Electronic supplementary information

Direct observation of reversible oxygen anion redox reaction in Li-rich manganese oxide, Li_2MnO_3, studied by soft X-ray absorption spectroscopy

Masatsugu Oishi,*[1] Keisuke Yamanaka,[2] Iwao Watanabe,[1,2] Keiji Shimoda,[1] Toshiyuki Matsunaga,[1] Hajime Arai, [1] Yoshio Ukyo, [1] Yoshiharu Uchimoto,[3] Zempachi Ogumi[1] and Toshiaki Ohta[2]

[1]*Office of Society-Academia Collaboration for Innovation*, *Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

[2]*SR Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*

[3]*Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan*

*__Corresponding author__: Masatsugu Oishi
Address: Gokasho, Uji, Kyoto 611-0011, Japan
Phone: +81-774-38-4940
FAX: +81-774-38-4996
E-mail: m-ooishi@saci.kyoto-u.ac.jp

Table S1. The parameters for the Li_2MnO_3 electrode samples used for XAS measurements. Sample numbers correspond to those in Fig. 1.

Sample No.	Cycle	Charge (V)	Discharge (V)	Capacity (mAh/g)	SOC	Change of Li ion concentration (mol)
1	1			0	0.0	0.00
2	1	4.6		170	37.0	0.74
3	1	4.8		360	78.4	1.57
4	1		3.6	54	11.8	0.24
5	1		2	235	51.2	1.02
6	2	3.5		113	24.6	0.49
7	2	4.2		184	40.1	0.80
8	2	4.8		257	56.0	1.12
9	2		3.6	48	10.5	0.21
10	2		3.2	88	19.2	0.38
11	2		2	169	36.8	0.74

SOC is calculated as SOC 100 % = 459 mAh/g

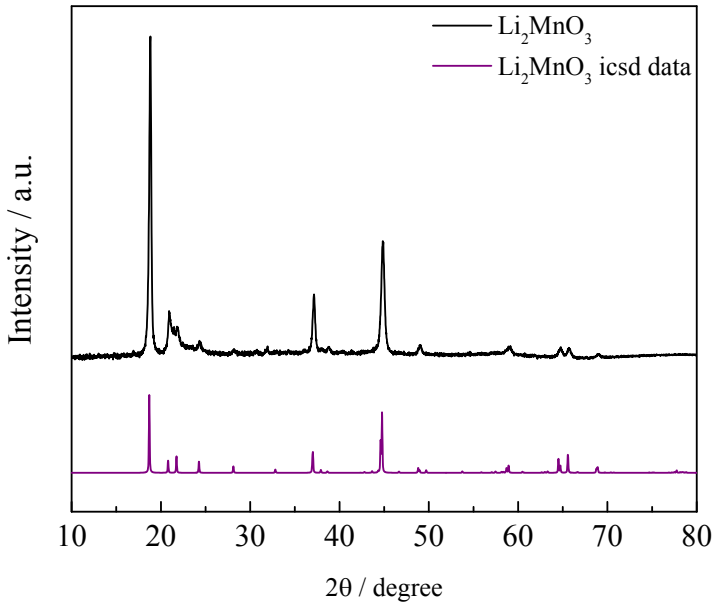


Figure S1. XRD pattern of the synthesized Li_2MnO_3 powder sample.

(a) (b)

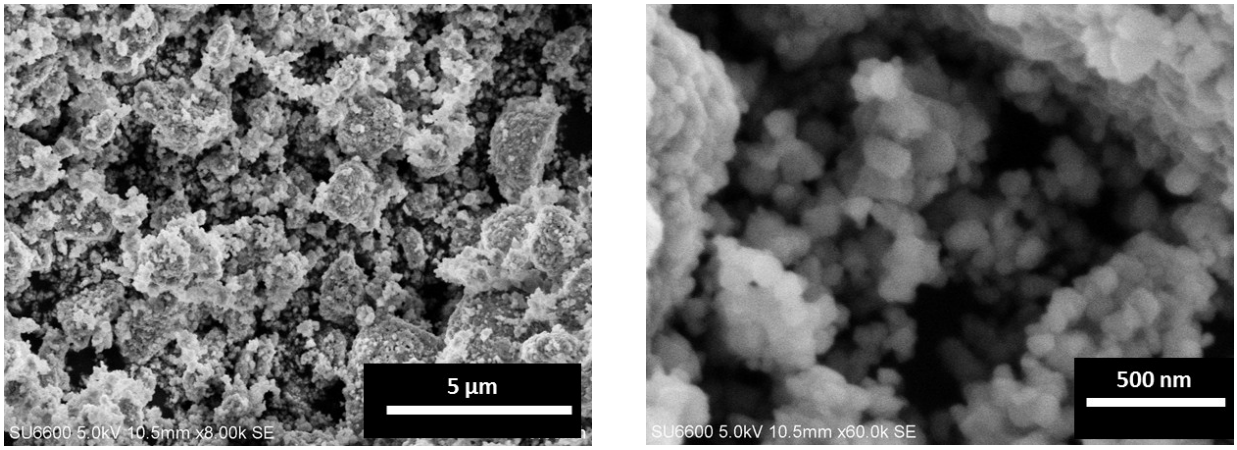


Figure S2. (a) Low and (b) high-magnification SEM images of the synthesized Li_2MnO_3 powder sample.

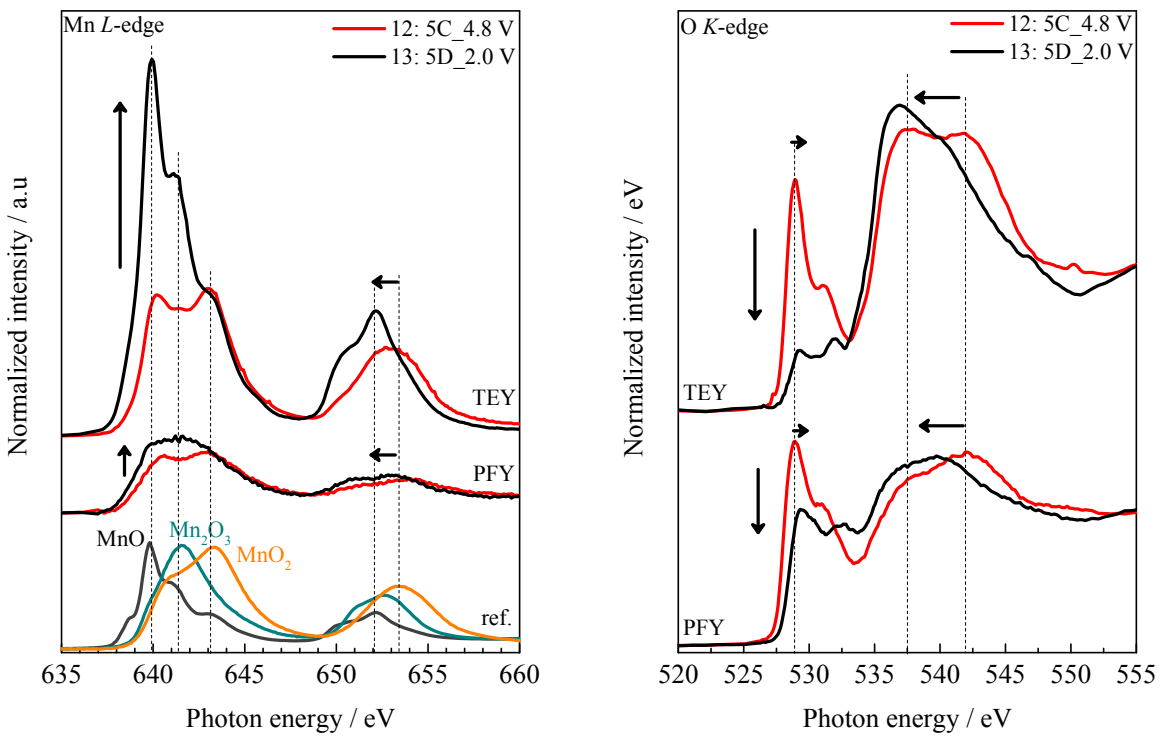


Figure S3. (a) Mn *L*-edge and (b) O *K*-edge XAS spectra for the Li_2MnO_3 electrode at fully charged (spectrum No.12) and fully discharged (spectrum No.13) states during the 5th cycle.

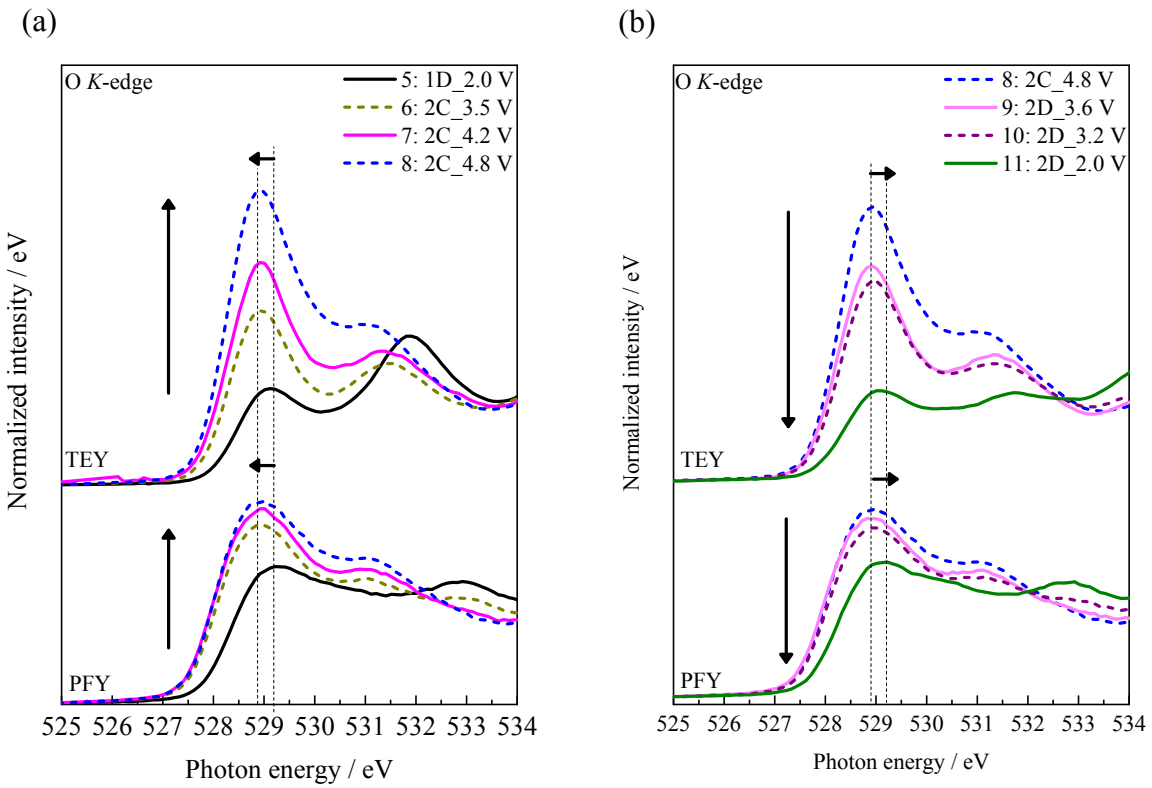


Figure S4. The pre-edge structures expanded from the O *K*-edge XAS for the Li_2MnO_3 electrode obtained during (a) charging and (b) discharging processes in the 2nd cycle, respectively.

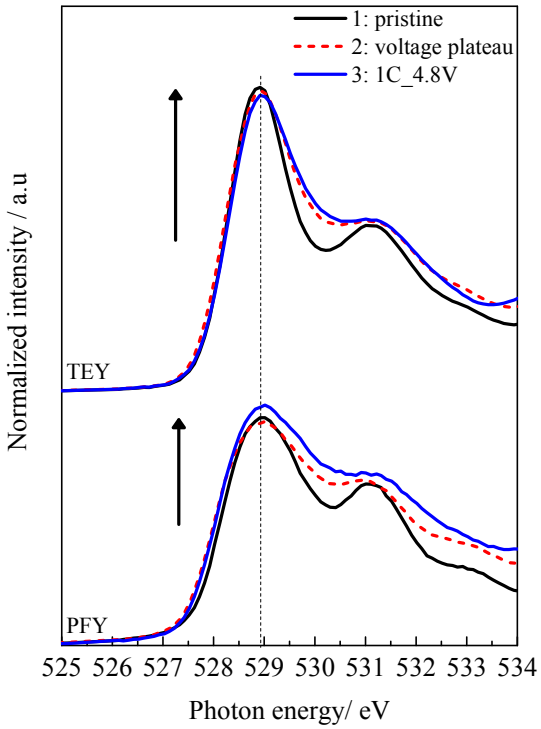
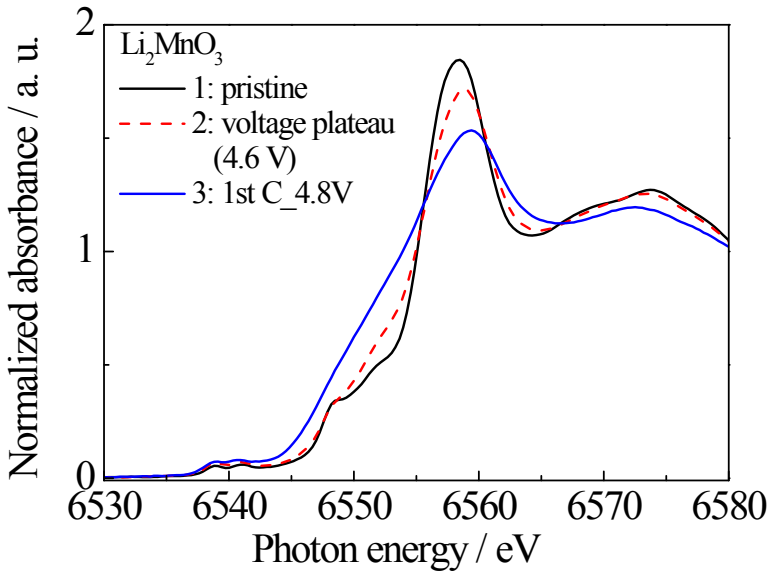


Figure S5. The pre-edge structures in the O *K*-edge XAS spectra for the Li_2MnO_3 electrode obtained during the initial charging process.

(a)



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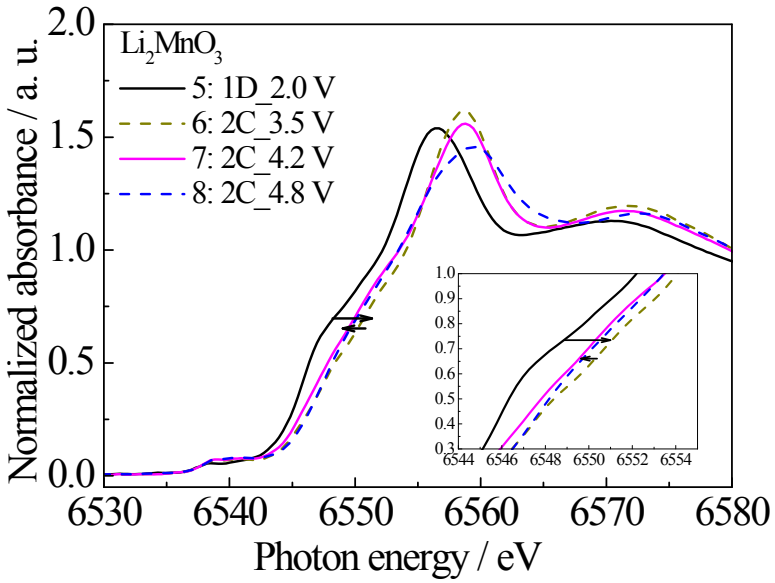
(b)



2
3

4 Figure S6. Mn *K*-edge XANES spectra of the Li_2MnO_3 electrodes obtained during (a) 1st
5 charging and (b) 2nd charging processes. The spectra changed drastically at the end of the 1st
6 charging (from No.2 to No.3 in Fig.(a)) indicating the reduction of Mn ions by the charge.
7 During the 2nd charging process the spectral change was not striking but similar behavior was
8 observed (Fig.(b)). The edge shifted to higher photon energy at first from 2.0 V to 3.5 V
9 implying the oxidation of Mn ions, then further charging lead to lowering of the edge energy
10 indicating the reduction of a part of Mn ions.