Supplementary Information

Operando resonant soft X-ray emission spectroscopy of $LiMn_2O_4$ cathode using an aqueous electrolyte solution

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Fabrication of $LiMn_2O_4$ powder and XRD measurement

Reagents were of commercial grade and used without purification. $LiMn_2O_4$ was synthesized by a sol-gel method. $Li(CH_3COO)$ (0.075M), $Mn(CH_3COO)_2·4H_2O$ (0.150 M) and citric acid (0.233 M) were dissolved into H_2O (40 ml). The precursor solution was obtained by aging the solution at 90 °C for 1 h. Then, the precursor solution was evaporated at 60 °C for 2 h using a rotary evaporator and was dried at 100 °C in vacuum for 12 h. The dried material was heat-treated at 800 °C for 1 h under air.

The powder X-ray diffraction (XRD) measurement was conducted on a Bruker D8 Advance using Cu *K*α X-ray source as shown in Fig. S1. The obtained XRD pattern was attributed to $LiMn_2O_4$.[S1,S2]

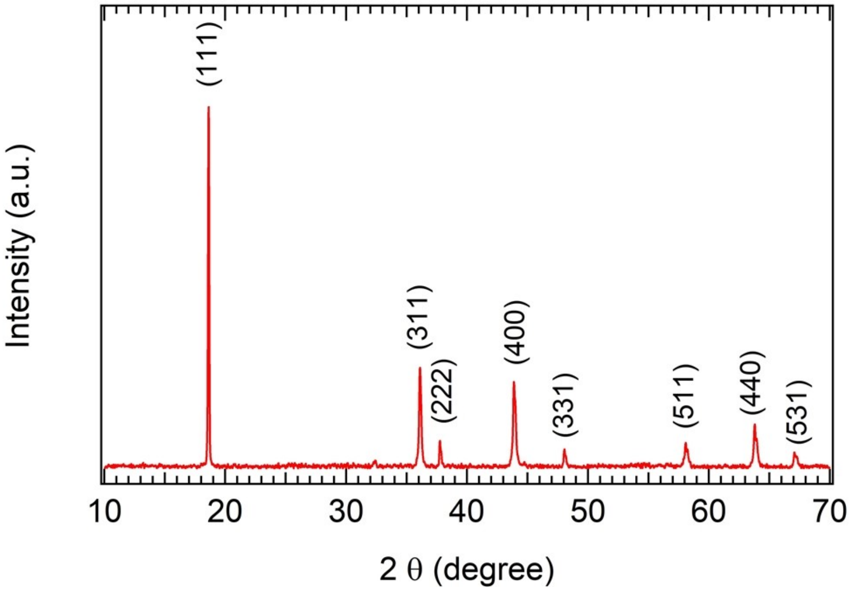

Fig. S1. XRD pattern of the $LiMn_2O_4$ powder (corresponding to the initial state). The wavelength of X-ray λ was 1.5418 Å (Cu *K*α).

Zig-zag scan of the window position for the XES measurement

The window position to the incident beam was refreshed by 4 min to reduce the beam damage. Figure S2 shows the details of the zig-zag scan. The distance for each movement along the vertical direction was 10 μm. When the beam reached near the top/bottom of Si_3N_4 window, the sample position was shift by 100 μm along the horizontal direction on the window. Then, the vertical scan resumed on the next vertical line. The beam spot size was 30 μm (h) × 2 μm (v) that is smaller than the distances of zig-zag scan.

For general XAS measurements except for dispersive XAS using energy-dispersed X-rays,[S3,S4] the incoming-photon energy must be scanned as a function of time. If we use the present RXES apparatus with the zig-zag scan for XES, the incoming-photon energy scan for XAS should be position dependent at each energy step. The position dependence as a function of the incoming-photon energy scan should not be negligible for the understanding of (averaged) electronic structure, since the $LiMn_2O_4$ sample was dried slurry, not thin film. For XES measurements, the emission energy is not needed to be scanned: Whole the energy region of each XES spectrum is simultaneously accumulated during the exposure time. The emission-energy profile is not mixed with the position dependence. We thus focused on XES rather than XAS in addition to the reasons of advantages of XES such as direct observation of *dd* excitation.

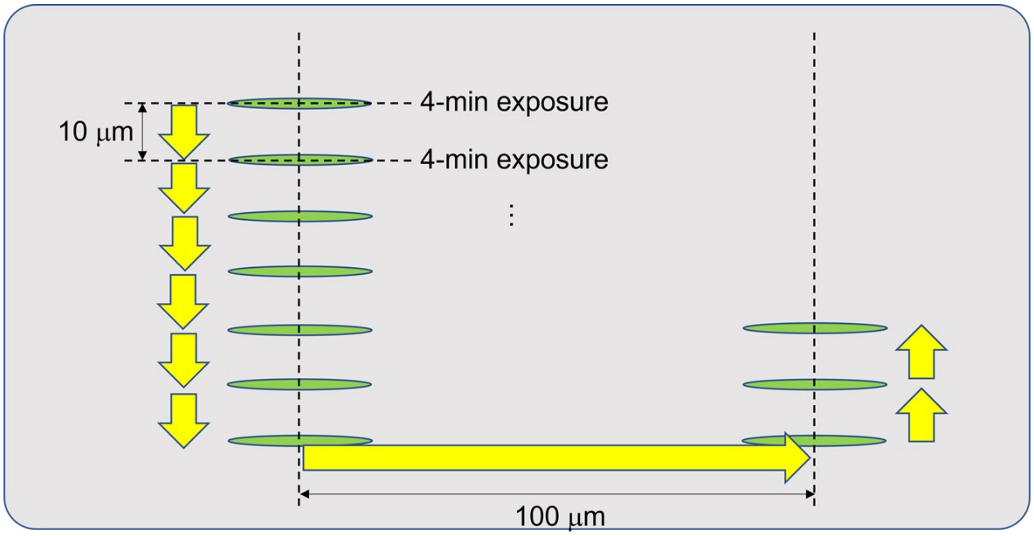

Fig. S2. A schematic picture of zig-zag scan of the Si_3N_4-based window to the incident soft X-rays. The green ellipses mean the beam spot.

Consideration about degradation of the $LiNO_3/H_2O$ electrolyte solution

We deduced that the deformation of the CV curve on the second cycle (Fig. 2(c) in the text) should be mainly caused by degradation of the $LiNO_3/H_2O$ electrolyte solution by the beam irradiation as follows. Because the *operando* cell with the Si_3N_4-based window was not broken during the XES measurement, the 1 mol·dm^{-3} $LiNO_3/H_2O$ solution should not boil by the beam irradiation. However, the fusion temperature of $LiNO_3$ as high as ~240 °C has been reported,[S5] indicating that the $LiNO_3$ should not be thermally robust. Then, the potential of 0.95 V vs. Ag/AgCl (at the charged state) for 1 mol·dm^{-3} $LiNO_3/H_2O$ solution is near the water oxidation potential.[S6] Thus, the intense beam irradiation (possibly with thermal and/or photo-induced effects) and electrochemical experiments during *operando* RXES were surely severe for the electrolyte solution. To reduce those effects, we refreshed the window position to the incident beam by 4 min in 10 μm steps.

Preliminary tests on cyclic voltammetry of $LiMn_2O_4$ using $LiNO_3/H_2O$ electrolyte solution

We have conducted preliminary charge-discharge experiments for the $LiMn_2O_4$ with $LiNO_3/H_2O$ electrolyte solution. The fabrication process of the $LiMn_2O_4$ powder, the composition of the $LiMn_2O_4$ slurry and the usage of 1 mol $\cdot dm^{-3}$ $LiNO_3/H_2O$ electrolyte solution are same as those for the *operando* experiments in the text, while the electrochemical experimental setup was partially different. The $LiMn_2O_4$ slurry was dropped on Au(10 nm)/Ti(3 nm)/Si_3N_4 substrate and dried, which is the working electrode. A titanium metal plate and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. We assembled three-electrode beaker cell using the electrodes and 1 mol $\cdot dm^{-3}$ $LiNO_3/H_2O$ electrolyte solution. The scan speed for the CV measurements was set to 0.5 mV/s.

Figure S3 shows the results of cyclic voltammetry (CV) until the fifth cycle. The CV profile for the first cycle is almost the same as that in the text, while the potential was shifted by 0.3 V probably due to the different counter and reference electrodes. For the second cycle, the profile is similar to that for the first cycle while the intensity (current) for all the oxidation/reduction peaks slightly reduced and the peak positions slightly shifted. Thus, the redox reaction should be almost reversible after the first cycle. Similar results have been reported in Refs. S7 and S8. After the second cycle, the profiles are almost maintained. Most likely, the slight enhancement of the structure around 0.56 V on the reduction process should be of some side reactions.

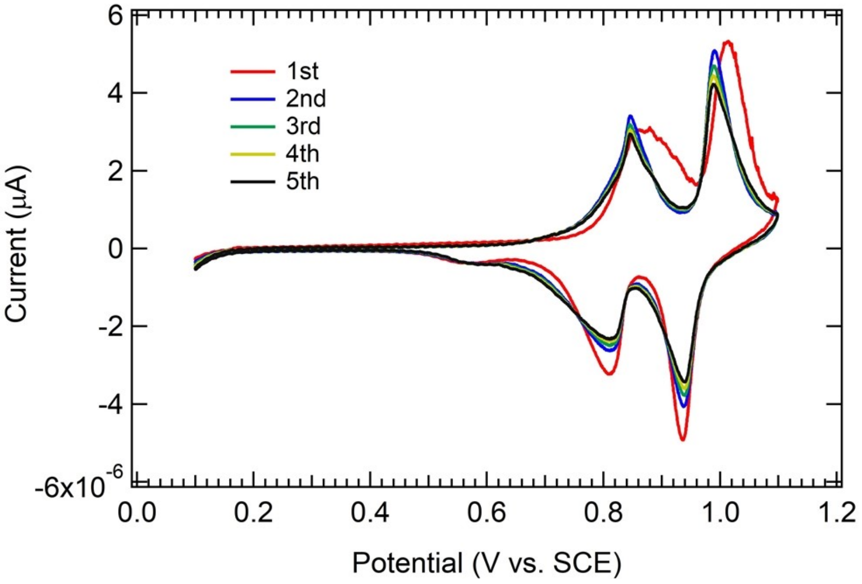

Fig. S3. CV tests for the $LiMn_2O_4$ with $LiNO_3/H_2O$ electrolyte solution.

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