

Oxygen Evolution Reaction Hot Paper

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Capturing Manganese Oxide Intermediates in Electrochemical Water Oxidation at Neutral pH by In Situ Raman Spectroscopy

Kang Hee Cho, Sunghak Park, Hongmin Seo, Seungwoo Choi, Moo Young Lee, Changwan Ko, and Ki Tae Nam*

Abstract: Electrochemical water splitting is a promising means to produce eco-friendly hydrogen fuels. Inspired by the Mn_4CaO_5 cluster in nature, substantial works have been performed to develop efficient manganese (Mn)-based heterogeneous catalysts. Despite improvements in catalytic activity, the underlying mechanism of the oxygen evolution reaction (OER) is not completely elucidated owing to the lack of direct spectroscopic evidence for the active Mn-oxo moieties. We identify water oxidation intermediates on the surface of Mn_3O_4 nanoparticles (NPs) in the OER at neutral pH by in situ Raman spectroscopy. A potential-dependent Raman peak was detected at 760 cm⁻¹ and assigned to the active $Mn^{IV}=O$ species generated during water oxidation. Isotope-labeling experiments combined with scavenger experiments confirmed the generation of surface terminal $Mn^{IV}=O$ intermediates in the Mn-oxide NPs. This study provides an insight into the design of systems for the observation of reaction intermediates.

Introduction

Electrochemical water splitting is an environmentally friendly process for producing hydrogen without the formation of unnecessary byproducts.^[1] However, the oxygen evolution reaction (OER) hinders the overall efficiency of the water splitting reaction due to its sluggish kinetics and complex reaction pathways leading to relatively high energy required for the water oxidation reaction to proceed.^[2,3] Therefore, the development of highly efficient electrocatalysts is essential to improve the overall efficiency of water electrolysis. Noble metal-based oxides, such as ruthenium oxide (RuO₂) and iridium oxide (IrO₂), are highly active under acidic conditions and NiFe-based electrocatalysts have been widely investigated under basic conditions.[4-8] The introduction of 2D framework for the hybridized materials was also considered as one of the strategies for efficient heterogeneous catalysis.^[9,10] Manganese (Mn)^[11-15] and cobalt (Co)-based^[16-18] electrocatalysts have been extensively studied as promising OER electrocatalysts at neutral pH; how-

the author(s) of this article can be found under: https://doi.org/10.1002/anie.202014551. ever, their performance is still lower compared to that reported under acidic and alkaline conditions.

In nature, the OER is efficiently catalyzed by the wateroxidizing complex (WOC) in photosystem II under neutral conditions. The WOC consists of a Mn₄CaO₅ cluster, which has a distorted cubane structure with a surrounding amino acid environment that stabilizes the Mn₄CaO₅ cluster.^[19] Inspired by this active Mn₄CaO₅ cluster, numerous studies have been performed on Mn-based electrocatalysts for the OER. However, many crystalline Mn-oxides exhibited low electrocatalytic activity under neutral pH conditions, which is attributed to the instability of Mn^{III} species.^[13] Therefore, various approaches were adopted to efficiently stabilize the Mn^{III} species generated during water oxidation, as follows: (1) formation of asymmetric Mn geometries by inducing distortion in the crystal lattice structure or introducing Mn-N bonding;^[20,21] (2) inducing structural disorder;^[22-24] or structural motif with mono- μ -oxo-bridges; $^{\left[25,26\right]}$ (3) changing the electronic configuration, such as the substitution of Mn^{IV} by Mn^{III} in Li Mn_2O_4 ;^[27] (4) formation of the Mn^{III} -rich phase;^[28] (5) introduction of metal support.^[29,30]

As an extension of these various strategies, previously in our group, sub 10 nm-sized Mn-oxide nanoparticles (NPs) were synthesized and we observed that Mn^{III} species are stabilized on the surface of the Mn-oxide NPs, resulting in the enhanced catalytic activity.^[31] In these crystalline Mn-oxide NPs, distinct mechanistic behavior was identified by the combined electro-kinetic and in situ spectroscopic analyses which is different from that of the crystalline bulk-sized Mnoxide counterparts. Specifically, concerted proton-coupled electron transfer (PCET) is the quasi-equilibrium step, generating Mn^{IV}=O intermediates prior to the rate-determining step (RDS).^[32] In addition, electrochemical impedance spectroscopy analysis indicated that the reaction rate constant (k) and transport properties are strongly correlated with the catalytic activity of film-type electrocatalysts.^[33] Moreover, we investigated the significance of the entropic contribution^[34] and interfacial band structure^[35] between the substrate and the Mn-oxide NPs in the water oxidation catalysis. Furthermore, the newly developed 4 nm Mn₃O₄ NPs exhibited superior catalytic activity than did any other Mn-based electrocatalyst under neutral conditions.[11] Recently, we highlighted the important aspects of highly active Mn-based heterogeneous electrocatalysts and the current understanding of their reaction mechanism for water oxidation.^[36] The Mn^{IV}=O water oxidation intermediates has not yet been directly identified by the vibrational spectroscopy such as

^[*] K. H. Cho, Dr. S. Park, H. Seo, S. Choi, M. Y. Lee, C. Ko, Prof. K. T. Nam Department of Materials Science and Engineering Seoul National University 1 Gwanak-ro, Gwanak-gu, Seoul 08826 (Republic of Korea) E-mail: nkitae@snu.ac.kr
Supporting information and the ORCID identification number(s) for

Raman or Infrared (IR) spectroscopy on Mn-based heterogeneous electrocatalysts so far.

In situ Raman and IR spectroscopy are beneficial to capture reaction intermediates because the diverse vibration modes attributed to metal-oxygen bonding can be sensitively distinguished. Determination of oxo-species during water oxidation using IR techniques has been previously reported. In situ observation of the surface Co^{III}-OO⁻ and Co^{IV}=O species on Co₃O₄ NPs by time-resolved Fourier-transform infrared (FTIR) spectroscopy was reported by the Frei group.^[37] From the agreement of the ¹⁸O isotope experiment and the O₂ gas product, different kinetics of surface intermediates was proposed in the photocatalytic cycle. Moreover, the Hamann group assigned the potential- and light-dependent absorption peak at 898 cm⁻¹ to the Fe^{IV}=O group on the surface of α -Fe₂O₃ during photoelectrochemical water oxidation in the experiments using isotope-labeled water and a hole scavenger.^[38]

In particular, in situ Raman spectroscopy is ideal for realtime monitoring of intermediate species in aqueous systems by virtue of the distinct vibration modes of the expected metal-oxo intermediates from those of H₂O, which show bands above 1600 cm⁻¹. Several observations of the structural changes and active oxo-species on electrocatalysts using in situ Raman spectroscopy have been reported. The Koper group reported Ni-OO⁻ species in NiOOH under alkaline conditions which shows a broad peak with an isotopic shift of 64 cm^{-1} .^[39] The active oxo-species was also detected in the

Co-based catalysts during water oxidation, such as µ-OO peroxide and superoxide moieties in Co₃O₄ and $Co-OO^$ species in CoOOH.^[40,41] In contrast, for heterogeneous Mn-oxide electrocatalysts, there still have been no reports regarding the spectroscopic capture of surface Mn-oxo intermediates using in situ Raman spectroscopy under neutral condition and only the structural phase transformations were reported before.[42-44] Mn-oxides exhibit extremely weak Raman bands owing to the relatively low Raman crosssection. In addition, laser-induced degradation of Mn-oxide can occur which results in the shift or broadening of the Raman peak.^[45]

In this study, we report the first direct observation of water oxidation reaction intermediates on the surface of Mn-oxide NPs by in situ Raman spectroscopy. All the Raman measurements were performed on Mn-oxide NPs under well-characterized conditions. Under the optimized measurement conditions, we confirmed the evolution of the surface terminal Mn^{IV}=O

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species on Mn-oxide NPs at 760 cm^{-1} during catalysis by combining isotope and scavenger experiment along with a comprehensive comparison of the results with those of previous studies.

Results and Discussion

Optimization of in situ Raman measurement conditions

The 4 nm Mn_3O_4 NPs were synthesized by a thermal decomposition method following a previously reported synthetic method.^[11] For Raman experiments, 4 nm Mn_3O_4 NPs/fluorine-doped tin oxide (FTO) electrodes with a catalyst thickness of 550 nm were used to eliminate possible spectral interferences from the Raman bands of FTO (Supporting Information, Figure S1). Indeed, no FTO peaks were observed in the measurement system (Supporting Information, Figure S2). Figure 1 a shows five spectral features at 291, 319, 371, 480, and 660 cm⁻¹, which correspond to the characteristic peaks of spinel Mn_3O_4 .^[12] Several control experiments were performed using the Mn_3O_4 NPs prior to the in situ Raman experiments to ascertain the system reliability.

As shown in Figure 1 a, the thickness of the electrolyte has significant influence on the relative intensity of the target materials. The Mn_3O_4 peaks gradually decreased by increasing the electrolyte thickness from 1.0 to 2.0 mm. When the electrolyte thickness was less than 1.0 mm, it was difficult to



Figure 1. Optimization of the in situ Raman measurement conditions for 4 nm Mn_3O_4 nanoparticles (NPs). a) Raman spectra of the Mn_3O_4 NPs in 1 M KHCO₃ electrolyte with different electrolyte thicknesses (1.0, 1.5 and 2.0 mm) and electrolyte volumes (5.5, 6.5 and 7.5 mL). b) Raman spectra of Mn_3O_4 NPs in sulfate, phosphate and carbonate electrolyte along with the reported region of high-valent Mn-oxo species. c) Effect of laser power on the Mn_3O_4 NPs. The laser power was varied from 0.05 to 2.5 mW. d) Five consecutive Raman spectra obtained at the same position on the catalyst surface with a laser power of 1.6 mW.

maintain the catalyst surface completely covered with a uniform electrolyte layer. Therefore, an electrolyte thickness of 1.0 mm was selected as the optimal condition for further analyses because the peaks of Mn-oxide are clearly evident.

Moreover, as the peak of the target high-valent Mn-oxo species can overlap with the Raman bands of the electrolyte, it is crucial to select a suitable electrolyte for the analysis. Based on previous studies of high-valent Mn-oxo species,^[46-54] the stretching vibrational Raman band of Mn-oxo was expected to be in the region of 707–803 $\rm cm^{-1}$ and 957–997 $\rm cm^{-1},$ as demonstrated in Figure 1b. In the case of phosphate and sulfate electrolytes, the peaks at 988 and 979 cm⁻¹ are overlapping with the target region for Mn-oxo species and are assigned to the symmetric stretching vibrational mode of PO₃ in HPO₄²⁻ and SO4²⁻, respectively.^[55,56] In contrast, the peaks of carbonate ions were positioned above 1000 cm⁻¹, indicating that the carbonate electrolyte is suitable for in situ Raman measurements. Although we previously observed the formation of Mn^{IV} species in phosphate electrolyte by



Figure 2. Electrochemical kinetic analyses of 4 nm Mn_3O_4 nanoparticles (NPs) film. a) Polarization-corrected cyclic voltammetry (CV) curves of the 4 nm Mn_3O_4 NPs with 550 nm thickness. b) Tafel plots of the Mn_3O_4 NPs in 1 M KHCO₃ electrolyte (pH 8.2). c) pH Dependency over a pH range from 7.6 to 9.2 in 1 M KHCO₃ electrolyte. d) Steady-state current densities of Mn_3O_4 NPs at different applied potentials (1.0 V, 1.2 V and 1.3 V vs. NHE) using chronoamperometry. Stability of Mn_3O_4 NPs was observed in the individual measurements.

in situ Raman spectroscopy,^[32] an earlier study reported the existence of interactions between phosphate groups and Mn ions.^[57] Thus, here, the in situ Raman experiments were performed in carbonate electrolytes to avoid the possible Raman bands originating from the interaction between phosphate and Mn ions.

Furthermore, the effect of laser power on Mn₃O₄ NPs was precisely verified for the reason that Mn-oxide are reported to be susceptible to local heating under laser irradiation.[45,58,59] As the laser power increased from 0.05 to 1.6 mW, the Raman signal of Mn_3O_4 gradually increased; however, when the laser power was higher than 2.5 mW, a phase transformation of the Mn-oxide was observed (Figure 1c). Thus, to exclude the possibility of any spectral change by the laser itself, a laser power of 1.6 mW was chosen for the characterization of the Mn₃O₄ catalysts. In addition, we examined whether the Raman spectra of Mn₃O₄ changed when continuous irradiation was applied to the catalyst surface. Figure 1 d shows five consecutive Raman spectra obtained at the same position with a laser power of 1.6 mW. As a result, the spectra remained identical even after the fifth acquisition, confirming that the Mn₃O₄ NPs are stable under the established measurement conditions.

Electrochemical kinetic analyses of Mn_3O_4 NPs

To investigate the electro-kinetic behavior of Mn_3O_4 NPs, several electrochemical analyses were performed on the Mn_3O_4 NPs electrode. Figure 2a shows the polarizationcorrected cyclic voltammetry (CV) curve of the 4 nm Mn_3O_4 NPs films in 1 M KHCO₃ buffer at pH 8.2. The polarizationcorrected CV curve shows that the Mn₃O₄ NPs are active under electrochemical water oxidation. Tafel and pH dependence analyses were then implemented to investigate the electro-kinetic behavior of Mn₃O₄ NPs. The Tafel plot of 4 nm Mn₃O₄ NPs was obtained by chronoamperometric measurements in 1 M KHCO₃ buffer at pH 8.2. As shown in Figure 2b, the Tafel slope was estimated to be $76 \text{ mV} \text{dec}^{-1}$ by plotting the current densities (mAcm⁻²) measured by chronoamperometry (CA) at different potentials. The Tafel slope (b) can be theoretically derived from the following relationship between the current density (j) and potential (E) as shown in Equation (1,2), where j_0 , α , F, E^0 , R, and T are the exchange current density, transfer coefficient, Faraday constant, thermodynamic equilibrium potential, gas constant, and temperature, respectively [Eqs. (1)-(4)].^[60]

$$\mathbf{j} = j_0 \exp\left(-\frac{\alpha F(E - E^0)}{RT}\right) \tag{1}$$

$$\mathbf{b} = \left(\frac{\partial \mathbf{E}}{\partial \log \mathbf{i}}\right) = \frac{2.3RT}{aF} \tag{2}$$

$$\alpha = n_{\rm p} + n_{\rm q}\beta \tag{3}$$

$$\left(\frac{\partial E}{\partial pH}\right)_{j,T,P} = -\left(\frac{\partial E}{\partial logj}\right)_{pH,T,P} \left(\frac{\partial logj}{\partial pH}\right)_{E,T,P}$$
(4)

The Tafel slope of 76 mV dec⁻¹ for the Mn_3O_4 NPs almost matches 2.3 RT/F in Equation (2) which indicates that the charge transfer coefficient (α) is 1. Slight deviation of Tafel slope compared to the expected value of 59 mV dec⁻¹

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(2.3 RT/F) can be explained probably by the inhomogeneous distribution of Mn sites in Mn-oxide NPs^[23] The broadening of the oxidation peak in the CV curve (Supporting Information, Figure S3) is also observed, supporting this hypothesis. The transfer coefficient (α) is given by the Equation (3), where n_p is the number of electrons transferred before the RDS, n_q is the number of electrons transferred during the RDS and β is a symmetry factor.^[61] The result indicates that the reversible one-electron transfer step occurred prior to the RDS.^[32,59,62]

Furthermore, the pH dependence against the current density of the 4 nm Mn₃O₄ NPs was investigated under neutral conditions. The potentials at a current density of 0.1 mA cm⁻² were measured at different pH and a linear relationship between pH and measured potential was observed with a slope of -72 mV pH^{-1} (Figure 2c). The proton reaction order is derived from Equation (4), showing the relationship between pH-dependent potential changes, Tafel slope and proton reaction order.^[62,63] Based on the values of the Tafel slope and pH-dependent potential changes obtained from Figure 2b and 2c, the first-order dependence of log(j) on pH was derived. The following electrochemical rate law for OER was determined using the experimental results of electrochemical kinetic analyses on Mn_3O_4 NPs, where k_0 and a_{H+} are the rate constant and proton activity, respectively [Eq. (5)].^[63]

$$\mathbf{j} = k_0 (a_{H^+})^{-1} \exp\left(\frac{FE}{RT}\right) \tag{5}$$

As depicted in Equation (5), we conclude that PCET occurred as a quasi-equilibrium step prior to the RDS in Mn_3O_4 NPs.

To further examine the stability of Mn_3O_4 NPs during water oxidation, both bulk electrolysis and chronopotentiometry were measured in 1 M KHCO₃ buffer at pH 8.2. Figure 2d shows the CA results measured at three different potentials (1.0 V, 1.2 V and 1.3 V vs. NHE), which were used in the in situ Raman experiment discussed later. As the purpose of stepwise CA experiments was to investigate whether Mn_3O_4 NPs are stable under the operating potential conditions for in situ Raman measurement, the stability was measured for 30 min. The results shown in Figure 2d confirmed that Mn_3O_4 NPs are stable in the electrochemical water oxidation. In addition, the constant current density of 1 mA cm^{-2} in the chronopotentiometric measurements supports the stable behavior of Mn_3O_4 NPs (Supporting Information, Figure S4).

In situ Raman spectroscopy analyses of Mn₃O₄ NPs

Figure 3 shows the potential-dependent spectral traces of Mn_3O_4 NPs measured in with the range of 200–1500 cm⁻¹ (1 M KHCO₃, pH 8.2), after the current density reached a steady state. The potential was varied from the open circuit potential (OCP) to 1.3 V vs. NHE, the potential at which OER occurs followed by the reverse potential were applied to the catalyst electrode. Two main spectral changes were observed during the insitu measurements: the reversible phase transformation between Mn_3O_4 and the more oxidized Mn-oxide phase and the evolution of a new broad peak centered at 760 cm⁻¹ (Figure 3a). In Figure 3b we compared the Raman spectra at the OCP and 1.3 V vs. NHE for a detailed explanation. At the OCP, spectral features of the Mn₃O₄ phase along with the vibration modes of carbonate ions were observed. Four peaks at 1015, 1064, 1310 and 1360 cm⁻¹ are attributed to the following vibration modes of carbonate ions, v(C-OH), $v_s(CO_3)$, $\delta(COH)$ and $v_s(CO_2)$, according to previous studies.[64-66]

Upon increasing the applied potential to 1.3 V vs. NHE, the peaks at 376, 507, 566 and 630 cm⁻¹ were newly observed along with the disappearance of the Mn_3O_4 phase, indicating a change in the Mn-oxide phase during the electrochemical water oxidation (Figure 3 b). In particular, among the various MnO_x polymorphs, the Raman spectra collected at 1.3 V vs. NHE are analogous to the hexagonal δ -MnO₂, $(Ba,H_2O)_2(Mn^{IV},Mn^{III})_5O_{10}$ and LiMn₂O₄, when considering the peak positions and their relative intensities (Figure 4).^[12,22,42-45,58,67-71] Based on the previous literatures,^[22,43,67] peaks at 507 and 630 cm⁻¹ can be interpreted as the out of plane symmetric stretching of Mn-O of MnO₆ and 566 cm⁻¹



Figure 3. In situ Raman spectra of Mn_3O_4 nanoparticles (NPs) films. a) Potential-dependent Raman spectra upon increasing the applied potential from open circuit potential (OCP) to 1.3 V and at reversely applied 0.6 V and 0.3 V in 1 M KHCO₃ electrolyte. The black dotted line indicates the reversible phase recovery of the initial Mn_3O_4 and the red dotted region demonstrates the evolution of the broad peak at 760 cm⁻¹, respectively. b) Comparison of the Raman spectra collected at OCP and 1.3 V. c) Magnified spectra of the red dotted region depicted in Figure 3 a. The peak at 760 cm⁻¹ shows the potential-dependent evolution during the water oxidation reaction. All the potentials are relative to NHE.



Figure 4. Raman peak positions of our results with the previously investigated Mn-oxide and highvalent Mn-oxo complexes. The size of the dots is proportional to the relative Raman intensity of Raman bands in the individual Mn-oxide. Bulk Mn_3O_4 powder was purchased from Sigma–Aldrich. Raman peak positions of pyrochroite $(Mn(OH)_2)$ was acquired from the RRUFF reference database. Brown dots denote the peaks of Mn-oxide measured under in situ conditions. The green and blue stars indicate the peaks of the previously reported $Mn^{V}=O$ and $Mn^{V}=O$ complexes in molecular catalysts. We adopted the table format in ref. [45] and further upgraded the various Raman bands of Mn-oxide along with our results.

band corresponds to the in-plane stretching vibration of octahedral layers in δ -MnO₂. In addition, the peak with lower intensity at 376 cm⁻¹ can be reasonably assigned as terminal Mn-O(H) tunnel or surface stretches.^[70] However, the Raman spectral features of MnO₂ can change depending on structural factors such as the distortion and interlayer distance of MnO₆ octahedra.^[43] Therefore, it is difficult to determine the exact status of our Mn-oxide during water oxidation as a specific phase solely based on the observed Raman spectrum.

When a reverse potential was applied, the main characteristic peak of Mn₃O₄ at 660 cm⁻¹ was recovered, as shown in the black dotted line in Figure 3a. This potential-dependent reversible phase transformation between spinel Mn₃O₄ and further oxidized Mn-oxide phases can be comprehended in terms of crystallographic characteristics. In the initial spinel Mn₃O₄ crystal structure, Mn^{II} cations occupy tetrahedral sites and Mn^{III} cations are located in the octahedral sites. Under the conditions in which anodic bias is applied to the Mn₃O₄ NPs, an oxidized spinel structure or disordered δ -MnO₂ are expected.^[22,72-74] In the case of the oxidized spinel structure, two octahedral sites are occupied by the isotropic Mn^{IV} and locally distorted Mn^{III} due to Jahn-Teller (J-T) distortion.^[71] The other possibility for disordered δ -MnO₂ can be explained by the water-driven phase transformation from spinel Mn₃O₄ to layered MnO₂ in aqueous conditions.^[72] The water molecule, when inserted into the spinel structure, offers thermodynamic driving force for phase transition, stabilizing δ -MnO₂. Moreover, the activation energy for the essential Mn migration during the transition is kinetically lowered by crystal water insertion. The formation of Mn^{IV} species is considered as a result of the applied oxidative potential rather than the disproportionation reaction^[13] of Mn^{III} into Mn^{IV} and Mn^{II} when considering that Mn^{III} is efficiently stabilized on the surface of Mnoxide NPs^[31,32] and the potentialdependent reversible phase transformation is observed (Figure 3 a). Similarly, the structural transformation between Mn₃O₄ and layered Mn-oxide has been previously reported in research fields such as ion batteries and electrochemical water oxidation reaction.^[73–78]

In addition, the peaks of carbonate ions showed different behaviors, where the peaks of v(C-OH), δ (COH) and v_s(CO₂) from HCO₃⁻ increased, while the peak of v_s(CO₃) from CO₃²⁻ significantly decreased. These changes could be attributed to the local pH change in the anode during OER, resulting in an increase in the amount of HCO₃⁻ near the electrocatalyst film. Moreover, the evolution of the two peaks at 836 and 910 cm⁻¹ indicated the formation of

soluble MnO_4^- species corresponding to $\nu_s(MnO_4)$ and $\nu_{as}(MnO_4)$, which are commonly observed for Mn-based electrocatalysts.^[79,80]

Interestingly, a prominent spectral change was observed in the region of 700 to 800 cm⁻¹, in which the vibration bands of high-valent Mn-oxo moieties are generally observed.[46-54] Notably, upon increasing the applied potential, a new broad peak centered at 760 cm⁻¹ appeared, which is indicated by the red dotted area in Figure 3a. The peak at 760 cm^{-1} was confirmed multiple times, producing consistent and reliable results (Supporting Information, Figure S5). In addition, the in situ Raman analyses on bare FTO substrate strongly support the peak at 760 cm⁻¹ to the Mn-oxo species generated during OER because no peak was newly observed in case of the bare FTO (Supporting Information, Figure S6). Evolution of the 760 cm⁻¹ band at an applied potential of 1.2 V and 1.3 V vs. NHE at which the OER occurs was clearly observed and this peak fully disappeared when a reverse potential was applied to the catalyst (Figure 3c). Moreover, complete disappearance of the 760 cm^{-1} band under the condition, where no further anodic potential is applied after in situ analyses, supports that it is the active intermediate species generated during the OER (Supporting Information, Figure S7). Based on the comparison of the Raman band at 760 cm⁻¹ to the previous studies on high-valent Mn-oxo species, we could potentially assign the newly evolved 760 cm⁻¹ peak to the terminal Mn^{IV}=O species (Figure 4). However, the Mn^{IV}=O species was not detected in bulk-sized Mn_3O_4 , which can be understood in terms of the different water oxidation mechanism between bulk-sized and nanosized Mn-oxide electrocatalysts (Supporting Information, Figure S8). And the high surface-to-volume ratio of 4 nm Mn_3O_4 NPs is also thought to have attributed to the observation of Mn^{IV} =O species.

Identification of the surface terminal $Mn^{N} = 0$ species by combined isotope and scavenger experiments

To corroborate the assignment of the peak at 760 cm⁻¹ to the reactive terminal Mn^{IV}=O intermediates, control experiments using electrolytes prepared with ¹⁸O-labeled water (H₂¹⁸O) and deuterium oxide (D₂O) were performed. Figure 5a shows a comparison between the insitu Raman spectra measured in 1 M KHCO₃ electrolyte containing H₂¹⁶O, D₂¹⁶O and H₂¹⁸O (at 1.3 V vs. NHE). No significant shift of the 760 cm⁻¹ peak was observed in D₂O and only the effect of the D isotope was observed in the peaks of the electrolyte denoted as v(C-OD) and δ (O-D) in Figure 5a. These two peaks originated from the carbonate ions and D₂O, respectively.^[66,79] The constant peak position at 760 cm⁻¹ in the D₂O electrolyte indicates that the intermediate species do not contain proton.

Further experiments using $H_2^{18}O$ were therefore performed to clearly identify the peak at 760 cm⁻¹. The broad peak at 760 cm⁻¹ redshifted to lower frequencies by 32 cm⁻¹ in the $H_2^{18}O$ electrolyte compared to the spectra obtained in the ¹⁶O-containing electrolyte (Figure 5b). The peak position of



Figure 5. Identification of $Mn^{V}=O$ species during electrochemical water oxidation on Mn_3O_4 nanoparticles (NPs) film. a) Effect of the isotope substitution on in situ Raman spectra of Mn_3O_4 NPs under the water oxidation reaction in 1 M KHCO₃ electrolyte containing $H_2^{16}O$, $H_2^{18}O$ or $D_2^{16}O$ collected at 1.3 V. b) Magnified in situ Raman spectra of the brown dotted region in Figure 5 a showing the isotopic shift of the peak at 760 cm⁻¹ to 728 cm⁻¹ in the ¹⁸O-labeled electrolyte. c) Hole scavenger experiments on Mn_3O_4 NPs showing the in situ Raman spectra before and after the addition of KI at an applied potential of 1.2 V. d) Proposed water oxidation mechanism of Mn_3O_4 NPs at neutral pH. All the potentials are relative to NHE.

the intermediate species along with its isotopic shift of 32 cm^{-1} support the assignment of the peak at 760 cm⁻¹ to the stretching vibrational mode of Mn^{IV}=O species. The observed isotopic shift of 32 cm⁻¹ is also in good agreement with the calculated value (33 cm⁻¹) for the Mn-O diatomic harmonic oscillator and with the detailed values of the ¹⁸O-isotopic shift reported for Mn^{IV}=O complexes (Supporting Information, Table S1). In addition, the effect of the ¹⁸O-substitution was observed in the isotopic peak-splitting of soluble MnO₄species with respect to the number of substituted ¹⁸O and the degree of shift within individual peaks was consistent with the previous study on ¹⁸O-enriched MnO₄⁻ ions (Supporting Information, Figure S9).^[81] Moreover, the two broad band features indicated as a green dotted region in Figure 5a are attributed to the overall sum of the different vibration modes of carbonate ions that occupy ¹⁸O.^[65]

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An additional experiment using potassium iodide (KI) were performed to prove the highly oxidative nature of $Mn^{IV}=O$ intermediate species that participate in OER. As shown in Figure 5c, no distinct spectral feature was observed when KI was introduced immediately after the observation of peak at 760 cm⁻¹ during the water oxidation reaction. The complete loss of the peak at 760 cm⁻¹ indicates that the highly reactive $Mn^{IV}=O$ species was consumed in iodide oxidation reaction. Additional CV and CA experiments on 4 nm Mn₃O₄ NPs in the presence of KI also showed the inhibitory effect of KI on the formation of $Mn^{IV}=O$ species (Supporting Information, Figure S10), which can be explained by the compar-

ison with previous studies by Hamann and Nakamura group.^[38,82] These control experiments directly confirm the high oxidative power of the terminal Mn^{IV}=O species generated in the OER on the surface of the Mn-oxide NPs.

It is interesting to note that the positions of the Raman band of bulk Mnoxide, which lies between 250 and 700 cm⁻¹, remained constant regardless of the isotope substitution (Supporting Information, Figure S11). In contrast, the stretching vibrational mode of surfacegenerated terminal Mn^{IV}=O species at 760 cm⁻¹ showed an isotopic shift. Previously, we constructed a schematic of the overall redox process for Mn-oxide NPs by the comprehensive study on electro-kinetic and spectroscopic analyses.^[32] First, the redox behavior and pH-dependent shift in the CV curves combined with the EPR data suggested the proton-coupled oxidation of Mn^{II}-H₂O to Mn^{III}-OH. In addition, the observation of broad UV/Vis band at 400 nm together with in situ XANES results showing the average Mn oxidation states that exceed +3 indicated the formation of Mn^{IV}. Aforementioned results and electro-kinetic studies that include Tafel slope, pH-dependence and proton reaction order confirmed a concerted one-

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proton and one-electron oxidation reaction from Mn^{III}-OH to Mn^{IV}=O as the quasi-equilibrium step, before the chemical RDS for the O–O bond formation. Taken together, based on the assumption of the acid base (AB) mechanism, we propose the following water oxidation steps in case of the Mn-oxide NPs (Figure 5 d). The proposed mechanism of Mn-oxide NPs is similar to those of previously investigated OER electrocatalysts in terms of reversible valency changes between Mn^{II} and Mn^{IV} and the O–O bond formation step via Mn^{IV}=O intermediates.^[37,57,83-85] However, the exact O-O formation step needs to be further interpreted using more advanced in situ techniques to perfectly reveal the reaction mechanism of OER.

Conclusion

In summary, using in situ Raman spectroscopy a new potential-dependent Raman band was observed at 760 cm⁻¹ in the OER under optimized measurement conditions. This intermediate peak showed an isotopic shift of 32 cm⁻¹ to a lower wavenumber in ¹⁸O-containing water, which was assigned to the stretching vibrational mode of the terminal Mn^{IV}=O species. Additional D₂O experiments and scavenger experiments using KI further corroborated the assignment of the above mentioned peak to the active Mn^{IV}=O species generated on the surface of the Mn-oxide NPs. Moreover, a thorough comparison of the Raman band position and isotopic shift of the Mn^{IV}=O species with previous studies validated the assignment to high-valent Mn^{IV}=O moieties. This work is meaningful in that the combination of our results with the proposed OER mechanism in Figure 5d, inferred from electrochemical kinetic analyses and our previous understanding, allow for direct observation of surface terminal Mn^{IV}=O species, which is the reaction intermediates for water oxidation, under the OER conditions. Different from spectroscopic tools such as XAS or UV/Vis, Raman spectroscopy can provide evidence characteristic of Mn-oxo. Further comparison of the Raman band position with that of homogeneous molecular complexes allow for the exact assignment of bonding characteristics between Mn-oxo whether it is single-, double- or triple-bonded. To the best of our knowledge, this is the first direct observation of highvalent Mn-oxo species using in situ Raman spectroscopy in heterogeneous Mn-oxide electrocatalysts. Our findings provide insights into heterogeneous electrocatalysts and efficient system design for intermediate capture. Furthermore, we expect that the electrochemical in situ Raman spectroscopy presented herein will serve as a promising tool for mechanistic investigation in various fields such as carbon dioxide reduction, nitrogen reduction, hydrogen peroxide production and water oxidation reaction.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Electrocatalysis · intermediates · manganese oxides · Raman spectroscopy · water oxidation intermediate

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