Supporting information for :

Design guidelines to use optical fibers as state of charge sensors: an operando micro wide and small angle X-ray scattering study of an IR-fiber equipped smart Na-ion battery

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Figure S1: Picture of the pouch cells in the sample holder at the beamline.

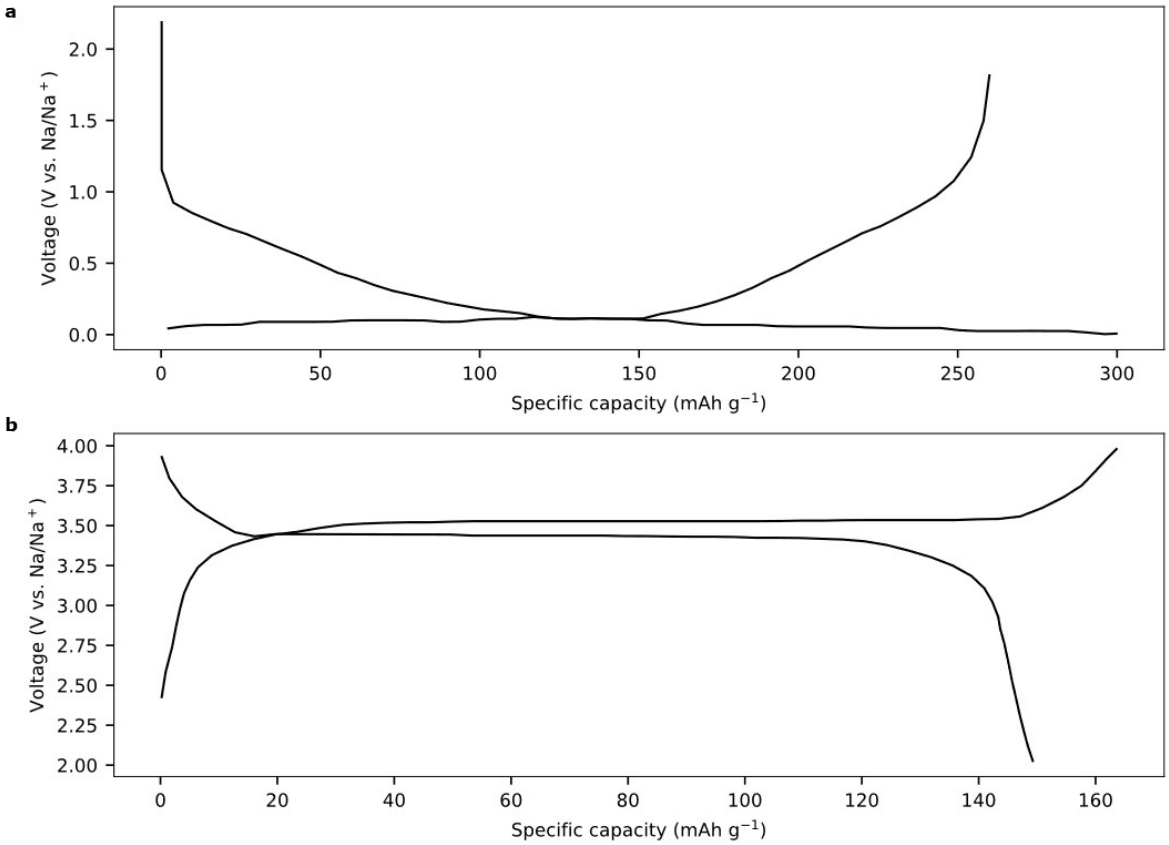

Figure S2 : The voltage profiles of (a) hard carbon (b) PBA Belcore free-standing electrodes.

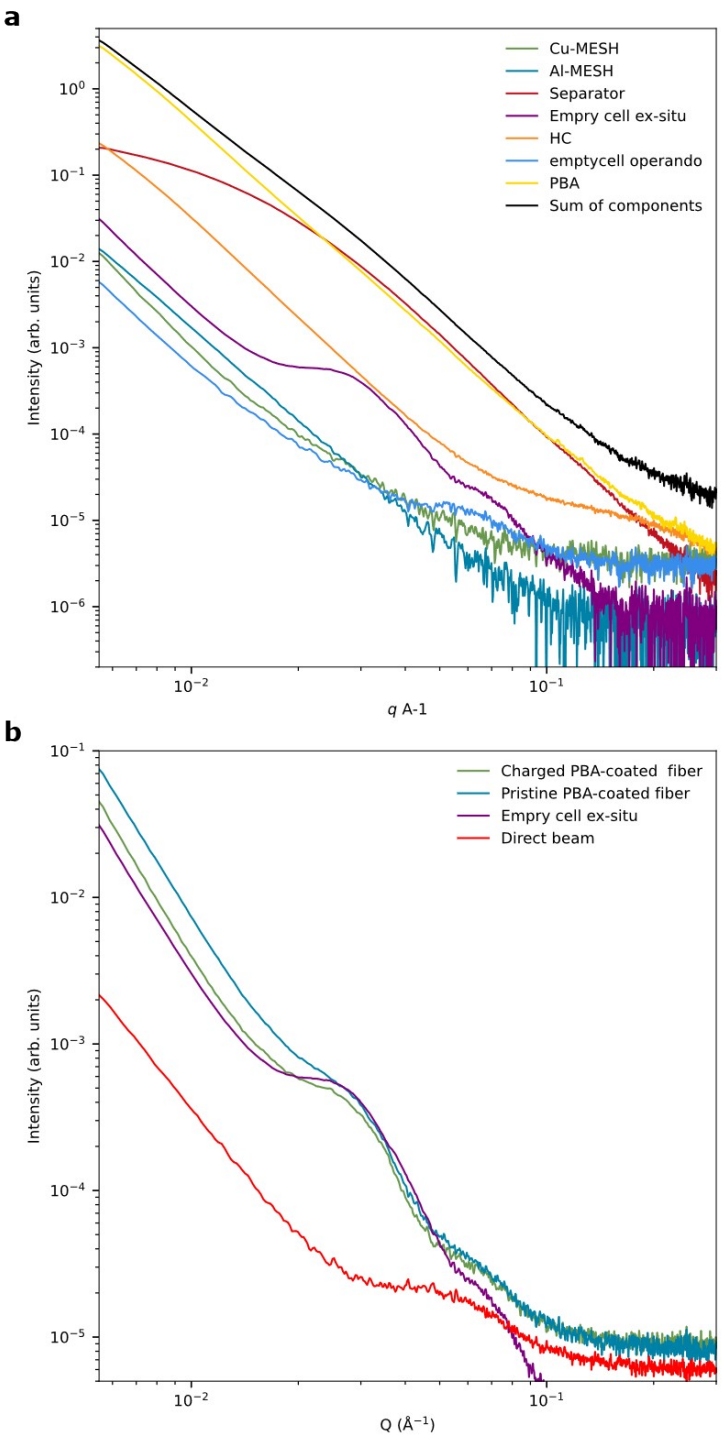

Figure S3 : (a) The SAXS profiles of different cell components. (b) The SAXS profiles of the charged PBA-coated, the pristine PBA-coated optic fiber, the direct beam, and the empty cell. The PBA-coated optic fiber samples were sealed in an empty cell. In the regions Q = 0.01 ~ 0.05 Å^{-1} and Q = 0.03 ~ 0.1 Å^{-1}, the SAXS intensity is mainly contributed by the empty cell and the direct beam. By contrast, the intensity difference observed at $Q = 0.0055 ~ 0.02 Å^{-1} originates from electron density variations associated with volume expansion and desodiation of charged PBA.

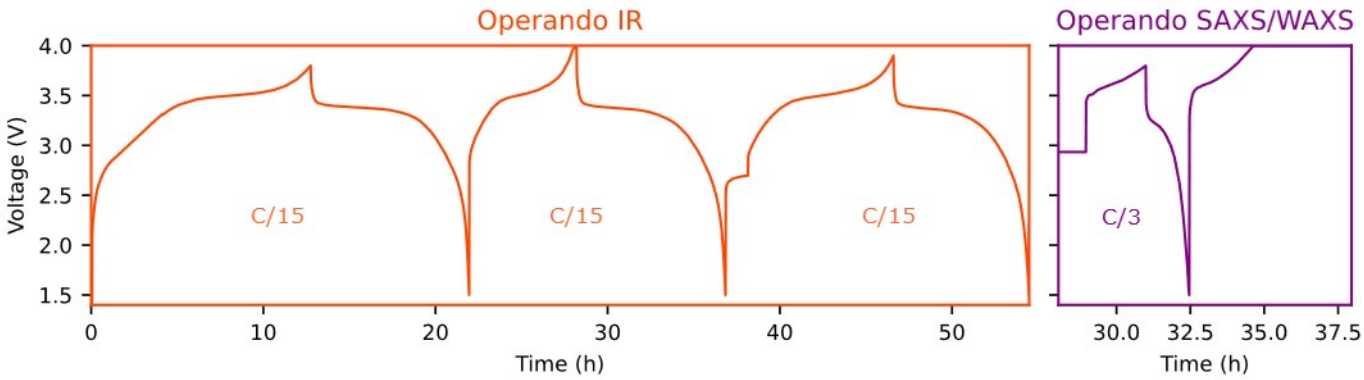

Figure S4 : The voltage profile of cell 2 during operando IR and operando SAXS/WAXS.

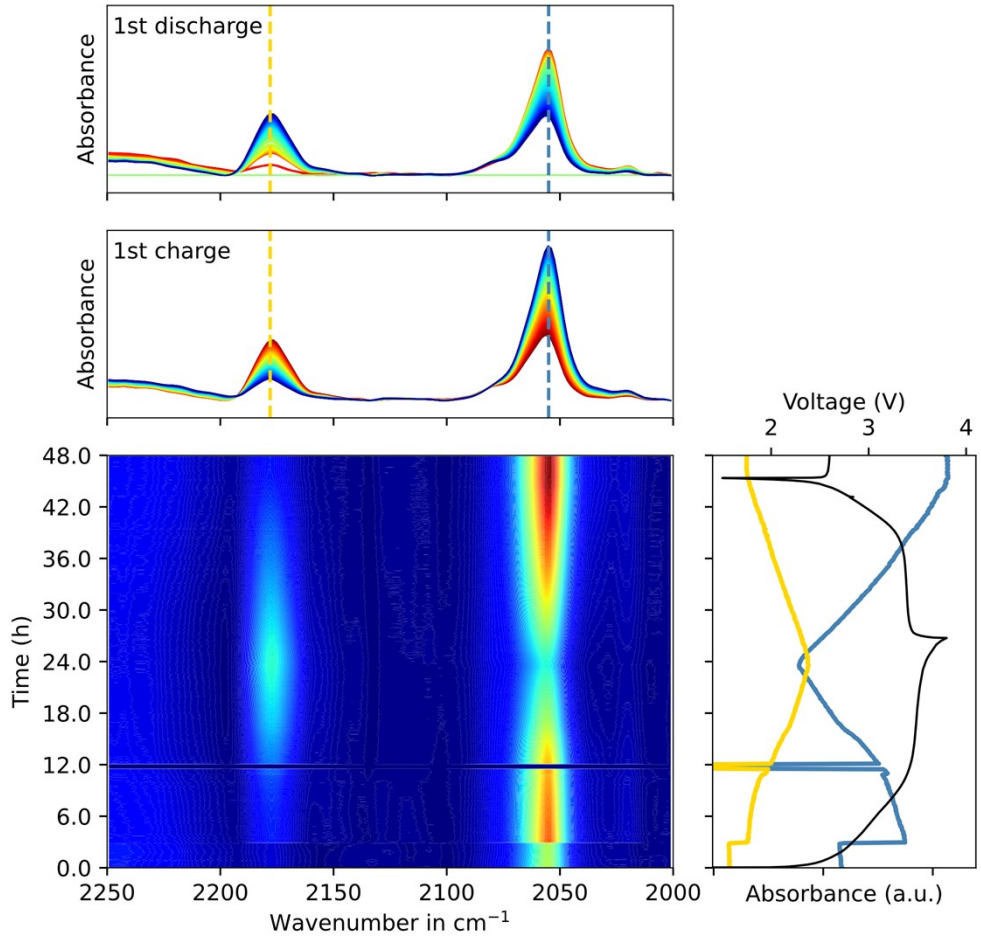

Figure S5: The operando IR contour of the first cycle of cell 1. Rainbow colours of the lines for the top graph correspond to different SoCs from blue to red (blue is the beginning of charge or discharge, and red is the end). The colour scale in the central panel corresponds to infrared signal intensity. Low intensity is blue and high intensity is red. Yellow and blue lines on the right side graph correspond to the absorbance at 2178 and 2055 cm^{-1}, respectively.

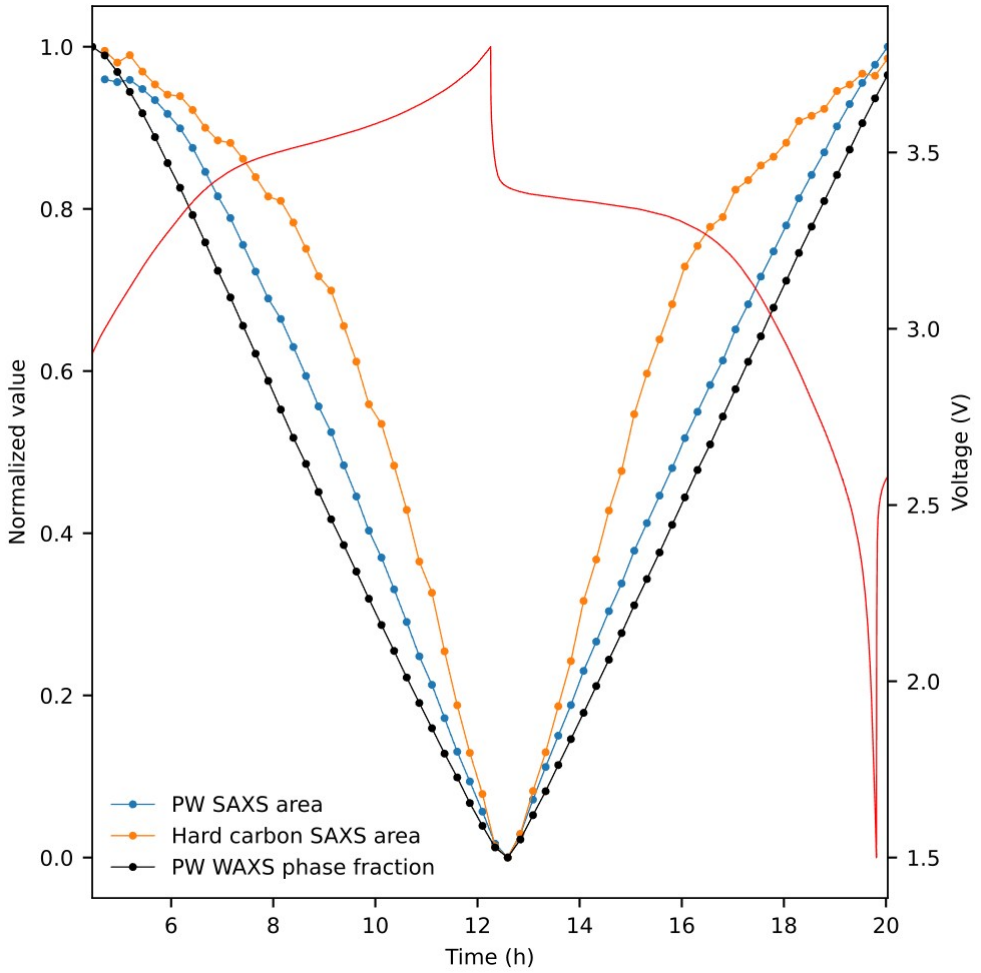

Figure S6 : The normalized profiles of integrated SAXS intensity in PBA and HC regions and PW WAXS phase fraction. All profiles are normalized from 0 to 1.

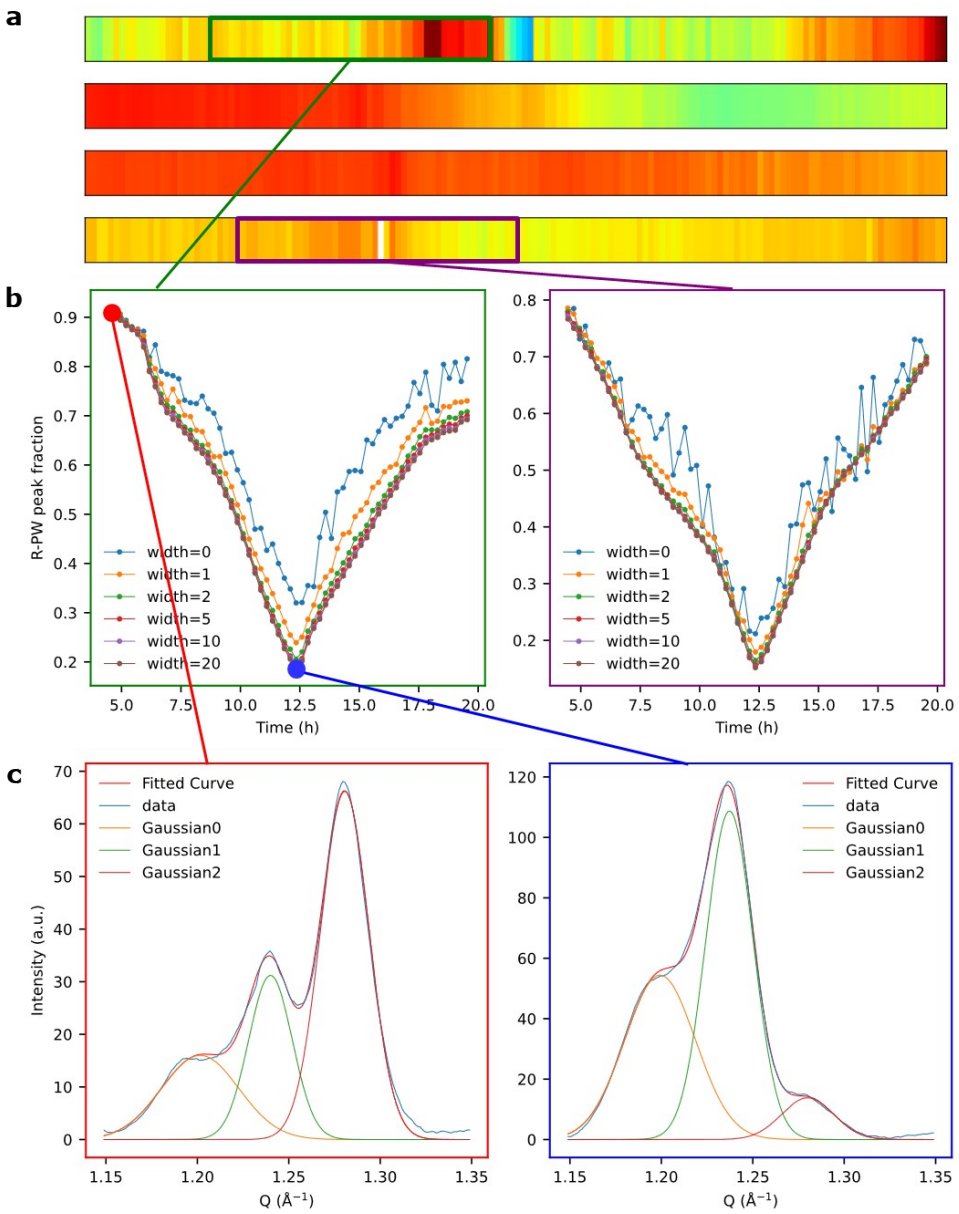

Figure S7: (a) Smallmaps composed of four line scans. The colorbar corresponds to the R-PW peak fraction as defined in the main text. Red and green corresponds to a high and low peak fraction, respectively. The green and purple rectangles are zones which will be analysed in more detail below. (b) WAXS R-PW peak fraction in different regions. The width parameter denotes the number of pixels averaged on the left and right sides of the fiber pixel, respectively. Thus, width = 0 corresponds to fiber pixels only, while width = 20 corresponds to the fiber pixels plus 40 surrounding pixels. The profiles converge at width = 1, indicating that the perturbation induced by the optical fiber is confined to its immediate vicinity. (c) Three-Gaussian peak fitting of background-removed WAXS profiles in the range 1.15–1.35 Å, shown at the beginning of charge (red) and at the end of charge (blue). The three Gaussian peaks correspond to $(200)_{T\text{-}PY}$, $(200)_{T\text{-}PY}$, and $(012)_{R\text{-}PW}$, respectively.

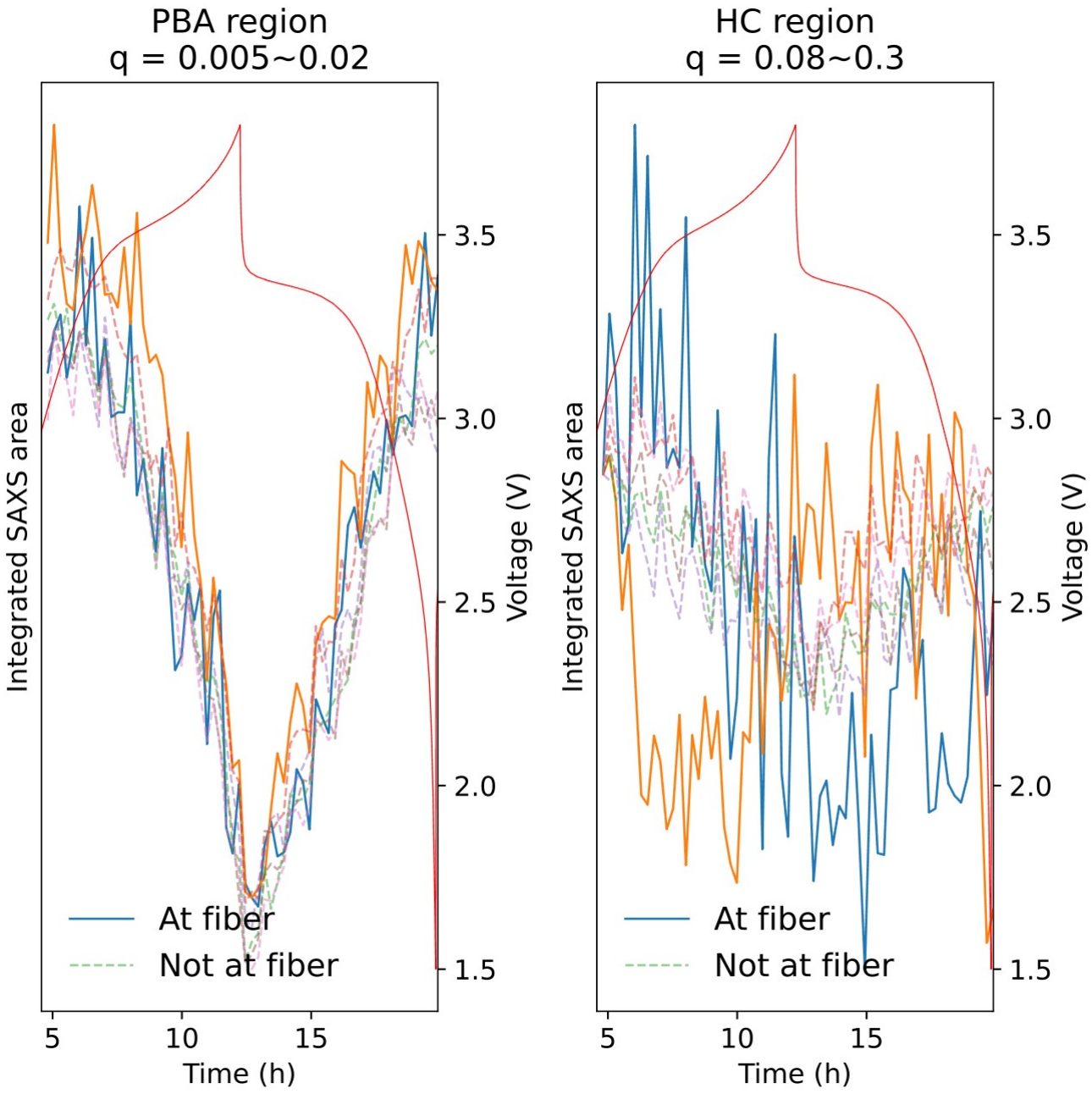

Figure S8: The integrated SAXS intensity profiles of different Smallmaps pixels. The solid lines show the profiles at the fiber position, and the dashed lines are profiles far from the fiber position. In the PBA region, the fiber has little effect on the SAXS intensity, while in the HC region, the fiber greatly affects the SAXS intensity, which makes analyzing the side effect on the HC anode induced by the optical fiber difficult.

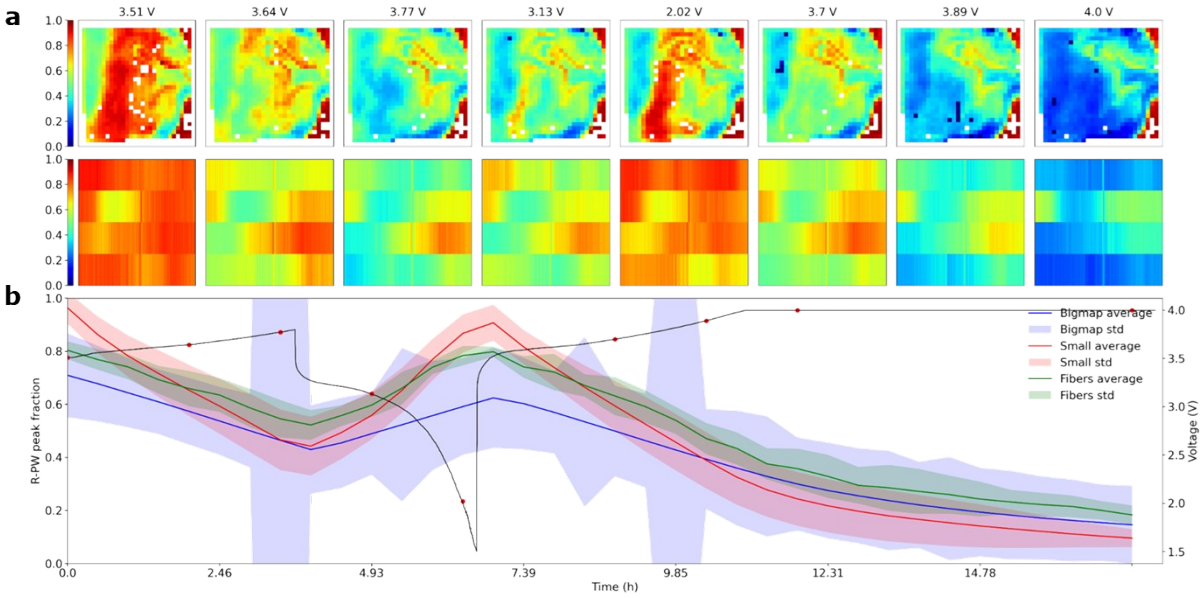

Figure S9 (a) Bigmaps (top) and Smallmaps (bottom) of the WAXS R-PW peak fraction for cell 2. (b) Voltage profile of the C/3 cycle, with red dots marking the voltages at which the maps in (a) were recorded. The panel also shows the average SoS (solid lines) and SoS distribution (shaded areas) for each region. At the higher C-rate, the sodiation rate—reflected in the slope of the profile—is significantly lower at the fiber position (green) compared to the surrounding region (red). This provides clear evidence that the reaction perturbation induced by the optical fiber is a general phenomenon, independent of the cell-specific sodiation heterogeneity patterns.

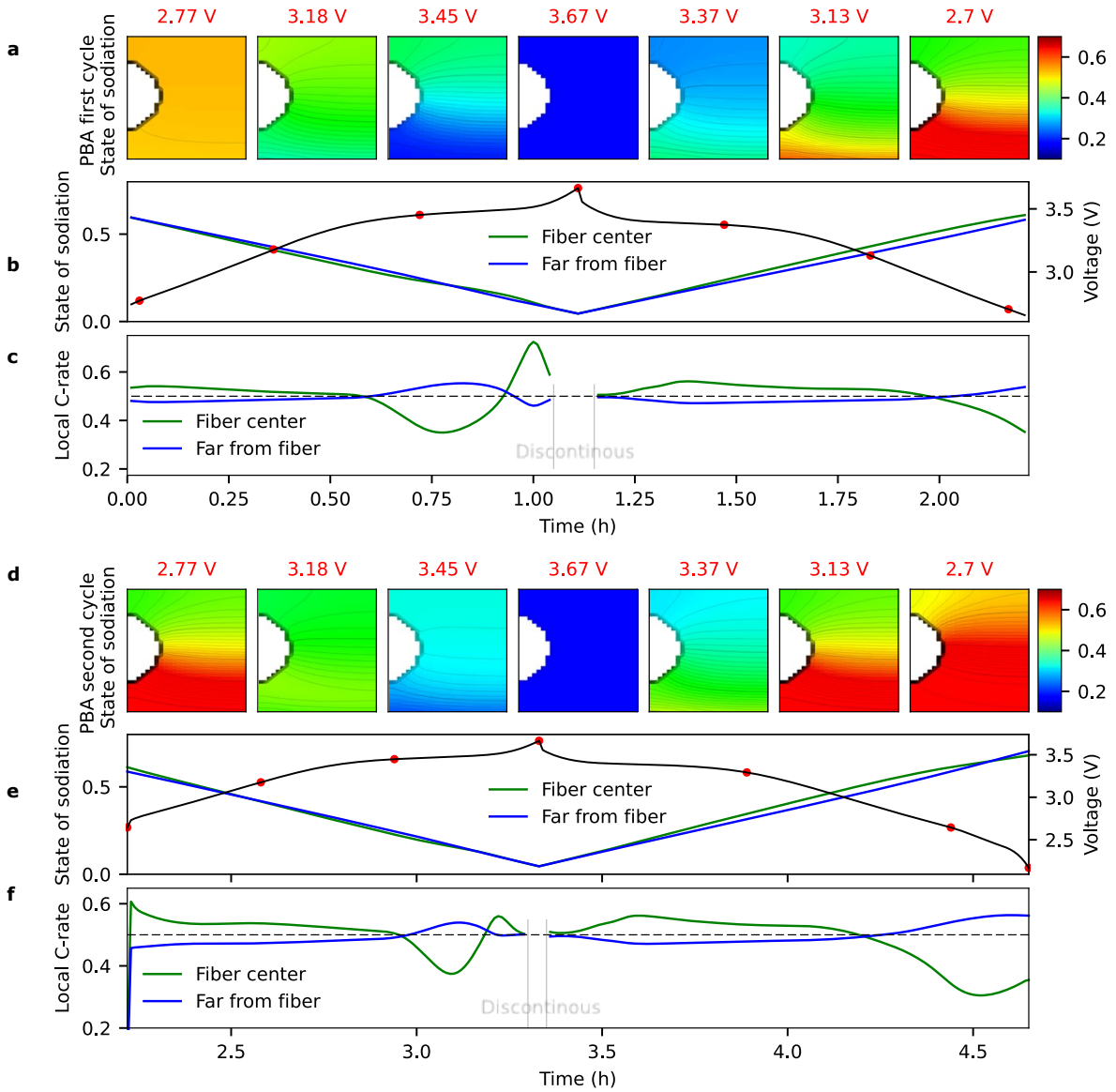

Figure S10 The P3D simulation of the uniform PBA porosity configuration (model 1). (a) and (b) The evolution of the sodium concentration distribution in the PBA cathode during the first cycle and the second cycle at a 0.5 C rate, respectively. (b) and (e) SoS profiles in the two regions of the first and the second cycle, plotted alongside the cell's OCV curve. Red dots correspond to the voltages of the snapshots shown in (a) and (d). (c) and (f) Local C-rates of the first and the second cycle, calculated by deriving the SoS curves. Blue and green lines correspond to the fiber position and far from the position, respectively.

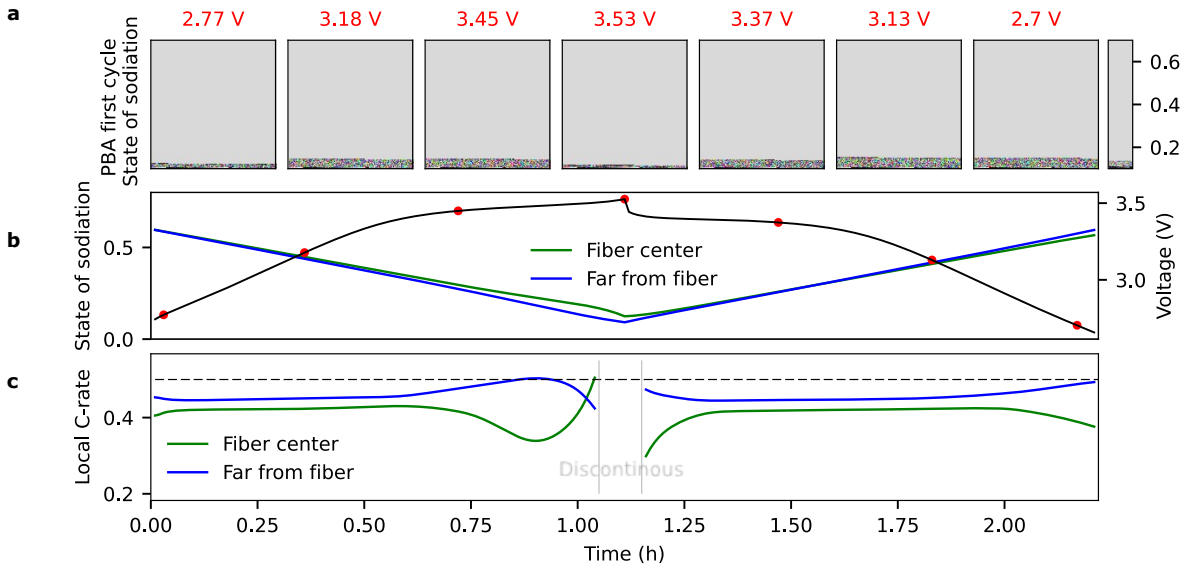

Figure S11 (a) Evolution of the sodium concentration distribution in the PBA cathode during the first cycle at a 0.5 C rate. (b) SoS profiles in the two regions, plotted alongside the cell's OCV curve. Red dots correspond to the voltages of the snapshots shown in (a). (c) Local C-rates of the first cycle, calculated by deriving the SoS curves. Blue and green lines correspond to the fiber position and far from the position, respectively.