

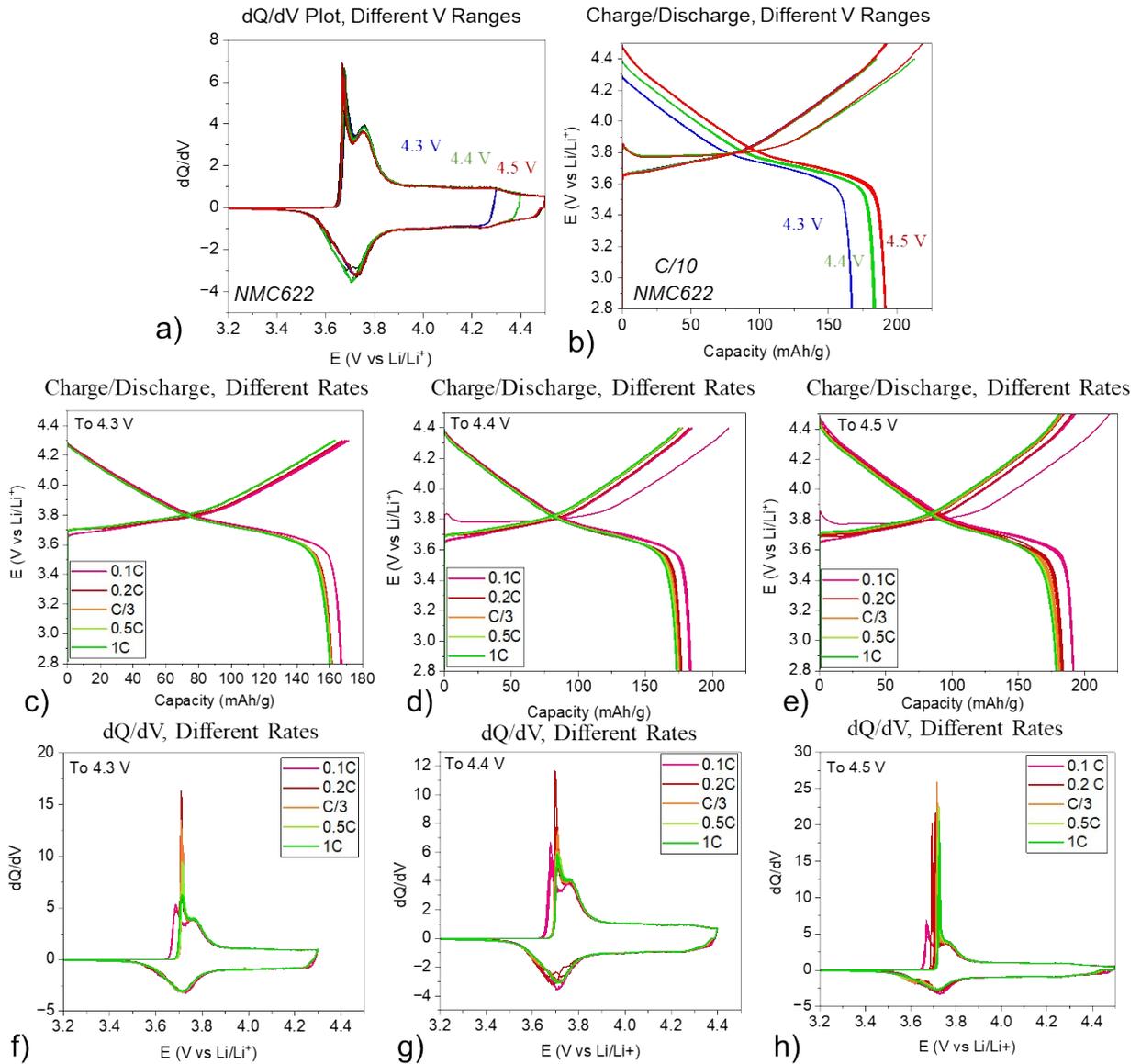
## Nickel-Dependent Interfacial Chemistry in Layered Oxide Cathodes: Insights from X-ray Photoelectron Spectroscopy and Electrochemical Quartz Crystal Microbalance

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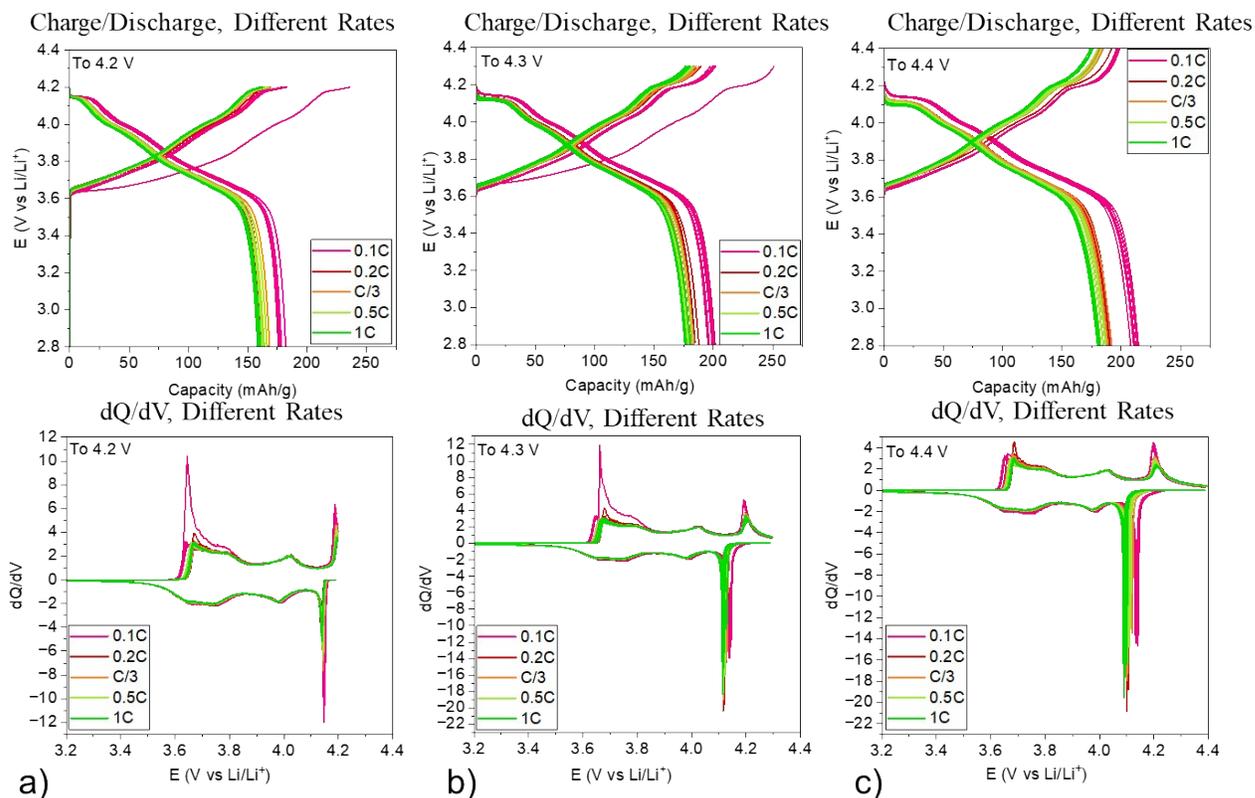
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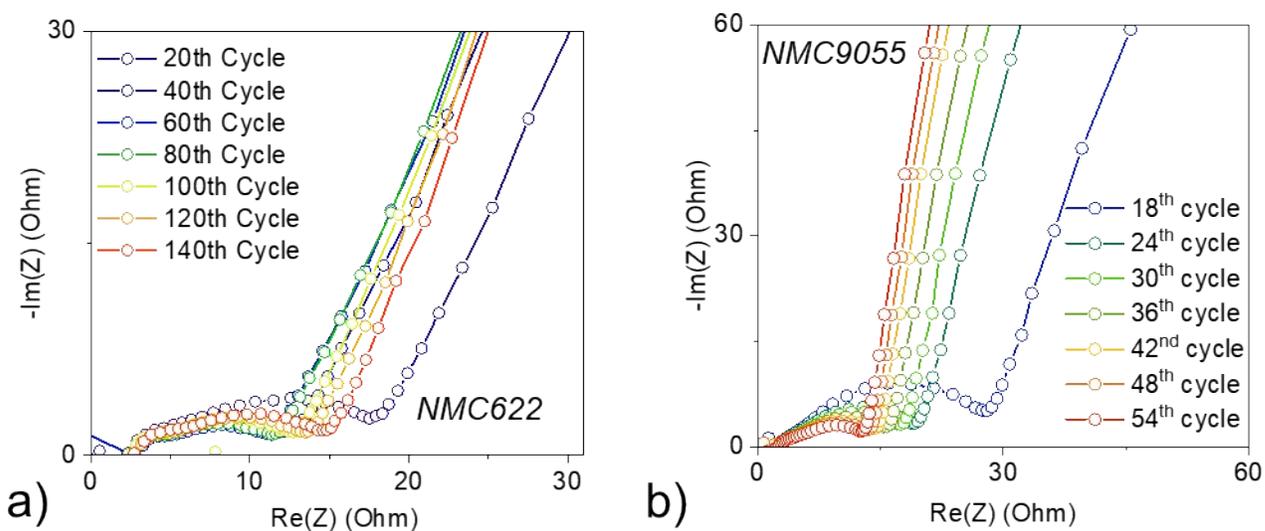
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**Figure S1.** a) dQ/dV plot for the first five cycles of lithium half cells with NMC622 cycled between voltage limits of 4.3 V, 4.4 V, 4.5 V and 2.8 V. b) Charge/discharge plot for the first five cycles of lithium half cells with NMC622 cycled between voltage limits of 2.8 and 4.3 V, 4.4 V, and 4.5 V, as indicated. Charge/discharge plot of NMC622 cycled between voltage limits of 2.8 V and c) 4.3 V d) 4.4 V and e) 4.5 V at various rates. dQ/dV plot of NMC622 cycled between voltage limits of 2.8 V and f) 4.3 V g) 4.4 V and h) 4.5 V at various rates.

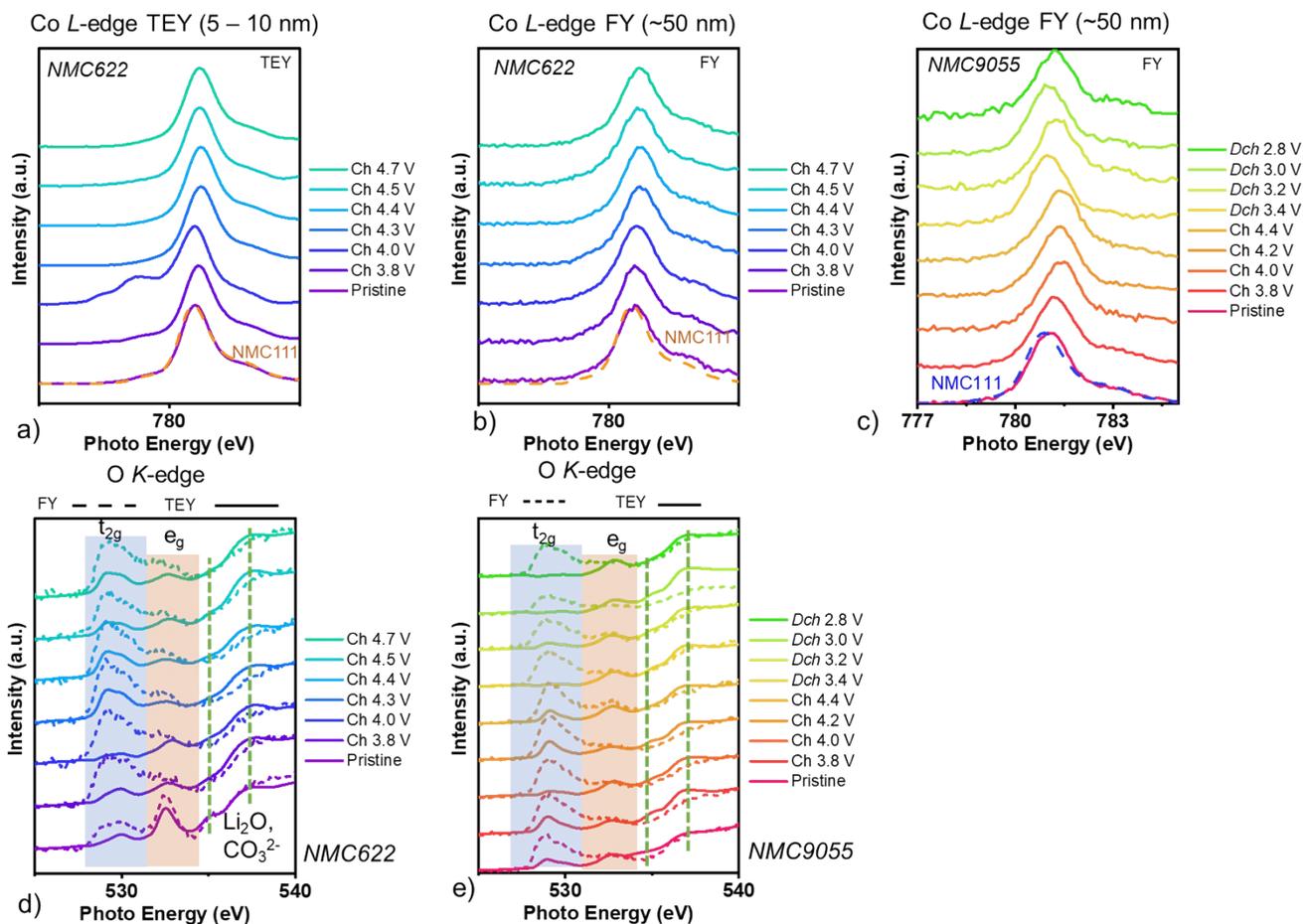


**Figure S2.** Charge/discharge plots and dQ/dV plots of lithium half cells with NMC9055 between voltage limits of 2.8 V and a) 4.2 V b) 4.3 V and c) 4.4 V at various rates.

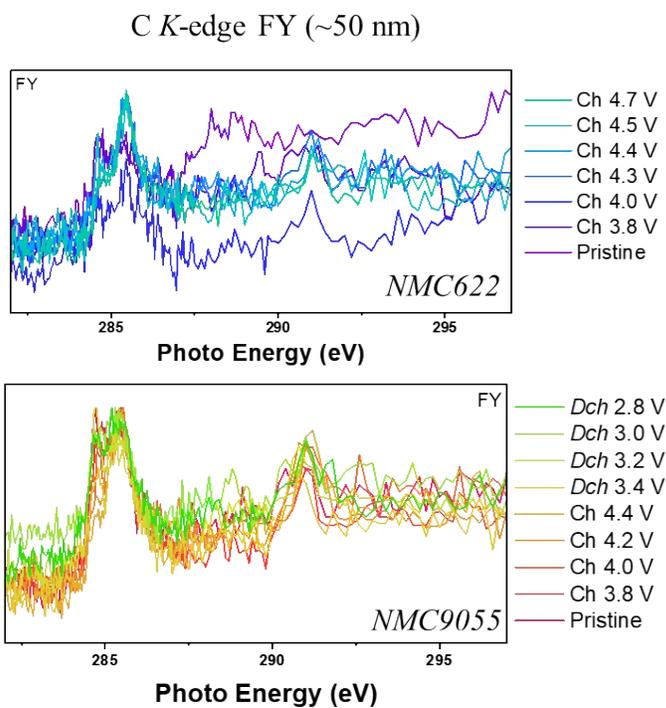


**Figure S3.** EIS measurements of lithium half-cells with an a) NMC622 cathode taken after each indicated cycle, where each cycle is a CCCV charge at a rate of 0.1C to 4.5 V followed by a

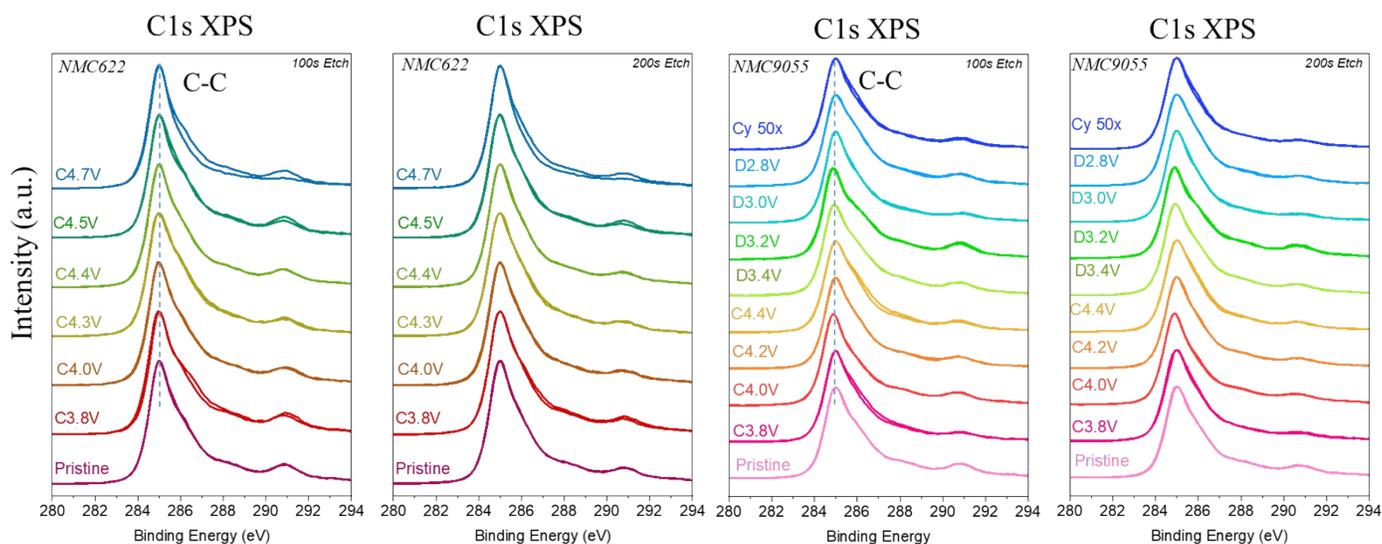
voltage hold at 4.5 V until the cell reached a current value of 0.02C and then a CC discharge at 0.1C to 2.8 V; b) NMC9055 cathode taken after each indicated cycle, where each cycle is a CCCV charge at a rate of 0.1C to 4.5 V followed by a voltage hold at 4.5 V until the cell reached a current value of 0.02C and then a CC discharge at 0.1C to 2.8 V.



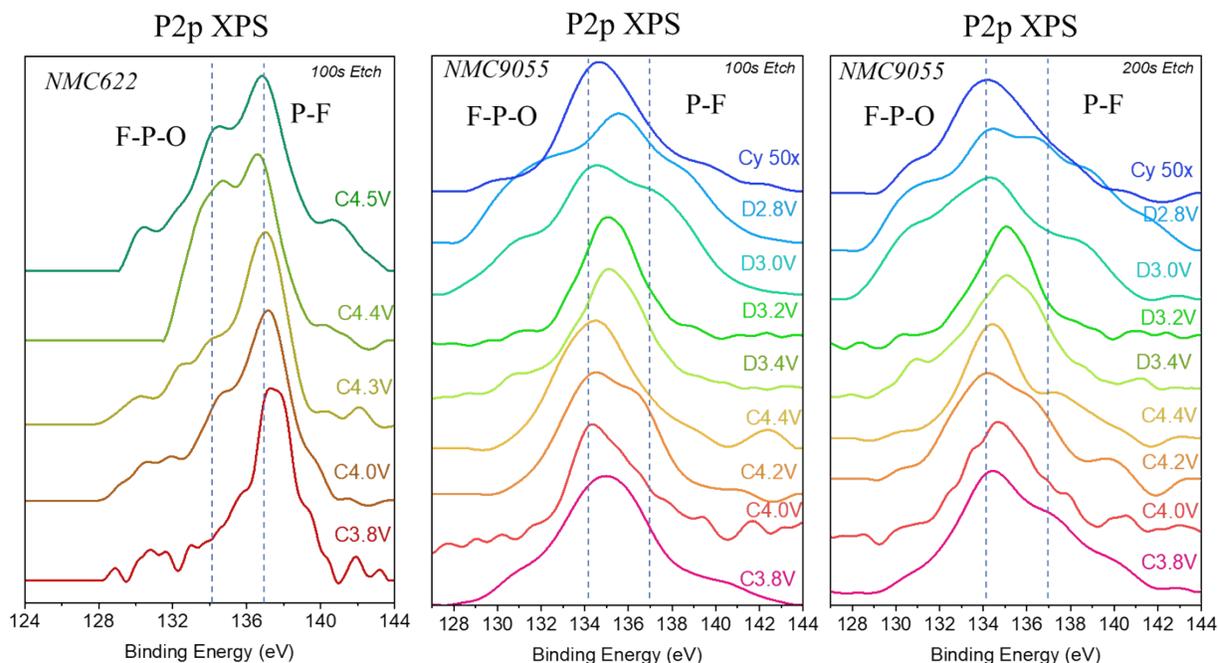
**Figure S4.** *Ex situ* Co L-edge X-ray absorption spectra in a) TEY and b) FY modes of NMC622 cathodes; *Ex situ* Co L-edge X-ray absorption spectra in c) FY mode of NMC9055 cathodes; *Ex situ* O K-edge X-ray absorption spectra in TEY and FY modes of d) NMC622 and e) NMC9055 cathodes removed from lithium-half cells cycled to the indicated voltage limits.



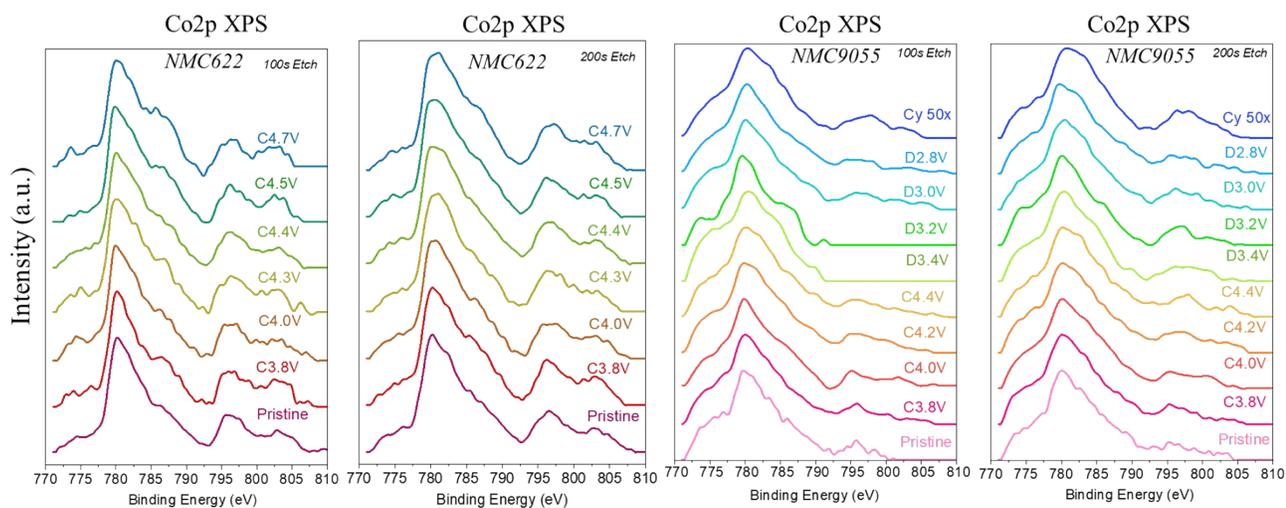
**Figure S5.** *Ex situ* C K-edge X-ray absorption spectra in FY mode (~50 - 100 nm depth) for NMC622 (top) and NMC9055 (bottom) electrodes removed from lithium half-cells at the indicated potentials.



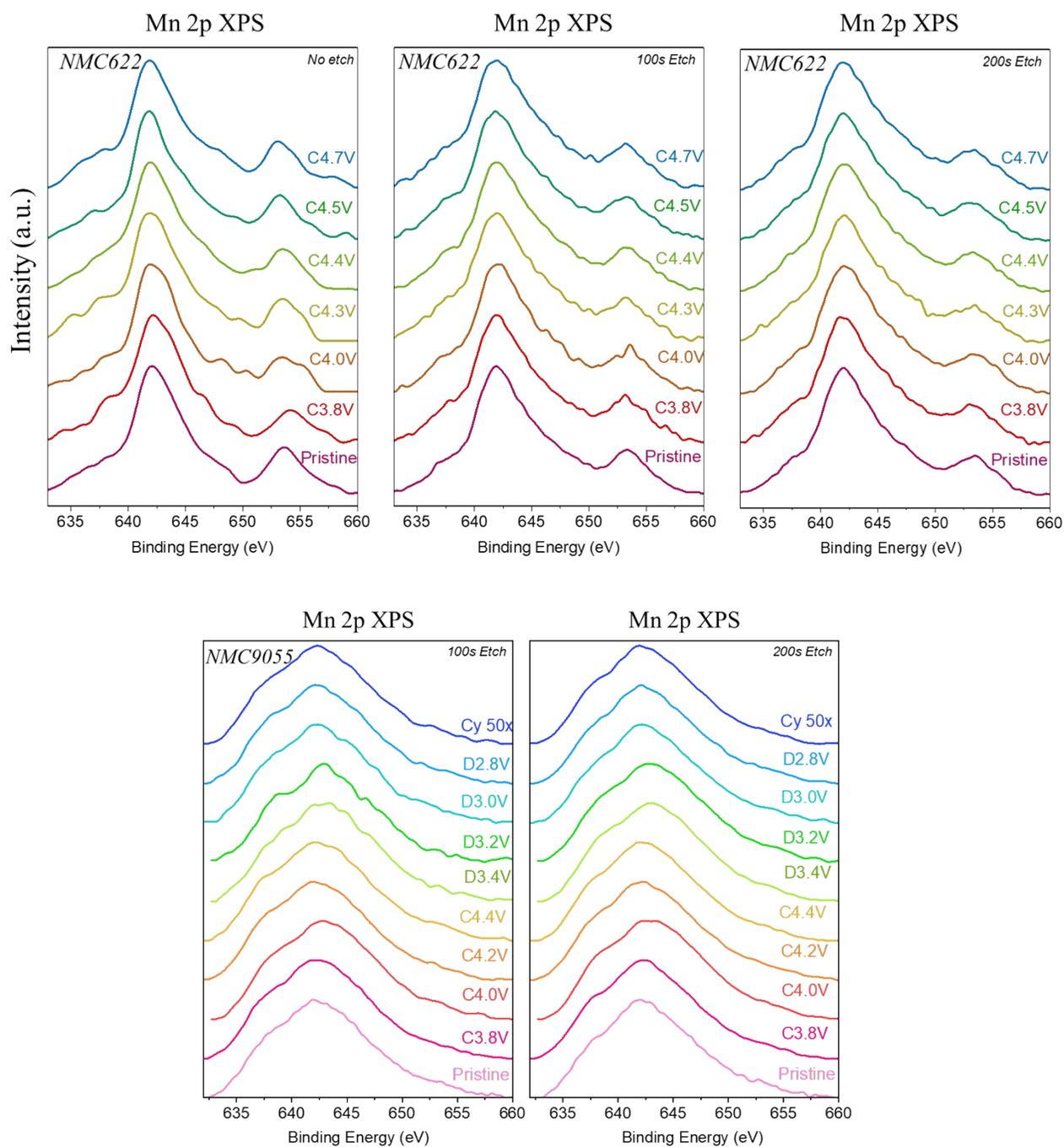
**Figure S6.** *Ex situ* C1s XPS depth profiling experiments on NMC622 and NMC9055 cathodes removed from Li half-cells at the indicated potentials. Samples were etched for either 100 s or 200 s.



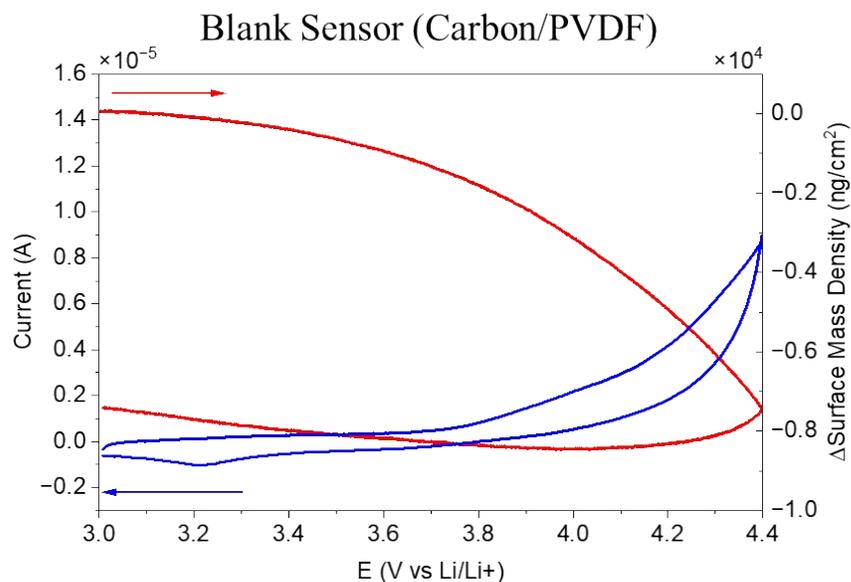
**Figure S7.** *Ex situ* P2p XPS depth profiling experiments on a) NMC622 and b) NMC9055 cathodes removed from Li half-cells at the indicated potentials. NMC622 cathodes were etched for 100 s and NMC9055 for 100 s and 200 s.



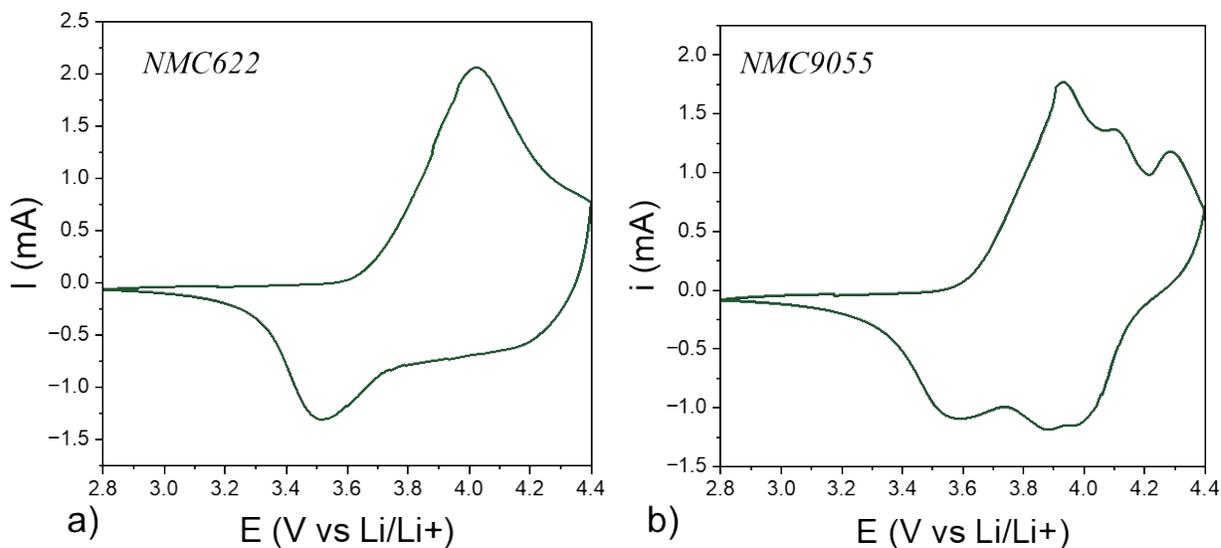
**Figure S8.** *Ex situ* Co2p XPS depth profiling experiments on NMC622 and NMC9055 cathodes removed from lithium half-cells at the indicated potentials after 100 s and 200 s of etch time.



**Figure S9.** *Ex situ* Mn2p XPS for NMC622 and NMC9055 cathodes removed from Li half-cells at the indicated potentials with no etching (NMC622 only), 100 s of etching, and 200 s of etching.



**Figure S10.** EQCM sensor with a film containing only carbon and PVDF, with no active material. The electrolyte was 2 M LiTFSI in 1:1 EC:DMC. Lithium foil was used as both the counter and reference electrode with the sensor used as the working electrode.



**Figure S11.** Coin cell CV of a) NMC622 and b) NMC9055 in 1 M LiPF<sub>6</sub>, 1:1 EC/DEC, at a scan rate of 0.3 mV/s.