

Electronic Supplementary information

New Insights into the Phase Evolution in CuS during Lithiation and Delithiation Processes

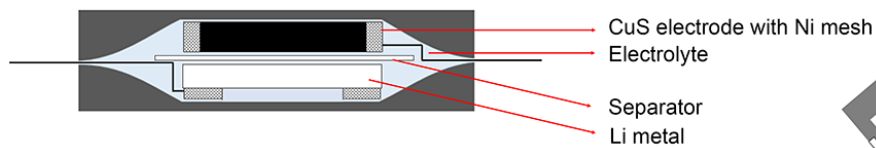
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Pouch type cell for *operando* XRD



Operando XRD, Transmission mode

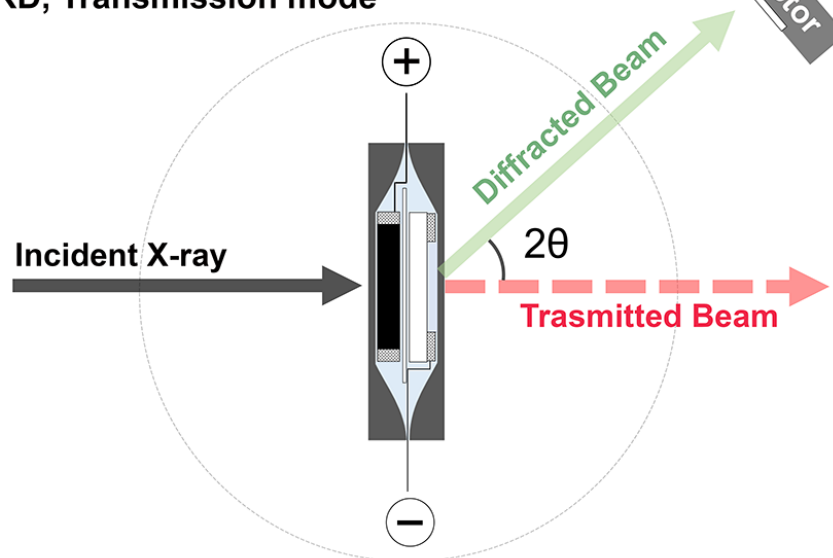


Figure S1. Schematics of the *operando* XRD pouch cell (top) and measurement configuration (bottom).

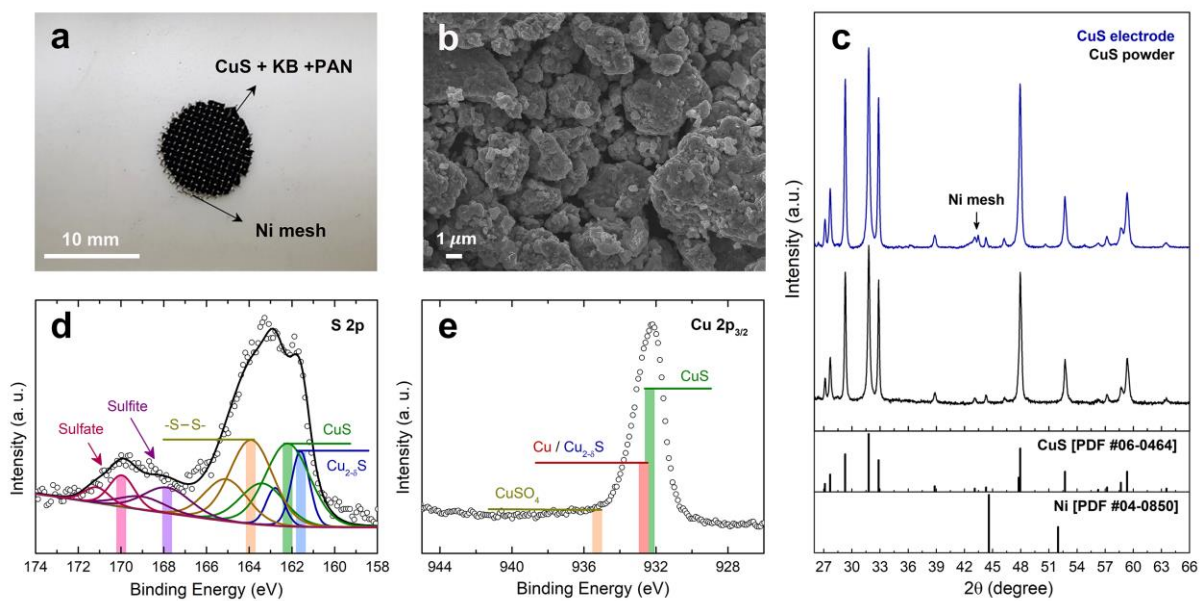


Figure S2. (a) Optical image and (b) SEM image of the as-prepared CuS/Ni mesh electrode; (c) XRD patterns of the commercial CuS powder and the electrode; XPS spectra of (d) S 2p and (e) Cu 2p_{3/2} core levels. The reference patterns of CuS and Ni are shown in the bottom panels of (c).

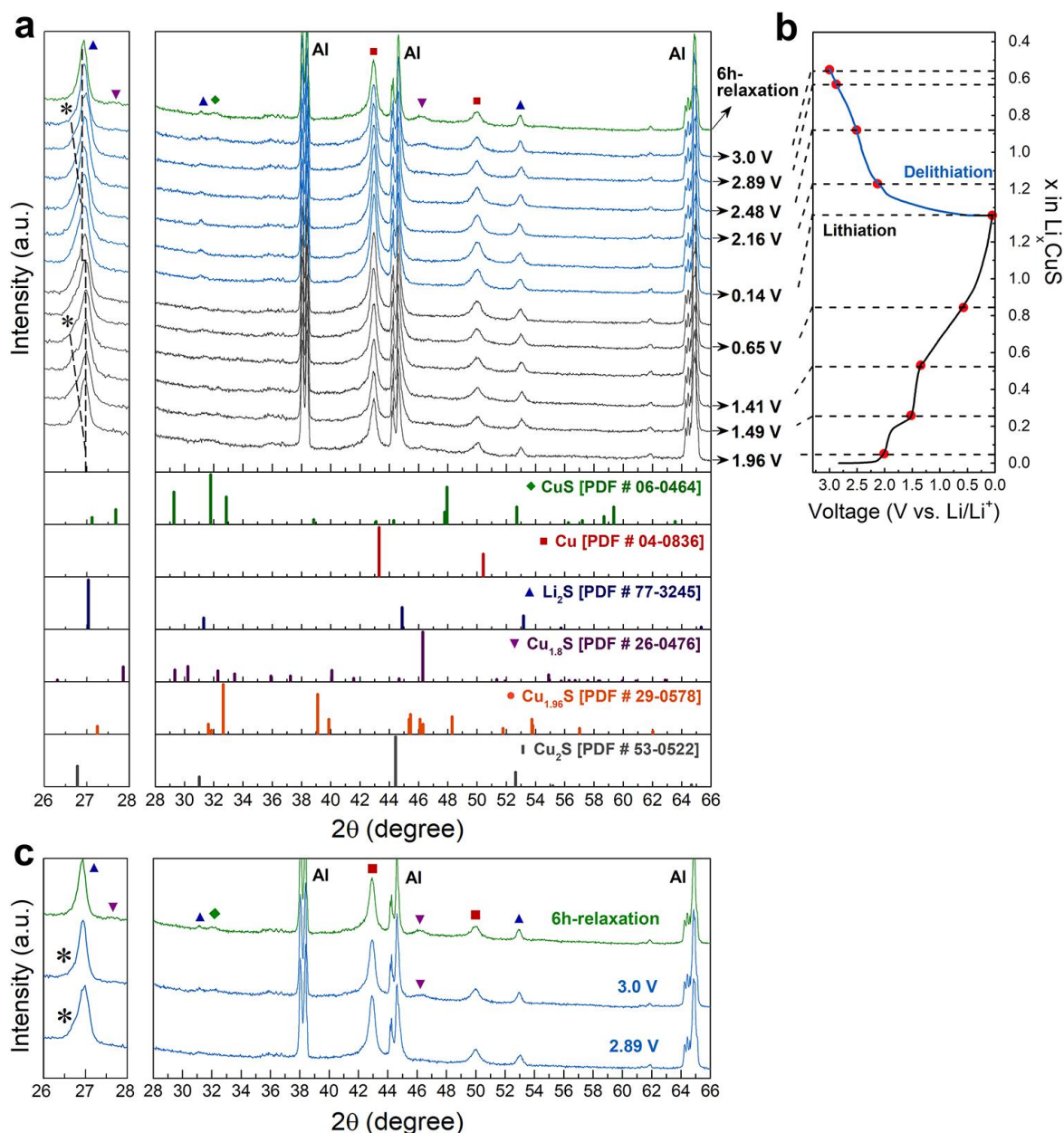


Figure S3. Operando XRD results for a Li|CuS cell during the second lithiation and delithiation in the voltage range of 0.05-3.0 V at a current density of 100 mA g^{-1} . (a) XRD; (b) voltage profile as a function of the Li amount (x) in Li_xCuS ; and (c) XRD patterns of the cells delithiated to 2.89 V (bottom), 3.0 V (middle), and followed by a 6h-relaxation (top). The reference XRD patterns of the CuS, Cu, Li_2S and $\text{Cu}_{2-\delta}\text{S}$ phases are displayed in the bottom panels of (a). The aluminum peaks originated from the laminated films of the pouch cell.

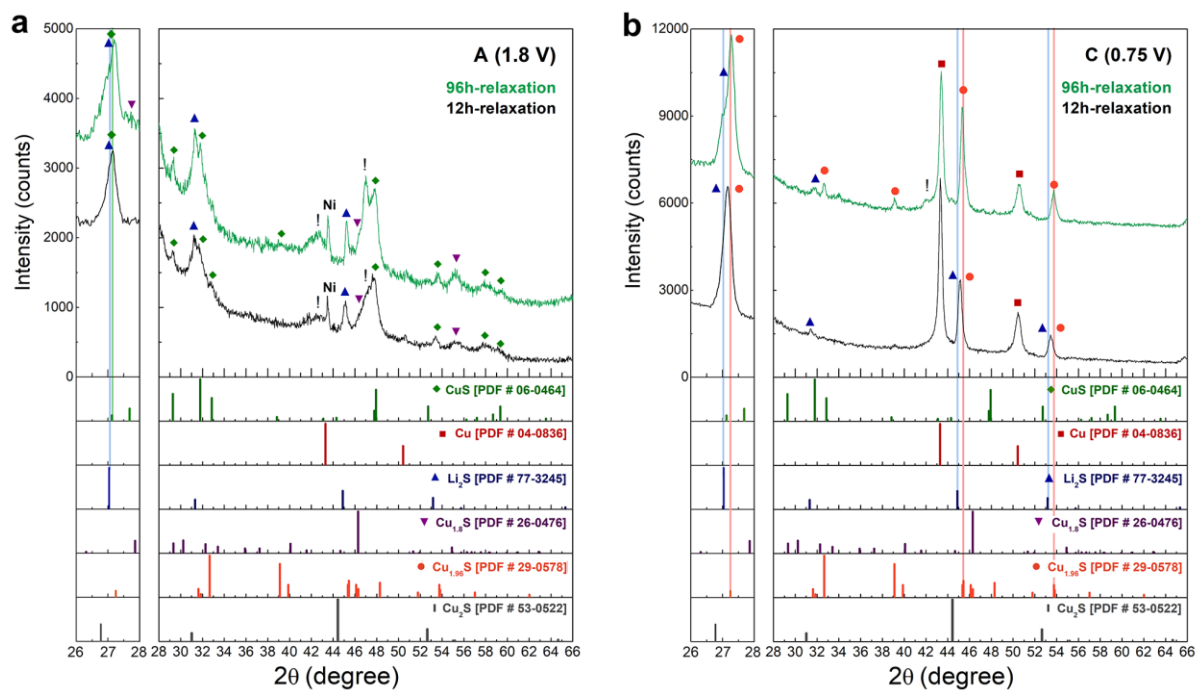


Figure S4. *Ex-situ* XRD patterns for a Li|CuS cell after lithiation down to (a) 1.8 V and (b) 0.75 V, followed by relaxation for 12 h and 96 h. The reference XRD patterns of the CuS, Cu, Li_2S and $\text{Cu}_{2-\delta}\text{S}$ phases are displayed in the bottom panels of (a) and (b).

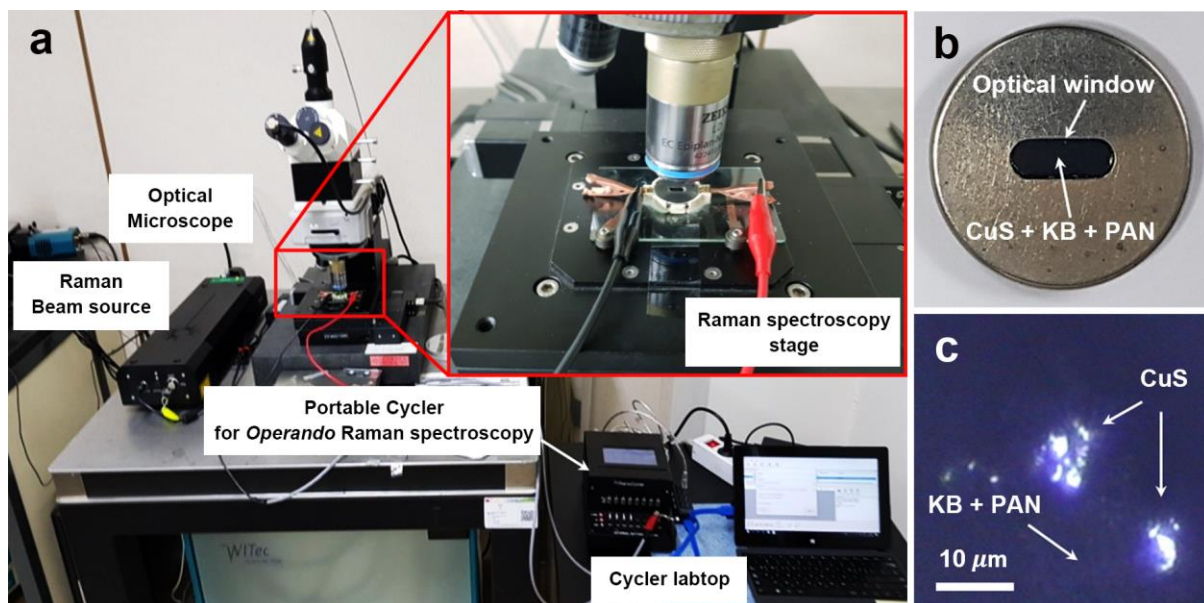


Figure S5. (a) Experimental set-up, (b) customized coin-type cell and (c) optical micrograph of the CuS electrode for *operando* Raman spectroscopy.

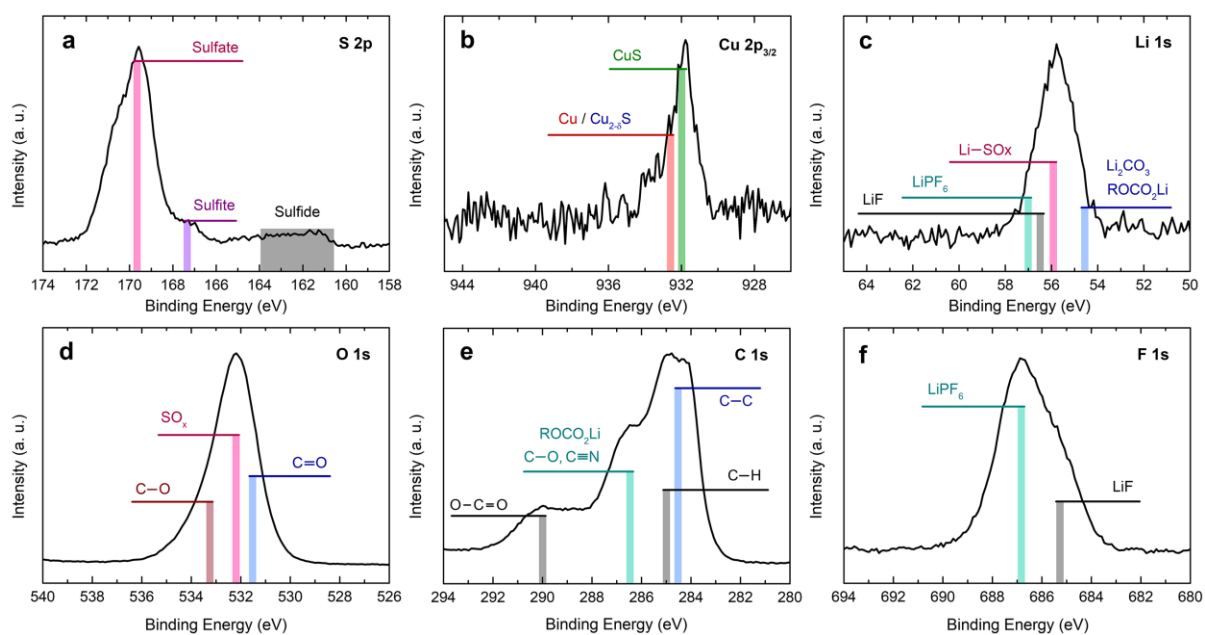


Figure S6. *Ex-situ* XPS spectra of the CuS electrode rested in the OCV state for 12 h without surface etching. (a) S 2p spectrum; (b) Cu 2p_{3/2} spectrum; (c) Li 1s spectrum; (d) O 1s spectrum; (e) C 1s spectrum; and (f) F 1s spectrum. Relevant reference components are indicated with colored lines.

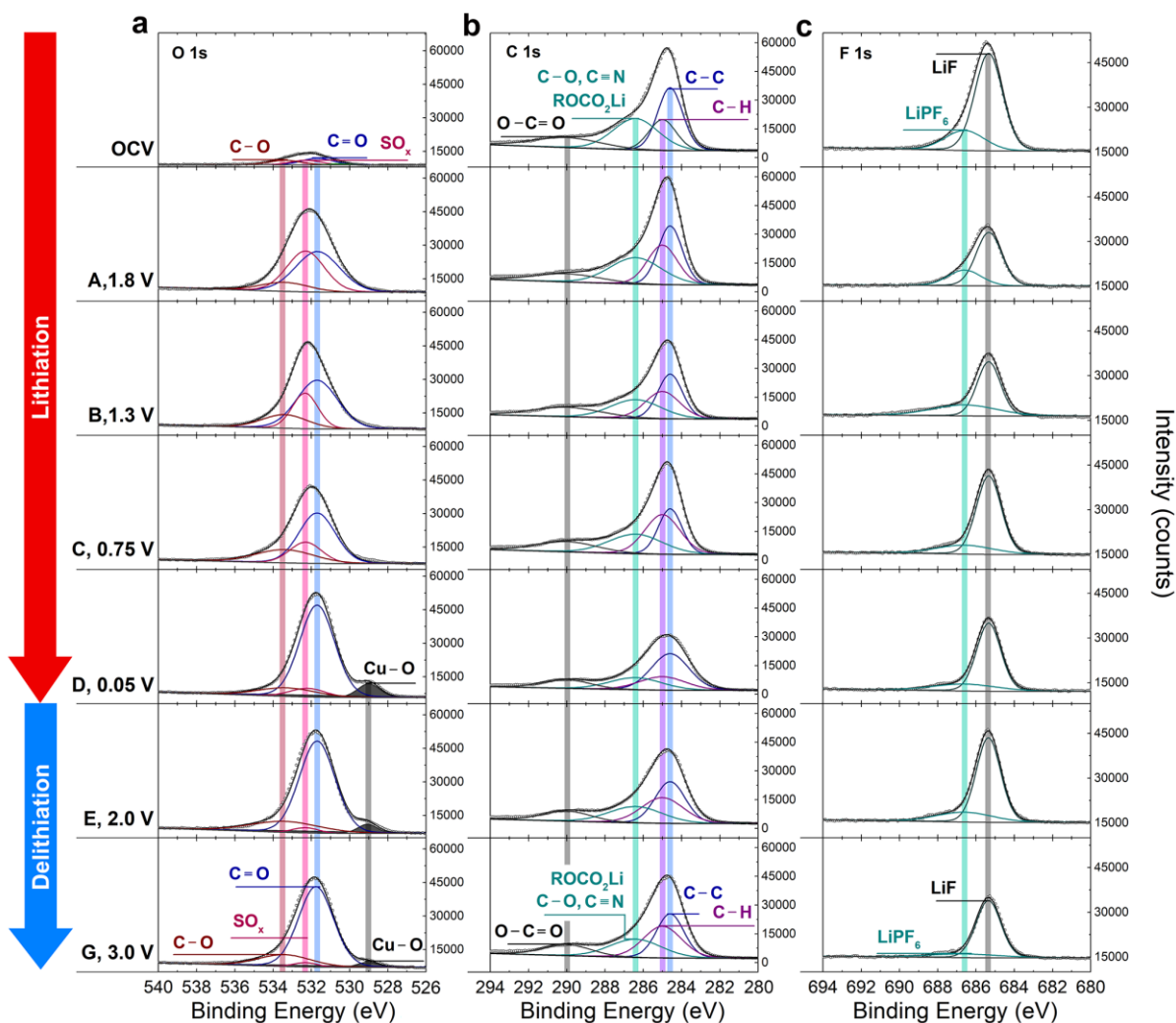


Figure S7. *Ex-situ* XPS spectra of CuS electrodes with different degrees of lithiation ('A'-'D') and delithiation ('E', 'G') during the first cycle in the voltage range of 0.05-3.0 V at a current density of 100 mA g⁻¹. (a) O 1s spectra; (b) C 1s spectra; and (c) F 1s spectra. Relevant reference components are indicated with colored lines.

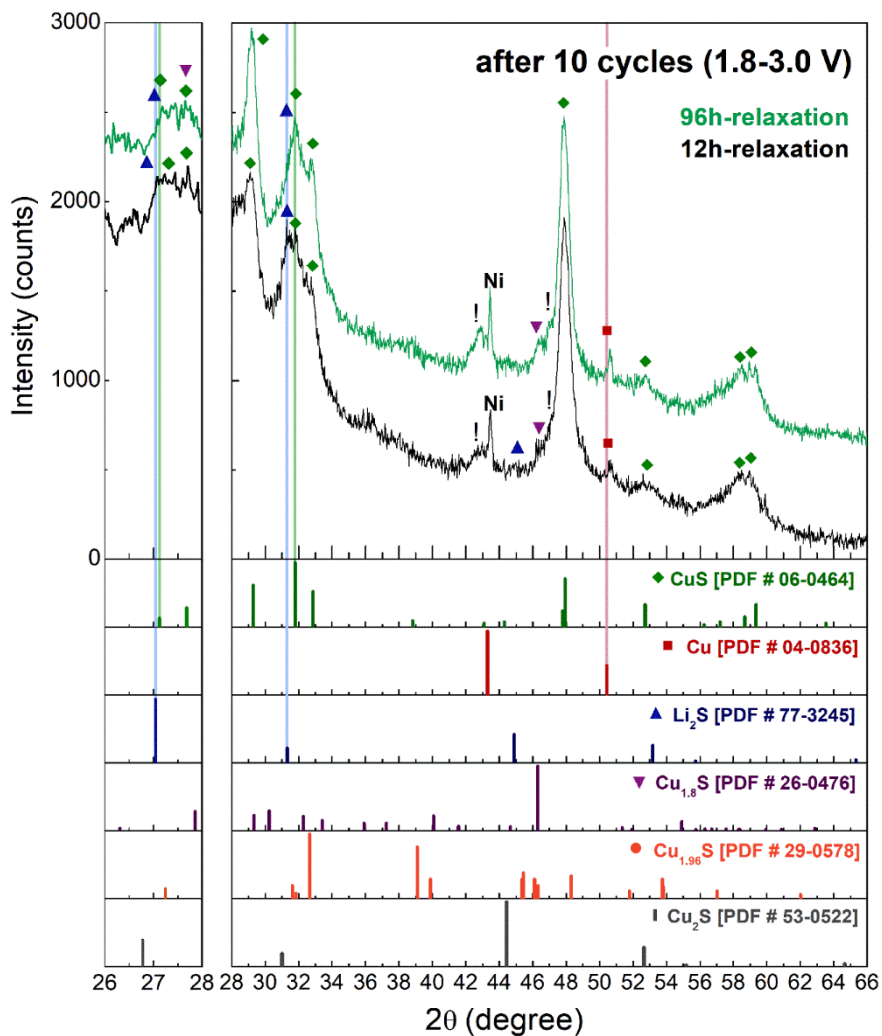


Figure S8. *Ex-situ* XRD patterns of the electrodes after 10 cycles in the voltage range of 1.8-3.0 V vs. Li/Li⁺, followed by relaxation for 12 h and 96 h. The reference XRD patterns of the CuS, Cu, Li₂S and Cu_{2-δ}S phases are displayed in the bottom panels.