Supporting Information

Participation of unstable lattice oxygen of cationexchanged δ -MnO₂ in water oxidation reaction

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Fig. S22 Graph for applied potential and current on Co^{2+}/MnO_2 with evolved oxygen molecules during DEMS measurement.

Table S1. Overpotential and TOF of cation-exchanged MnO₂

Experimental Section

Material synthesis: Based on sol-gel method, we synthesized birnessite-type δ -MnO₂. 0.25 M KMnO₄ (\geq 99.0%, Sigma-Aldrich) aqueous solution was mixed with 0.3 M C₄H₄O₄ (\geq 99.0%, Sigma-Aldrich). The mole fraction of KMnO₄ to C₄H₄O₄ was 3:1. When two kinds of chemicals were mixed, the color of solution turned from deep purple to brown color immediately. The mixture was stirred for 30 min at room temperature for gelation. After the reaction, brown suspension, amorphous Mn(OH)₂ particle, started to settle. The precipitate was separated from the mixture by centrifugal separation with 8000 rpm for 10 min and rinsed several times using D.I. water (18.2 M Ω , Milipore). To remove the H₂O molecules between MnO₆ layers in birnessite-type δ -MnO₂, the precipitate was dried in a vacuum oven at 80 °C for 48 h with being pressed by glass substrate. For uniform particle size, Dried sample was milled by a mortar and designated as K⁺/MnO₂. For cation exchange from K⁺ to other metal, we dispersed the separated precipitate before drying in each 0.025 M CaCl₂ (Sigma-Aldrich), NiCl₂ (Sigma-Aldrich), and CoCl₂ (Sigma-Aldrich) aqueous solution using a bath sonicator for 60 min, and then stirred for 60 min. Cation-exchanged δ -MnO₂ samples were also separated in a centrifugal separator and dried in a vacuum oven at the same condition with K⁺/MnO₂. We named cation-exchanged δ-MnO₂ samples by CaCl₂, NiCl₂, CoCl₂ as Ca²⁺/MnO₂, Ni²⁺/MnO₂, and Co^{2+}/MnO_2 , respectively.

Characterizations: The crystal structures of K⁺/MnO₂, Ca²⁺/MnO₂, Ni²⁺/MnO₂, and Co²⁺/MnO₂ were characterized by X-ray diffraction (XRD, SmartLab, Rigaku) using Cu K α as X-ray anodization source (k=0.15406 nm). The overall morphologies of samples were observed by a Field-Emission Scanning Electron Microscope (HR FE-SEM, Hitachi) and High-Resolution Transmission Electron Microscopy (HR-TEM, JEM-2100F, JEOL Ltd.). Atomic ratio of metal in cation-exchanged δ -MnO₂ samples were determined by Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES, JY ACTIVA, Horiba). Oxygen species and Mn oxidation state of the samples were investigated by X-ray Photon Spectroscopy (XPS) in Korea Basic Science Institute. Further analysis for Mn oxidation state at Pohang Accelerator Laboratory. Standard materials were MnO₂ (Sigma-Aldrich), Mn₃O₄ (Sigma-Aldrich), and MnO (Sigma-Aldrich) for designation of edge energy position as function of Mn oxidation state. The powder samples were loaded on a sample holder with a

1-3 mm of thickness. The XAS spectra of the samples were calibrated using Mn reference foil for Mn K-edge energy using an ionization chamber. The obtained data were processed by the Athena instrument fitting program for EXAFS spectra.

Electrochemical measurements: Electrochemical analysis were carried out with a potentiostat/galvanostat (VSP, Biologic) in three-electrode configuration. Reference and counter electrodes were double junction Hg/HgO (in 1 M KOH) after calibration and graphite rod or Pt wire, respectively. All the measurements were shown in the reversible hydrogen electrode (RHE) scale as following equation.

$$E(V_{RHE}) = E(V_{Hg/HgO}) + 0.059 \times pH + 0.109$$
(1)

Working electrode was prepared by drop-casting method with catalyst ink on a glassy carbon of rotating disk electrode (RDE, PINE, electrode area=0.2475 cm²). The catalyst ink was a dispersion solution of 20 mg of catalyst powder, 5 mg of conductive carbon (Vulcan XC-72R, CABOT), and 10 ul of Nafion resin solution in a solvent mixture of 1.2 ml of D.I. water and 0.8 ml of 2-propanol (Junsei). After dispersing in a bath sonication for 30 min, 9.9 ul of the catalyst ink was loaded on RDE and dried in an oven at 60 °C for 10 min. OER activity of the electrocatalyst was measured in N2-saturated 1 M KOH (99.98%, Sigma-Aldrich) by cyclic voltammetry (CV) method from 0.935 to 1.8 V_{RHE} at a scan rate of 5 mV/s. During the CV measurement, RDE was rotated with 1,600 rpm continuously. 85% iR compensation was applied using the solution resistance (R_s) value estimated from EIS measurement at 100 kHz. The double-layer capacitance (C_{dl}) was estimated by integral of the CV area from 0.8 to 1.4 V_{RHE}. To figure out the pH dependence on OER activity, we used four kinds of KOH electrolyte (pH 12.5, pH 13, pH 13.5, and pH 14) by controlling KOH concentration. Cation dependence was checked using 1 M TMAOH (Sigma-Aldrich, 1 M in water) as electrolytes. Regarding turnover frequency (TOF), it is common to estimate the number of participated catalyst atoms using metal redox peak for surface concentration of active metal species, however δ -MnO₂ doesn't show redox peak near OER potential range. Therefore, we use the molecule number of loading catalyst layer on the RDE and assume molar mass of four catalysts is same with MnO₂ (86.93 g/mol). The turnover frequencies (TOF) were calculated using following equation.

$$TOF = \frac{j}{4 \times F \times n}$$

where j is the current density at 1.75 V_{RHE} and N_A is the Avogadro number (6.023 x 10²³). 4 is the number of electrons transferred to evolve a O₂ molecule, *F* is the Faraday constant, and *n* is the molecule number of catalyst layer on the RDE. For OER activity comparison, we used commercial catalysts from Sigma-Aldrich (Mn₃O₄, Mn₂O₃, MnO₂, Co₃O₄, and IrO₂) except for MnO₂ (Alfa Aesar) and prepared the working electrode by drop-casting method on RDE (loading amount = 0.08 mg/cm²)

Dissolved metal quantification: Co reconstruction occurs through two oxidation reaction around 1.2 and 1.5 V_{RHE} , so we have applied four kinds of constant potentials (OCP, 1.35 V_{RHE} , 1.55 V_{RHE} , 1.75 V_{RHE} for OER) to Co²⁺/MnO₂ electrode for 1 hr and collected the electrolyte (200 ml of 1 M KOH) after each chronoamperometry (CP) experiment for Inductively coupled plasma mass spectrometry (ICP-MS) measurement. To inhibit the redeposition of dissolved metal cation, the electrolyte was continuously stirred at high rotating speed and replaced with new electrolyte after each CP. ICP-MS measurement was done by Agilent Techologies 7900 after calibration with ICP-MS standard solution.

 O_2 diffusion coefficient: To compare O₂ diffusion coefficient, chronoamperometry (CA) was carried out in O₂-saturated 6 M KOH with a rotating speed of 2,000 rpm to ignore the effect of mass transfer limitation. We chose high KOH concentration to alleviate the effect of reactant concentration limitation. Despite harsh pH condition for O₂ diffusion coefficient measurement, MnO₂ structures maintained due to lower potential than MnO₂/MnO₄²⁻_(aq) as presented in Figure S13 [M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE International, Houston, 1974]. During CA, a potential for oxygen intercalation is applied to the catalyst, and then the CA data were plotted as current vs. the inverse square root of time (*i* vs. t^{-1/2}). D₀ can be calculated using equation as following,

$$\lambda = a (D_0 t)^{-1/2}$$

where λ is dimensionless shape factor and a is the radius of catalyst particle. $t^{-1/2}$ is obtained from the intercept value (i = 0) in i vs. $t^{-1/2}$ plot. A can be estimated by the relation about a spherical geometry approximation as below

$$S = \frac{6}{2a\rho}$$

where S is the surface area of catalyst determined from BET analysis and ρ is the theoretical density.[*Nat. Commun.*, 11, 2002 (2020)]

 O_2 -Thermal programmed desorption spectroscopy: We compared the instability of lattice oxygen in cation-exchanged δ -MnO₂ samples by O₂ thermal programmed desorption spectroscopy (O₂-TPD). To evaporate the moisture on the sample, 0.5 g of catalyst powder on alumina crucible was preheated at 100 °C for 30 min with 50 ml/min of N₂ (99.999%) gas stream, and cooled down to room temperature. Then, mixture gas of O₂ and N₂ (5:95) was purged to the alumina crucible with a flow rate of 50 ml/min for 30 min at room temperature to stabilize the thermal conductivity detector (TCD) in a gas chromatography. To remove the physisorbed O₂ on the catalyst, 50 ml/min of N₂ gas was purged again into alumina crucible. For O₂ –TPD measurement, temperature was linearly increased from 30 to 850 °C at a ramping rate of 5 °C/min in the N₂ atmosphere and the desorbed O₂ gas was measured by TCD.

In-situ Raman spectroscopy: Changes of Mn-O bond and oxygen species in K⁺/MnO₂ and Co²⁺/MnO₂ catalyst along with the elevated bias were observed by *in situ* Raman spectroscopy (X-ploRA, Horiba) with a 60× water immersion objective and home-made electrochemical cell for the measurement. As shown in **Figure S14**, home-made electrochemical cell consisted of Cu plate as current collector, nano-patterning Au substrate for surface-enhanced Raman scattering effect, leakage-free Ag/AgCl electrode as reference electrode, and Pt wire for counter electrode. Working electrode was prepared by drop-casting method on Au substrate with the catalyst ink which used in the electrochemical analysis. Prior to casting, Au substrate was cleaned by ethanol and D.I. water several times. Lens in the water immersion objective contacted directly to the electrolytes (1 M KOH in ¹⁶O-H₂O or ¹⁸O-H₂O (≥98 atom%, Sigma-Aldrich)). Laser excitation was conducted at 532 nm with a laser power of 0.3 mW at a grating 1200 1 mm⁻¹. The scattered light was collected by the water immersion objective and directed to charge coupled device (CCD) detector. Before the measurement, we calibrated the Raman shift using 520 cm⁻¹ peak of standard Si sample. After capturing of electrode images, all of *in situ* Raman spectra were obtained for 10 s by accumulating 10 times During recording the

spectrum, the constant potential was applied for 300 s *via* a potentiostat/galvanostat (PGSTAT101, AUTOLAB). The potential was increased in phases every 0.05 V from -0.05 to 0.8 $V_{Ag/AgCl}$. In the case of ¹⁸O-labeled OER experiment, we applied the constant OER potential (0.725 $V_{Ag/AgCl}$) in 1 M KOH in ¹⁸O-H₂O electrolyte to substitute ¹⁶O in metal oxide bond to ¹⁸O for 3 min. After the reaction, we washed the electrolyte thoroughly and rinsed using D.I. water several times. Then, we acquired the Raman spectrum with applying OER potential in 1 M KOH in ¹⁶O-H₂O.

Anion exchange membrane water electrolysis (AEMWE): To evaluate the performance of Co^{2+}/MnO_2 as anode catalyst in AEMWE, we fabricated a membrane electrode assembly (MEA) comprising anion exchange membrane (Sustainion Alkaline AEM X37-50, grade T, Dioxide Materials) and two electrodes. Cathode catalyst was commercial 46.7% Pt/C (Tanaka Kikinzoku). Catalyst was loaded on a gas diffusion layer (MGL 190, AvCarb, area = 3x3 cm²) by hand-spraying method with a catalyst ink. Target loading amounts of cathode and anode were 1 mg_{Pt}/cm² and 10 cm_{Mn}/cm², respectively. The AEMWE performance of as-prepared MEA was evaluated by IV-curve in alkaline water electrolyzer station (Scitech Korea Inc.). IV curve measurement was carried out with constant current mode by increasing 10 mA/cm2 every 10 s from open circuit voltage to 1.8 V. During the measurements, temperature of both cell and electrolyte tank was kept at 60 °C.

Online differential electrochemically mass spectroscopy (DEMS): For online DEMS measurement, we used flow-type cell with three electrodes and ion exchange membrane between working and counter electrode. The working electrode was prepared by drop-casting method on Pt current collector. Ag/AgCl and Pt wire were used as reference and counter electrode, respectively. The cell was directly connected to HPR-40 DEMS instrument (HIDEN analytical). Similar with *in situ* Raman spectroscopic analysis, we first labelled lattice oxygen in Co^{2+}/MnO_2 with ¹⁸O-H₂O by applying OER potential (1.75 V_{RHE}). After changing the electrolyte to 1 M KOH in ¹⁶O-H₂O, we tracked the evolved O₂ amount (³²O₂, ³⁴O₂, ³⁶O₂) during LSV measurement.



Fig. S1 Atomic ratio of metal cation in (cation-exchanged) δ -MnO₂ samples.



Fig. S2 SEM and EDS mapping images of (a), (b) Co^{2+}/MnO_2 and (c), (d) K^+/MnO_2 .



Fig. S3. HR-TEM and EDS mapping images of (a), (b) Co²⁺/MnO₂ and (c), (d) K⁺/MnO₂. (e) Relative atomic percentage of Mn, Co, K in Co²⁺/MnO₂ and K⁺/MnO₂.



Fig. S4 Relationship between Mn oxidation state and energy position at 0.5 normalized intensity. (Void circles = Mn oxide reference samples; Mn_3O_4 , Mn_2O_3 , MnO_2)



Fig. S5 XPS spectra in Mn 3s orbital region for (a) standard Mn oxide samples and (b) (cationexchanged) δ -MnO₂ samples. ΔE means the magnitude of peak splitting for Mn oxidation state identification.



Fig. S6. XPS spectra in O 1s with three deconvoluted peaks for K⁺/MnO₂, Ca²⁺/MnO₂, Co²⁺/MnO₂, and Ni²⁺/MnO₂.



Fig. S7 XPS spectra in O 1s region of (a) Co^{2+}/MnO_2 with three different oxygen vacancy concentrations and K⁺/MnO₂. Deconvoluted XPS spectra in O 1s region of (b) K⁺/MnO₂, (c) 0.5 Co²⁺/MnO₂, (d) 1.0 Co²⁺/MnO₂, and, (e) 2.0 Co²⁺/MnO₂.



Fig. S8 OER activities of Co^{2+}/MnO_2 with three different oxygen vacancy concentrations and K^+/MnO_2 in 1 M KOH.



Fig. S9 (a) OER activities in 1 M TMAOH and 1 M KOH) for (black) K^+/MnO_2 and (orange) Co^{2+}/MnO_2 . Tafel plot of (b) Co^{2+}/MnO_2 and K^+/MnO_2 .



Fig. S10 Comparison of OER activity with (a) other commercial Mn-based oxides, (b) Co_3O_4 , and IrO_2 in 1 M KOH with a RDE rotating speed of 1,600 rpm.



Fig. S11 Stability test of Co^{2+}/MnO_2 in N₂-saturated 1 M KOH. (Applied current = 50 mA/cm²)



Fig. S12 SEM images of (a), (b) Co^{2+}/MnO_2 on carbon paper before stability test and (e), (f) after stability test. EDS mapping images and atomic percentage for Mn, Co, O of (c), (d) Co^{2+}/MnO_2 on carbon paper before stability test and (g), (h) after stability test.



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Fig. S15 CV graph of commercial Co₃O₄ (Sigma-Aldrich) in 1 M KOH.



Fig. S16 Nyquist plots of (a) K⁺/MnO₂, (b) Co²⁺/MnO₂, and (c) Ni²⁺/MnO₂ and Bode plots of (d) K⁺/MnO₂, (e) Co²⁺/MnO₂, and (f) Ni²⁺/MnO₂ in 1 M KOH at various potentials (V_{RHE}).



Fig. S17. (a) XRD patterns of V^{3+}/MnO_2 , Al^{3+}/MnO_2 , and K^+/MnO_2 . OER activities depending on the electrolyte pH of (b) V^{3+}/MnO_2 and (c) Al^{3+}/MnO_2 . (d) pH-dependence of four kinds of catalysts.



Fig. S18 Schematic image of home-made electrochemical cell for *in situ* Raman spectroscopy analysis.



Fig. S19 Chronoamperometry (CA) at 1.16 V_{RHE} for 300 sec of K⁺/MnO₂, Ca²⁺/MnO₂, Co²⁺/MnO₂, and Ni²⁺/MnO₂ for calculation of O ion diffusion coefficient.



Fig. S20 Raman spectra of cation-exchanged MnO_2 (solid) before and (dotted) after O_2 diffusion coefficient measurement. (v_1 = out-of-plane Mn-O bond, v_2 = in-plane Mn-O)



Fig. S21 XPS spectra in Mn 3s of (a) K⁺/MnO₂, (b) Ca²⁺/MnO₂, (c) Ni²⁺/MnO₂, and (d) Co²⁺/MnO₂ before and after OER process.



Fig. S22 Graph for applied potential and current on Co²⁺/MnO₂ with evolved oxygen molecules during DEMS measurement.

	Overpotential @ 5 mA/cm ²	Overpotential @ 10 mA/cm ²	Turnover frequency
K ⁺ /MnO ₂	0.54 V	Not detected	0.0084 s ⁻¹
Ca ²⁺ /MnO ₂	0.50 V	Not detected	0.0141 s ⁻¹
Ni ²⁺ /MnO ₂	0.40 V	0.44 V	0.0751 s ⁻¹
Co ²⁺ /MnO ₂	0.40 V	0.43 V	0.230 s ⁻¹

Table S1. Overpotential and TOF of cation-exchanged MnO_2