

SUPPORTING INFORMATION

Operando Observations of a Manganese Oxide Electrocatalyst for Water Oxidation using Hard/Tender/Soft X-ray Absorption Spectroscopy

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Index	Page
i) Schematic images of operando XAFS measurements	S2
ii) Film thickness of K:MnO _x catalyst	S3
iii) Current and cycle measurement of Mn K-edge XAFS	S4
iv) Curve fitting analysis of K:MnO _x using δ-MnO ₂ and γ-MnO ₂ structures	S5
v) Curve fitting analysis of K:MnO _x at different electrode potential	S6
vi) Comparison of O K-edge XAFS spectra and current during operando condition	S7
vii) K K-edge XAFS during electrodeposition and current during operando condition	S8

i) Schematic images of operando XAFS measurements

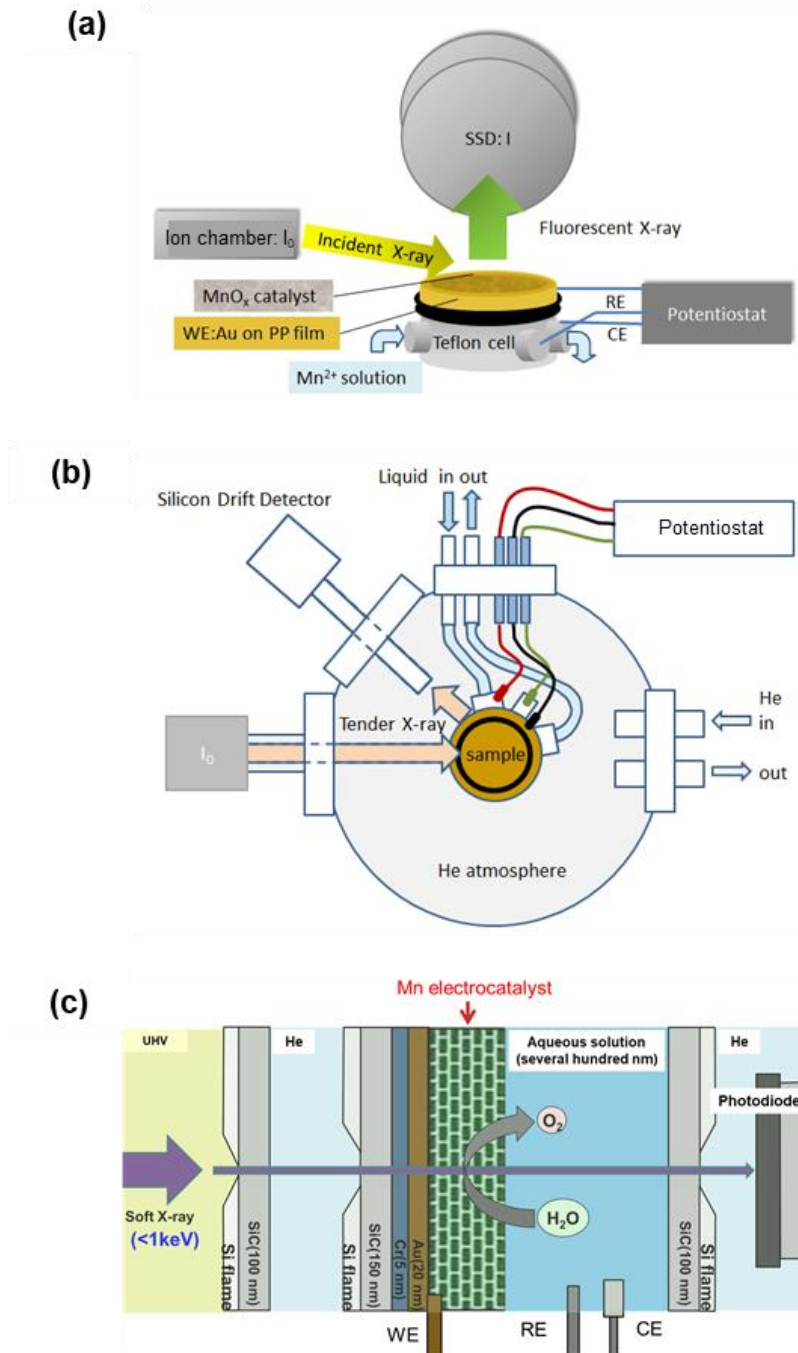


Figure S1. Schematic images of process used to obtain operando XAFS measurements using (a) hard X-rays, (b) tender X-rays, and (c) soft X-rays.

ii) Film thickness of K:MnO_x catalyst

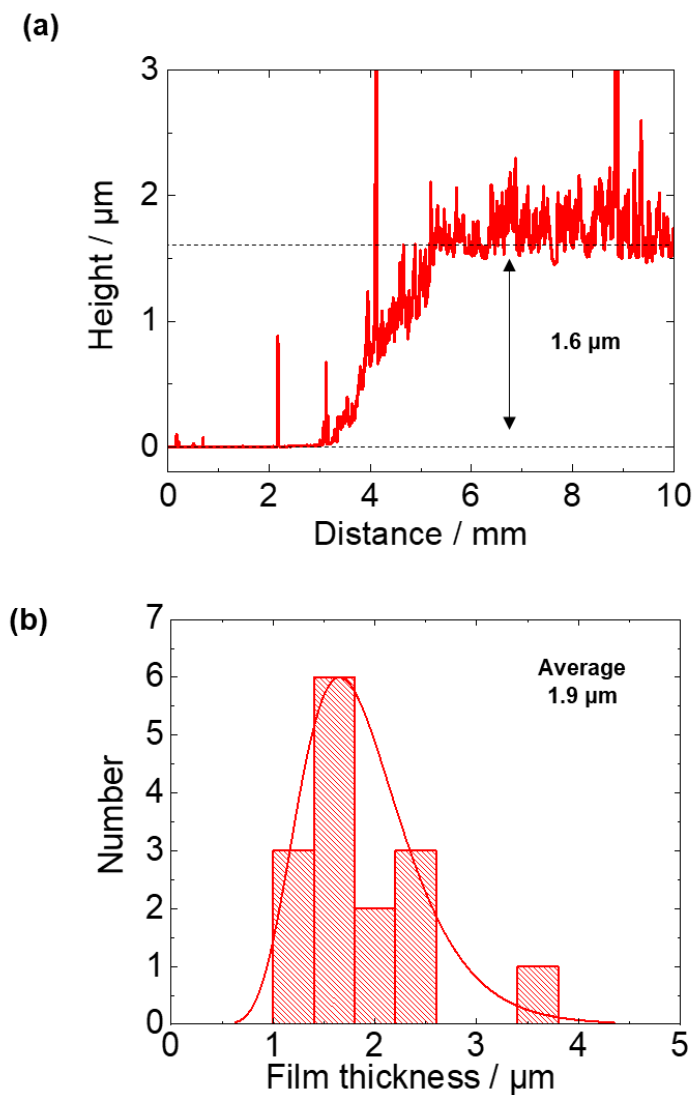


Figure S2. (a) Surface profilometry of a K:MnO_x catalyst electrodeposited on ITO substrate. (b) Film thickness distribution of 15 samples of K:MnO_x catalyst. The average film thickness was estimated as ca. 1.9 μm .

iii) Current and cycle measurement of Mn K-edge XAFS

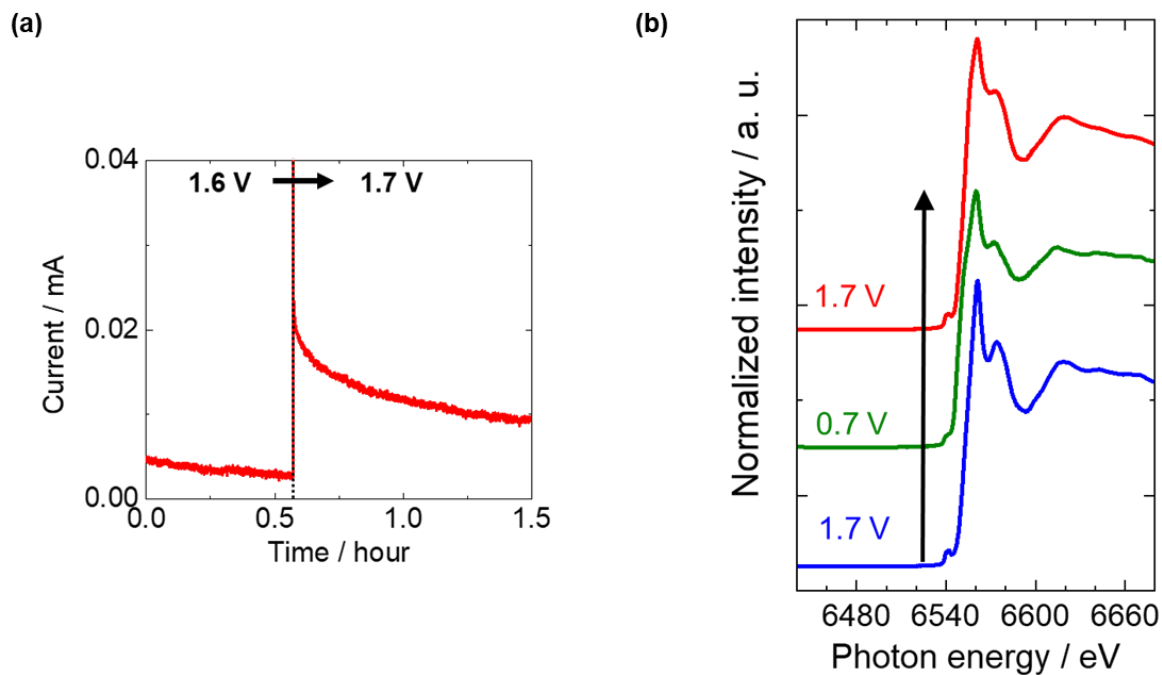


Figure S3. (a) Time course of OER current during operando Mn K-edge XAFS condition for K:MnO_x catalyst at 1.7 V vs. RHE in phosphoric acid buffer solution at pH 8, confirming that the spectra were obtained under operando measurements. (b) Cycle measurement of operando Mn K-edge XAFS for K:MnO_x catalyst in phosphoric acid buffer solution at pH 8.

iv) Curve fitting analysis of K:MnO_x using δ -MnO₂ and λ -MnO₂ structures

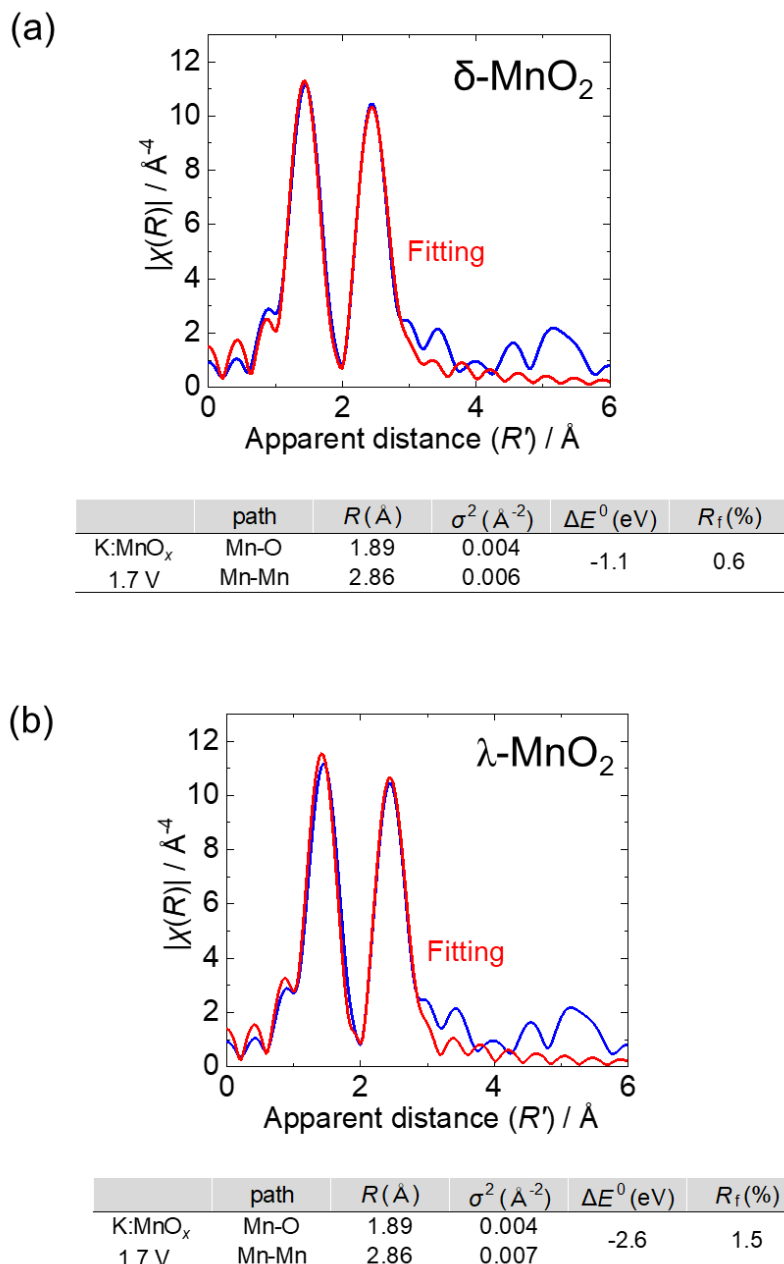


Figure S4. Curve fitting analysis of Mn K-edge XAFS for K:MnO_x at 1.7 V vs. RHE using single crystal structure data of (a) δ -MnO₂ and (b) λ -MnO₂. The coordination number was fixed to 6. The result shows that K:MnO_x catalyst was more consistent with the δ -MnO₂ structure than with the λ -MnO₂ structure.

v) Curve fitting analysis of K:MnO_x at different electrode potential

	path	$R(\text{\AA})$	$\sigma^2(\text{\AA}^{-2})$	$\Delta E^0(\text{eV})$	$R_f(\%)$
$\delta\text{-MnO}_2$	Mn-O	1.90	0.005	-1.4	0.9
	Mn-Mn	2.88	0.007		
K:MnO _x 0.7 V	Mn-O	1.89	0.010	-4.3	8.6
	Mn-Mn	2.87	0.011		
K:MnO _x 1.7 V	Mn-O	1.89	0.004	-1.1	0.6
	Mn-Mn	2.86	0.006		

Figure S5. Curve fitting analysis of Mn K-edge XAFS for $\delta\text{-MnO}_2$ powder and K:MnO_x at 0.7 and 1.7 V vs. RHE. The coordination number was fixed to 6. The result indicates that Debye–Waller factor(σ^2) is changing by electrode potential.

vi) Comparison of O K-edge XAFS spectra and current during operando condition

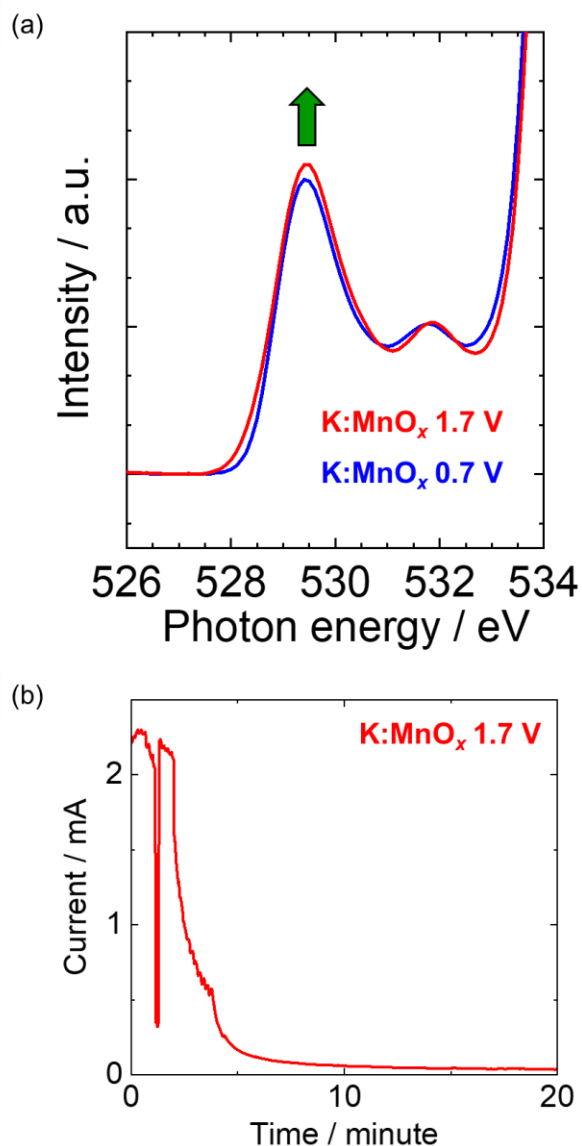


Figure S6. (a) Comparison of operando O K-edge XAFS spectra from 1.0 to 0.0 V for K:MnO_x catalyst in phosphoric acid buffer solution at pH 8. A slight increase in the lower energy peak was observed for the spectrum at 1.7 V vs. RHE. (b) Time course of OER current during operando O K-edge XAFS for K:MnO_x catalyst in phosphoric acid buffer solution at pH 8, confirming that the spectra were obtained under operando measurements. Note that the current is decreasing with time, because the flow of electrolyte solution is restricted due to the electrolyte thickness of several hundred nanometers.

vii) K K-edge XAFS during electrodeposition and current during operando condition

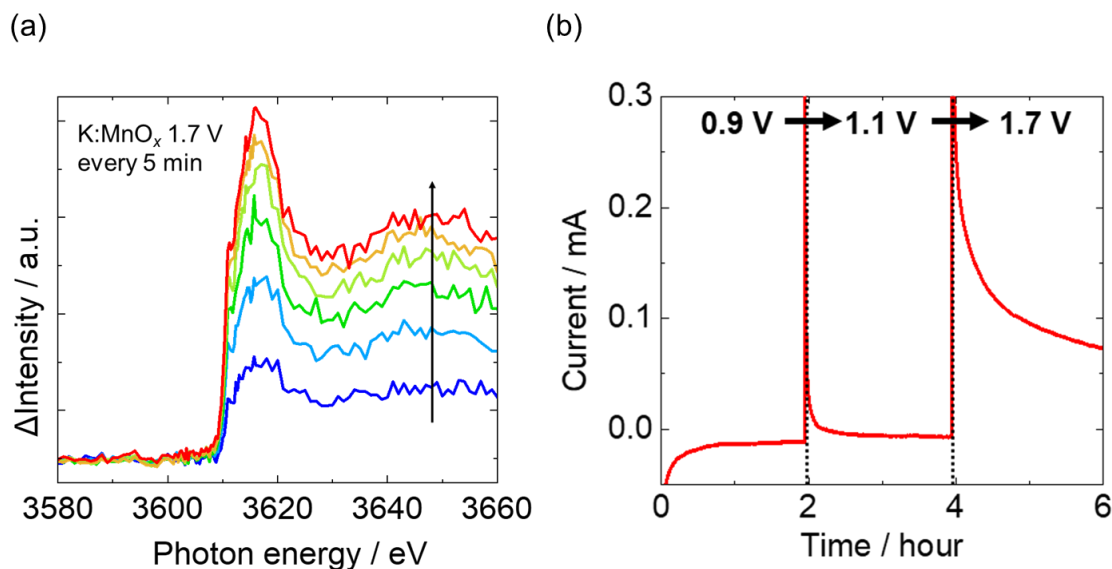


Figure S7. (a) *In situ* K K-edge XAFS spectra for electrodeposition process of K:MnO_x catalyst at 1.7 V vs. RHE in methylphosphonic acid solution containing MnCl₂·4H₂O at pH 8. To avoid the effect of K⁺ in the electrolyte solution, the intensity of each spectrum was subtracted by that of the K spectrum before applying electrode potential. The intensity increased with the amount of electrodeposited catalyst, indicating that the spectra could be attributed to the K species in the K:MnO_x. (b) Time course of OER current during operando K K-edge XAFS condition for K:MnO_x catalyst in phosphoric acid buffer solution at pH 8, confirming that the spectra were obtained under operando measurements.