Electronic Supplementary Information

Highly reversible capacity at the surface region of a lithium-rich manganese oxide: A model study using an epitaxial film system

Sou Taminato,[a] Masaaki Hirayama,[a,*] Kota Suzuki,[a] Norifumi L. Yamada,[b] Masao Yonemura[b], Jin-Young Son,[c] and Ryoji Kanno[a]

[a] *Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan*

[b] *Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 203-1 Shirakata, Tokai, Ibaraki 319-1106, Japan*

[c] *Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Koto, Sayo, Hyogo 679-5198, Japan*

*Corresponding author, TEL: +81-45-924-5403, Fax: +81-45-924-5403, e-mail: hitrayama@echem.titech.ac.jp

S1. In-plane XRD patterns of an epitaxial Li_2MnO_3 film

Fig. S1 shows the 020 and 060 diffraction peaks are observed along the in-plane [1-10] direction at 20.7° and 65.3°, respectively. The 020 peak is attributed to a superlattice structure with honeycomb Li/Mn ordering in the transition metal layer, confirming the formation of a lithium-rich layered structure. Fig. S2 shows the rocking curve of the 020 reflection indicates six-fold symmetry at intervals of 60°. Although the 020 reflection should have two-fold symmetry, the six-fold symmetry demonstrates that the Li_2MnO_3(001) film was composed of 60°-rotated domains:

Li_2MnO_3[010]//$SrTiO_3$[110], Li_2MnO_3[010]//$SrTiO_3$[011] and Li_2MnO_3[010]// $SrTiO_3$[101].

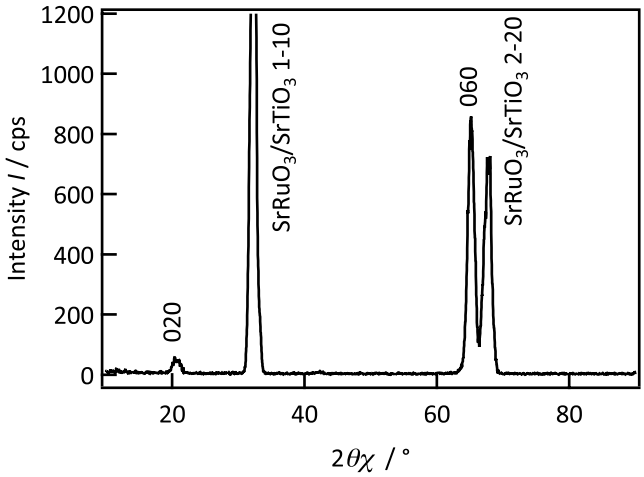

Fig. S1 In-plane XRD pattern for a Li_2MnO_3 film on $SrRuO_3$(111)/Nb:$SrTiO_3$(111).

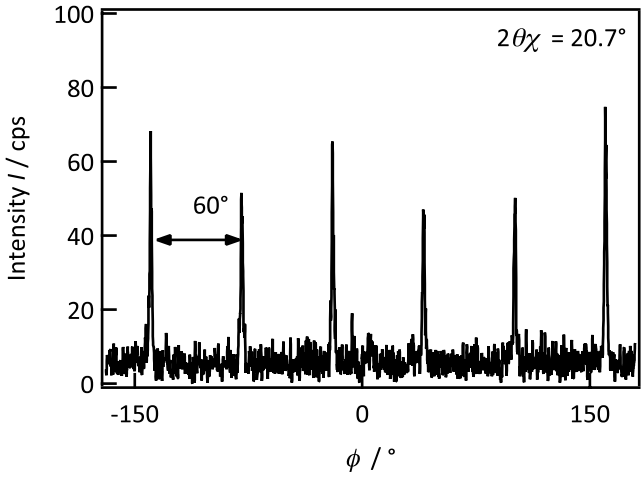

Fig. S2 In-plane phi scan XRD pattern for a Li_2MnO_3 film on $SrRuO_3$(111)/Nb:$SrTiO_3$(111).

S2. Comparison of XRD and XANES results among Li_2MnO_3 films with different thicknesses

Fig. S3 shows XRD patterns of 12.6, 29.8, and 45.1 nm-thick Li_2MnO_3(001) films synthesized under the same PLD conditions except for the deposition time.

Whereas the intensities of the 00*l* and 0*k*0 diffraction peaks increased with the film thickness, no significant changes in cell parameters and intensity ratios of 00l to 0k0 peaks were observed in the thickness range. These results indicate that those films had a similar crystal structure and composition. Fig. S3 shows Mn-K edge XANES spectra of 12.6 and 29.8 nm-thick Li_2MnO_3(001) films. The similar spectra reveal the same coordination environment of Mn ions in both films, which is consistent with the XRD results. Hence, we conclude that the Li_2MnO_3(001) films with different thicknesses had a similar structure and lithium and oxygen deficiency.

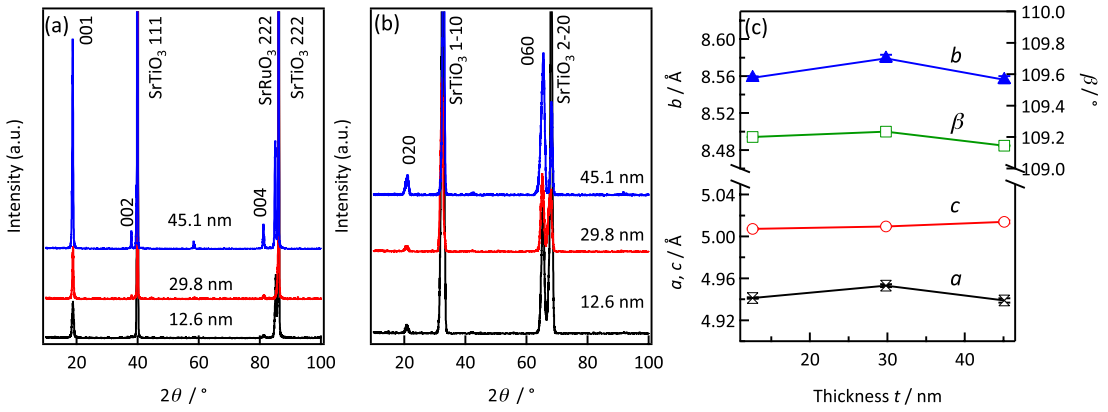

Fig. S3 (a)Out-of-plane and (b) in-plane XRD patterns and (c) cell parameters of 12.6, 29.8, and 45.1 nm-thick Li_2MnO_3(001) films.

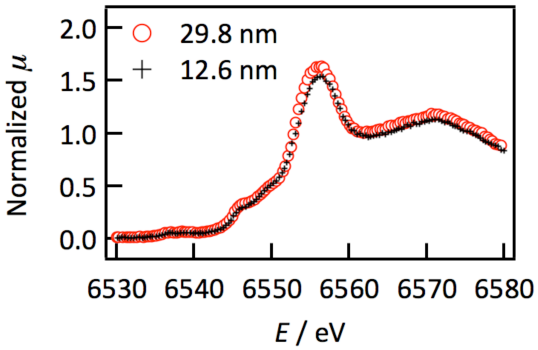

Fig. S4 XANES spectra of Mn-K edge of 12.6 and 29.8 nm-thick Li_2MnO_3(001) films.