Supplementary Information

In situ X-ray Raman spectroscopy and magnetic susceptibility study on Li[Li$_{0.15}$Mn$_{1.85}$]O$_4$ oxygen anion redox reaction

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Experimental

Preparation and characterization

A powder sample of $Li[Li_{0.15}Mn_{1.85}]O_4$ was prepared by a two-step solid-state reaction technique as previously reported.[1] The obtained sample was characterized by X-ray diffraction with Fe-Kα radiation (D8 ADVANCE, Bruker AXS) and scanning electron microscopy (S-3600 N, Hitachi High-Technologies). Rietveld analysis was performed using the RIETAN-FP software,[2] and the crystal structure was drawn using the VESTA software.[3]

Electrochemical measurements

The electrochemical properties of $Li[Li_{0.15}Mn_{1.85}]O_4$ were examined in a non-aqueous lithium cell. A mixed electrode (diameter = 16 mm) consisting of 88 wt% $Li[Li_{0.15}Mn_{1.85}]O_4$, 6 wt% acetylene black (AB, Denka), and 6 wt% polyvinylidene fluoride (PVdF, Kureha) was used as the working electrode, and a lithium metal sheet pressed onto a stainless-steel (SUS) plate (diameter = 19 mm) was used as the counter electrode. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (EC/DMC = 3/7 by volume, Kishida Chemical). Two sheets of the porous polyethylene membrane (TonenGeneral Sekiyu K. K.) were used as a separator. The cell was fabricated in an Ar-filled glove box, and then operated at a current of 0.3 mA ($\simeq$ 0.15 mA·cm^{-2}) at 298 K. The voltage range was 3.0–5.0 V for initial three cycles, and then changed to 3.0–5.3 V for subsequent thirty cycles. The charge/discharge curves of the initial three cycles are shown in Fig. 1(c), while those of the subsequent thirty cycles are shown in Fig. 1(d).

In situ XRS/XAS measurements

Recently, we developed an in situ XRS system to clarify the electronic structures of C_6Li and $C_{12}Li$.[4] We used the same XRS system to investigate the O K-edge spectra of $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$ samples with $y \geq 0$. The lithium cell was packed into an Al-laminated film with a size of 80 mm × 50 mm and exposed to hard X-rays at the BL33XU beamline

at SPring-8. The mix electrode was prepared by the same method described above, but a lithium metal sheet (diameter = 19 mm) without the SUS plate was used as the counter electrode. The thickness of the mix electrode was 53 μm and the weight of the active material (Li[Li$_{0.15}$Mn$_{1.85}$]O$_4$) was 21.38 mg. Before the XRS/XAS measurements, the Al-laminated cell was operated at 3.0–4.2 V for three cycles as a conditioning. The applied current was 0.3 mA and the environment temperature was 298 K. As shown in Fig. S1, these charge/discharge curves almost trace those in Fig. 1(c), suggesting that in situ lithium cell was successfully fabricated.

After charging the Al-laminated cell up to 4.5 or 5.3 V at the current of 0.3 mA, XRS/XAS measurements were performed at $\sim$298 K under an open circuit condition (not monitored during the measurements). Fig. S2(a) shows the experimental setup for the in situ XRS/XAS measurements. Furthermore, Figs. S2(b) and S2(c) show schematic arrangements of the Al-laminated cell for the XRS and XAS measurements, respectively. The Al-laminated cell was slightly tilted for the XRS measurements, where the angle between the Al-laminated cell and incident X-ray was 5 °. We selected an energy of 9.8 keV as the incident X-ray because signals of scattered X-ray reached the maximum at 9.8 keV in the case of XRS measurements on C$_6$Li and C$_{12}$Li.[4] However, the acquisition time for one XAS spectrum was at least 11 h. We also measured the O K-edge spectrum of Li$_2$CO$_3$ (Wako Pure Chemical Industries) with an acquisition time of 24 min. After each XRS measurement, Mn K-edge X-ray absorption near edge structure and extended X-ray absorption fine structure spectra were acquired by conventional XAS measurements. In contrast to the XRS measurements, the Al-laminated cell was set to be perpendicular to the incident X-ray. The analysis region for the XAS measurements was estimated to 3 mm $\times$ 10 μm, which was approximately 1.5 $\times$ 10^{-2} % of the surface area of the mix electrode ($\simeq$ 2 cm^2). The analysis region for the XRS measurements is similar with that for the XAS measurements.
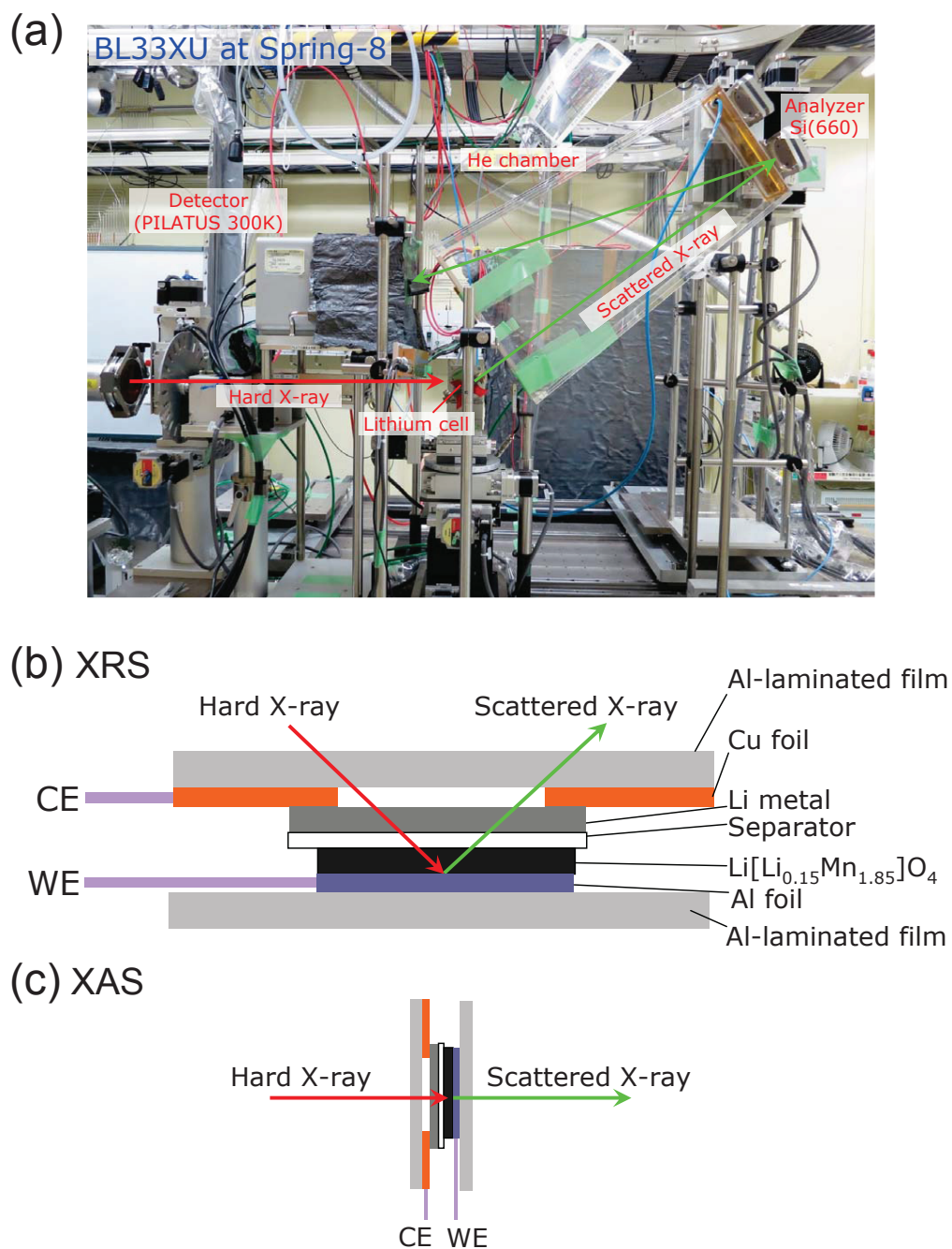
χ measurements

The χ (= M/H) values were determined using a superconducting quantum interference

device (SQUID) magnetometer (MPMS, Quantum Design), where M is the magnetization and H is the applied magnetic field. M was measured in field-cooling mode with $H = 10$ kOe and cooling from 400 to 5 K. Delithiated $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$ samples with $y > 0$ were prepared by the electrochemical reaction. Each $Li[Li_{0.15}Mn_{1.85}]O_4/Li$ cell was charged up to a desired Li composition at the current of 0.3 mA, and rested for 5 h to reach a stable open circuit voltage. Charge curves for the χ measurements are shown in Fig. S3. The weight of active material ($Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$) was approximately 15 mg. Each mix electrode consisting of $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$, AB, and PVdF was removed from the cell in the Ar-filled glove box, and packed into two sheets (20 mm × 20 mm) of Al foils to avoid reactions with moist air. Finally the $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$ sample was fixed to the sample rod of the SQUID magnetometer with a Cu wire. Above procedure was essentially same with χ measurements on $Li_{1-y}[Ni_{1/2}Mn_{3/2}]O_4$[5] and $Li_{1+y}[Li_{1/3}Ti_{5/3}]O_4$.[6]
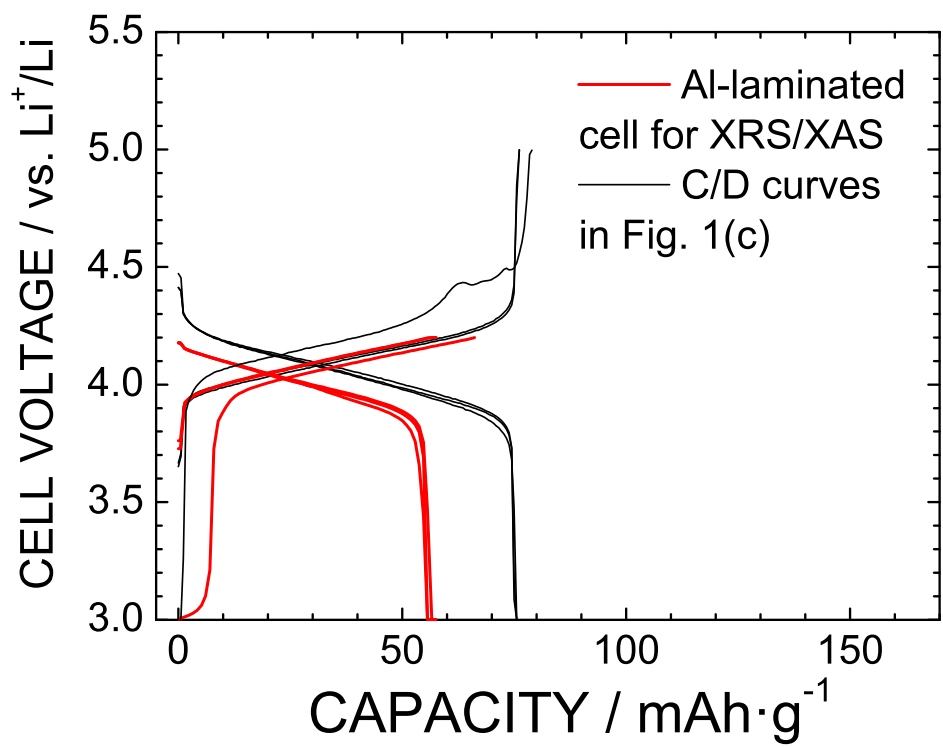
Fig. S1: Conditioning charge/discharge (C/D) curves of the Al-laminated lithium cell for the XRS/XAS measurements. C/D curves in Fig. 1(c) are also shown for comparison.

Fig. S2: (a) Setup of in situ XRS measurements and schematic arrangements of the Al-laminated cell for the (b) XRS and (c) XAS measurements.
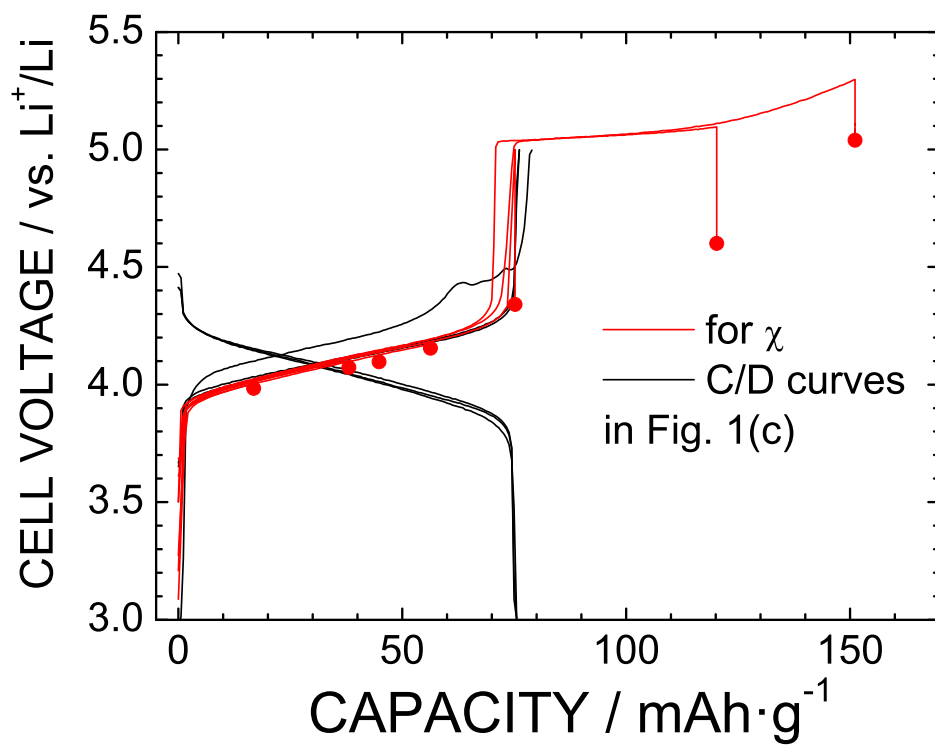
Fig. S3: Charge/discharge (C/D) curves for the χ measurements. The closed circles indicate open circuit voltages just before χ measurements. C/D curves in Fig. 1(c) are also shown for comparison.

**Table S1**: Structural parameters of the Li[Li$_{0.15}$Mn$_{1.85}$]O$_4$ sample determined by Rietveld analysis

Atom	Wyckoff position	Occupancy	x	y	z	B_{iso} / Å^2
Li1	8a	1.0	0.125	0.125	0.125	0.9(1)
Li2	16d	0.075	0.5	0.5	0.5	0.8(1)
Mn1	16d	0.925	0.5	0.5	0.5	0.8(1)
O	32e	1.0	0.262(1)	0.262(1)	0.262(1)	1.8(1)
Space group: $Fd\bar{3}m$, $a_{\text{c}} = 8.1899(1)$ Å, $R_{\text{wp}} = 2.82$ %, and $S = 1.27$.						
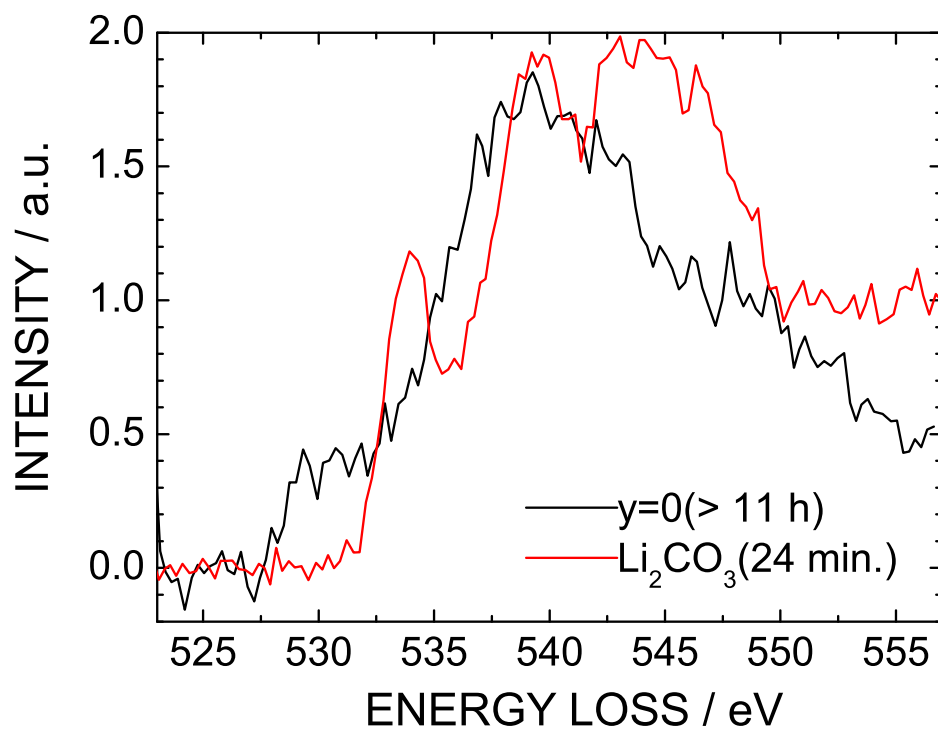
Fig. S4: O K-edge spectrum of Li_2CO_3 obtained by the XRS measurement. O K-edge spectrum of the $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$ ($y = 0$) sample is also shown for comparison.
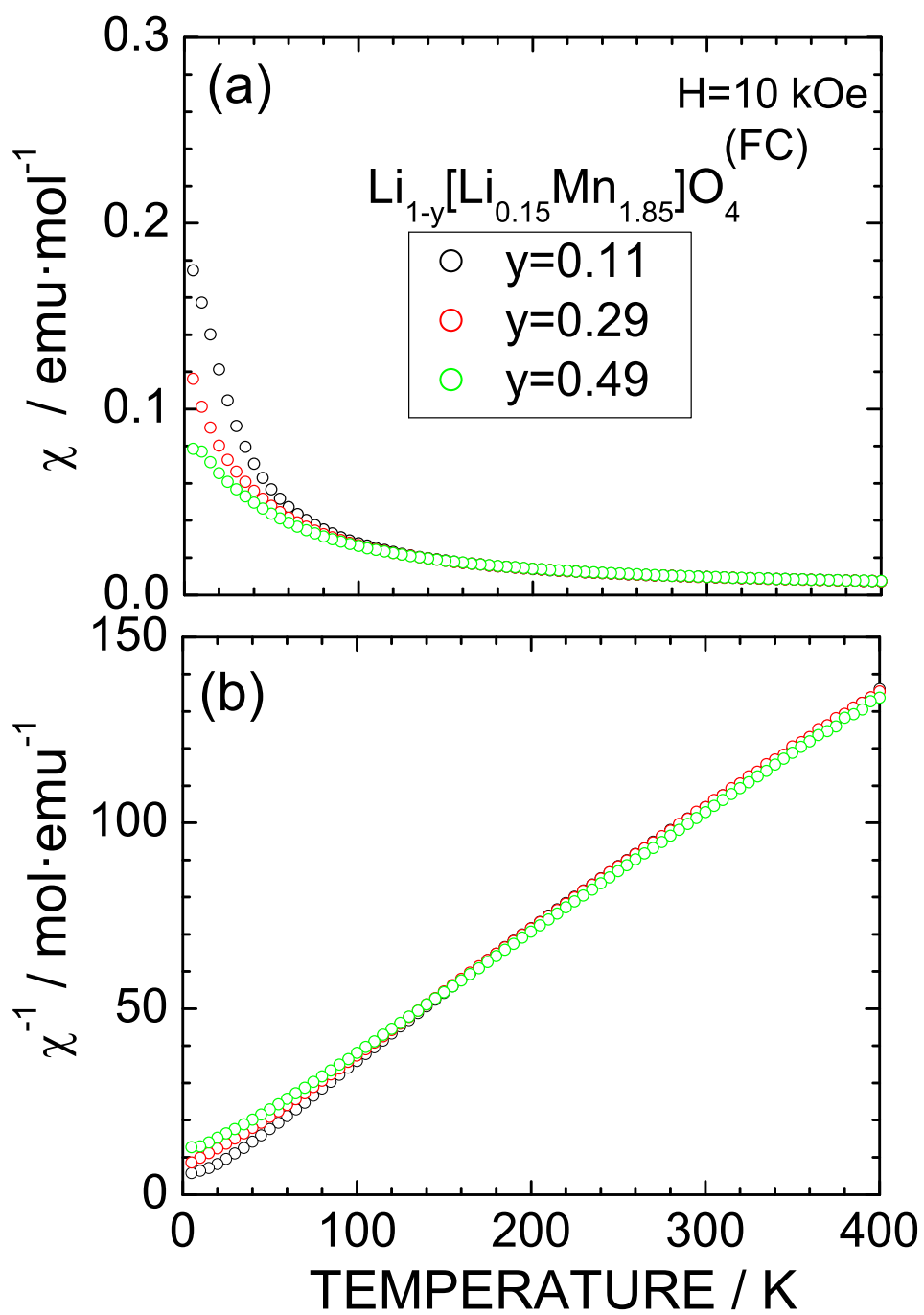
Fig. S5: (a) χ and (b) χ^{-1} of the $y = 0.11$, 0.22, and 0.49 samples measured in field-cooling mode with $H = 10$ kOe.

Table S2: Curie–Weiss parameters of the $Li_{1-y}[Li_{0.15}Mn_{1.85}]O_4$ samples

y	OCV / V	μ_{eff} / μ_B	Θ_p / K
0	–	3.93(2)	−62(3)
0.11	3.985	3.84(4)	−19(2)
0.25	4.073	3.62(4)	−11(1)
0.29	4.098	3.57(2)	−12(1)
0.38	4.154	3.56(3)	−13(2)
0.49	4.341	3.56(4)	−13(1)
0.78	4.601	3.57(3)	−19(1)
0.98	5.039	3.68(3)	−40(1)

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