

Supplementary Material (ESI)

Voltage-dependent charge compensation mechanism and cathode electrolyte interface stability of the lithium-ion battery cathode materials LiCoO_2 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ studied by photoelectron spectroscopy

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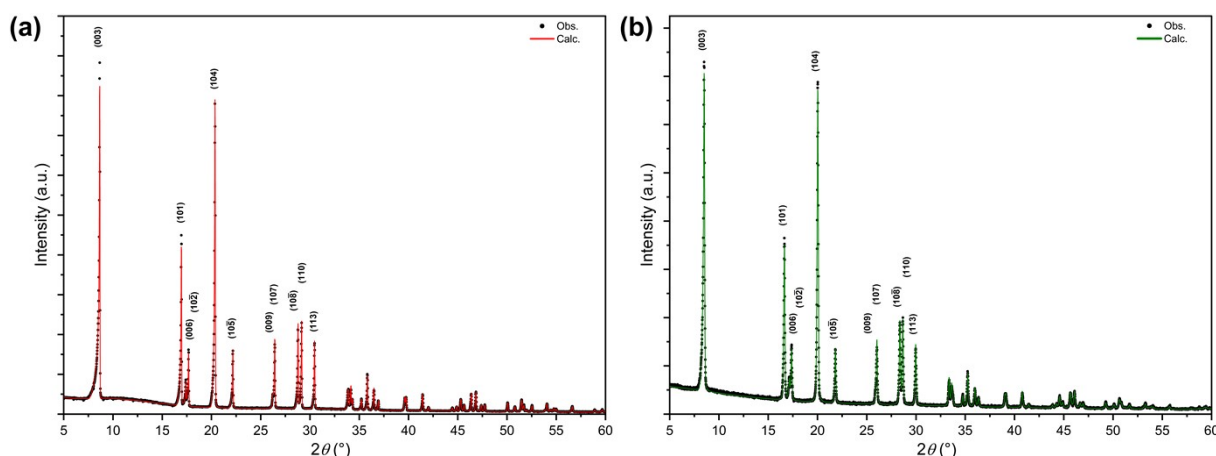


Figure S1. Powder diffraction pattern of pristine LCO and NMC333 with Rietveld refinement (Calc.).

Cell parameter	
LCO	Space group: $R\bar{3}m$ $a=2.8161 \text{ \AA}$; $c=14.0532 \text{ \AA}$; $c/a= 4.99$; $V= 96.5 \text{ \AA}^3$; $w_R= 5.953\%$
NMC333	Space group: $R\bar{3}m$ $a=2.8584 \text{ \AA}$; $c=14.2217 \text{ \AA}$; $c/a= 4.98$; $V= 100.6 \text{ \AA}^3$; $w_R= 6.015\%$

Table S1. Lattice parameter, c/a ratios, volumes and w_R -values for pristine LCO and NMC333 obtained by Rietveld refinement.

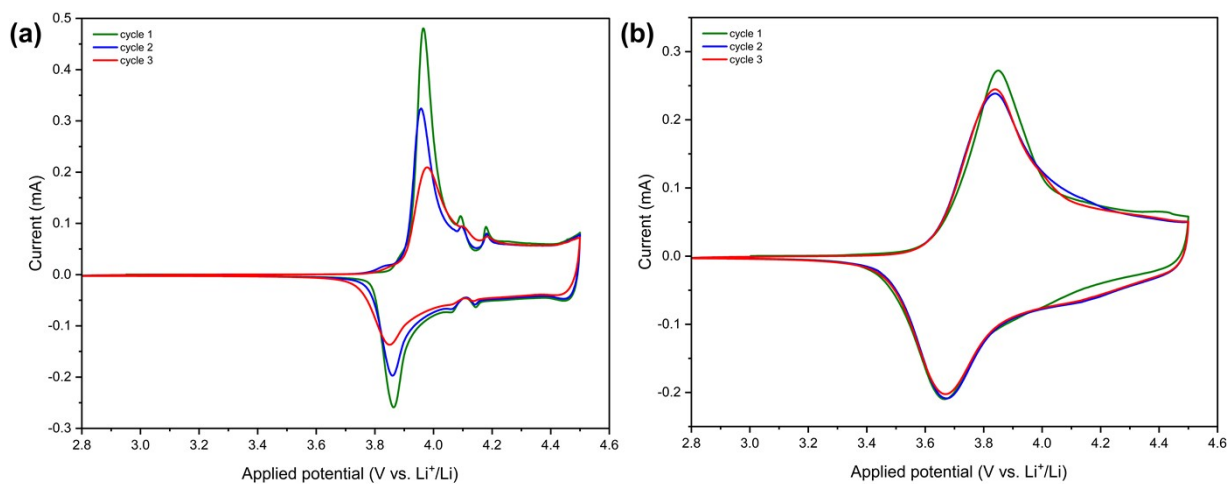


Figure S2. CV of LCO (a) and NMC333 (b) in the range of 2.8 V to 4.5 V vs. Li⁺/Li.

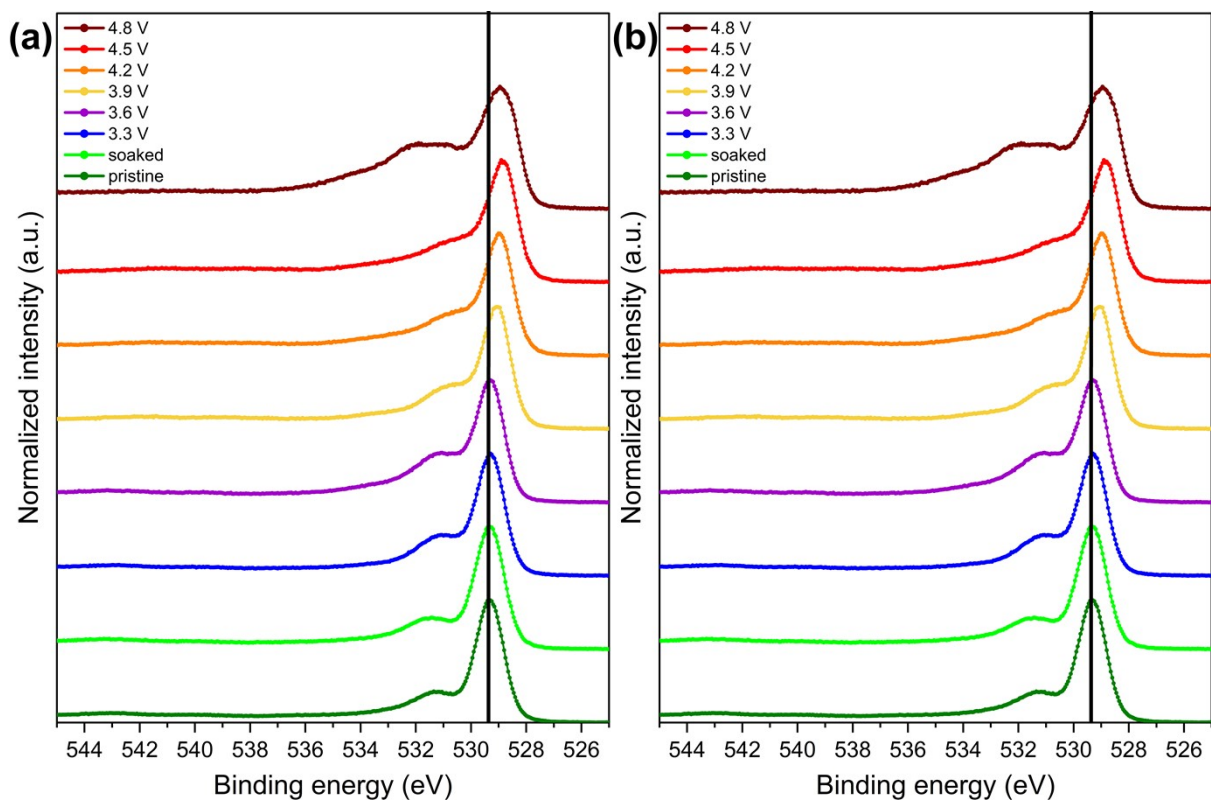


Figure S3. (a) Oxygen 1s spectra of LCO scratched and (b) NMC333 scratched with a vertical line as a guide for the eye to show the binding energy shift.

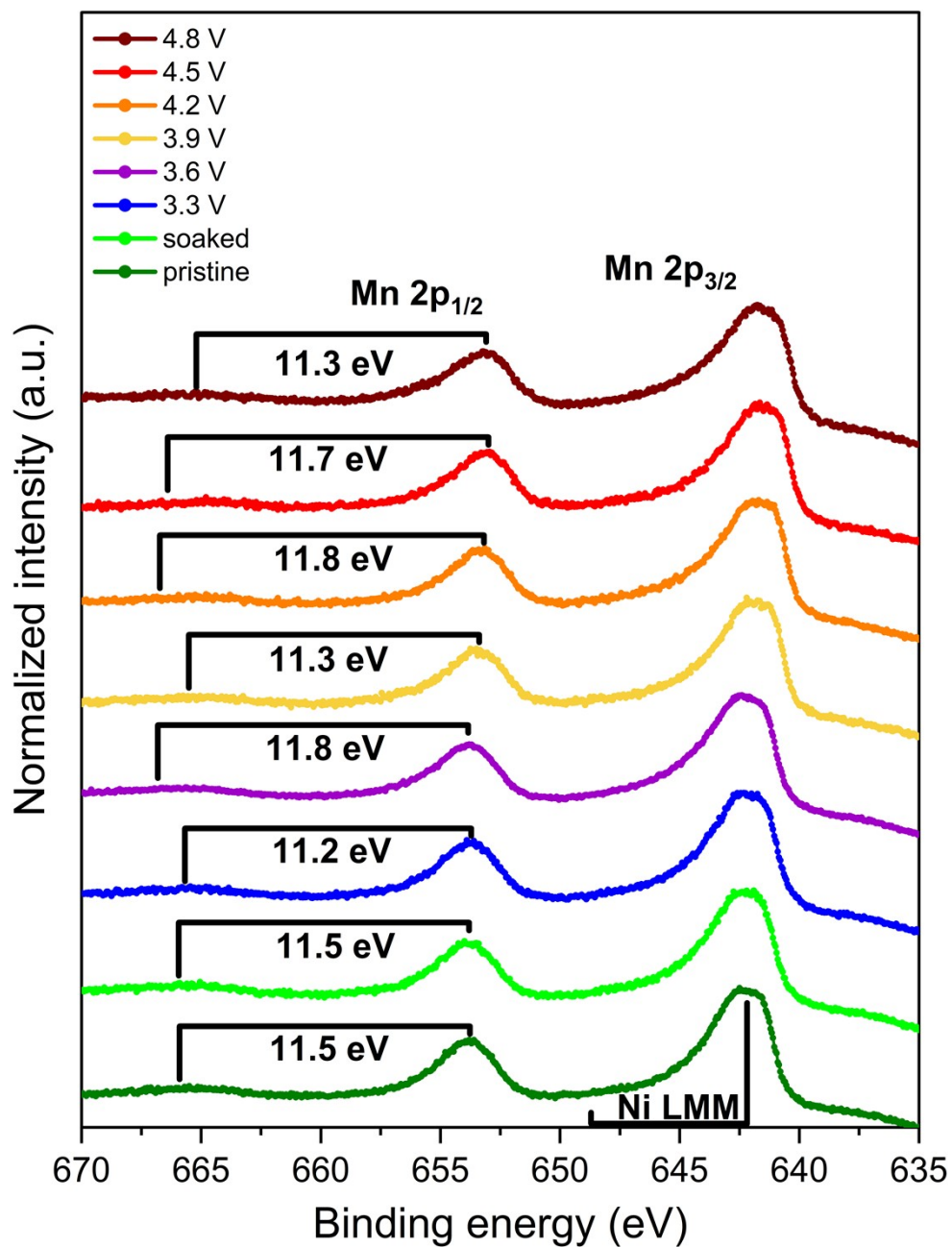


Figure S4. Mn 2p spectra of NMC333 scratched. The Ni LMM Auger overlaps with the Mn2p_{3/2} peak.

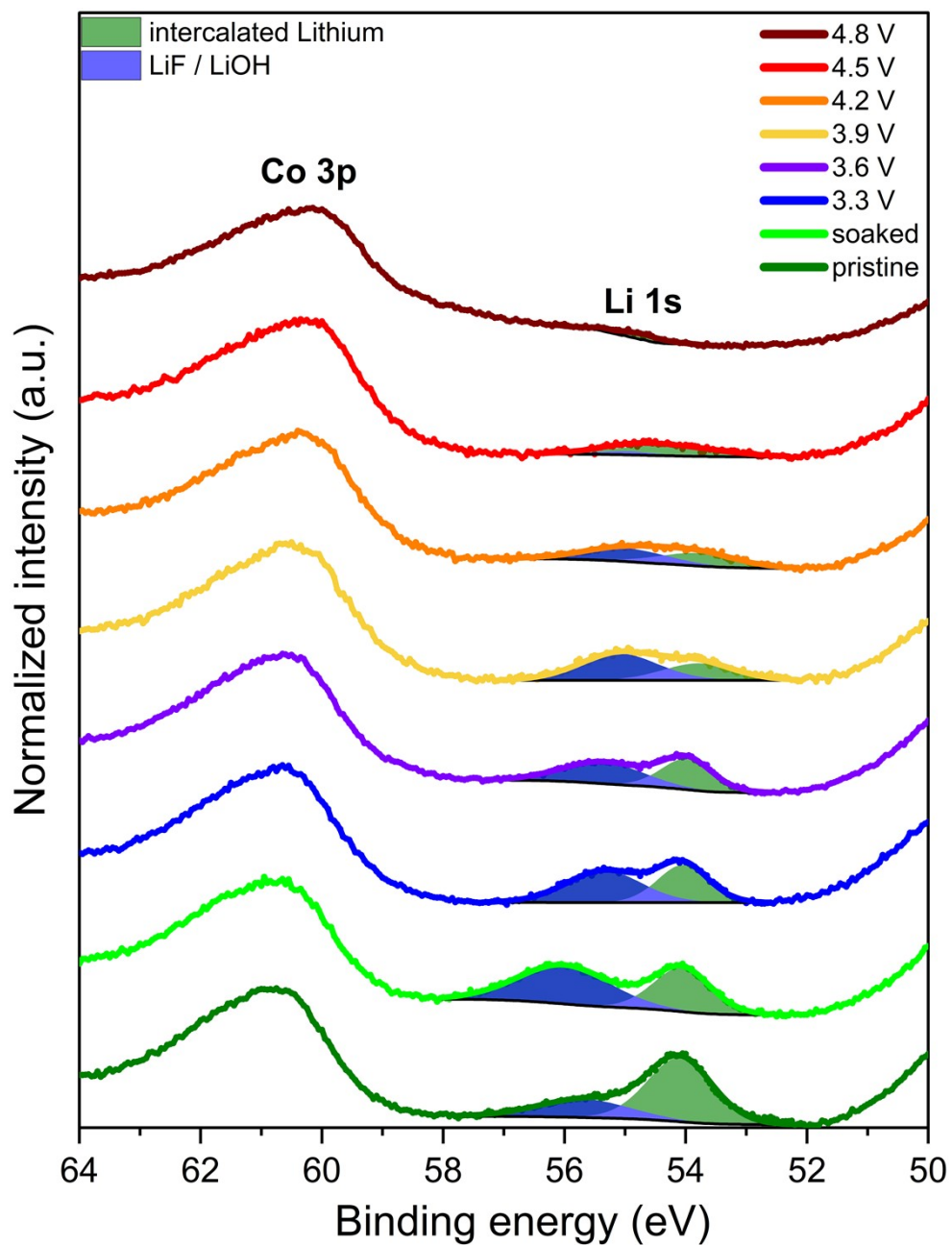


Figure S5. Li 1s and Co 3p spectra of NMC333 discharged to different voltages collected before performing in-vacuo scratching.

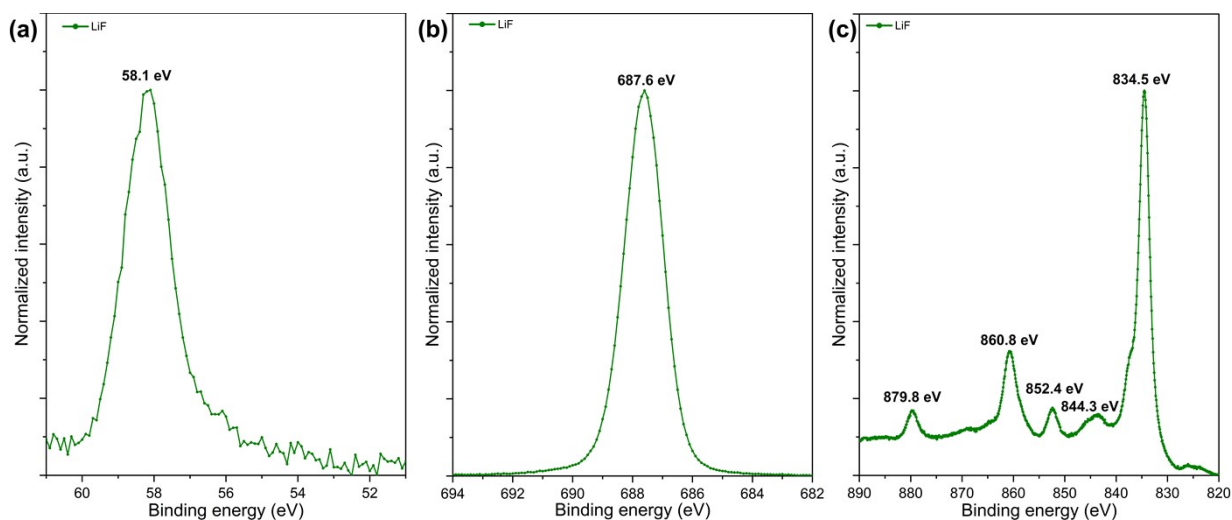


Figure S6. a) Li 1s, F 1s and F KLL of sputtered LiF on Si111 normalized to F 1s main to 684.6 eV.

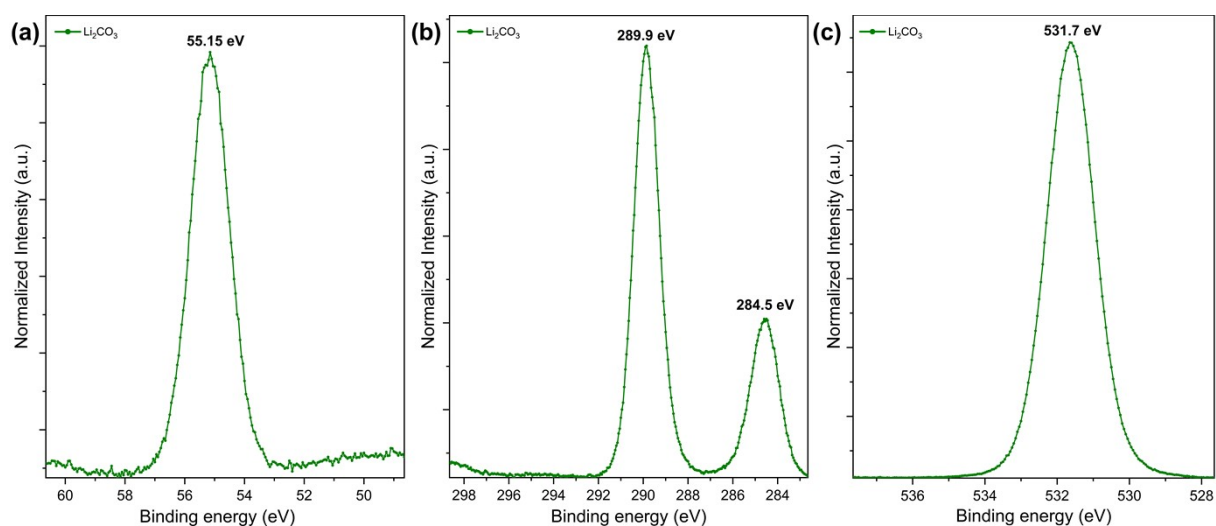


Figure S7. a) Li1s, C1s and O1s of in-vacuo scratching Li_2CO_3 were normalized to C-C at 284.5 eV.

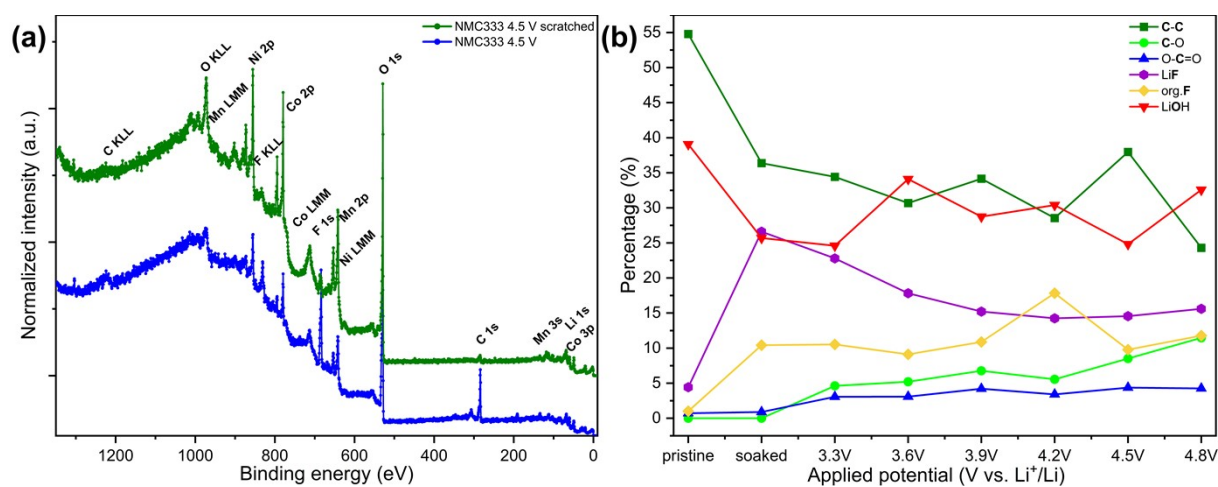


Figure S8. (a) Survey spectra of NMC333 charged to 4.5 V as an example for showing the significant reduction in the intensity of the carbon 1s and fluorine 1s peak with scratching. (b) The composition of the CEI at different voltage states.

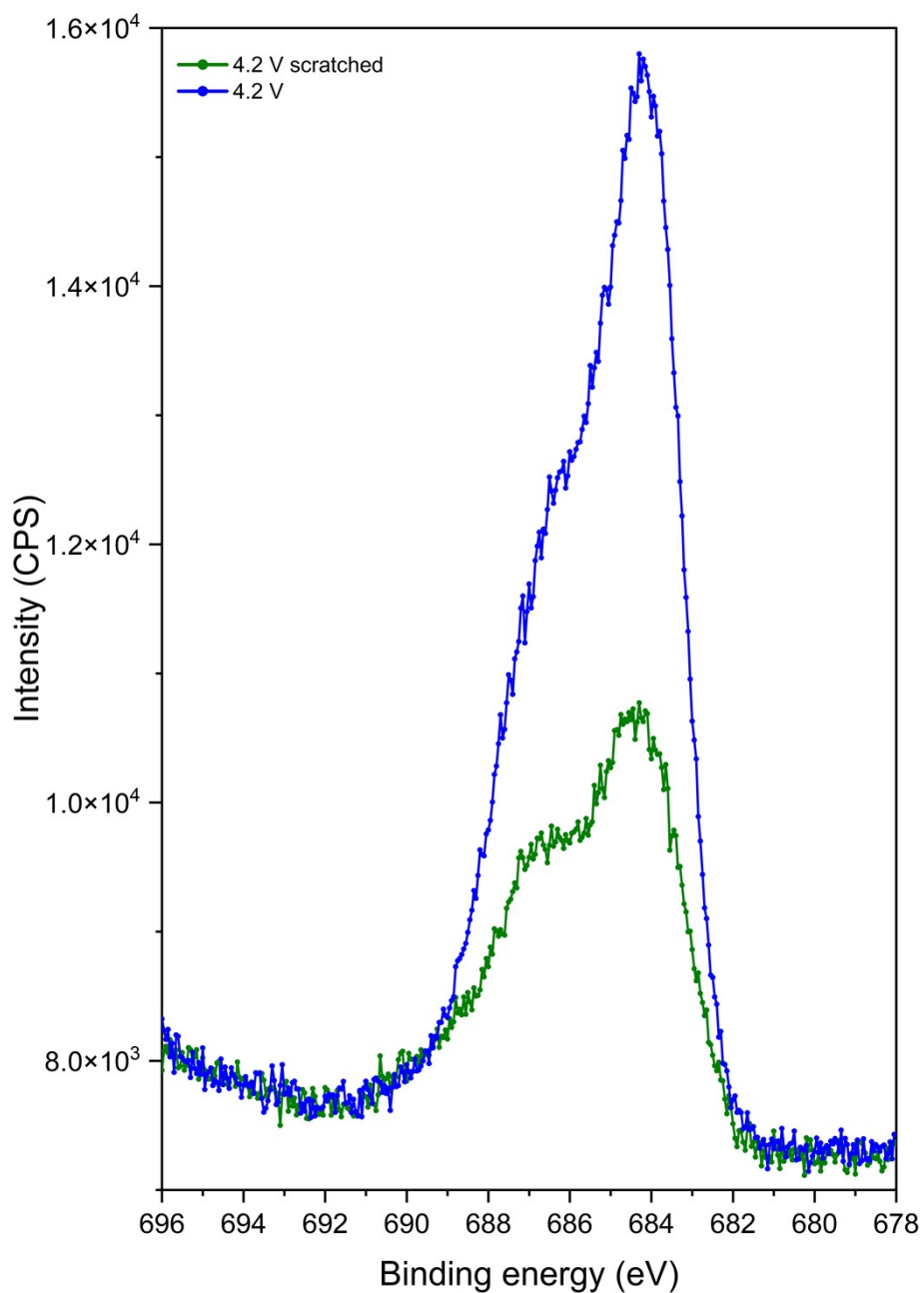


Figure S9. (a) F 1s spectra of NMC333 charged to 4.2 V before and after scratching, showing the reduction in the intensity of the carbon 1s peak by in-vacuo scratching.