

Supplementary information

Probing Sodium Structures and Dynamics in Hard Carbon for Na-ion Batteries using ^{23}Na *Operando* Solid-State NMR Spectroscopy

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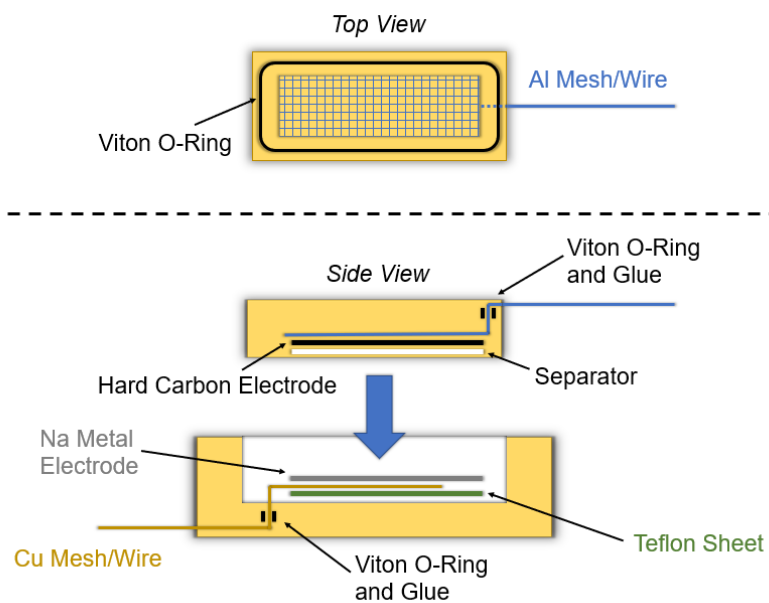


Figure S1. Scheme of the in-situ cell with a description of the parts.

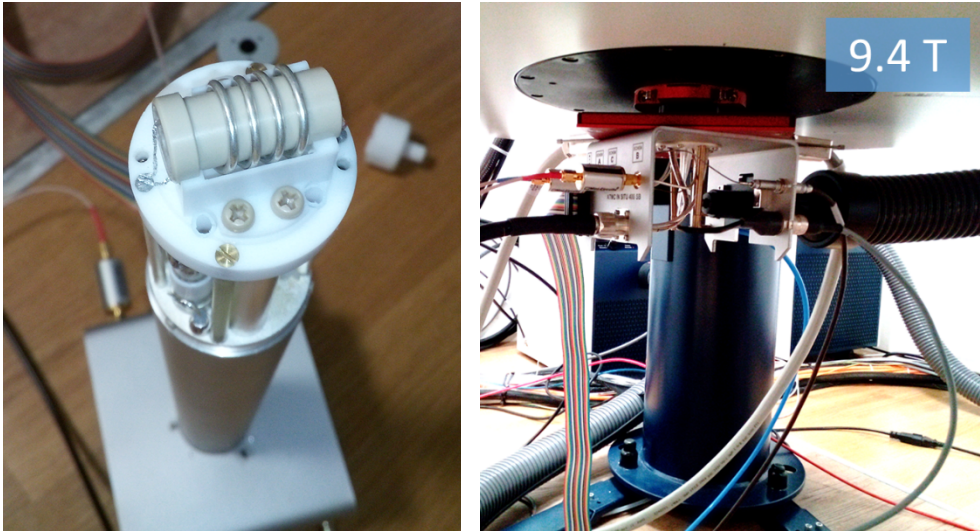


Figure S2. Experimental setup: In-situ probe with added cell (left) and placement of the probe in the NMR spectrometer (right).

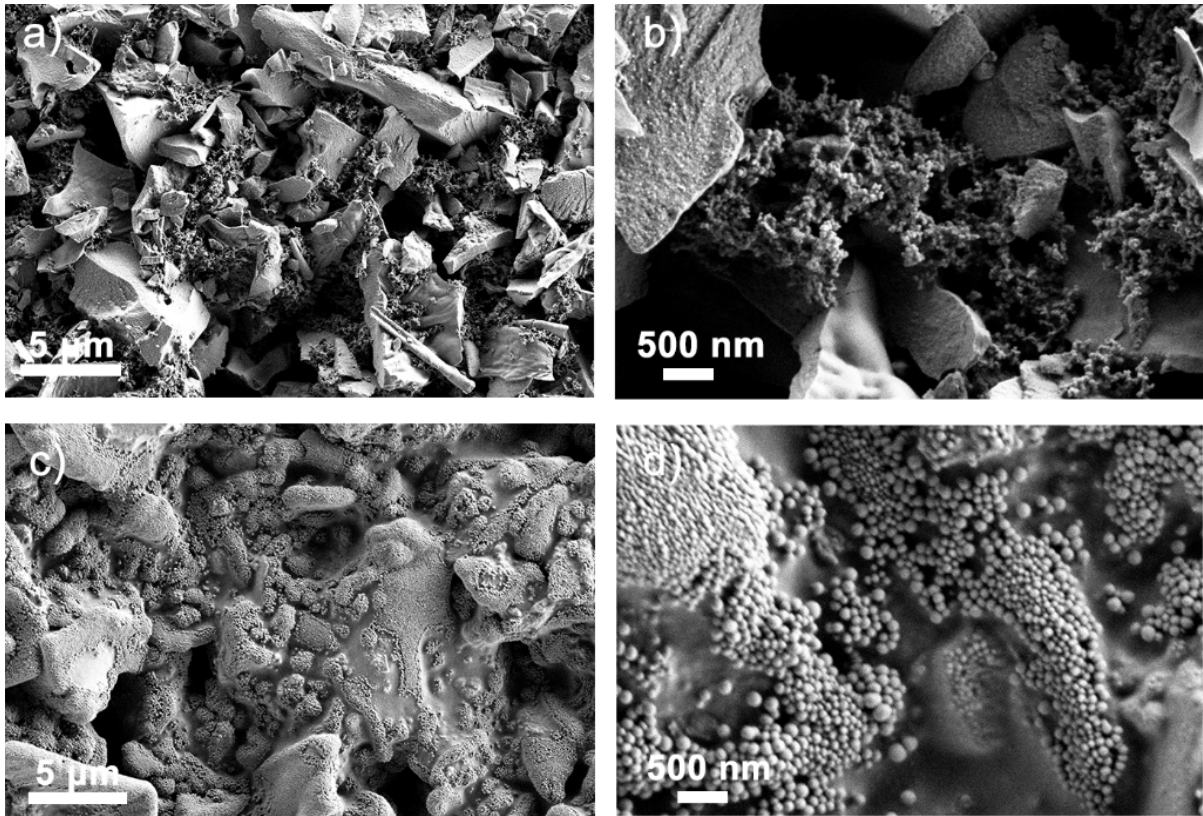
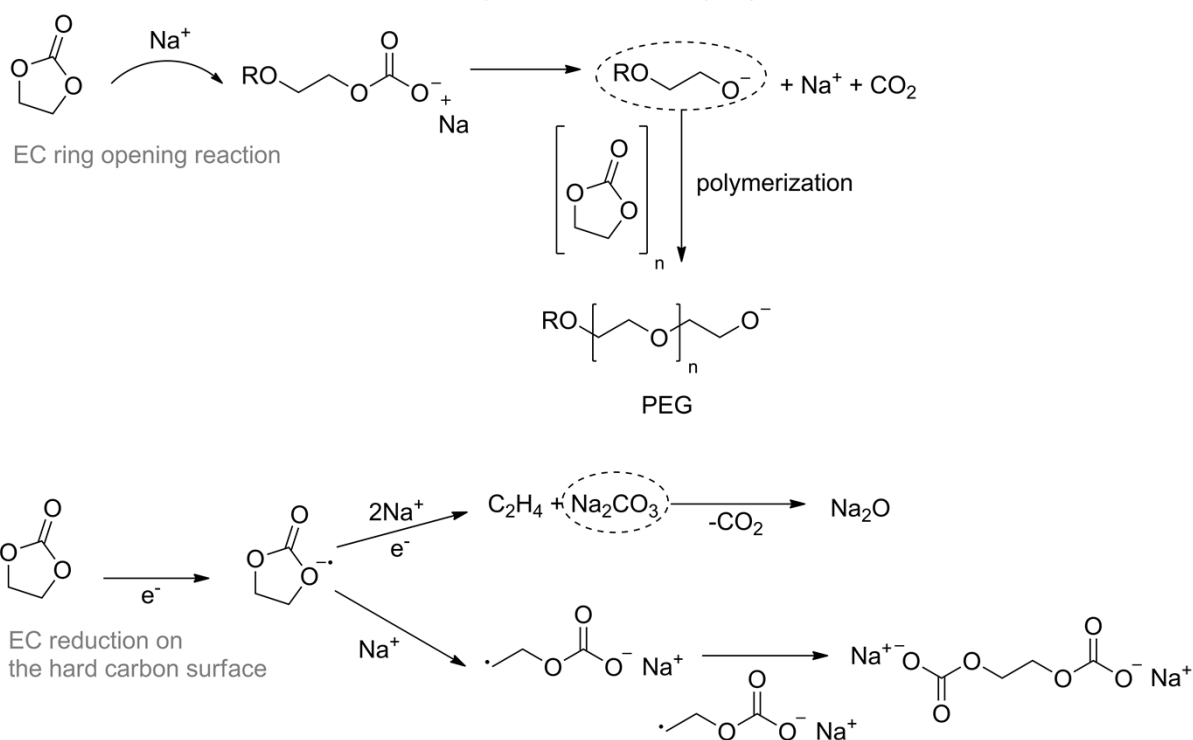


Figure S3. SEM micrographs of a, b) pristine CC@1400°C electrode and c, d) CC@1400°C electrode sodiated at 5 mV vs Na/Na⁺ at a current density of C/10.

Some of possible ethylene carbonate (EC) decomposition reactions:



Some of possible dimethyl carbonate (DMC) and NaPF₆ decomposition reactions:

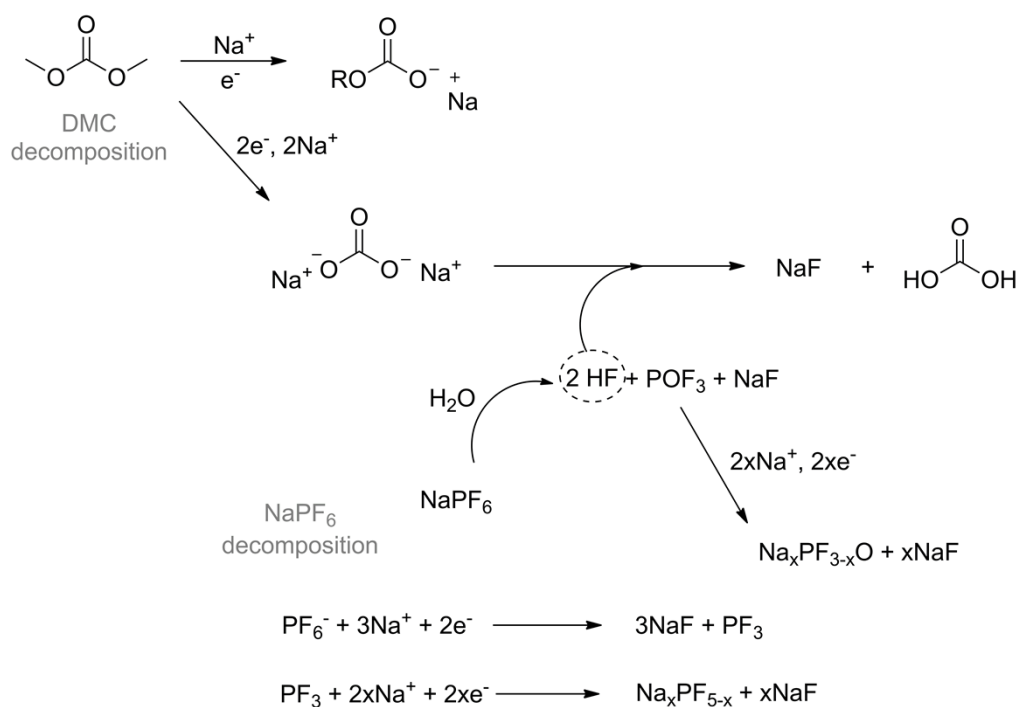


Figure S4. Some of the possible ethylene carbonate, dimethyl carbonate and NaPF₆ decomposition reactions and products in the SEI at the hard carbon electrodes surface.

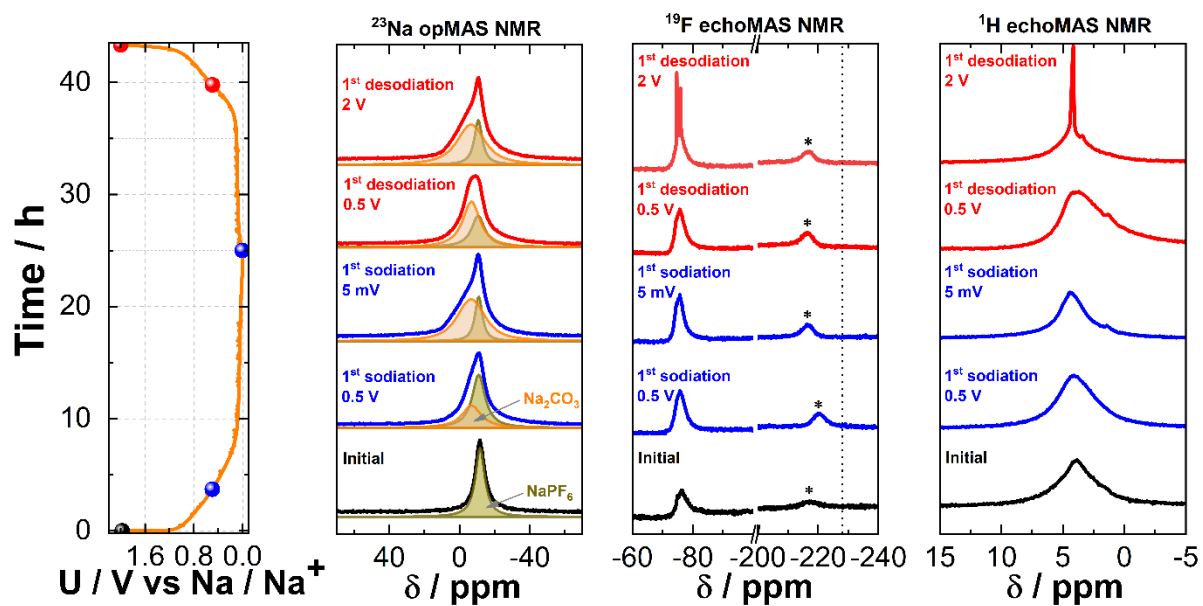


Figure S5. First cycle electrochemistry with related ^{23}Na , ^{19}F and ^1H ex-situ solid-state MAS NMR spectra of CC@1400°C powder extracted in the sodiated and desodiated state. The black circle on the galvanostatic curve indicates the position of the initial potential, the blue circles indicate the sodiated points, and the red circles indicate the two desodiated points. The dashed line in the ^{19}F graph shows the predicted position for the NaF signal.

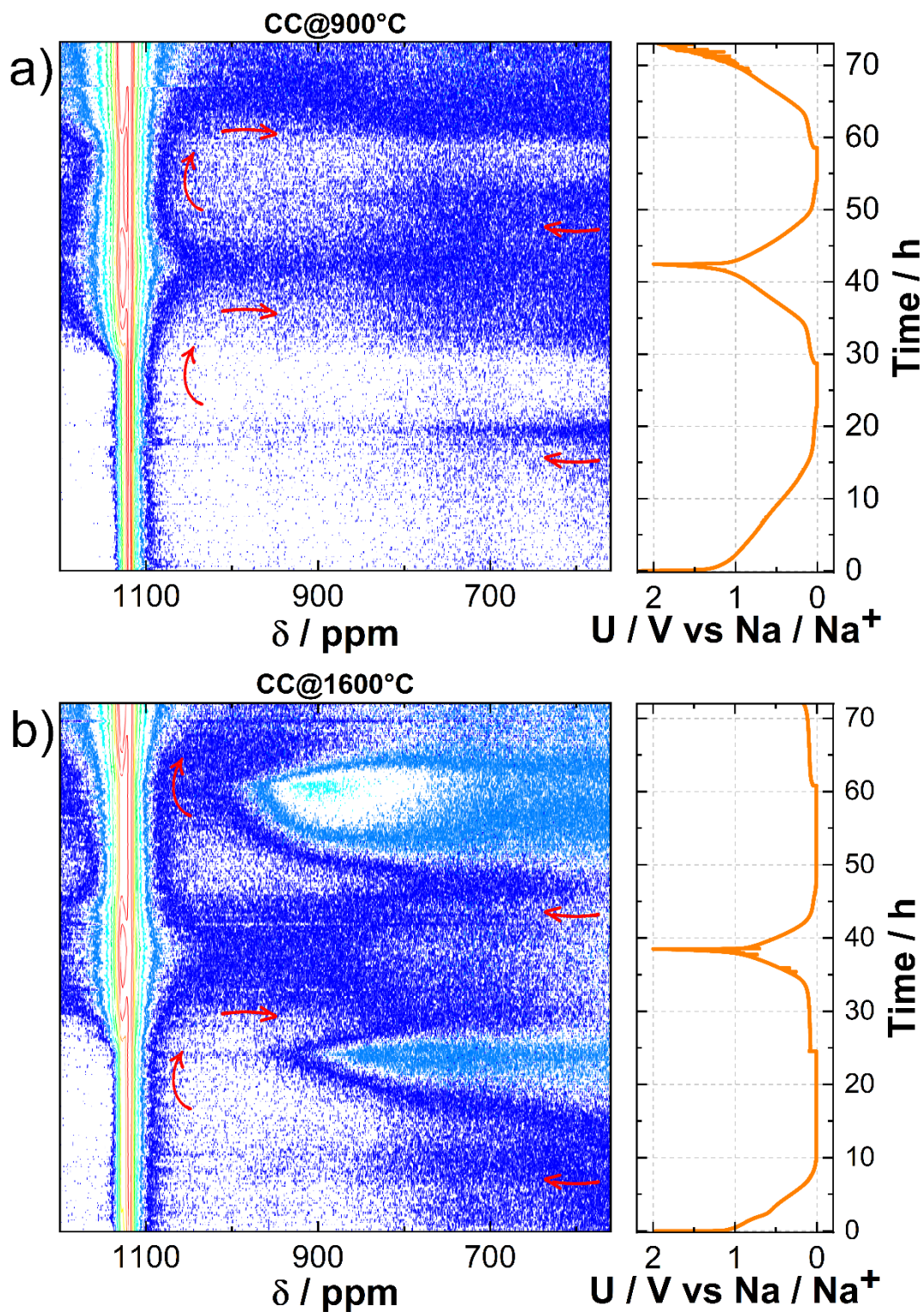


Figure S6. Spectrum of ^{23}Na operando solid-state NMR a) Na||CC@900°C and b) Na||CC@1600°C half cell at 90° orientation with respect to the external magnetic field of the spectrometer shown with a logarithmic plot of NMR signal intensity levels. Red arrows indicate the movement of an additional signal. Related galvanostatic curves of both measurements are added to the right.

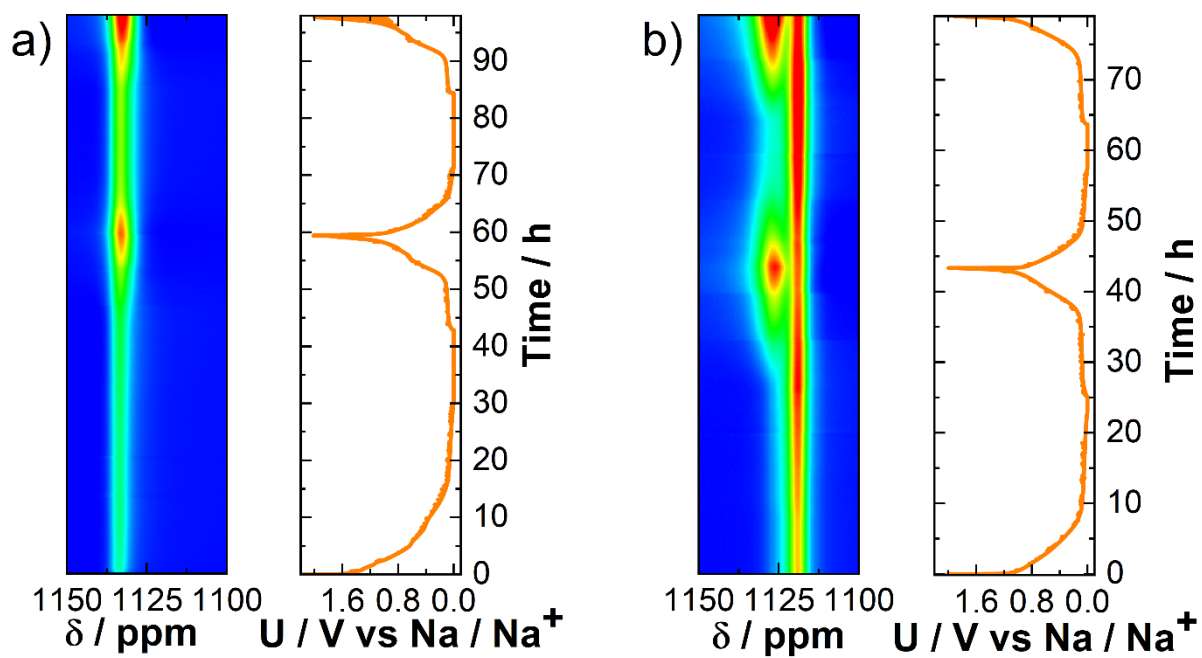


Figure S7. ^{23}Na operando solid-state NMR of metal Na signal $\text{Na}||\text{CC}@1400^\circ\text{C}$ half cell at 0° a) and 90° b) orientation with respect to the external magnetic field of the spectrometer. Related galvanostatic curves of both measurements are added to the right.

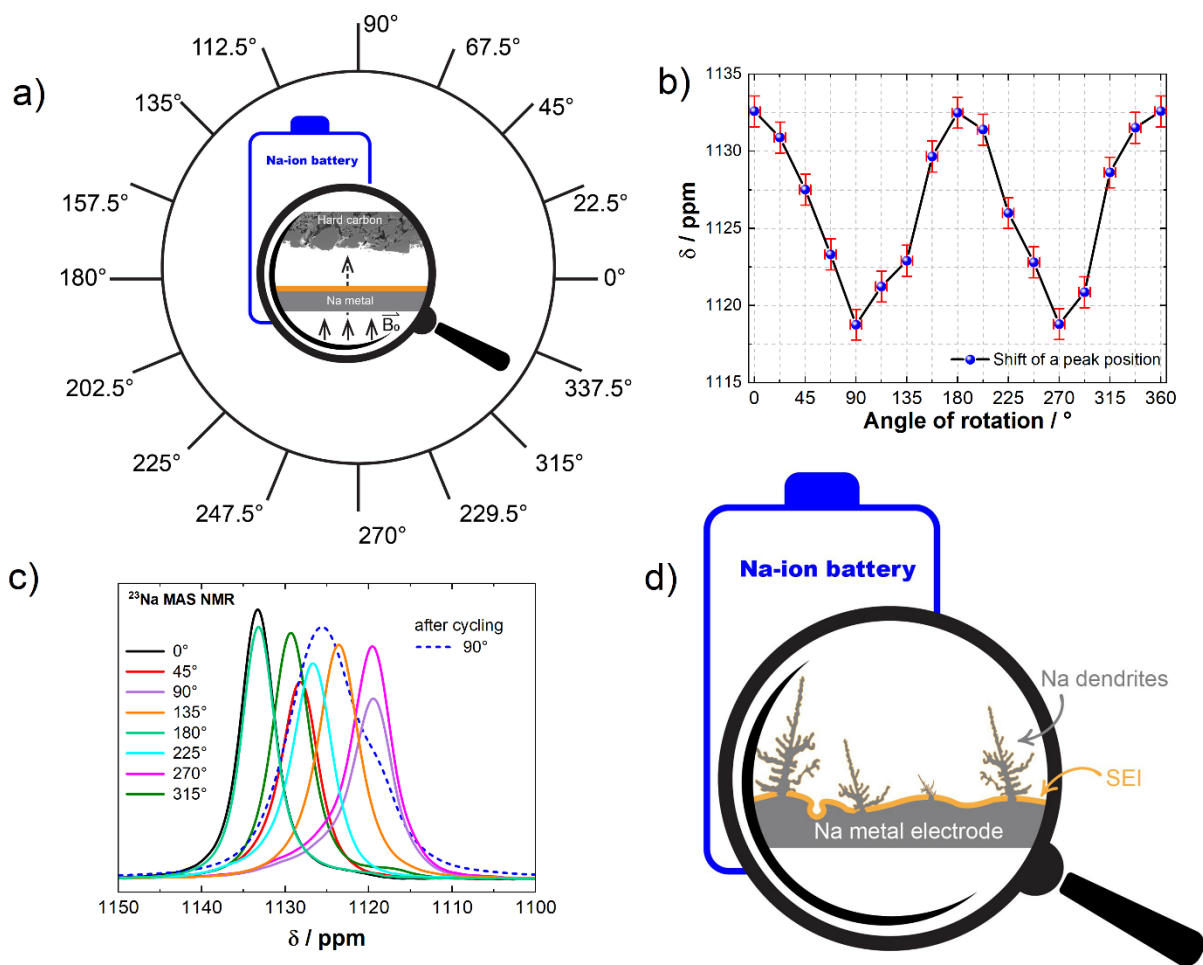


Figure S8. a) Schematic of the Na metal electrode position relative to the magnetic field of the spectrometer. b) Measured chemical shift as a function of angle relative to the magnetic field of the spectrometer. c) Measured spectra at each position of the electrode relative to the external magnetic field of the spectrometer. d) Sketch of dendrites on the surface of the Na metal electrode. The position of the SEI layer on the electrode surface is shown in orange.

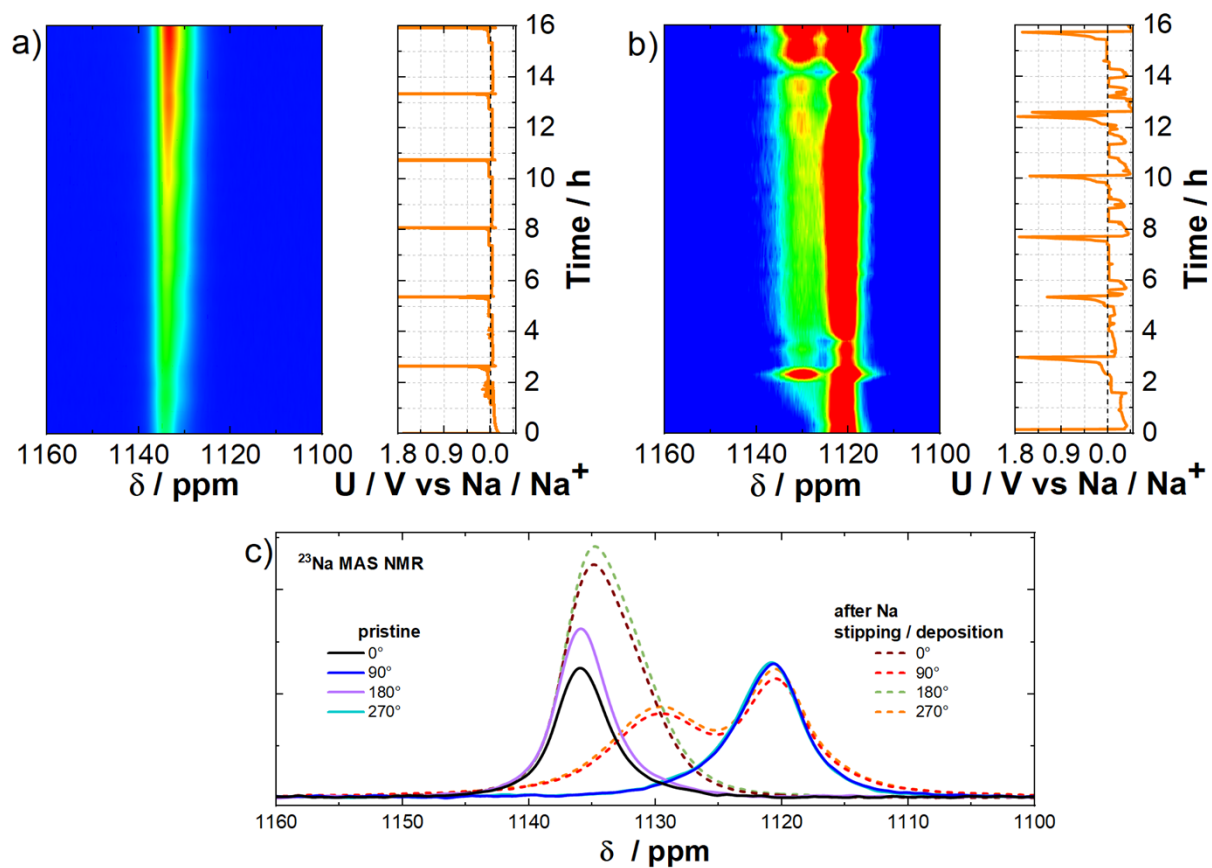


Figure S9. Spectrum of ^{23}Na operando solid-state NMR $\text{Na}||\text{Cu}$ cell at 0° a) and 90° b) orientation with respect to the external magnetic field of the spectrometer. Related galvanostatic curves of both measurements are added to the right. c) In-situ solid-state NMR spectrum before and after operando measurement at 4 different orientations of the $\text{Na}||\text{Cu}$ cell with respect to the external magnetic field.

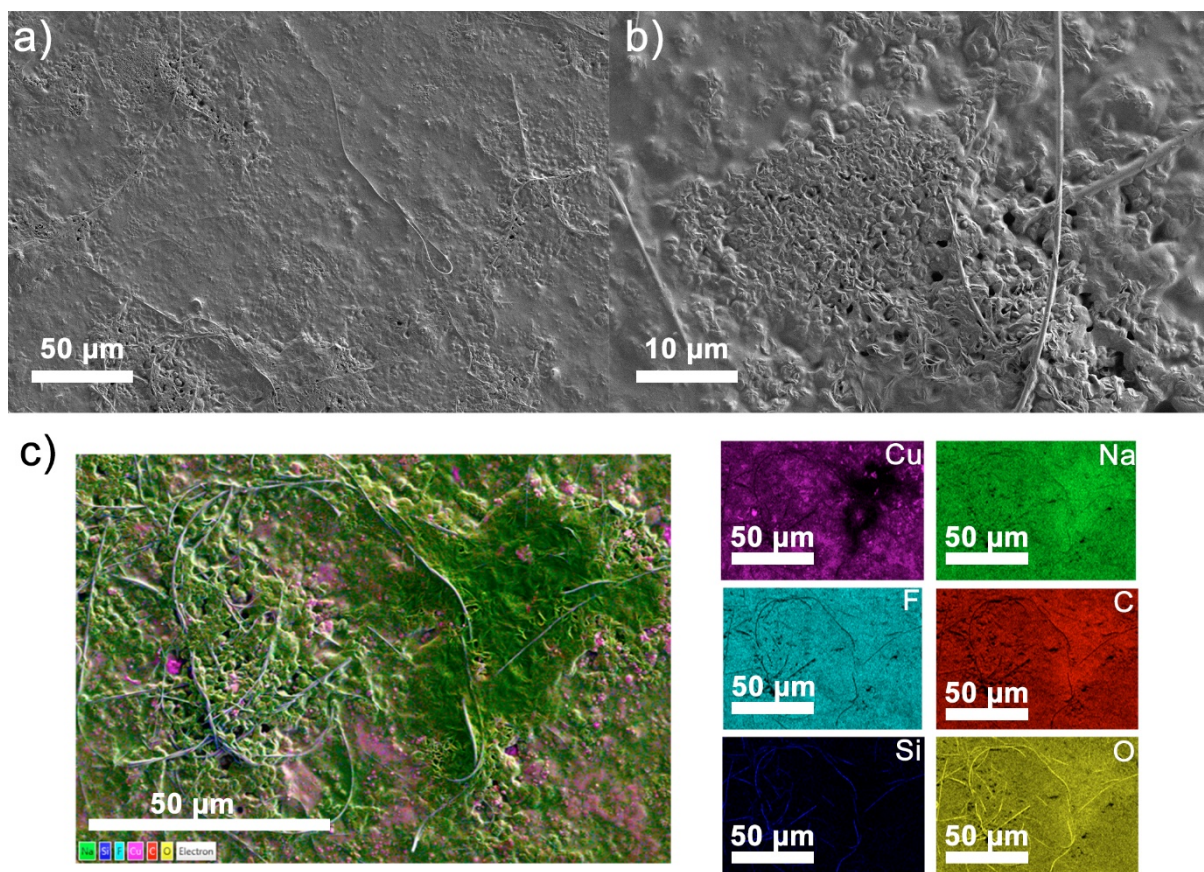


Figure S10. a) SEM micrographs of Cu electrode after stripping and deposition in Na||Cu cell; b) higher magnification of Na deposits on Cu electrode and c) EDX mapping of the Cu electrode after stripping and deposition in Na||Cu cell.

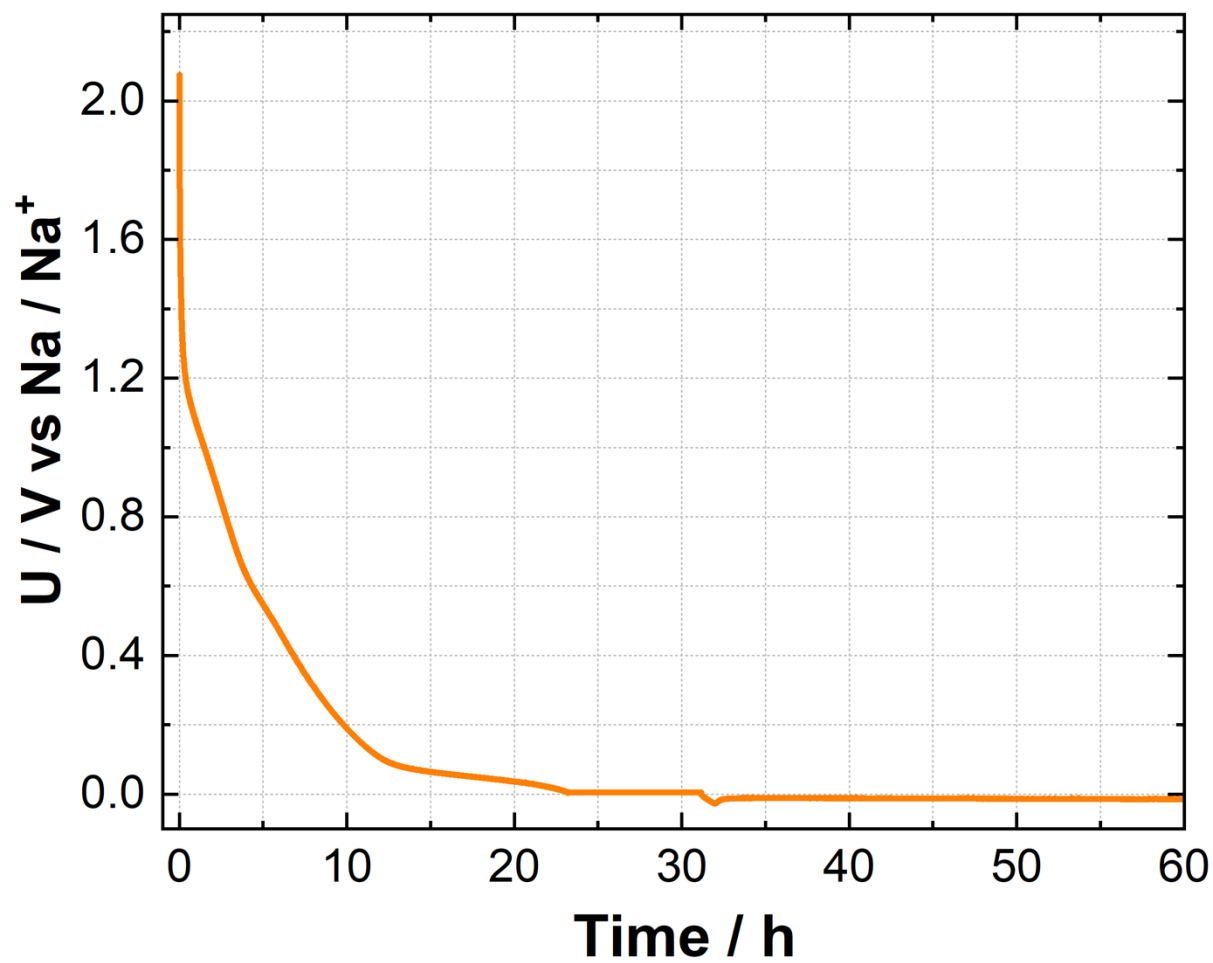


Figure S11. Voltage profile of CC@1400°C when sodiated to negative potentials.