

## Supporting information

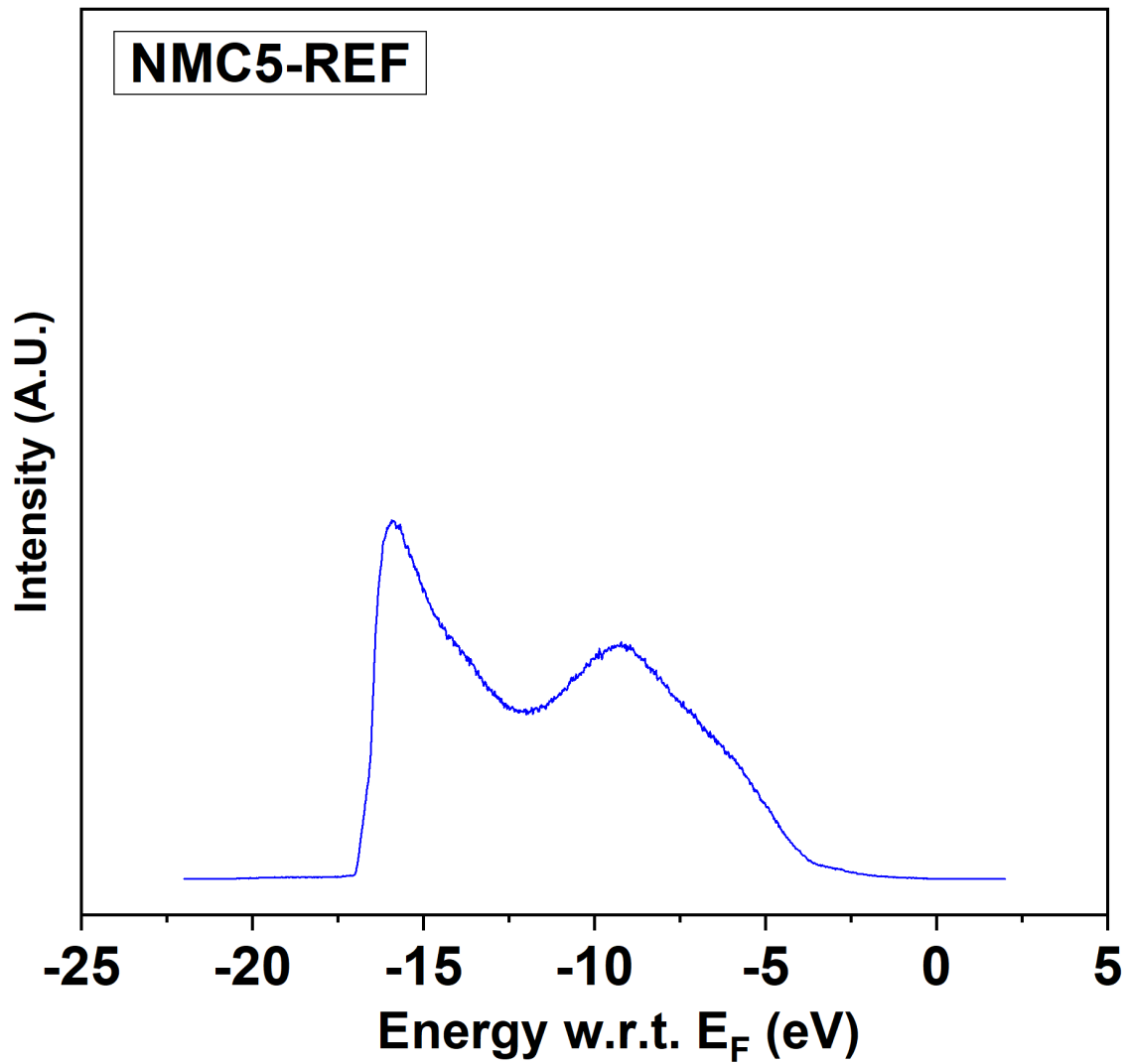
### **Understanding the active formation of a cathode–electrolyte interphase (CEI) layer with energy level band bending for lithium-ion batteries**

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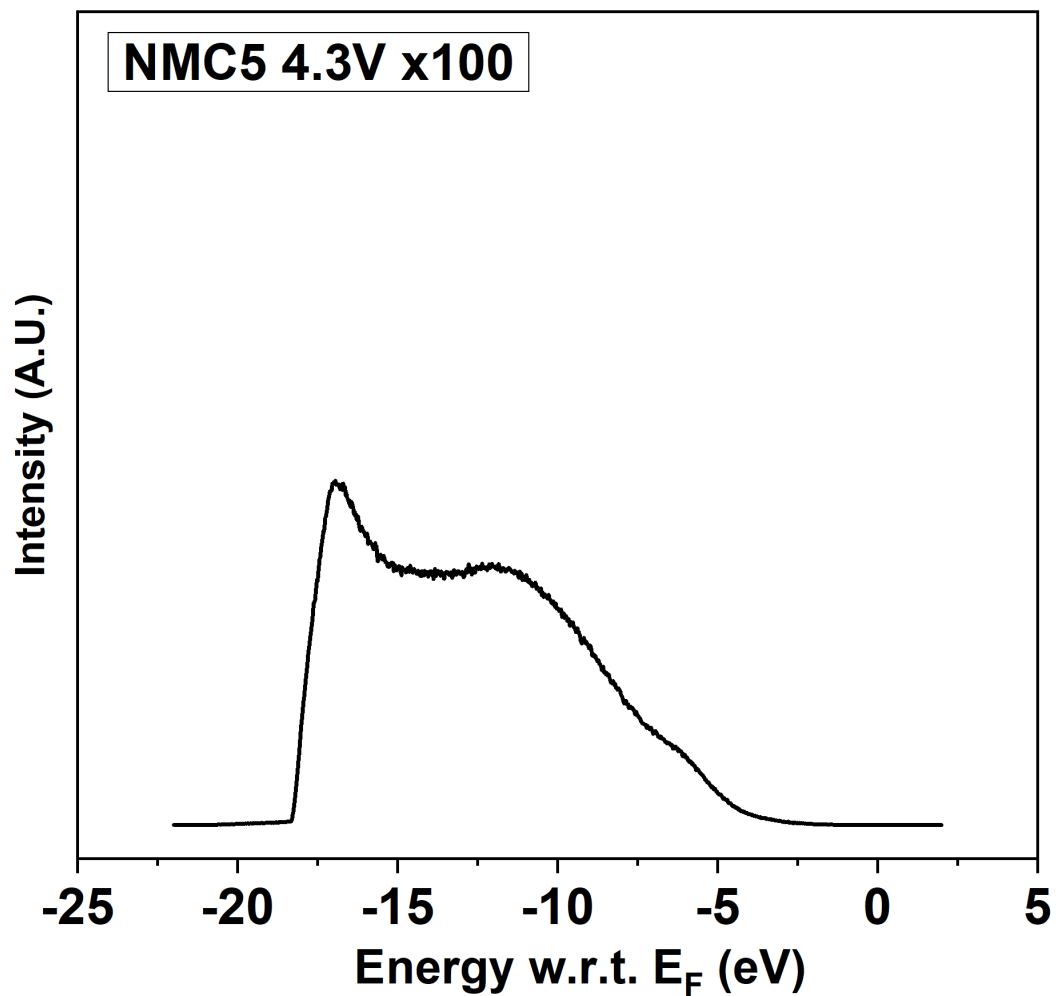
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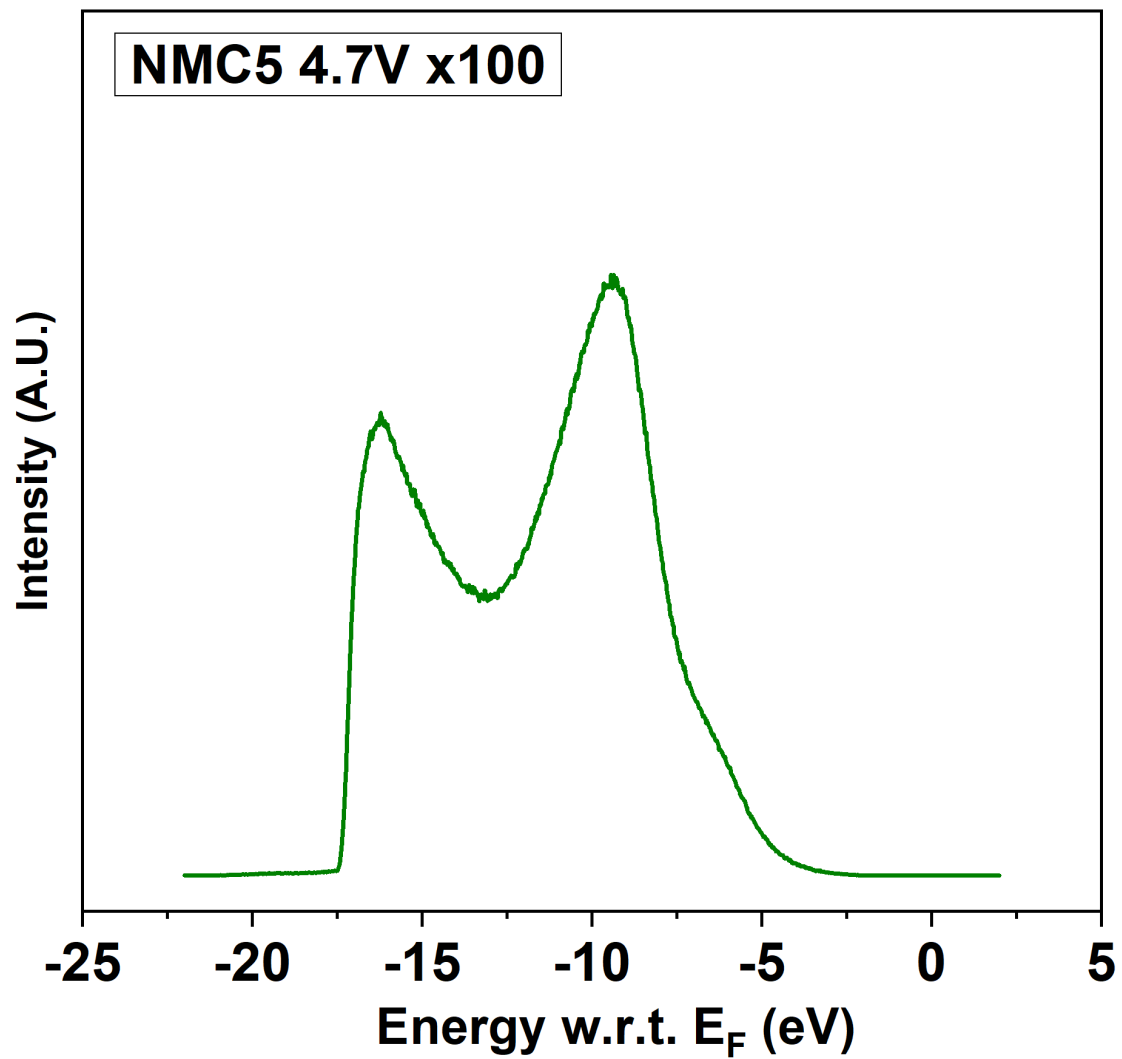
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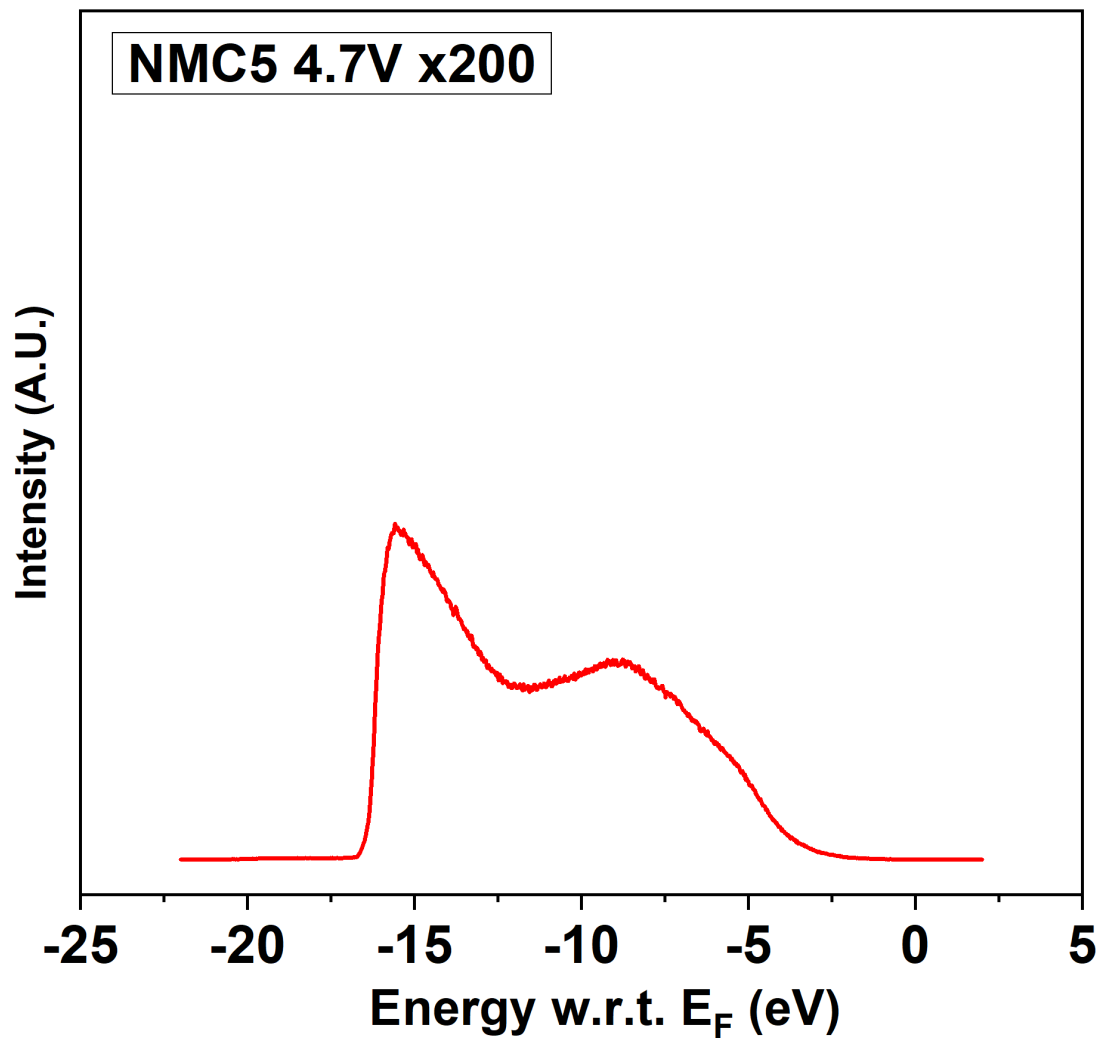
**Fig. S1.** Full spectrum obtained from the ultraviolet photoemission spectroscopy (UPS) measurements on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  at reference state (REF).



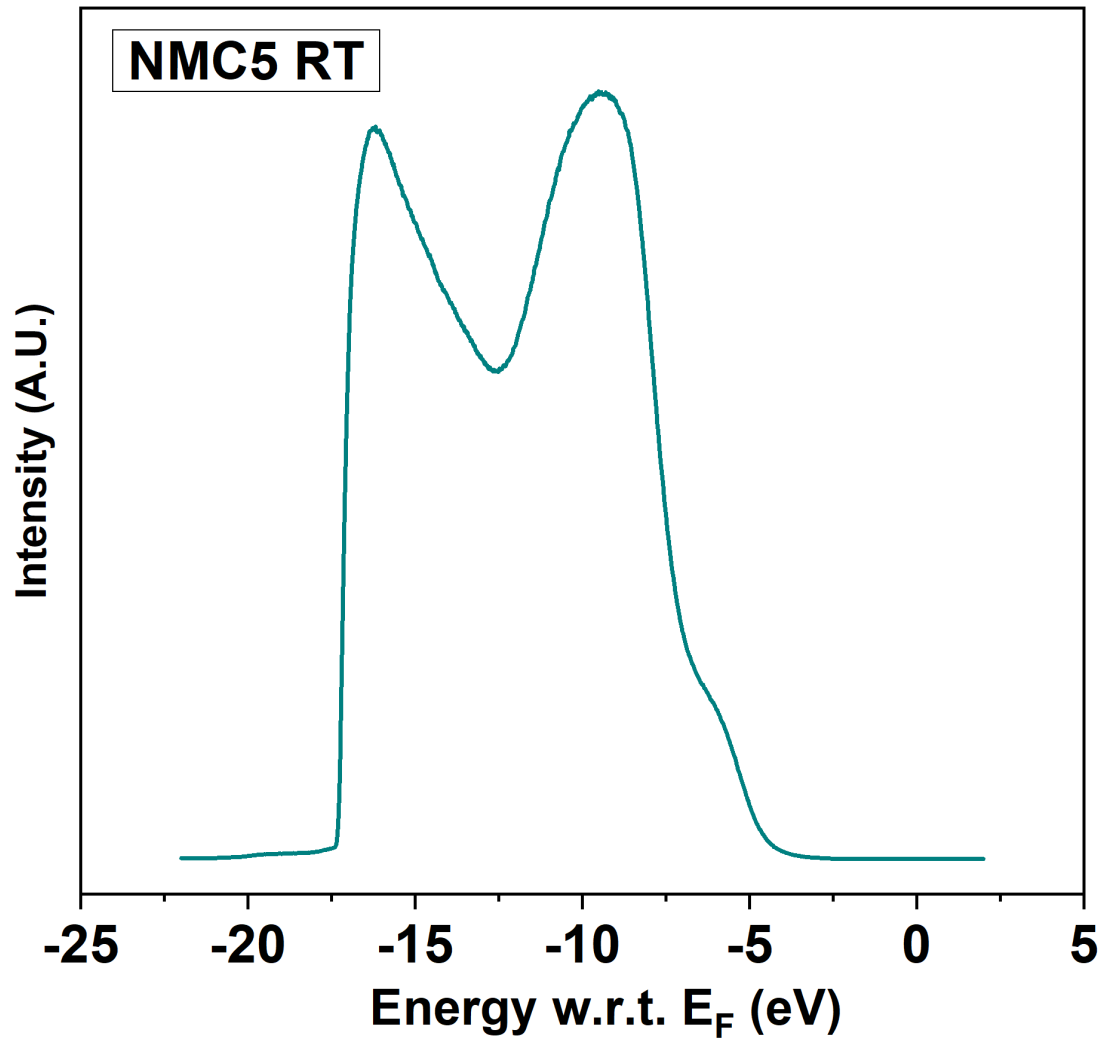
**Fig. S2.** Full spectrum obtained from the ultraviolet photoemission spectroscopy (UPS) measurements on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  after 100 cycles in the voltage range of 2.8 – 4.3 V with 0.4C current applied.



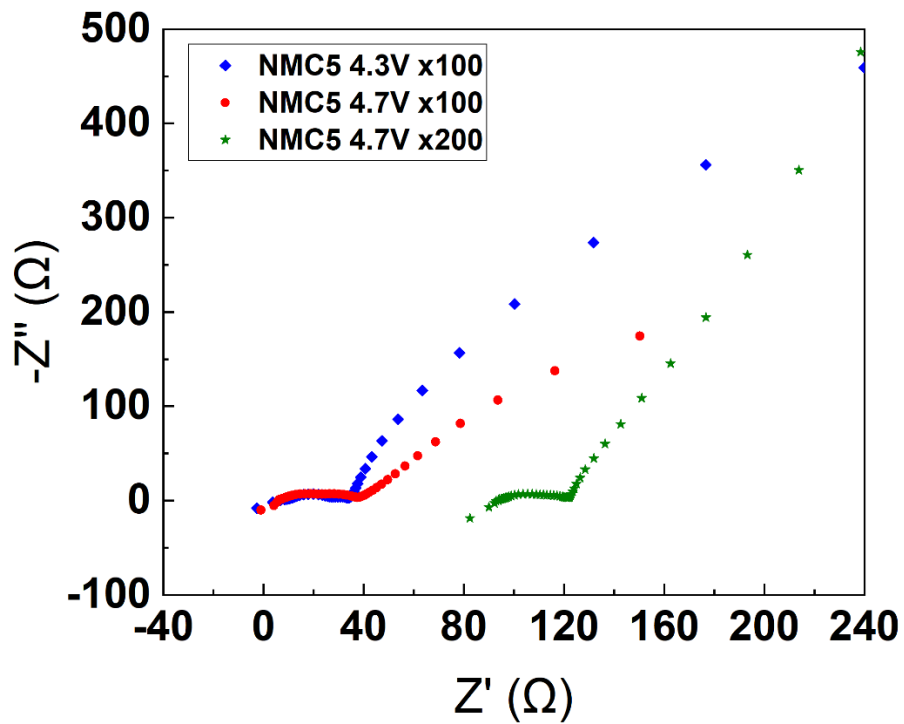
**Fig. S3.** Full spectrum obtained from the ultraviolet photoemission spectroscopy (UPS) measurements on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  after 100 cycles in the voltage range of 2.8 – 4.7 V with 0.4C current applied.



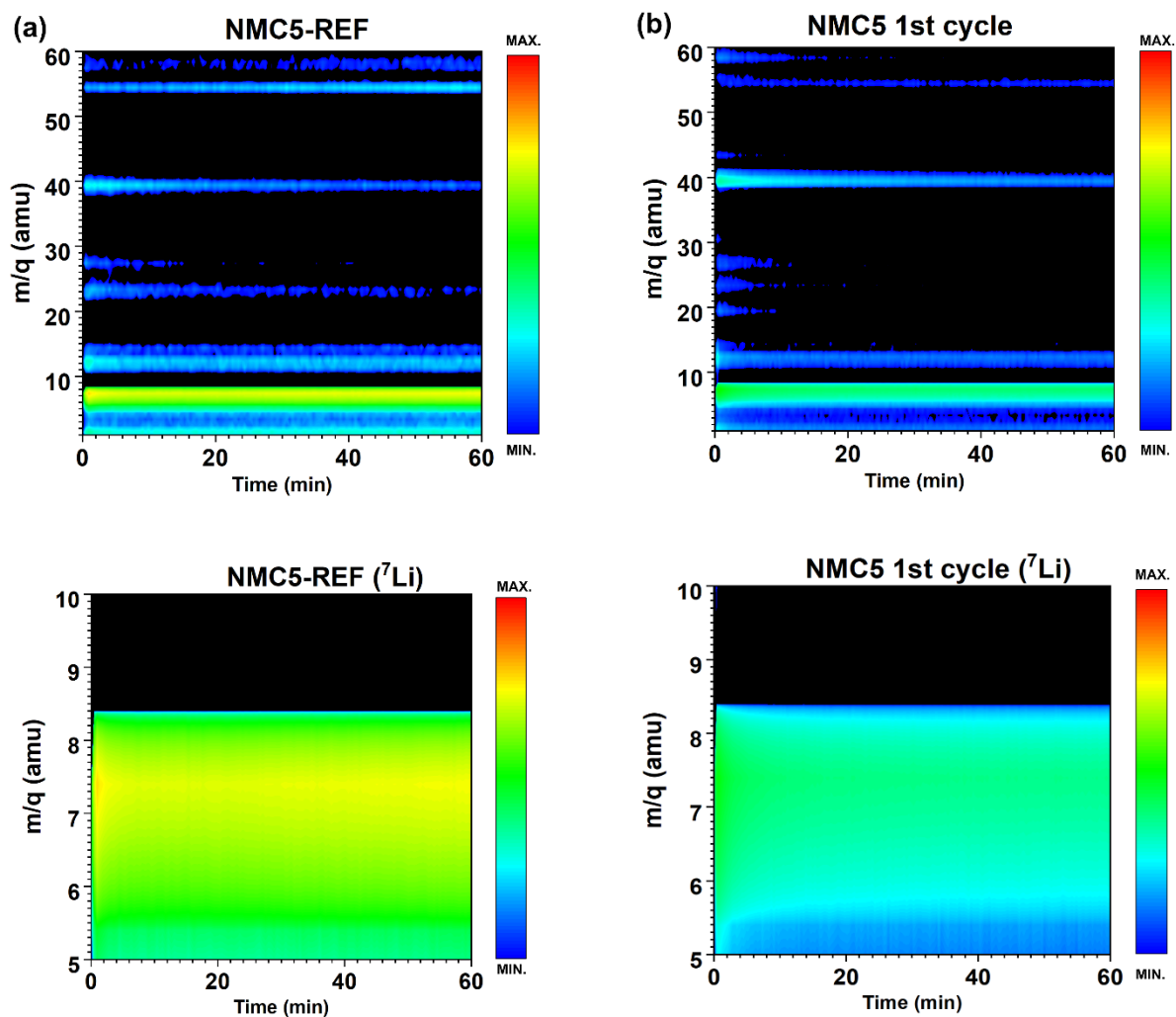
**Fig. S4.** Full spectrum obtained from the ultraviolet photoemission spectroscopy (UPS) measurements on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  after 200 cycles in the voltage range of 2.8 – 4.7 V with 0.4C current applied.



**Fig. S5.** Full spectrum obtained from the ultraviolet photoemission spectroscopy (UPS) measurements on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  after 40 cycles with dynamic current rates from 0.125 C to 0.25 C to 0.4 C and back to 0.125 C in the voltage range of 2.0 – 4.5 V.

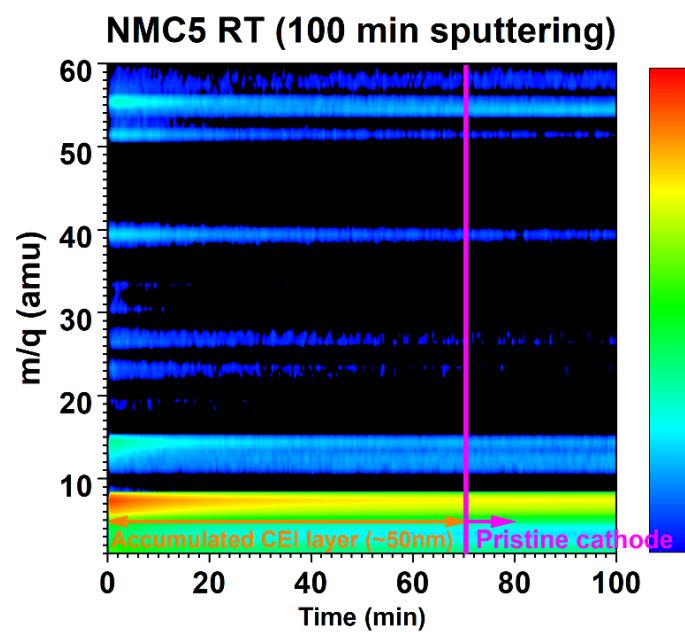


**Fig. S6.** EIS measurements (Nyquist plot) on  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  (NMC5) after 100 cycles in the voltage range of 2.8 – 4.3 V (at 0.4C-rate), after 100 cycles in the voltage range of 2.8 – 4.7 V (at 0.4C-rate), and after 200 cycles in the voltage range of 2.8 – 4.7 V (at 0.4C-rate).



**Fig. S7.** Visualization of the cathode-electrolyte interphase (CEI) formation by SIMS positive-ion detection (PID) mode on (a) NMC5 (REF) at reference state, and (b)  $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2})\text{O}_2$  (NMC5) after 1<sup>st</sup> cycle in the voltage range of 2.8 – 4.7 V with 0.4 C current applied. Comparison of the  $^7\text{Li}$  distribution between NMC5-REF and NMC5 with initial cycle.





**Fig. S8.** Visualization of the accumulated CEI layer and the pristine part of the NMC5 RT cathode based on the SIMS positive-ion detection mode.