Supporting Information for:

Aluminum chloride-based Catholytes for Stable High-voltage Solid-state Sodium Batteries

*Erick Ruoff and Arumugam Manthiram**

Materials Science and Engineering Program & Walker Department of Mechanical Engineering,

The University of Texas at Austin, Austin, TX 78712, USA

*Corresponding Author. Tel: +1-512-471-1791; fax: +1-512-471-7681.
E-mail address: manth@austin.utexas.edu (A. Manthiram)

List of Supporting Figures

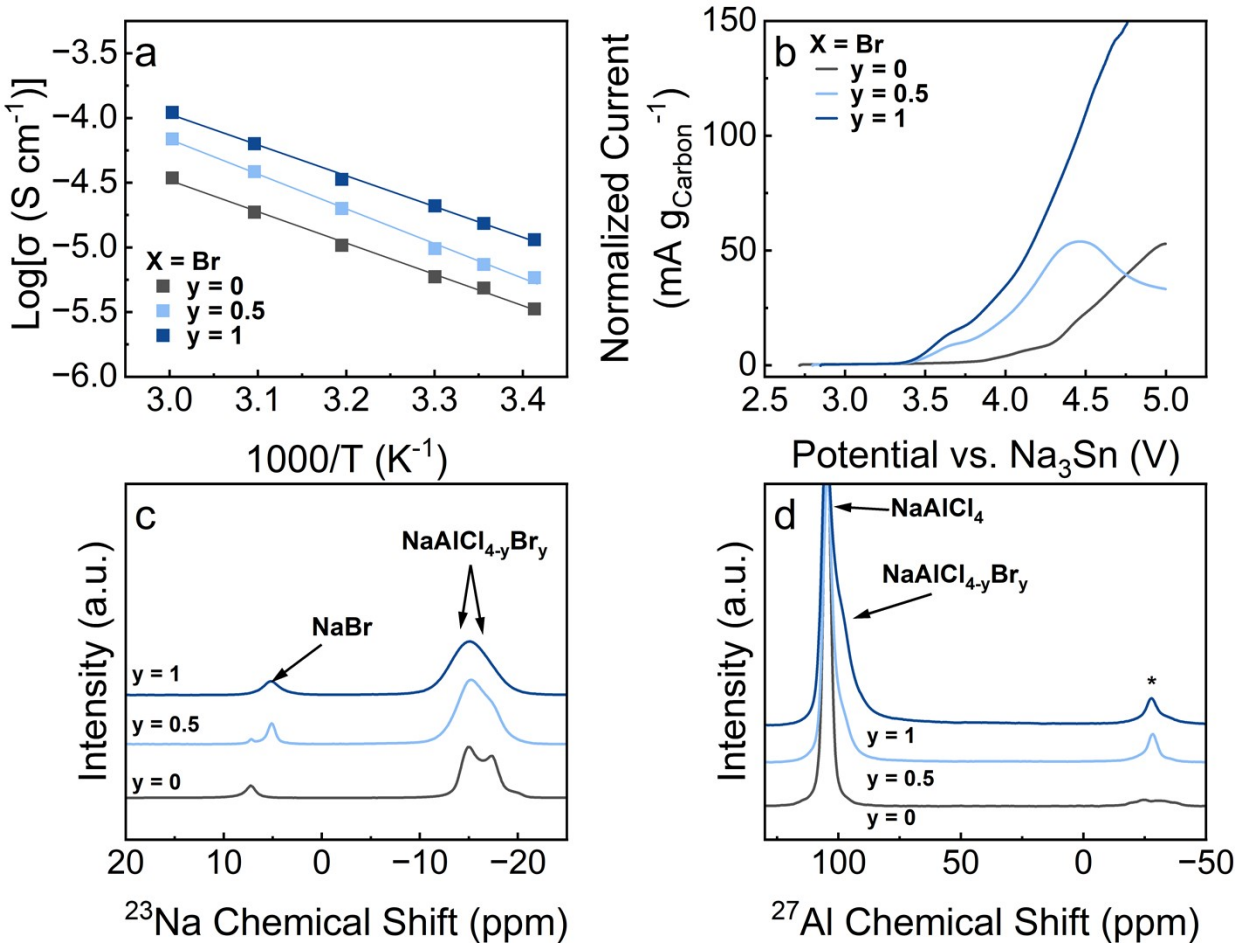

Figure S1. Characterization of [(1-y)NaCl + yNaX +$AlCl_3$] SE series for X = Br. (a) Arrhenius plots of ionic conductivity. (b) LSV curves. (c) ^{23}Na and (d) ^{27}Al solid-state magic angle spinning NMR spectra, "*" signs indicate spinning side bands.

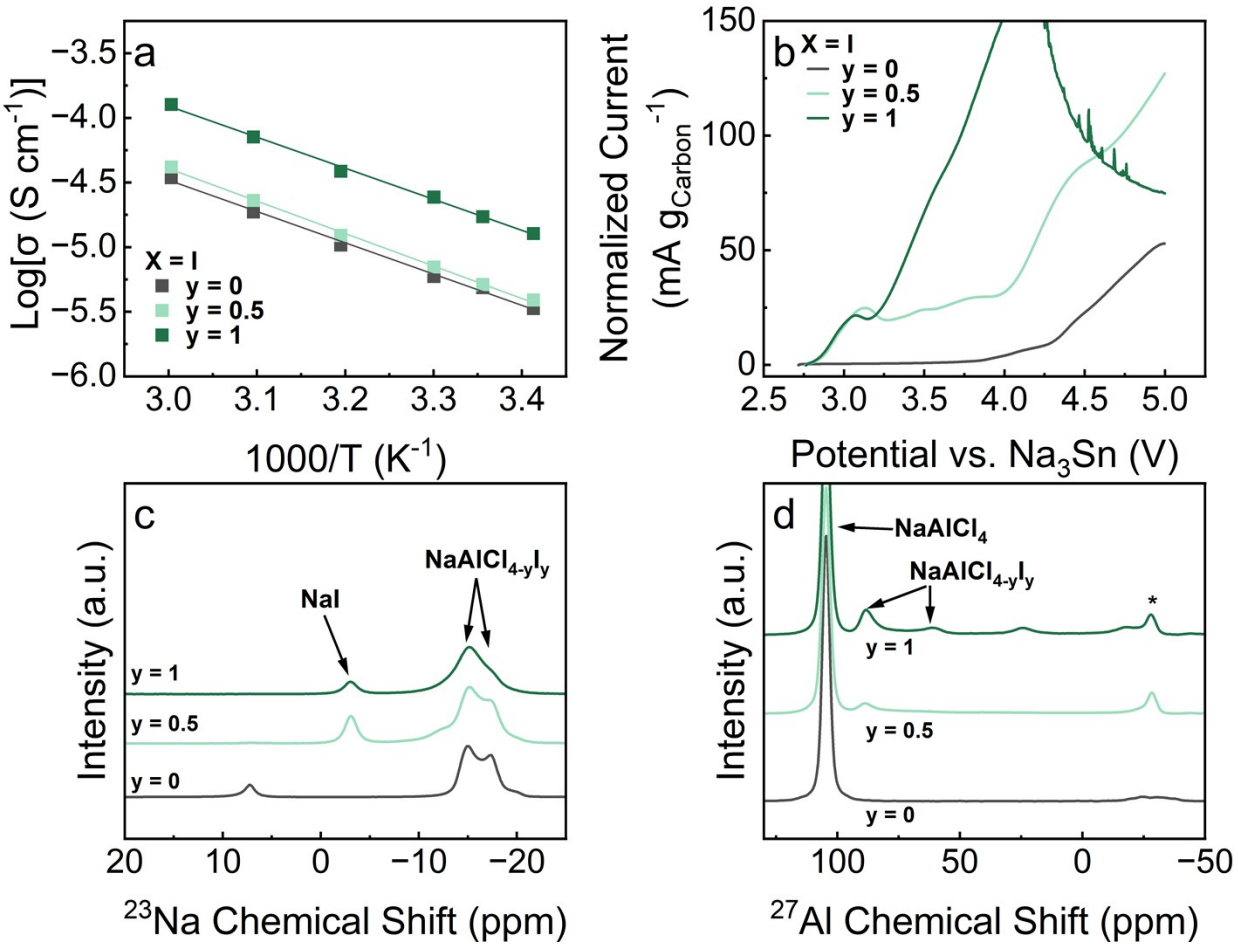

Figure S2. Characterization of [(1-y)NaCl + yNaX +$AlCl_3$] SE series for X = I. (a) Arrhenius plots of ionic conductivity. (b) LSV curves. (c) ^{23}Na and (d) ^{27}Al solid-state magic angle spinning NMR spectra, "*" signs indicate spinning side bands.

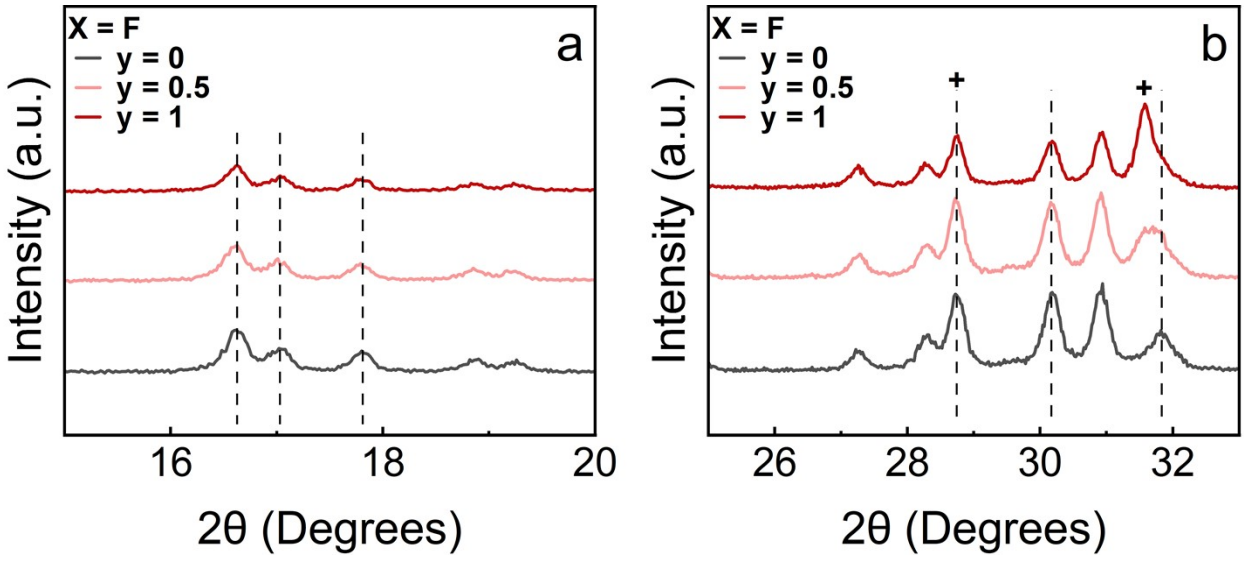

Figure S3. XRD patterns of the [(1-y)NaCl + yNaX +$AlCl_3$] SE series for X = F, zoomed in on ranges from (a) 15-20° and (b) 25-33°, with the + sign referring to reflections from NaCl.

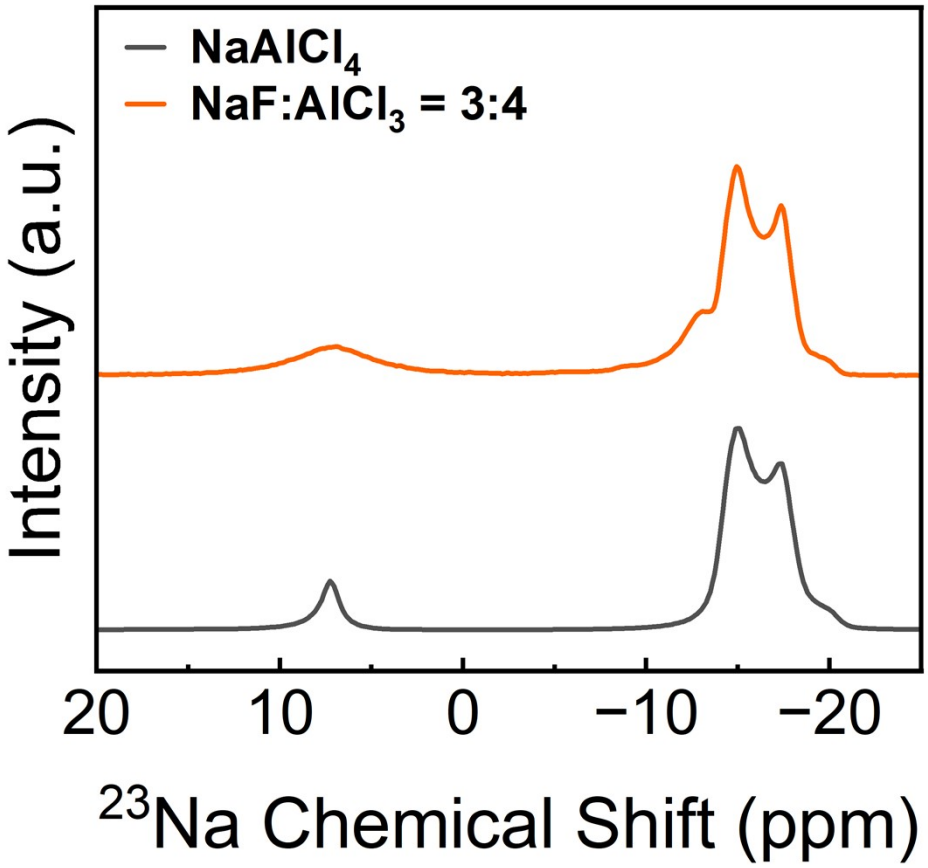

Figure S4. ^{23}Na solid-state magic angle spinning NMR spectra of NaF : $AlCl_3$ = 3 : 4 SE.

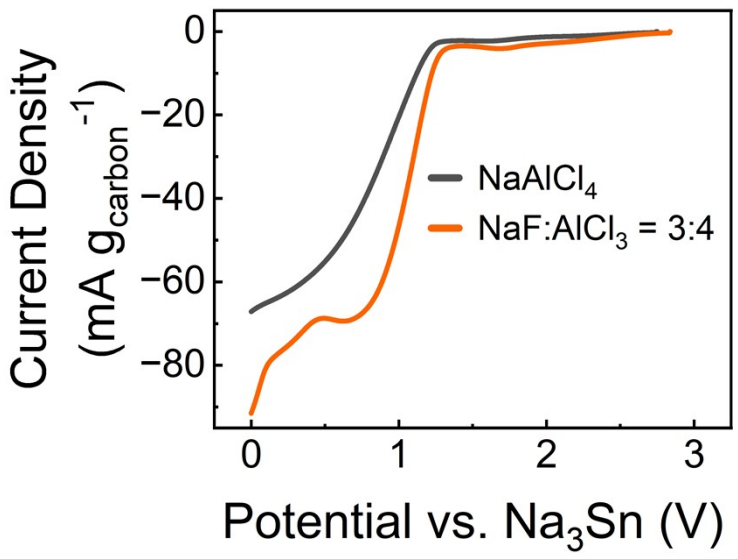

Figure S5. LSV curves of selected SE samples at a scan rate of 0.1 mv s^{-1}.

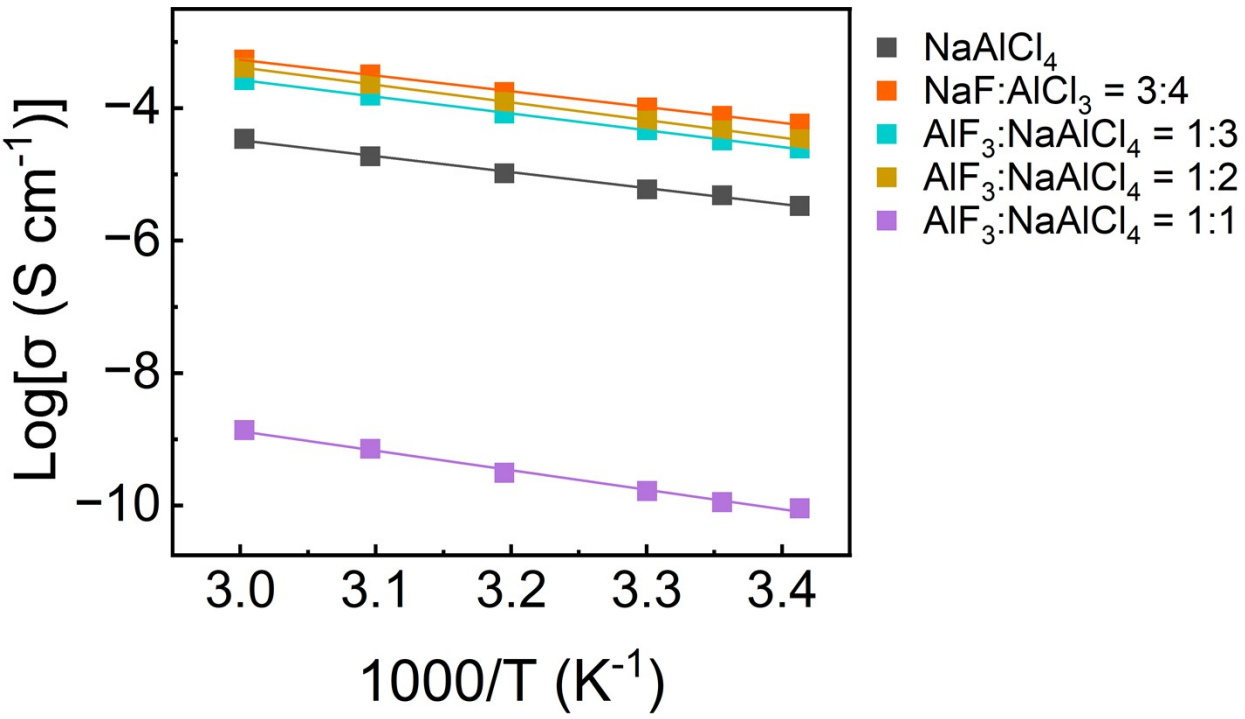

Figure S6. Arrhenius plots of ionic conductivity of various AlF_3 : $NaAlCl_4$ composite SEs.

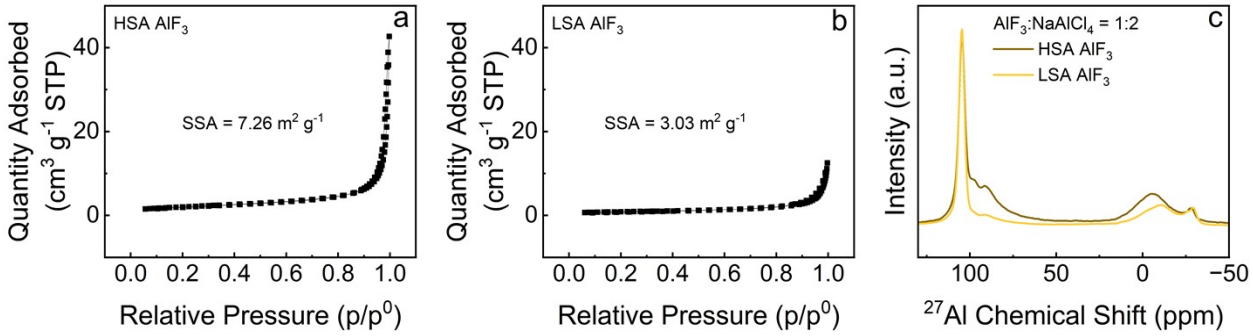

Figure S7. BET isotherms for (a) HSA AlF_3 and (b) LSA AlF_3. (c) ^{27}Al NMR spectra of AlF_3 : $NaAlCl_4$ = 1 : 2 composite SEs with HSA and LSA AlF_3 prepared by a melt reaction method.

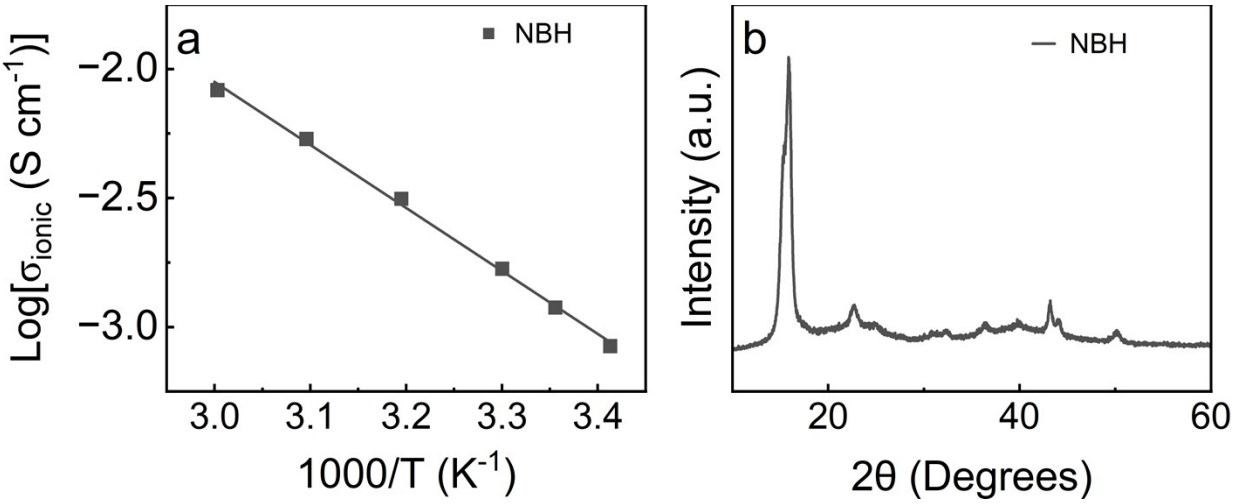

Figure S8. Arrhenius plot of ionic conductivity and XRD pattern of NBH SE.

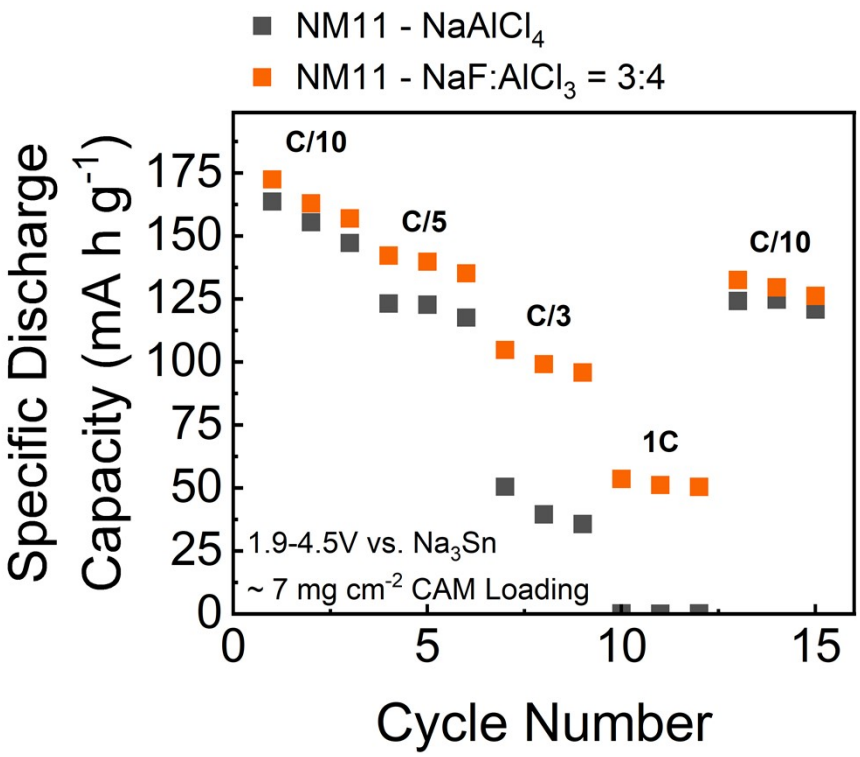

Figure S9. Rate capability testing of selected ASSBs.

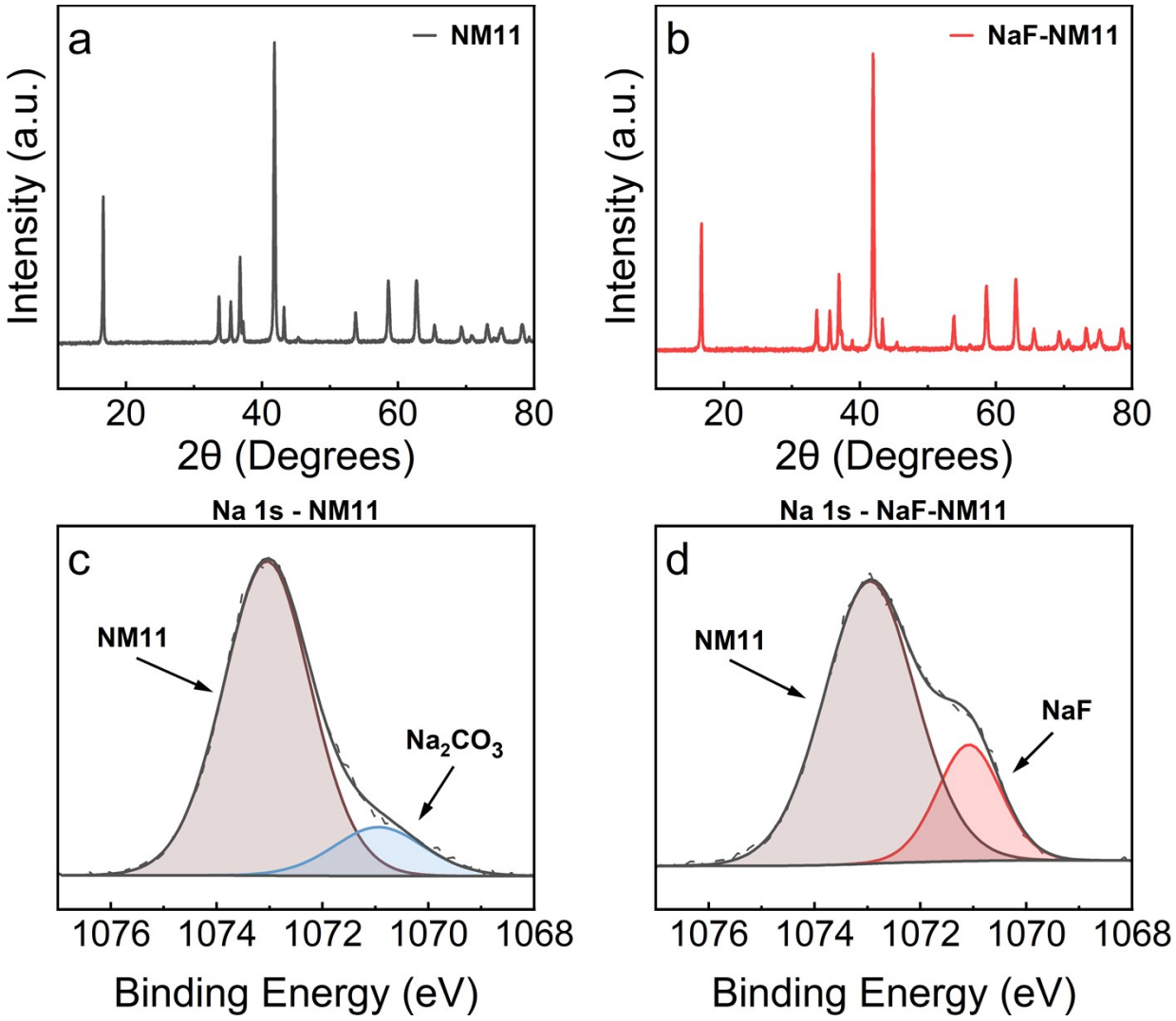

Figure S10. XRD pattern of (a) pristine and (b) NaF coated NM11 CAM. Na 1s XPS spectrum of (c) pristine and (d) NaF coated NM11 CAM.

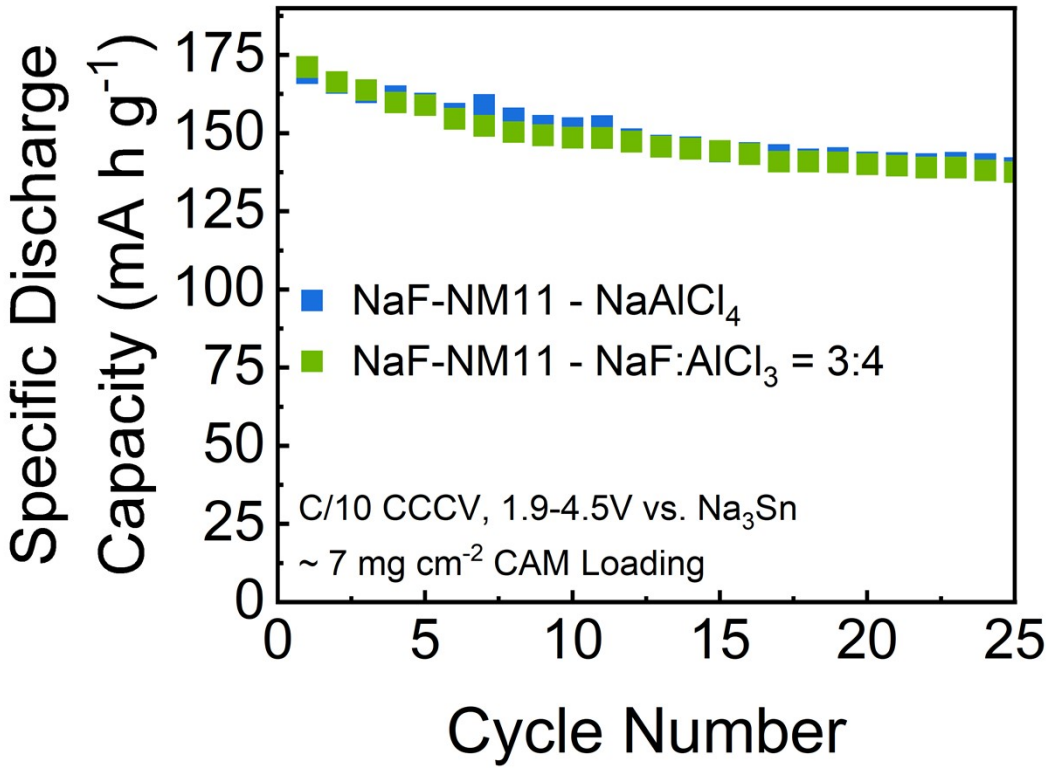

Figure S11. Initial ASSB cycling performance with NaF coated NM11 CAM.

List of Supporting Tables

Table S1. Predicted reaction pathways and formation energies for the $AlCl_3$ + NaF reactants. Calculated from The Materials Project Interface Reactions application.[1]

Reaction	E_{rxn} (kJ mol^{-1})
0.25 $AlCl_3$ + 0.75 NaF → 0.75 NaCl + 0.25 AlF_3	-63.8
0.2 $AlCl_3$ + 0.8 NaF → 0.2 $NaAlF_4$ + 0.6 NaCl	-57.4

REFERENCES

(1) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater* 2013, *1* (1), 011002. https://doi.org/10.1063/1.4812323.