Transition metal speciation as a degradation mechanism with the formation of solid-electrolyte interphase (SEI) in Ni-rich transition metal oxide cathode

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Table S1. Linear fitting with Curie-Weiss law (150 K – 300 K) for the magnetic measurement. Electrode is active-material: Carbon black: PVDF = 80:10:10 wt%.

Sample	μ_{exp} (BM)	Curie const. (emu·K/mol)	Curie-Weiss temp. (K)	Mn^{4+}	Mn^{3+} (LS)	Co^{3+}	Ni^{2+}	Ni^{3+} (LS)	Ni^{3+} (HS)
				(mole ratio)					
REF	3.0112	1.1402	-95.439	0.29	0.01	0.2	0.412		0.088
4.2 V	2.7226	0.9321	-66.4243	0.2331	0.0669	0.2	0.375	0.125	
4.5 V	3.0345	1.1579	-95.8893	0.285	0.015	0.2	0.390		0.110
4.8 V	2.6563	0.8873	-63.4693	0.22	0.08	0.2	0.32	0.18	

Table S2. Rietveld refinement fitting parameters and phase quantification (Trigonal: R-3m + Cubic: Fd-3m). NMC5-REF indicates the pristine $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode. NMC5 4.2 V, NMC5 4.5 V, and NMC5 4.8 V represent the NMC5 electrodes cycled at 2.0 – 4.2 V, 2.0 – 4.5 V, and 2.0 – 4.8 V, respectively, for 100 times with the current rate of 0.4 C.

Sample	a-lattice (Å)	c-lattice (Å)	O position	NMC5 (%)	SPINEL (%)	Spinel a-lattice (Å)	R_{wp}	R_{exp}
NMC5-REF	2.87091	14.24743	0.23460	100			2	3.12
NMC5 4.2 V	2.87181	14.2516	0.23767	99.1155	0.88	8.2383	4.07	3
NMC5 4.5 V	2.8558	14.33194	0.23505	100			11.12	3.02
NMC5 4.8 V	2.86042	14.23003	0.23424	60.14182	39.85	7.58864	3.7	3.08

Table S3. EIS fitting results. NMC5-REF indicates the pristine $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode. NMC5 4.2 V, NMC5 4.5 V, and NMC5 4.8 V represent the NMC5 electrodes cycled at 2.0 – 4.2 V, 2.0 – 4.5 V, and 2.0 – 4.8 V, respectively, for 100 times with the current rate of 0.4 C.

Initial Charge			
Sample	R_{el} (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
NMC5 4.2 V	6.59	13.89	5.81
NMC5 4.5 V	9.69	7.56	15.90
NMC5 4.8 V	7.67	52.00	12.09

100 cycles					
Sample	R_{el} (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)	Warburg coefficient, σ	D_{Li} (cm^2s^{-1})
NMC5-REF				2.54	5.78082E-10
NMC5 4.2 V	4.99	3.29	16.08	4.10	1.41624E-11
NMC5 4.5 V	19.39	3.44	34.33	2.97	9.44337E-11
NMC5 4.8 V	4.89	12.00	60.68	2.85	3.56263E-11

Table S4. Supplement information corresponding to Fig. 5 Mass spectroscopy analyses.

Cycle No.	Corresponding time from C1 (sec)	Between 1 cycle (sec)
C10	101	11
C50	543	
C100	1097	
C200	2204	
C300	3311	
C400	4418	
C500	5525	

AMU	Corresponding elements or compounds
7.0	Li, Li-based SEI species
12.0	Carbon (based)
27.0	LiF
44.0	C_2F from electrolyte decomposition in relation to PVDF binder
47.0	PO from electrolyte decomposition
52.0	OF_2 from electrolyte decomposition
60.0	^{60}NiO and/or $^{12}C_5$
55.0 – 61.0	Transition metal species (Mn, Co, and Ni)
74.0	^{58}NiO

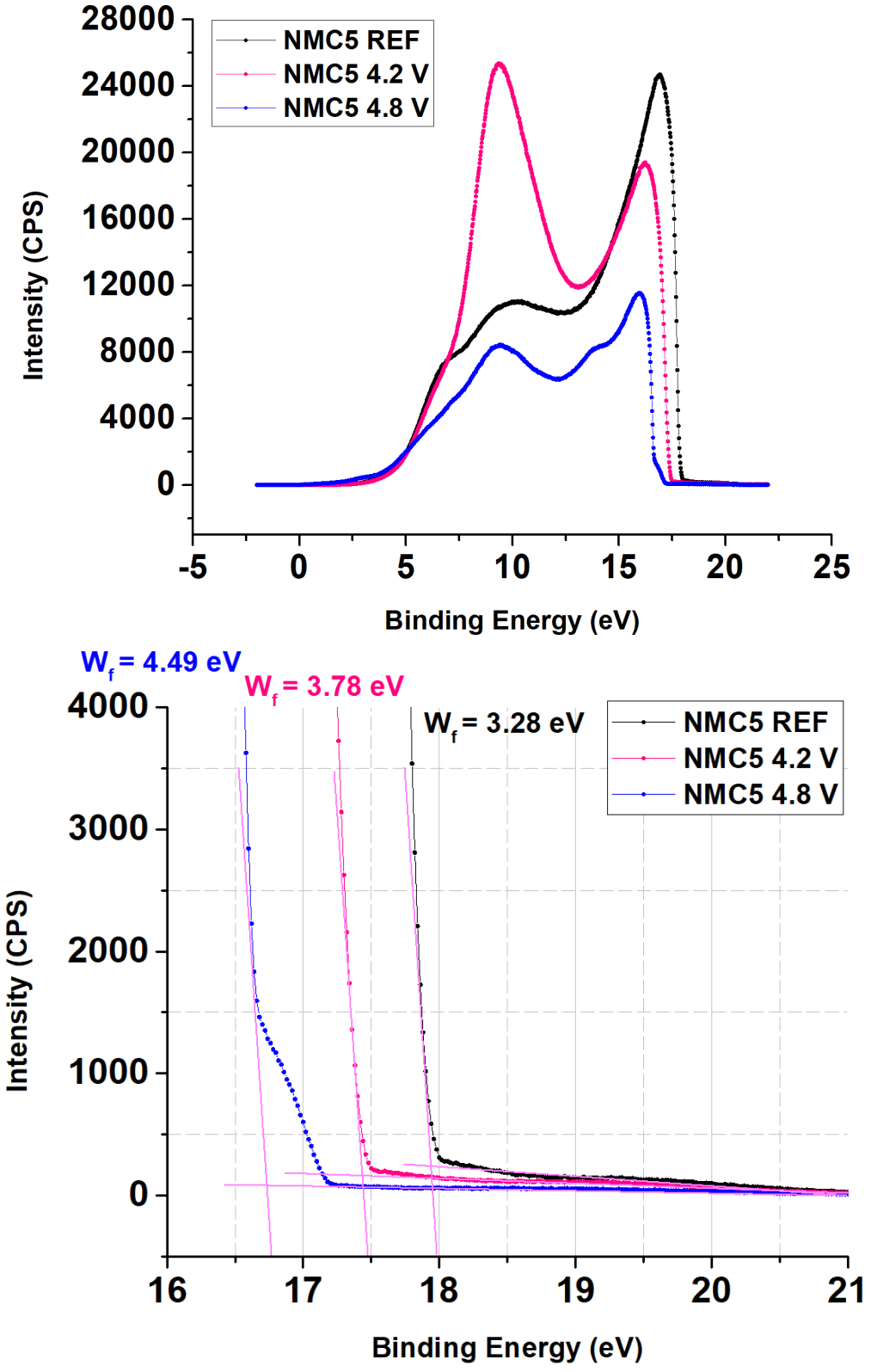


Fig. S1. (Top) Ultraviolet photoelectron spectroscopy (UPS) measurements on NMC5 REF, NMC5 4.2 V, and NMC5 4.8 V. (Bottom) Work function calculation for each electrode. REF indicates reference state where no current was applied. NMC5 is the $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode. UPS photons were emitted by Helium gas (He I: 21.22 eV). W_F is work function for each electrode.

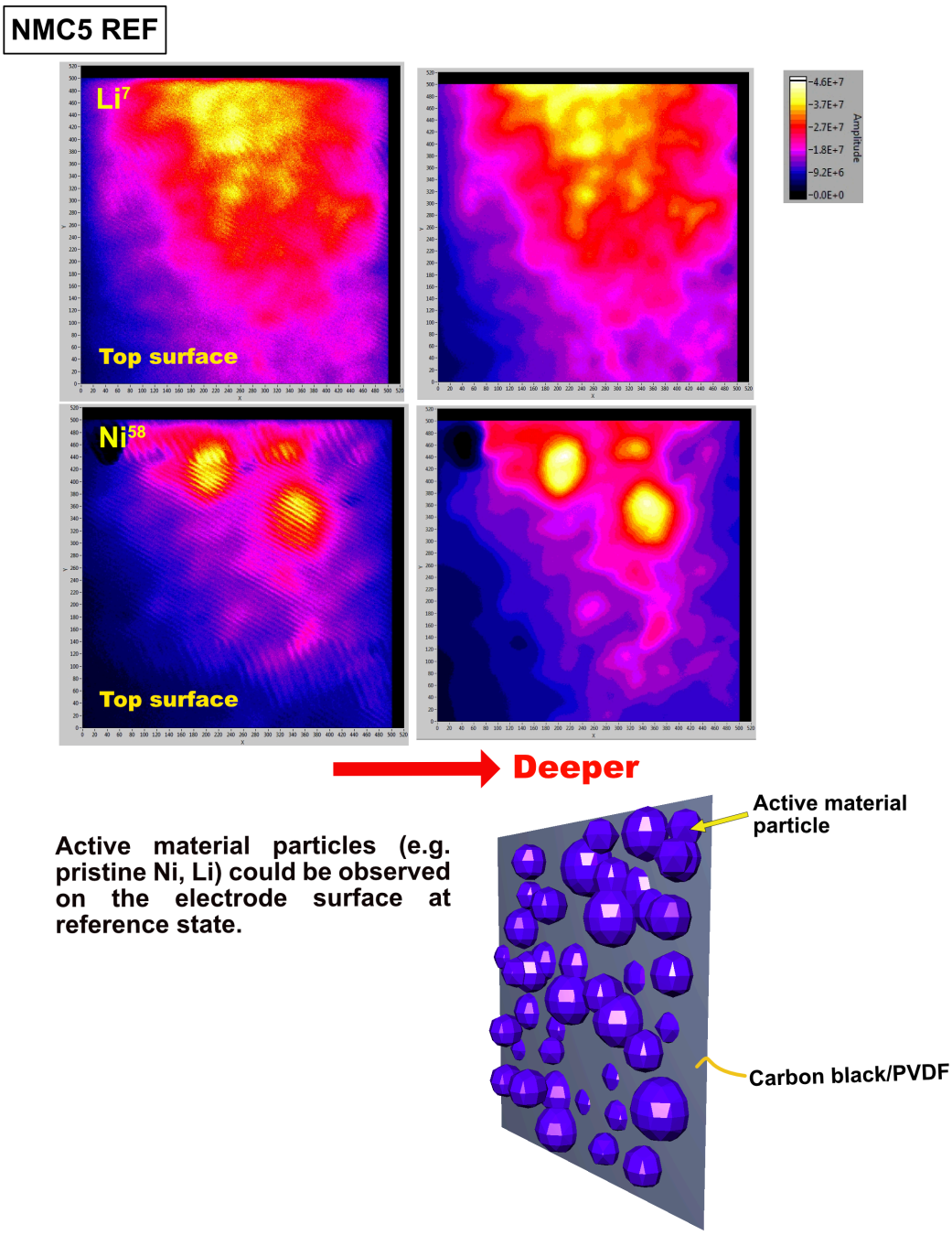


Fig. S2. SIMS mapping with ^{7}Li and ^{58}Ni elements of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode. At reference state (NMC5 REF), where no current was applied, the mapping revealed Ni and Li distributions along with the active material particles. It showed a good consistency with depth.

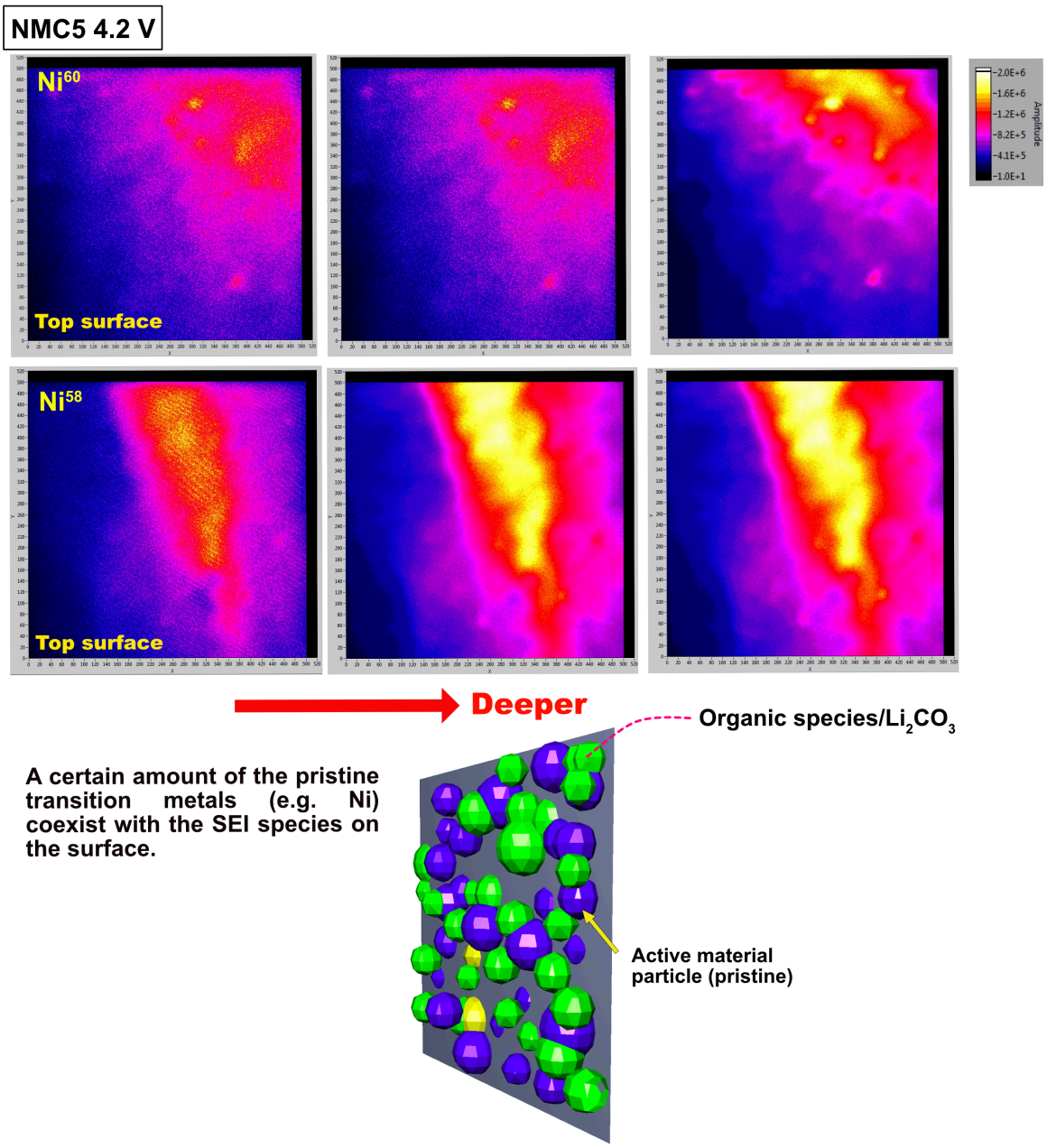


Fig. S3. SIMS mapping with ^{58}Ni and ^{60}Ni elements of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode, at two different points, respectively. The cathode was cycled in the voltage range of 2.0 – 4.2 V (0.4 C-rate). The Ni elements of the top surface showed relatively lower concentration as compared with the NMC5 REF (Fig. S2.), but it recovered its signal with depth. The interphase is likely to be mixed with some SEI species.

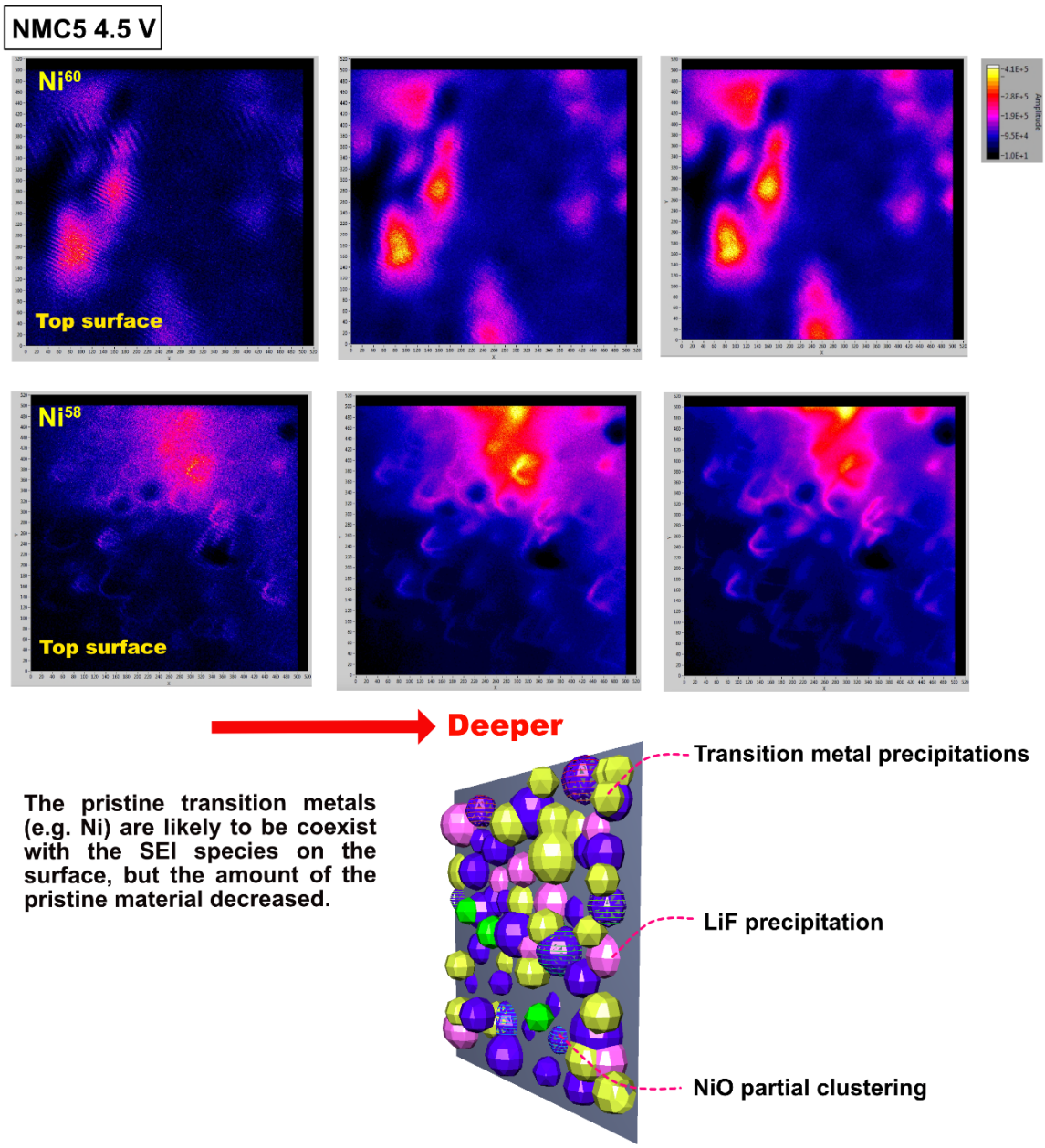


Fig. S4. SIMS mapping with ^{58}Ni and ^{60}Ni elements of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode, at two different points, respectively. The cathode was cycled in the voltage range of 2.0 – 4.5 V (0.4 C-rate). The Ni elements of the top surface showed relatively lower concentration as compared with the NMC5 REF and NMC5 4.2 V (Fig. S2.). It slightly recovered its signal with depth, but the amount of the pristine transition metal (Ni) obviously decreased.

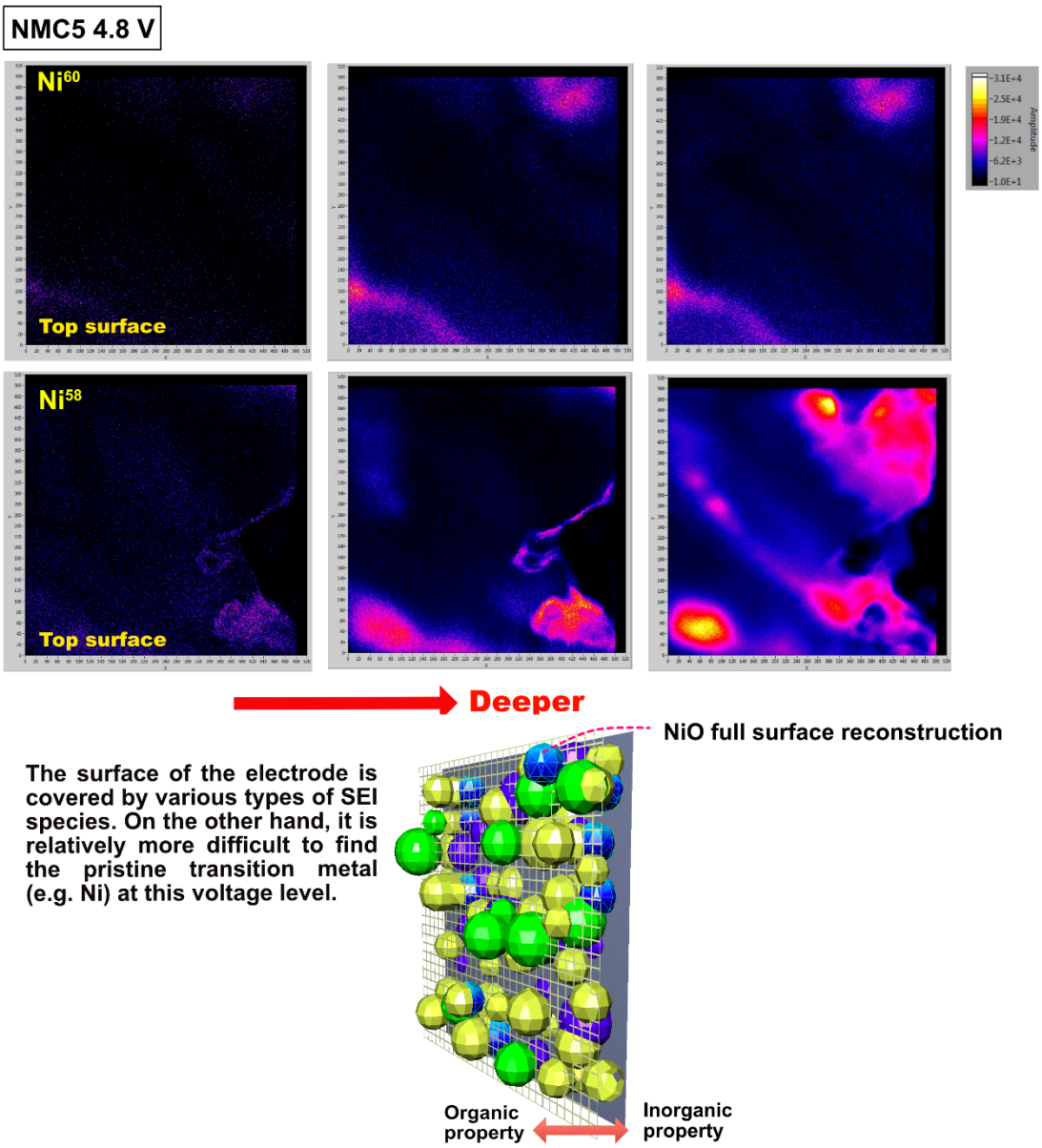
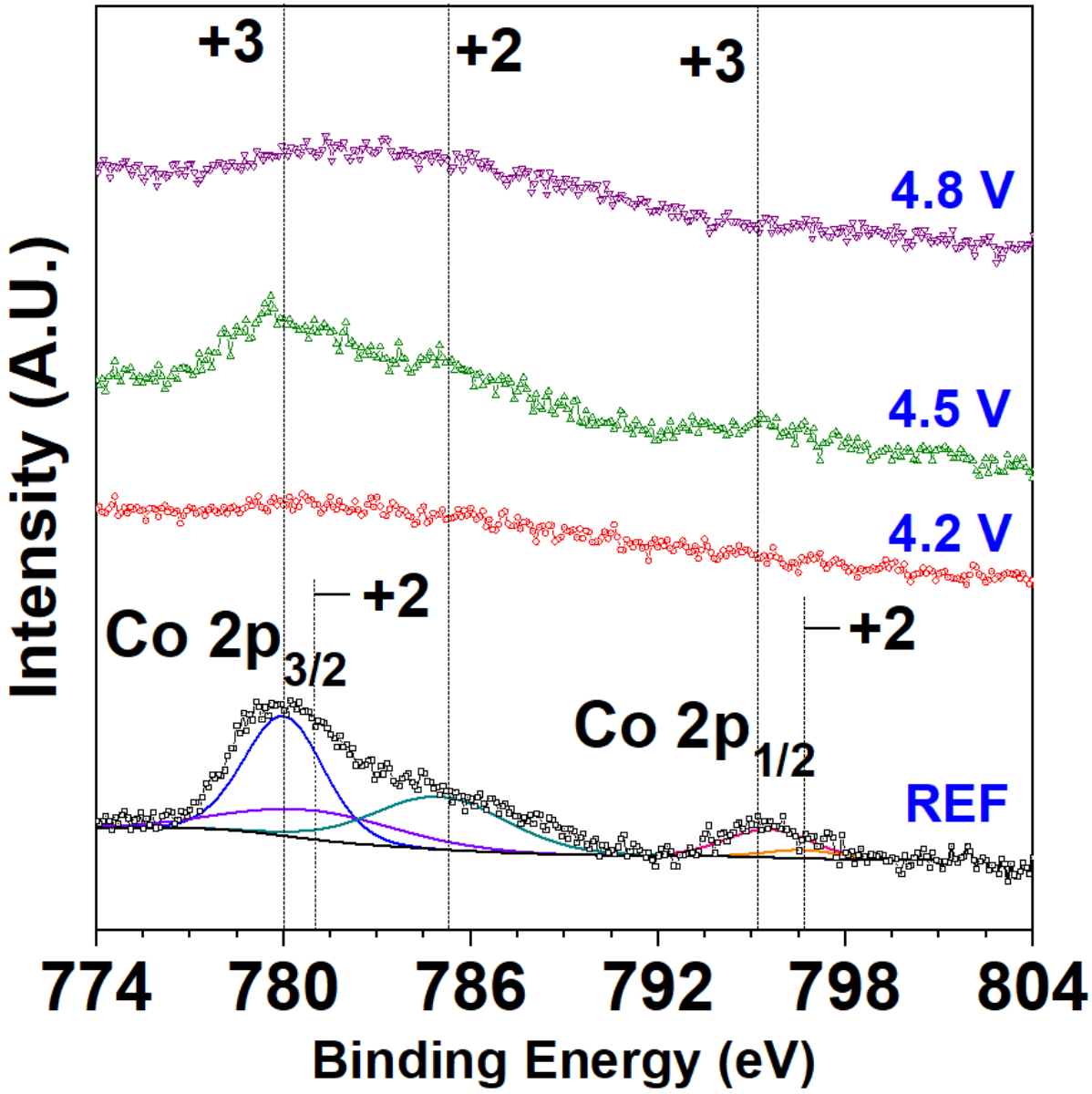


Fig. S5. SIMS mapping with ^{58}Ni and ^{60}Ni elements of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ electrode, at two different points, respectively. The cathode was cycled in the voltage range of 2.0 – 4.8 V (0.4 C-rate). The top surface of the interphase is likely to be covered by organic SEI species. On the other side, it can be suggested that the SEI layer close to the electrode substrate mainly consist of inorganic SEI species such as decomposed metallic precipitates (e.g. NiF_2, NiF_3, MnF_2, LiF_2, CoF_3).



Type	B.E.	State
Co $2p_{3/2}$	780.0 eV	+3
Co $2p_{1/2}$	795 eV	+3
Co sat. Peak	785 eV	+2
Co sat. Peak	802.7 eV	+2
Co weak Peak	781.01 eV	+2 (at pristine)
Co weak Peak	796.6 eV	+2 (at pristine)

Fig. S6. Ex situ XPS spectra of NMC5 REF, NMC5 4.2 V, NMC 5 4.5 V, and NMC5 4.8 V electrodes after 100 cycling with the constant current of 0.4 C at Co 2p.