Electronic Supplementary Information

Oxidation behaviour of lattice oxygen in Li-rich manganese-based layered oxide studied by hard X-ray photoelectron spectroscopy

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	Sampling	Potential / V	Capacity /	Li content x in
	point		mAh/g	Li _x Ni _{0.20} Mn _{0.55} O _{1.93}
1 st cycle	1	OCV	0.0	1.25
	2	4.24	32.4	1.15
	3	4.45	51.5	1.09
	4	4.58	88.7	0.98
	5	4.61	227.6	0.56
	6	4.80	308.8	0.31
	7	4.00	-32.2	0.41
	8	3.50	-93.2	0.60
	9	2.00	-171.5	0.83
5 th cycle	(10)	2.00	0.0	0.76
	(11)	3.39	21.7	0.69
	(12)	4.03	118.0	0.40
	(13)	4.80	217.6	0.10
	(14)	4.20	-21.4	0.16
	(15)	3.65	-82.4	0.35
	(16)	2.00	-214.6	0.75

Table S1. Delithiated/relithiated samples of $Li[Li_{0.25}Ni_{0.20}Mn_{0.55}]O_{1.93}$ prepared for HAX-PES measurements.

	Sampling	Potential / V	Capacity /	Li content x in Li _x Mn _{0.67} O ₂
	point		mAh/g	
1 st cycle		OCV	0.0	1.33
	2	4.72	32.4	1.24
	3	4.80	56.8	1.17
	4	3.26	-15.2	1.21
	5	2.00	-32.5	1.26
5 th cycle	6	2.00	0.0	1.24
	7	3.40	14.6	1.20
	8	4.15	28.3	1.16
	9	4.80	40.7	1.12
	10	3.75	-6.0	1.14
	(11)	3.26	-14.5	1.16
	(12)	2.00	-36.5	1.23

Table S2. Delithiated/relithiated samples of Li_2MnO_3 prepared for HAX-PES measurements.



Fig. S1. X-ray diffraction profile of the pristine Li[Li_{0.25}Ni_{0.20}Mn_{0.55}]O_{1.93} sample, which is indexed with *C*2/*m*, and the refined lattice parameters are a = 4.951 Å, b = 8.558 Å, and c = 5.028 Å, $\beta = 109.213^{\circ}$ respectively.



Fig. S2. Charge-discharge profiles of Li_2MnO_3 electrodes for the 1st and 5th cycles. Sampling points for HAX-PES measurements are marked on the figure.



Fig. S3. Mn $2p_{3/2}$ photoelectron spectra of Li₂MnO₃ electrodes for (a) the 1st and (b) 5th cycles. The sampling points are cited from Fig. S1. Asterisks in (a) and (b) indicate the multiplet splitting. The vertical lines show the reference positions from ref. 33 in the main text rescaled with the acetylene black peak position at 284.5 eV in C 1s spectra.



Fig. S4. Li 1s + Mn 3p photoelectron spectra of Li_2MnO_3 electrodes for (a) the 1st and (b) 5th cycles. The sampling points are cited from Fig. S1.



Fig. S5. Li 1s + Mn 3p photoelectron spectra of $\text{Li}[\text{Li}_{0.25}\text{Ni}_{0.20}\text{Mn}_{0.55}]O_{1.93}$ electrodes for (a) the 1st and (b) 5th cycles. The sampling points are cited from Fig. 1.



Fig. S6. O 1s photoelectron spectra of Li_2MnO_3 electrodes for the 1st cycle. The sampling points are cited from Fig. S1.



Fig. S7. O 1s photoelectron spectra of Li[Li_{0.25}Ni_{0.20}Mn_{0.55}]O_{1.93} electrode disassembled at 309 mAh/g (Sampling point #6), which were acquired on a laboratory XPS system with/without Ar⁺ sputtering (PHI5000 VersaProbe II, monochromated Al $K\alpha$ radiation; 1486.6 eV, sputtering condition; 4 keV, 10 μ A, 1 min).

Fitting procedure of the O 1s HAX-PES spectra

The O 1s HAX-PES spectra were decomposed with three or four Gaussian functions as follows. As a first step, we start with the pristine sample (Fig. S8, sp. #1). The pristine sample can be separated into three components. The signal centred at 532.7 eV is ascribed to surface-deposited oxygen species. The lattice oxygen peak was successfully fitted with two Gaussian components. One is a sharp component set at 529.4 eV, and the other is a relatively broad component located at 530.0 eV. It may be possible to consider that the former is the component coming from the Li₂MnO₃-like domain and the latter is from the $LiMO_2$ -like and/or the other-type domain in the active material. Alternatively, the lattice oxygen in the active material can be simply expressed as an asymmetric peak. Therefore, the lattice O²⁻ signal from the active material was fitted with the two components in the spectral decompositions for the charged/discharged samples. The 529.4-eV component was fitted without any constraints, but the 530.0-eV component was done with the constraints in peak position, width, and amplitude with respect to the 529.4-eV one. On the spectral fittings for the charged/discharged samples, a fourth component was introduced at ca. 530.5 eV (Fig. S8, sps. #3,6,8,9). The fourth component was fitted without any constraints (except for #9), and its peak position was slightly shifted at between 530.2 and 530.8 eV. In the fully discharged spectra (Sp. #9), the width of the signal at ca. 530.5 eV was restricted to be less than 1.5 eV, and the signal at the highest energy, which can be assigned to surface-deposited oxygen and/or Li₂CO₃, was restricted to be higher than 531.5 eV in position to provide a reasonable fitting result. Fig. S9 shows the O 1s decomposition results for the 5th cycle samples, where the same fitting procedures were applied.



Fig. S8. Examples of the O1s spectral decomposition for the 1st cycle. The sampling points are cited from Fig. 1.



Fig. S9. Examples of the O1s spectral decomposition for the 5th cycle. The sampling points are cited from Fig. 1.