Liquid-solid phase separation induced interfacial degradation in solid-state Na-ion batteries with Na-K liquid anodes

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Supplemental figures and tables

Table S1 Calculated Na diffusivity in Na-K alloy at 373 K, as a function of K concentration.[2]

wt%K in NaK	D_{Na} (10^{-5} cm^2s^{-1})
10	4.169
20	4.360
30	4.547
40	4.723
50	4.909
60	5.097
70	5.270
80	5.451
90	5.649

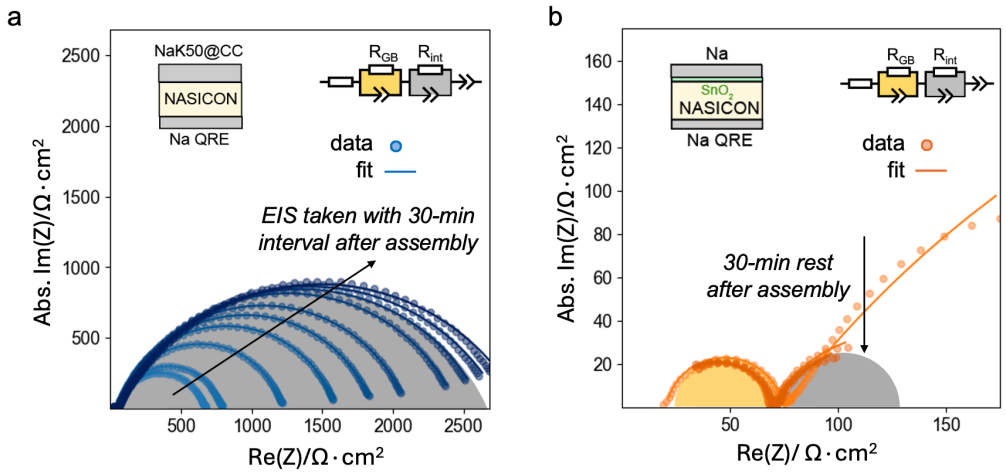

Figure S1 a Post-assembly EIS spectra evolution of a NaK50/NASICON/Na cell without a SnO_2 coating on NASICON. **b** Post-assembly EIS spectra evolution of a NaK50/SnO_2-NASICON/Na cell.

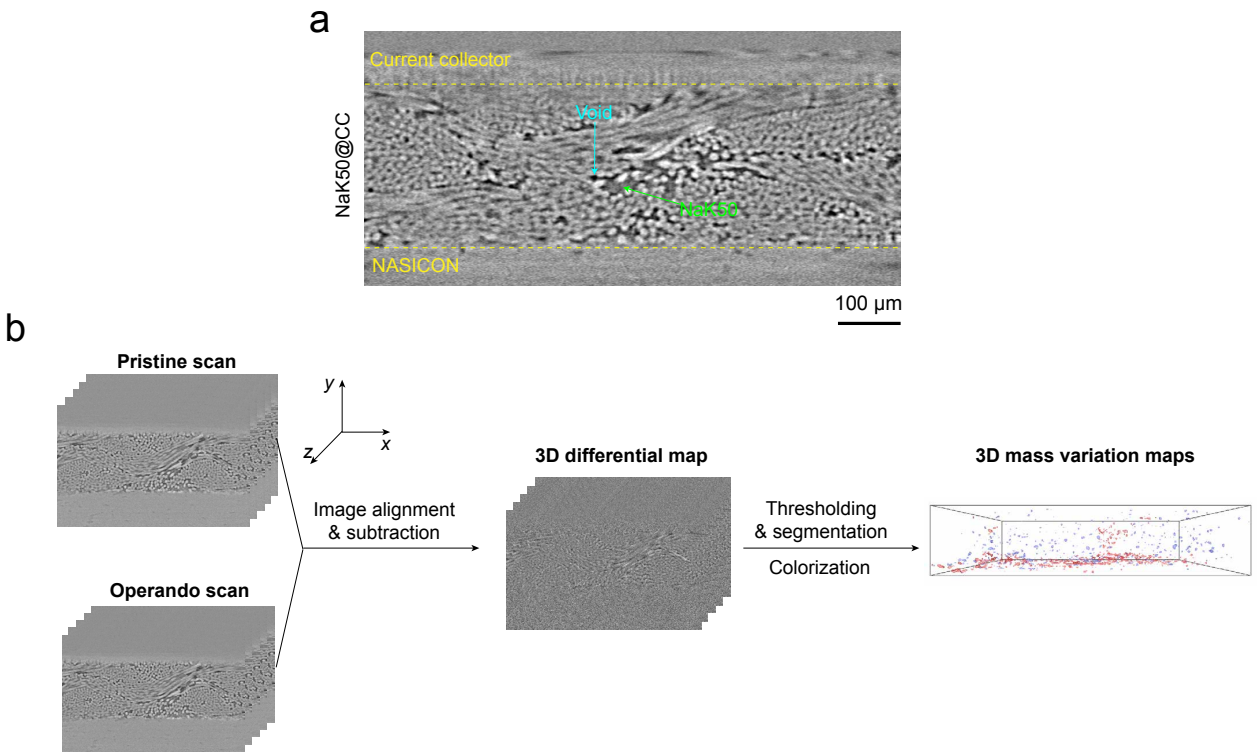

Figure S2 a A single virtual cross-section image from the pristine synchrotron XCT scan of the *operando* cell. **b** 3D image processing workflow to obtain 3D mass variation maps.

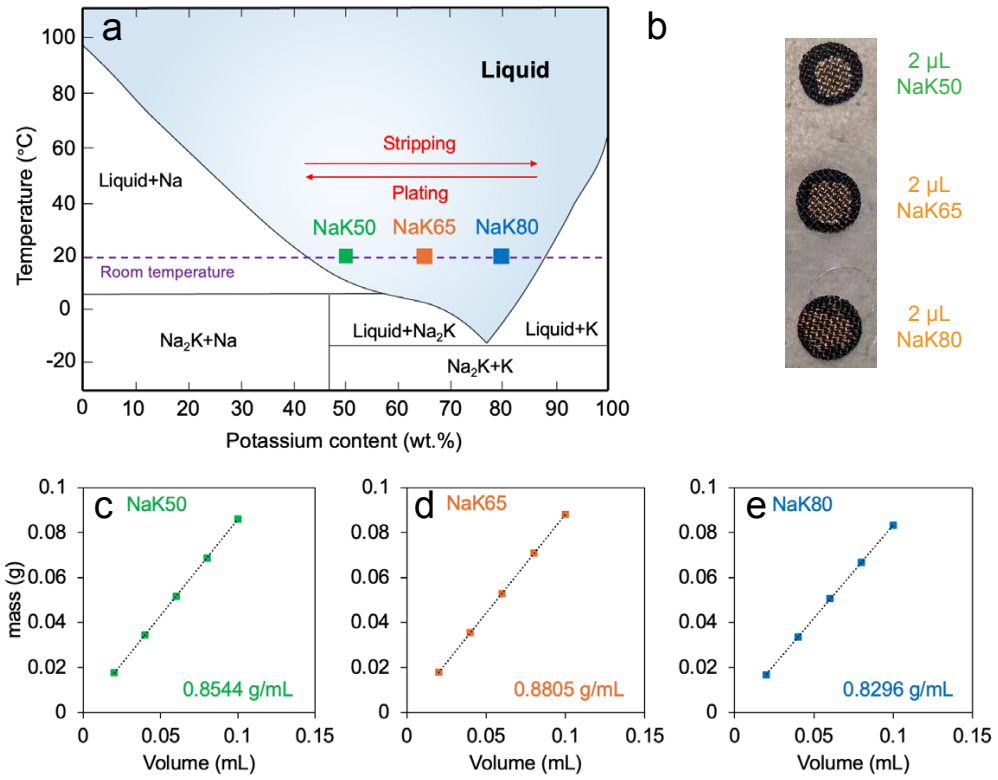

Figure S3 a Na-K phase diagram.[1] **b** NaK spreading experiment where 2 μL of NaK50, 65 or 80 liquid was dropped onto a 6 mm carbon cloth piece. **c-d** Density measurement results on NaK liquids.

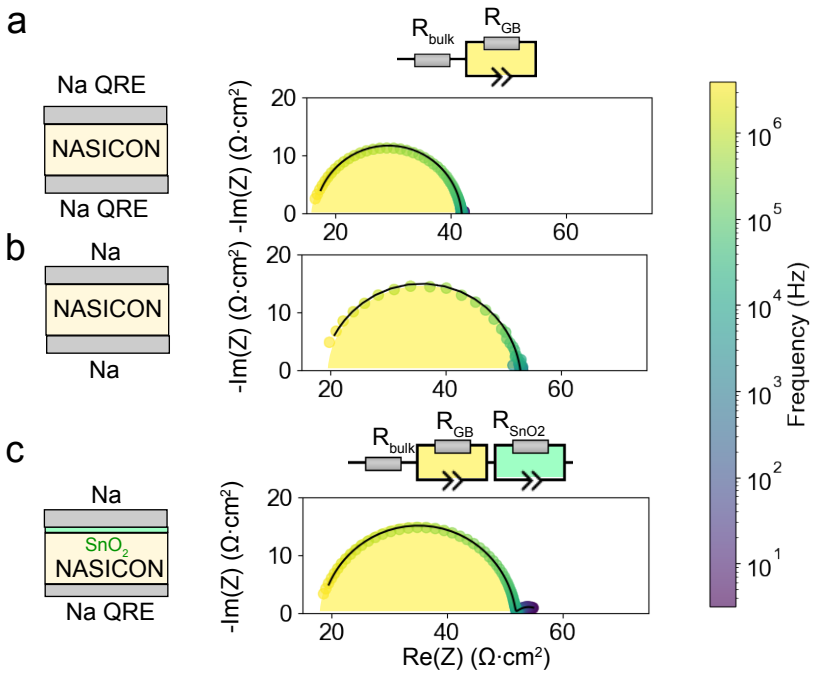

Figure S4 a-b EIS collected on a NaQRE/NASICON/NaQRE and Na/NASICON/Na symmetric cells under 10 MPa external pressure showing no interfacial resistance. **c** EIS collected on Na/SnO_2-NASICON/NaQRE asymmetric cell showing contributions from the SnO_2 coating on the working electrode side.

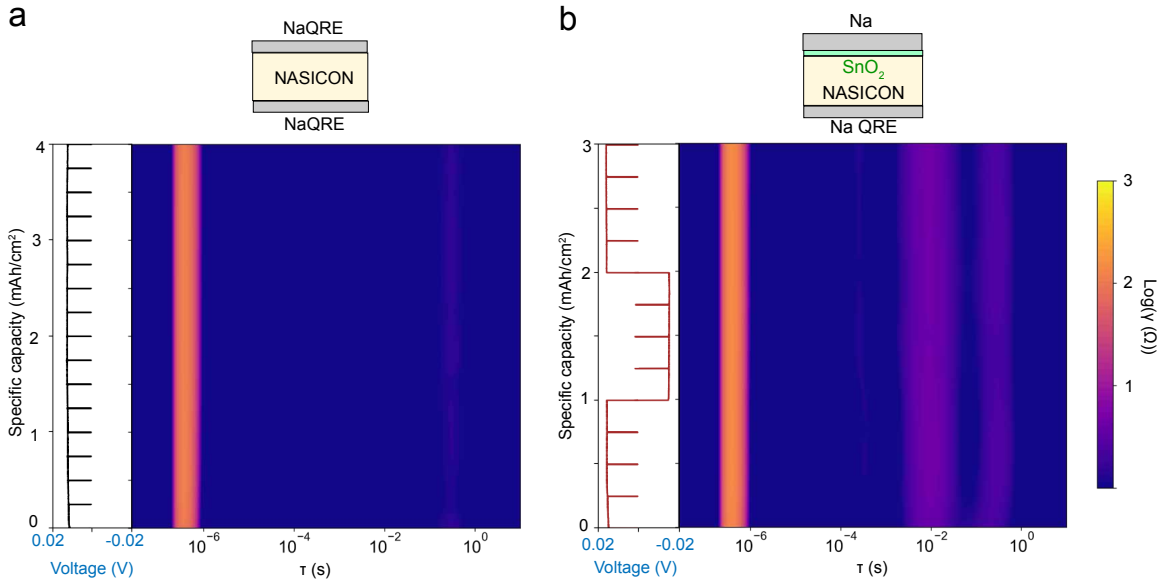

Figure S5 Impedance evolution represented by DRT over **a** Na stripping (plating) process of Na-QRE, **b** Na stripping-plating-stripping process of Na metal. Insets show cell configuration.

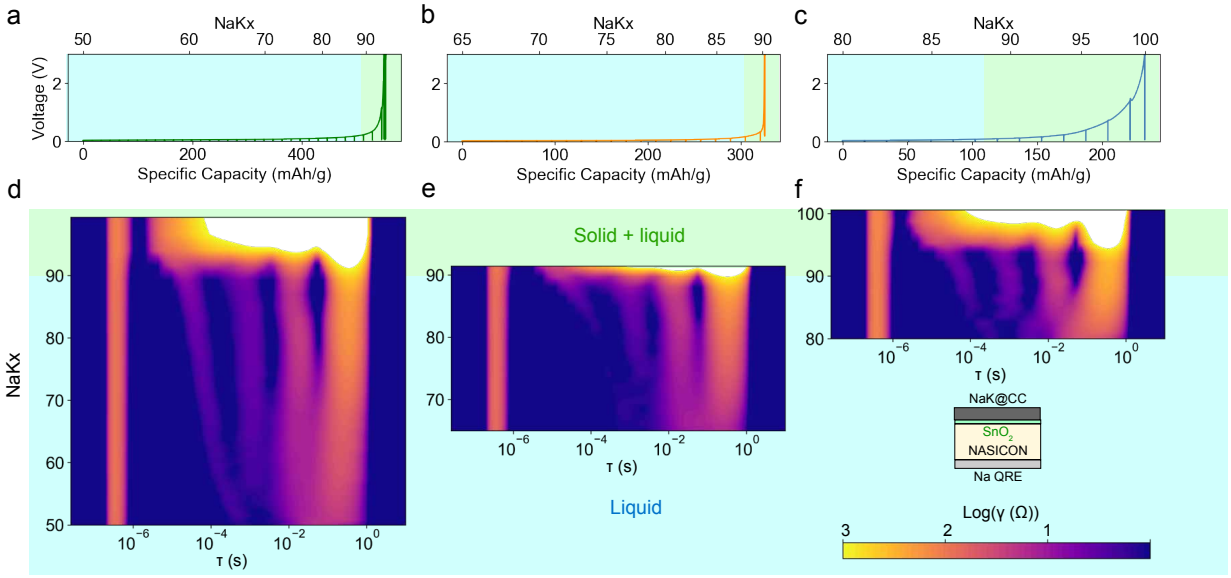

Figure S6 Voltage profile & DRT spectra evolution during the critical stripping process of **a,d** NaK50; **b,e** NaK65 and **c,f** NaK80. All cells ran under an external pressure of 10 MPa.

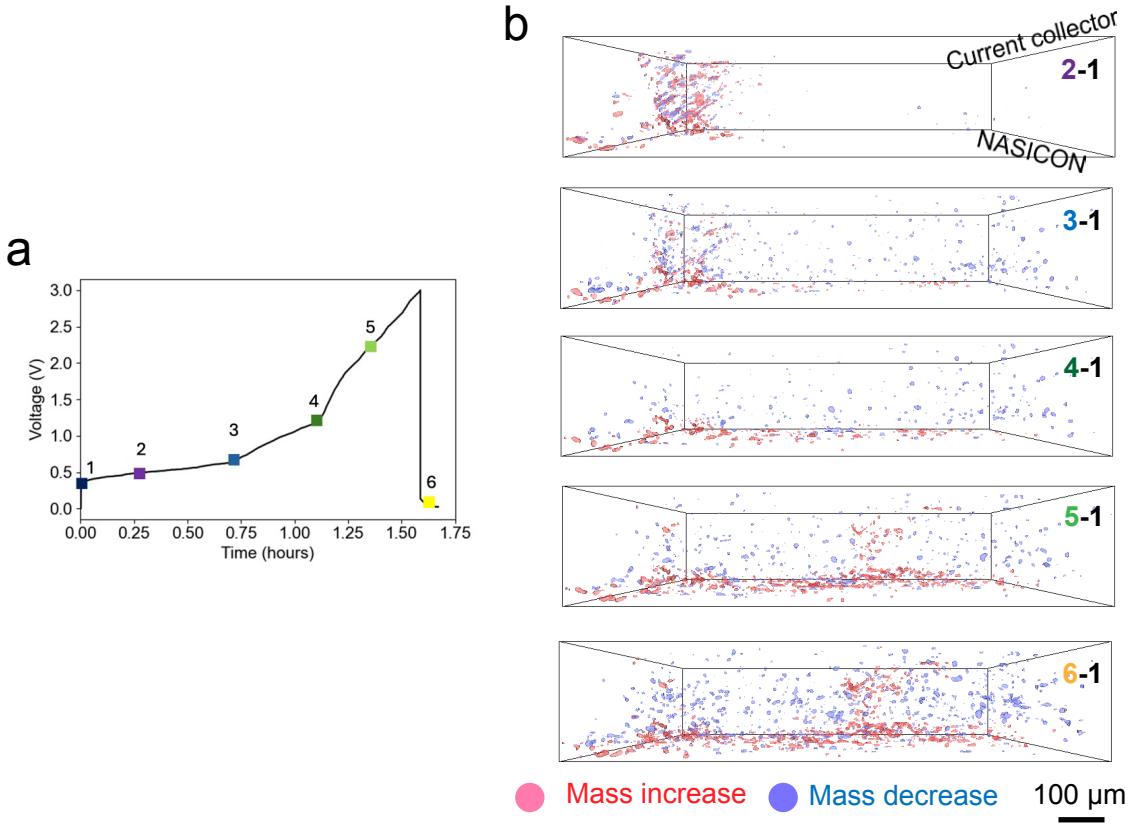

Figure S7 a Voltage profile of the *operando* cell that went through critical stripping process. **b** 3D mass variation maps of the NaK50@CC anode area collected during the critical stripping process.

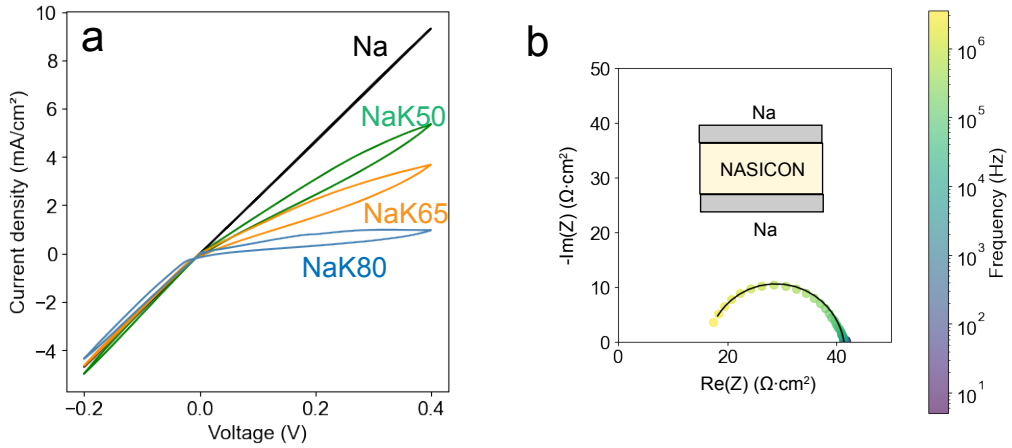

Figure S8 a First-cycle CV of Na metal and NaK liquid anodes. **b** EIS of Na/NASICON/Na symmetric cell after 1st CV cycle showing zero interfacial resistance. CV of Na metal was collected with a symmetric cell setup, CV of NaK liquids were collected with a Na metal counter electrode.

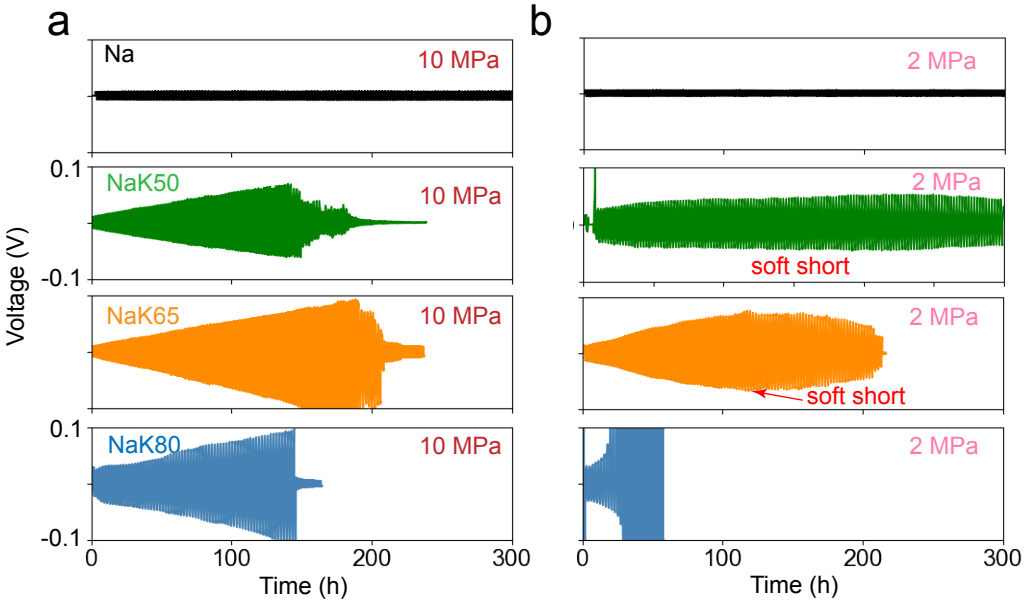

Figure S9 Long-term cycling test on Na & NaK alloys with symmetric cell setups at 0.1 mA/cm^2 and **a** 10 MPa external pressure and **b** 2 MPa external pressure

References

(1) Leonchuk, S. S.; Falchevskaya, A. S.; Nikolaev, V.; Vinogradov, V. V. NaK alloy: underrated liquid metal. *J. Mater. Chem. A* **2022**, *10*, 22955–22976.

(2) Gopala Rao, R. V.; Murthy, A. K. Self diffusion in liquid Na-K alloy. *Pramana* **1977**, *9*, 587–592.