist plots of exposed NACO0.2125

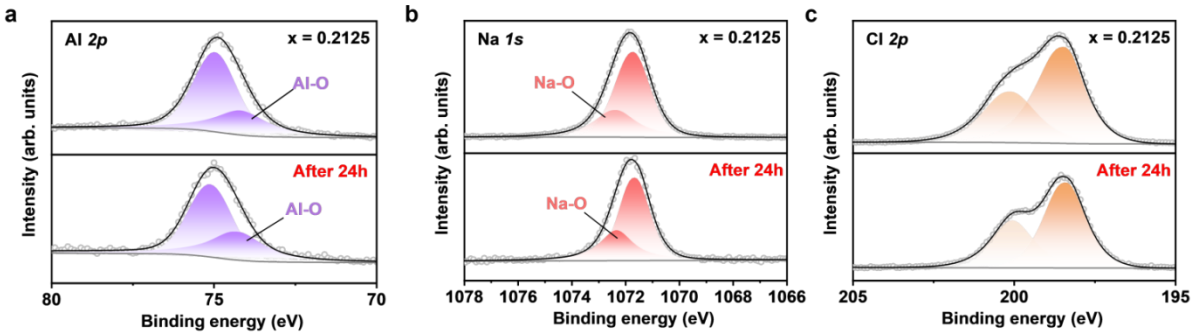

Figure S14 (a) Al *2p*, (b) Na *1s* and (c) Cl *2p* X-ray photoelectron spectroscopy (XPS) spectra of NACO0.2125 and exposed NACO0.2125.

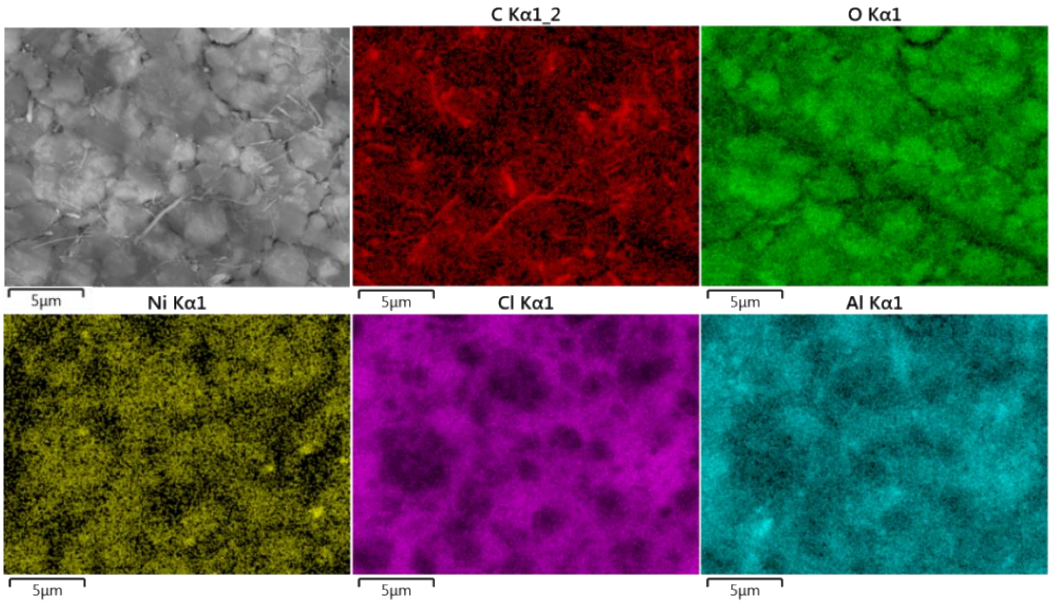

Figure S15 SEM image and mapping of composite cathode.

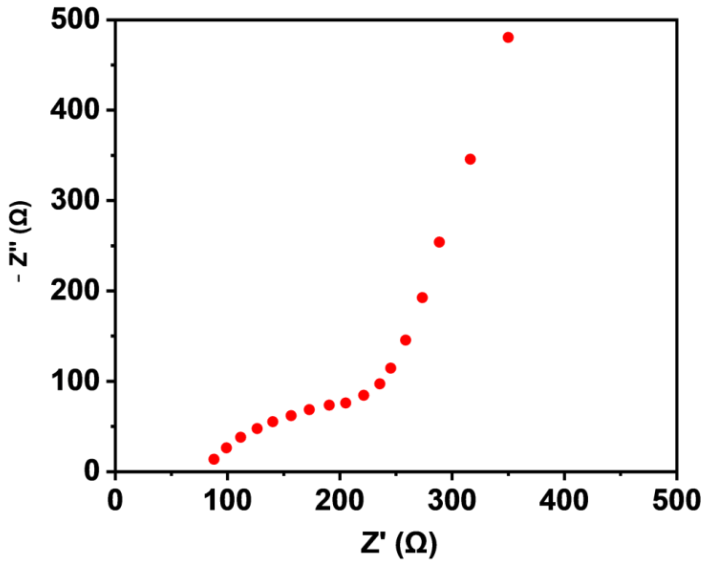

Figure S16. Nyquist plots of Na_3PS_4.

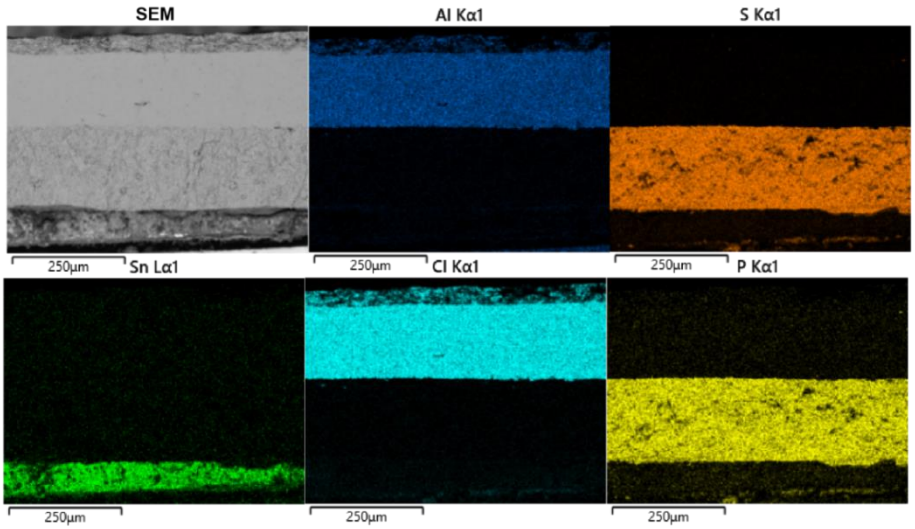

Figure S17. Cross-sectional SEM image and mapping of ASSB.

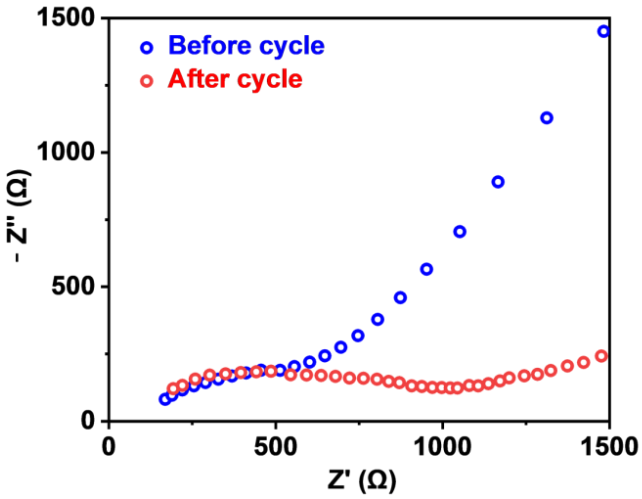

Figure S18. Nyquist plots of ASSB.

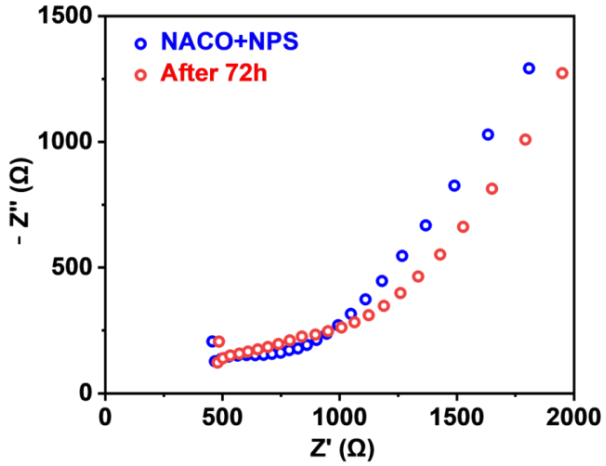

Figure S19. Nyquist plots of Na_3PS_4 and NACO0.2125.

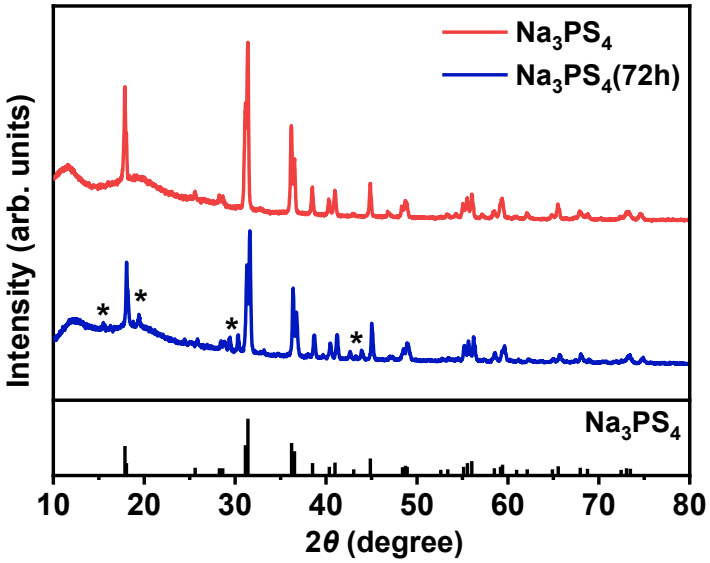

Figure S20. XRD patterns of Na_3PS_4

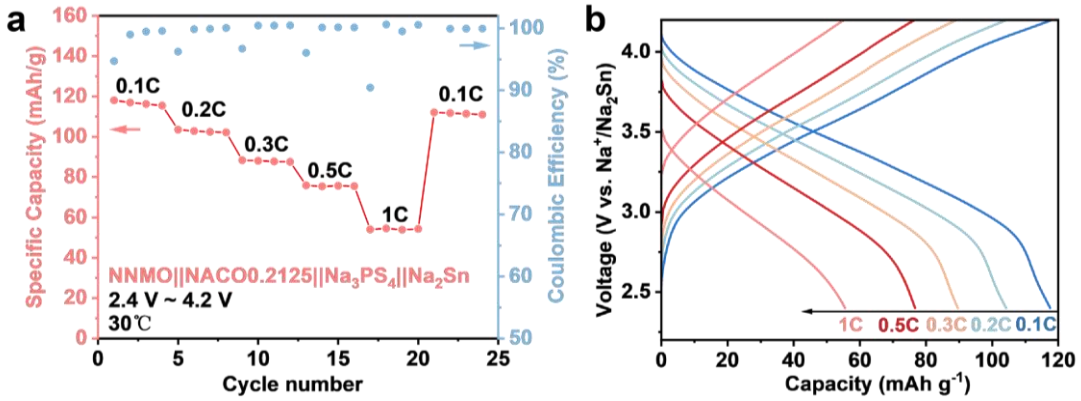

Figure S21. (a) Rate performance of ASSB, (b) Charge-discharge profiles at different rate.

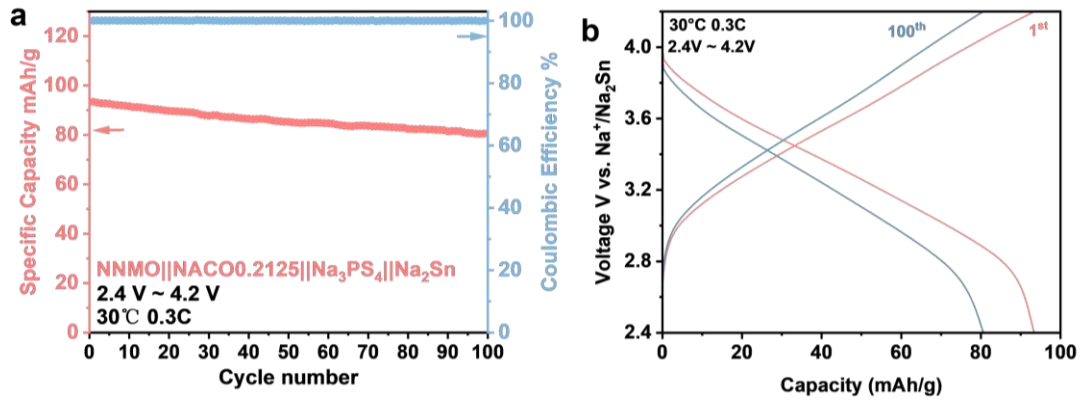

Figure S22. (a) Cycle performance of ASSB, (b) Charge-discharge profiles at different cycles.

Table S1. XRD refinement results of $Na_{0.4625}Al_{0.25}Cl_{0.7875}O_{0.2125}$.

Component： $Na_{0.4625}Al_{0.25}Cl_{0.7875}O_{0.2125}$ **Space group：** *Fm*-3*m* **Lattice Parameters：** $a = b = c = 5.6311(3)$ Å,V = 178.56 (1) Å^3, $\alpha = \beta = \gamma = 90°$						
Atom	x	y	z	Wyckoff	Occupancy	Uiso
Na1	0.00000	0.00000	0.00000	4*a*	0.462	0.00036
Cl1	0.50000	0.50000	0.50000	4*b*	0.787	0.04973
Al1	0.00000	0.00000	0.00000	4*a*	0.162	0.00036
Al2	0.25000	0.25000	0.25000	8*c*	0.044	0.00045
O1	0.50000	0.50000	0.50000	4*b*	0.213	0.04973
Rwp=4.094%　GOF=1.73%						