Electronic Supplementary Material (ESI) for Nanoscale.

Miniature all-solid-state heterostructure nanowire Li-ion batteries for nanoscale diagnosis of electrochemical processes

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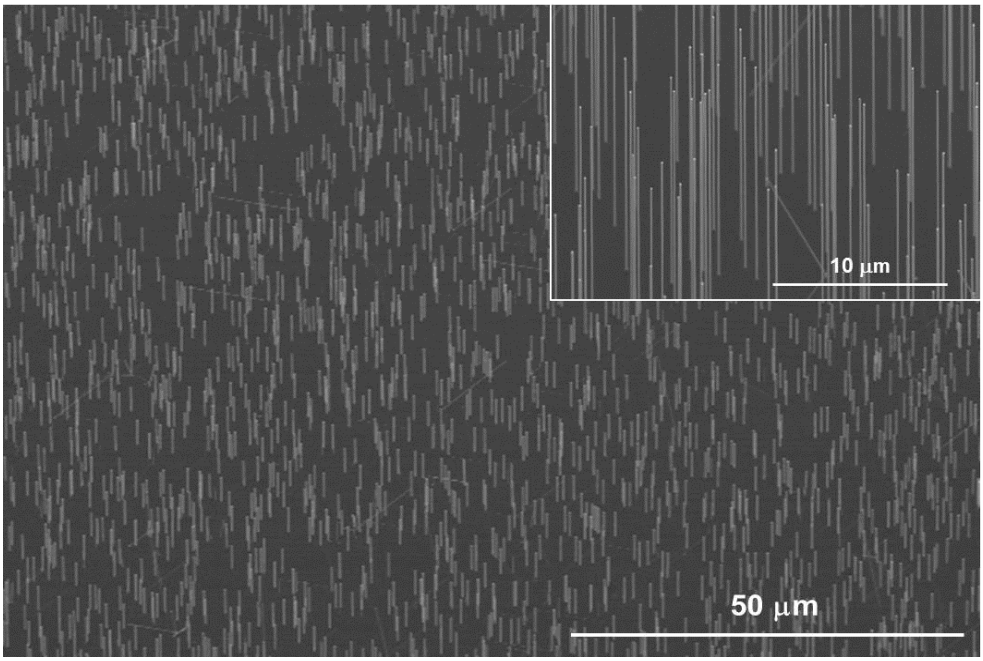


Fig. S1. FESEM, VLS-grown uniform single-crystalline Si NWs grown on a (111) Si wafer.

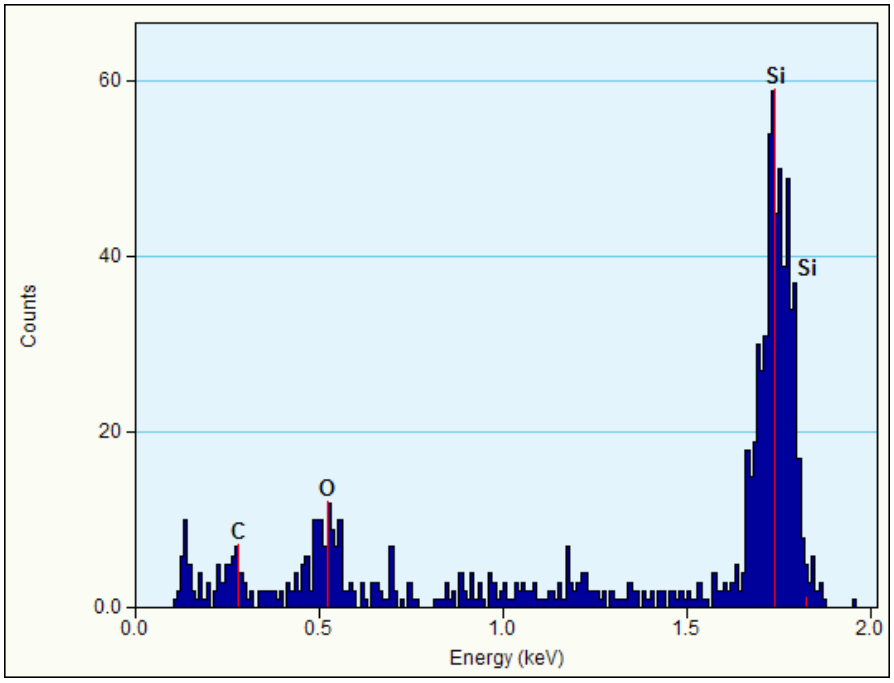
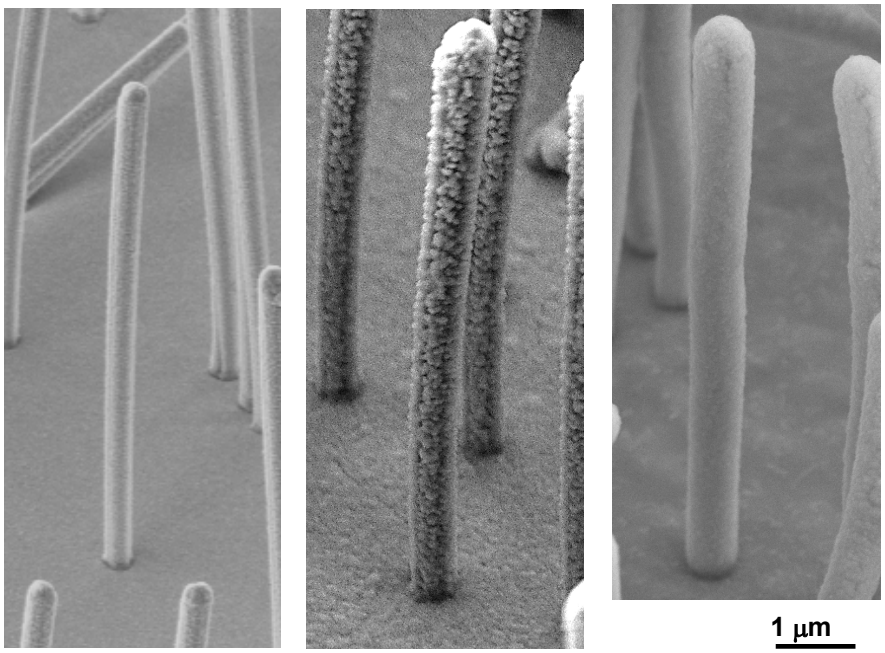
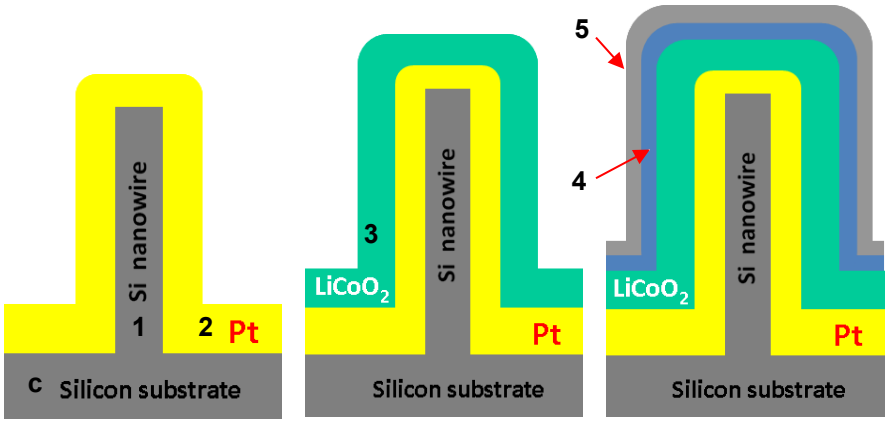
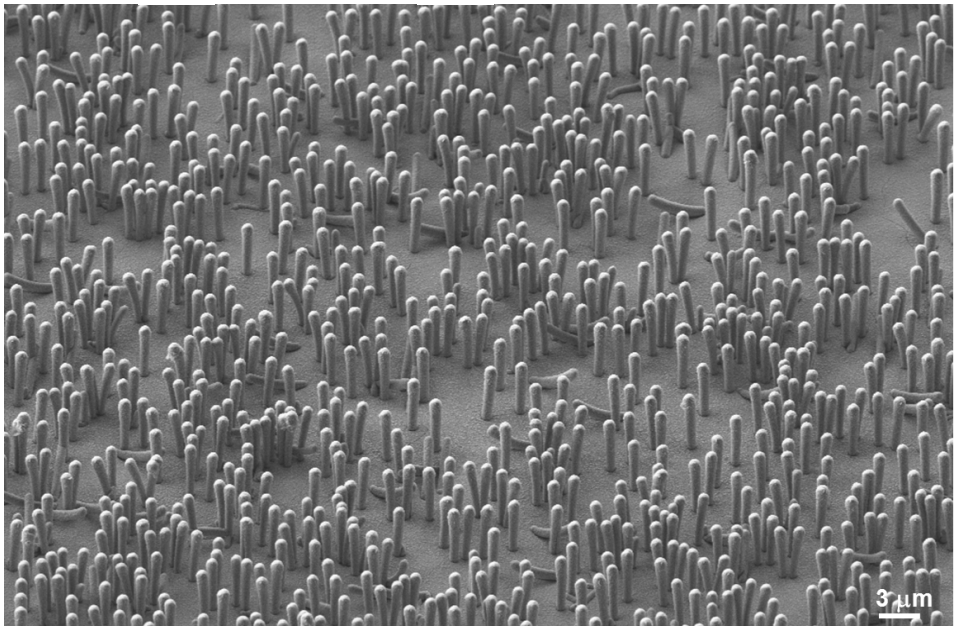


Fig. S2. X-ray spectrum acquired at the native oxide layer showing the Si-K peak at 1.74 keV and the O-K peak at 0.52 keV


1 μm


Si nanowire
1
2
Pt
c
Silicon substrate
a
3
LiCoO2
Si nanowire
Pt
Silicon substrate
b
5
4
LiCoO2
Si nanowire
Pt
Silicon substrate
c

d


3 μm

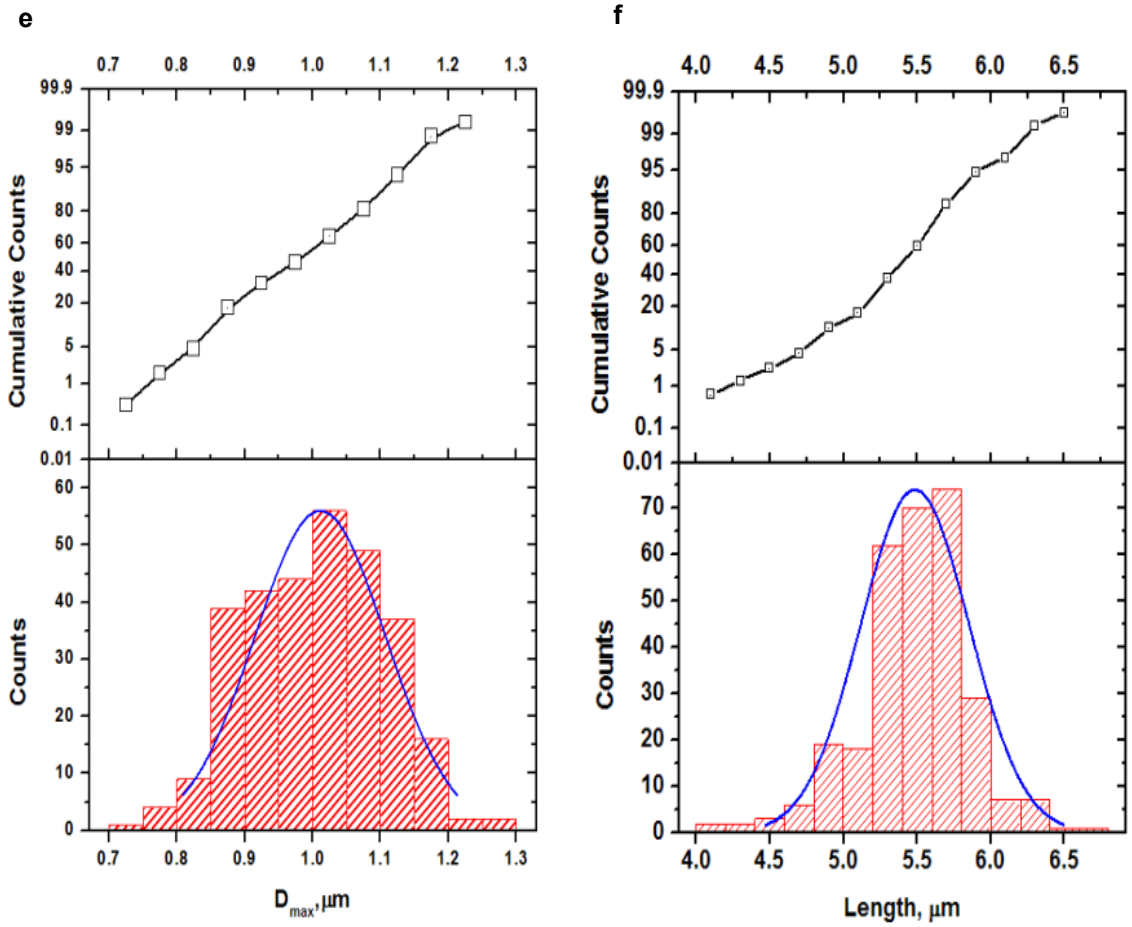


Fig. S3. Electron images and schematic illustrating different stages of battery fabrication. (a-c) FESEM, after deposition of an initial metal collector layer (a), after deposition of a $LiCoO_2$ cathode layer (b), after deposition of a top *n*-Si amorphous anode layer (c). (d) Large field of view of as deposited NW-LiBs at 45° tilt and (e, f) cumulative and differential histograms on NW-LiB's maximum diameter (d_{max}) and length (l) distributions, respectively, N = 300 with the following statistical parameters: d_{max} (mean = 1.0 µm, SD = 0.1 µm, min = 0.75 µm, max = 1.3 µm, range = 0.5 µm, median = 1.0 µm); l (mean = 5.5 µm, SD = 0.4 µm, min = 4.2 µm, max = 6.6 µm, range = 2.5 µm, median = 5.5 µm). Blue line shows normal distribution curves with the same parameters.

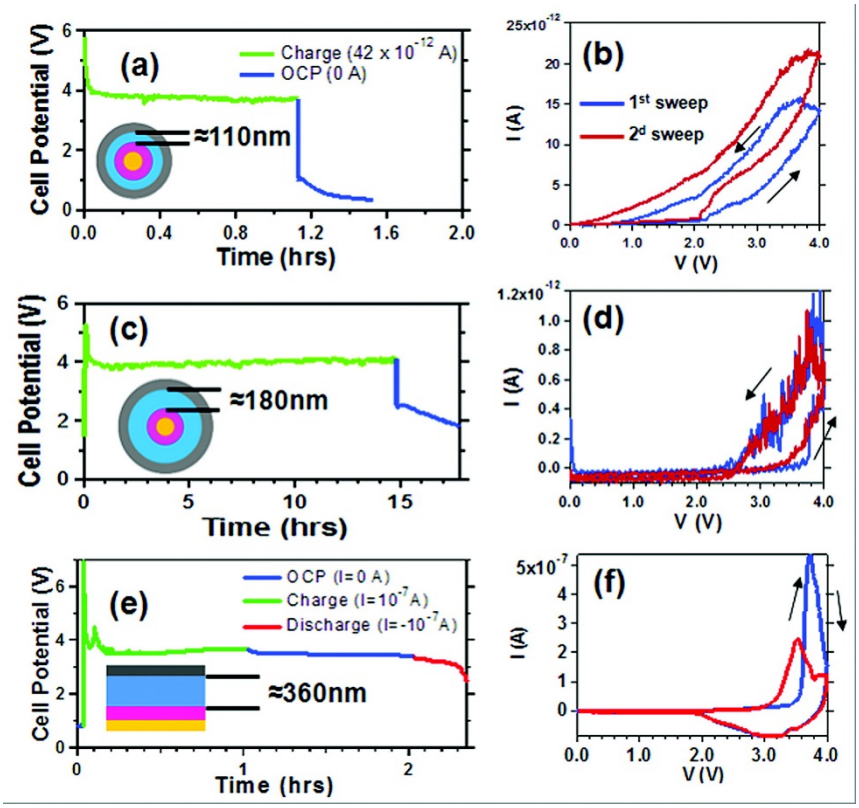


Fig. S4. Constant current charging – open circuit potential curves and (a) slow scan linear voltammetry *I–V* characteristics; (b) a NW-LiB with 110 nm thick LiPON; (c, d) a NW-LiB with 180 nm thick LiPON; and (e, f) a thin film LiB with 360 nm thick LiPON (discharge shown in red)[37]. The voltage scan rate for *I–V* curves is 0.16 mV/s.

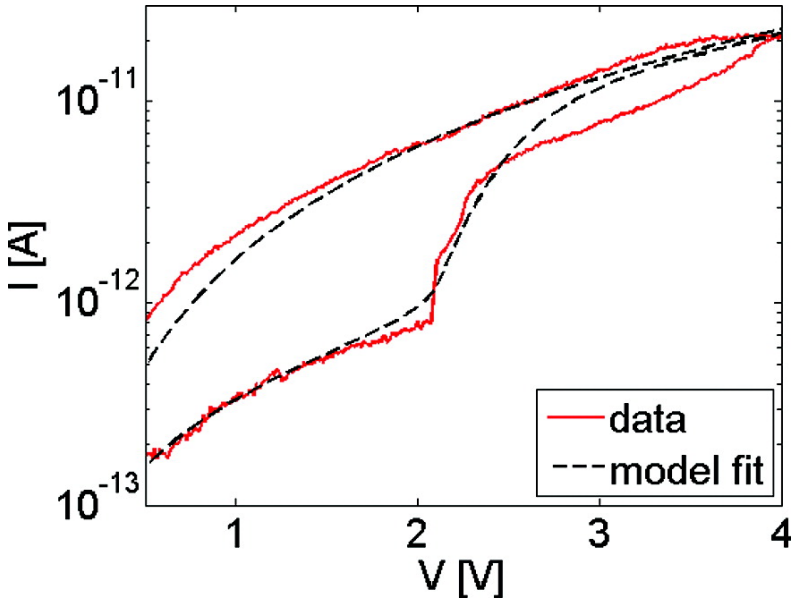


Fig. S5. Measured vs. calculated *I*–*V* characteristics for the NW-LiB with LiPON ≈ 110 nm (same data as in Fig. S4b)[37]. Model parameters are: $N_c = 2 \times 10^{19}$ cm^{-3}, $n_0 = 3.5 \times 10^{16}$ cm^{-3}, $\mu = 4.5 \times 10^{-9}$cm^2/V·s, $N_t = 10^{18}$ cm^{-3}, $\delta = 32$, $l = 10$.

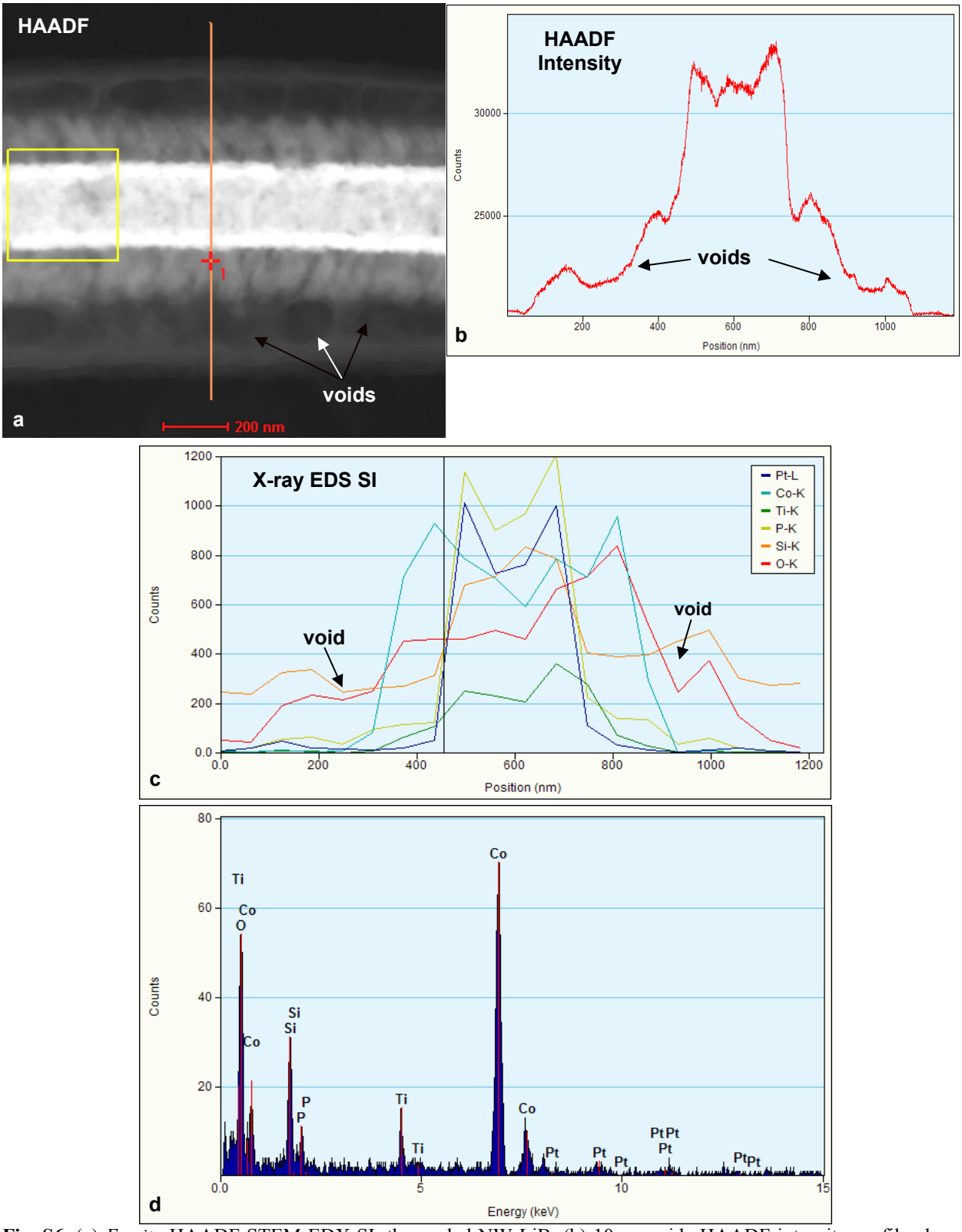


Fig. S6. (a) *Ex situ* HAADF STEM-EDX SI, the cycled NW-LiB, (b) 10 nm-wide HAADF-intensity profile along the orange line in (a), and (c) drift-corrected X-ray EDS SI line profile along the orange line in (a). (d) X-ray spectrum acquired in the point marked by red cross in (a). Note drops in intensities of phosphorus and oxygen X-ray lines at both LiPON-$Li_{1-x}CoO_2$ interfaces.