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Molybdenum-Doped Manganese Oxide as a Highly Efficient and Economical Water Oxidation Catalyst

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ABSTRACT: The development of efficient and noble-metal-free electrocatalysts for the challenging oxygen evolution reaction (OER) is crucial for sustainable energy solutions. In this work, a facile co-precipitation method, followed by thermal postsynthetic treatment in N₂/air, was developed to synthesize molybdenum-doped α -Mn₂O₃ materials (Mn₂O₃:1.72%Mo, Mn₂O₃:2.64%Mo, Mn₂O₃:32.23%Mo and Mn₂O₃:49.67%Mo) as low-cost water-oxidizing electrocatalysts. Powder X-ray diffraction (PXRD), extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM) investigations showed the presence of strong distortions in the molybdenum-doped α -Mn₂O₃ host lattice (Mn₂O₃:2.64%Mo) and an average oxidation state of Mn^{2.8+}. Several test assays demonstrated that these structural features significantly promote the OER activity. Mn₂O₃:2.64%Mo was found to exhibit very good activity among the series in cerium ammonium nitrate (CAN)-assisted water oxidation with a maximum turnover frequency (TOF) of 585 $\mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$, which is a 15-fold improvement of the pure α -Mn₂O₃ activity and higher than the value of the previously reported benchmark Mn-based catalyst, birnessite. The optimized catalyst (Mn₂O₃:2.64%Mo) excelled through a low onset potential (η = 300 mV) and a promising overpotential of 570 mV for OER at a current density of 10 mA cm⁻², which is only 20 mV above that of the noble metal benchmark RuO₂ electrode and competitive with that of the most active Mn-based OER catalysts reported to date. Electrochemical impedance spectroscopy (EIS) studies demonstrated that the catalytically active surface area of Mn₂O₃:2.64%Mo is much higher than that of α -Mn₂O₃ for the OER at the applied potential. In addition, stability during 30 h without degradation was achieved, which exceeds that of a wide range of current noble-metal-free electrocatalysts. Our study provides a facile and effective approach for the preparation of economical and high-performance manganese-based electrocatalysts for water oxidation.

KEYWORDS: water oxidation, OER, molybdenum/manganese oxides, XAS, HRTEM, electrocatalysts, low-cost metals

Introduction

The design of efficient, economical and robust electrocatalysts is essential for the oxygen evolution reaction (OER), which is a central yet challenging process in rechargeable metal-air or metal-O₂ batteries and in water splitting.¹ Water oxidation catalysts (WOCs) are the current bottleneck for clean hydrogen generation from artificial photosynthesis,^{2,3} i.e., the splitting of water into hydrogen and oxygen.⁴⁻⁸ To date, the large-scale electrochemical production of hydrogen from water electrolysis is greatly limited by the high overpotential and the lack of catalyst stability, especially of noble-metal-free electrode materials.^{9,10} This has triggered intense research interest in the development of efficient, low-cost,¹¹ stable, eco-friendly,¹² and earth-abundant WOCs.^{13,14} In comparison with high-performance nickel- and cobalt-containing WOCs, manganese oxides are generally earth abundant,¹⁵ environmentally friendly, and inexpensive, which renders them very attractive resources for large-scale applications.^{16,17} Moreover, the facile access to widespread resources of mineable manganese cores with a high Mn concentration¹⁸ renders investments into Mn-based WOCs economically attractive. Manganese is the key element of natural photosynthesis, where it assists water oxidation through the central calcium-manganese oxide of photosystem II (PSII).^{4,7,19,20} Since the 1970s, this has inspired a wide scientific community to mimic this natural process using Mn-based catalysts¹² as functional models of the {CaMn₄O₅} cluster in PSII.²¹ Over the last years, many studies focused on developing new Mn-based molecules as model complexes for this natural benchmark using various ligand types, including Schiff bases,²²⁻²⁶ pyridine-based ligands,^{27,28} and porphyrins.²⁹ Due to the “distorted cube” structure of nature’s {CaMn₄O₅}

cluster,²⁰ the family of Mn oxocubanes attracted particular interest.^{30,31} However, most of these Mn-based model complexes are not stable under water oxidation conditions and they are converted into oxide phases.³²⁻³⁶ Manganese oxides are thus more promising as environmentally friendly catalysts, and their optimization is a sustainable way to generate highly sought-after robust materials for technological applications.^{37,38} Interestingly, the coexistence of Mn with molybdenum-rich minerals in nature and marine ecosystems³⁹ inspired materials scientists to explore Mn/Mo-based systems as catalysts for key electrochemical reactions⁴⁰⁻⁴⁵ and organic transformations.^{46,47} Previous studies have shown that Mo doping into Mn oxides leads to reduction in crystallinity, high surface area, and changes in morphology and electronic properties. The distorted structure improves the water oxidation performance of MoMnO_x oxides due to higher stability in the presence of water molecules,⁴⁸ while leading to weakly bonded lattice oxygen and an increasing number of active sites. Charge-compensation mechanisms and average oxidation state (AOS) results show that the fraction of Mn³⁺ species is notably reduced after Mo substitution. Relatively long Mn-O bonds and weaker lattice oxygen stabilities result in flexible lattice oxygen, which undergoes rapid exchange with molecular oxygen for efficient catalysis.^{46,49} While Mn/Mo mixed electrodes were introduced by Hashimoto and co-workers for seawater electrolysis,⁴¹ their chemical and structural features are largely unexplored, especially with respect to the productive role of Mo dopants.

Herein, we report on a molybdenum-doped manganese oxide Mn₂O₃:x%Mo (x = 1.72, 2.64, 32.23, 49.67) catalyst series for chemical, photochemical, and electrochemical water oxidation.

Among the synthesized series, highly active Mn_2O_3 :2.64%Mo was found to exhibit a very good water oxidation performance with cerium ammonium nitrate (CAN) media, reaching a maximum turnover frequency (TOF) of $585 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$. This 15-fold improvement of the activity of pure $\alpha\text{-Mn}_2\text{O}_3$ through Mo doping is superior to the values reported for the most active Mn-based catalysts.⁵⁰ Moreover, we present a comprehensive structural study about the productive effect of Mo doping on the WOC activity of the $\alpha\text{-Mn}_2\text{O}_3$ matrix through combination of different spectroscopic and analytical techniques, such as extended X-ray absorption fine structure (EXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and electrochemical impedance spectroscopy (EIS).

Results and Discussion

Influence of Mo doping on the $\alpha\text{-Mn}_2\text{O}_3$ Host Lattice.

The carbonate precursors with different initial molybdenum contents, in the following referred to as MnCO_3 :1.72%Mo, MnCO_3 :2.64%Mo, MnCO_3 :32.23%Mo, and MnCO_3 :49.67%Mo, were annealed in a nitrogen flow (400°C , 60 mL min^{-1}) to generate the Mo-doped MnO intermediates. Powder X-ray diffraction (PXRD) patterns demonstrate that they were converted into a MnO-type structure (Figures 1 and S1), as observed for the reference reaction with pure MnCO_3 under the same conditions (N_2 flow, 400°C , 60 mL min^{-1}) (Figure S1, red pattern). Thermogravimetric analysis (TGA) showed smaller mass losses at lower temperatures, followed by a significant mass loss at 400°C , which is attributed to carbonate decomposition (Figure S2). Afterwards, the Mo doped MnO intermediates were calcined at 400°C ($12^\circ\text{C min}^{-1}$) for 24 h in air to form the molybdenum-doped manganese oxides $\alpha\text{-Mn}_2\text{O}_3$ (Mn^{3+}) exhibiting the bixbyite structure (Figure S3). In contrast, analysis of the PXRD pattern of a pure manganese carbonate precursor after the direct calcination process in air shows that it was converted into MnO_x (Figures 1b and S4) containing Mn_5O_8 (Mn^{3+} and Mn^{4+}) with a minor percentage of $\alpha\text{-Mn}_2\text{O}_3$, which is in line with previous reports.^{51,52}

Furthermore, scanning electron microscopy (SEM) images confirm that the pure MnO precursor was converted into a mixed structure after calcination in air with different spherical and cubic morphologies (MnO_x), corresponding to the above-mentioned mixture of cubic $\alpha\text{-Mn}_2\text{O}_3$ and spherical Mn_5O_8 (Figure S5).

Interestingly, other than for the undoped precursor, the final structure obtained from molybdenum-doped precursors after calcination in air at 400°C was quantitatively changed to pure bixbyite-type $\alpha\text{-Mn}_2\text{O}_3$. This points to a stabilizing effect of molybdenum dopants on the Mn^{3+} sites within the bixbyite lattice (Figures 1b and S3). Results from Rietveld refinement of the PXRD patterns of calcinated Mn_2O_3 :2.64%Mo and Mn_2O_3 :1.72%Mo (Figures S3 and S6), and their refined lattice parameters (Table S1), show that Mo doping does not change the space group $Ia\bar{3}$ (#206) of the $\alpha\text{-Mn}_2\text{O}_3$ host lattice. However, the cell parameters and the cell volume decrease slightly upon Mo doping. Based on the refined atomic positions, both Mn1 and Mn2 are replaced with Mo1 atoms (Table S1), with the Mo2 atoms located in distorted octahedral units next to the Mn2 atoms (Figure 1a).

As the average Shannon crystal radii⁵³ of $\text{Mo}^{4+}/\text{Mo}^{6+}$ ($0.76 \text{ \AA}$) and Mn^{3+} ($0.785 \text{ \AA}$) are quite related, replacement of Mn^{3+} by Mo atoms in the $\alpha\text{-Mn}_2\text{O}_3$ lattice appears plausible, thus accounting for the decrease of d -spacing in $\alpha\text{-Mn}_2\text{O}_3$ and the observed peak shift to higher 2θ values as shown in Figure S7. For Mn_2O_3 :2.64%Mo, the observed morphology reflected the formation of pure Mo-doped $\alpha\text{-Mn}_2\text{O}_3$ with cubic symmetry (Figure 2a).

Figure 1. (a) Ball and stick representation of the crystal structure of pure $\alpha\text{-Mn}_2\text{O}_3$ and Mn_2O_3 :2.64%Mo along the [222] crystallographic zone axis. (b) Synthesis conditions and annealing temperature used for Mn_2O_3 :2.64%Mo.

Scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX) further confirmed the uniform dispersion of Mo in the $\alpha\text{-Mn}_2\text{O}_3$ lattice (Figures 2b-d and S8). The composition of Mn/Mo was derived from SEM-EDX and inductively coupled plasma mass spectrometry (ICP-MS) measurements (Table S2), which show a similar trend in the elemental ratios. However, it should be noted that while SEM-EDX is a surface-sensitive method, ICP-MS monitors the bulk composition and thus provides a more accurate overall atomic ratio.

High-resolution transmission electron microscopy (HRTEM) images (Figure S9), scanning transmission electron microscopy (STEM) and high-angle annular dark field (HAADF) elemental mapping of Mn_2O_3 :2.64%Mo provided further evidence that the molybdenum atoms were doped into the manganese oxide host structure (Figures 2e-h and S10). As a reference, $\alpha\text{-Mn}_2\text{O}_3$ was checked by HAADF-STEM-EDX to confirm that the Mo signal detected in the Mn_2O_3 :2.64%Mo specimen was neither noise nor background (Figure S11). While the characteristic IR bands of $\alpha\text{-Mn}_2\text{O}_3$ are slightly shifted to higher wavenumbers in Mn_2O_3 :2.64%Mo, no additional bands indicating the presence of extra lattice Mo oxide species were detected (Figure S12).

Figure 2. (a) SEM image of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. (b-d) SEM-EDX element mapping of (b) manganese, (c) oxygen, and (d) molybdenum in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. (e-h) High-angle annular dark-field imaging-scanning transmission electron microscopy-energy-dispersive X-ray analysis (HAADF-STEM-EDX) mapping of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$.

PXRD data show significant structural changes with increasing Mo content. As confirmed from Rietveld refinement, $\text{Mn}_2\text{O}_3:1.72\%\text{Mo}$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ display a decreased lattice constant compared to the cubic bixbyite structure (Figures S3, S6 and Table S1). Based on the PXRD results, samples with higher molybdenum content ($\text{Mn}_2\text{O}_3:32.23\%\text{Mo}$ and $\text{Mn}_2\text{O}_3:49.67\%\text{Mo}$) clearly showed an additional manganese molybdate phase, $\text{Mn}(\text{MoO}_4)$ (Figure S13). In comparison with the $\alpha\text{-Mn}_2\text{O}_3$ PXRD pattern, the (222) peak position of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ and $\text{Mn}_2\text{O}_3:1.72\%\text{Mo}$ is slightly shifted to higher 2θ values, indicating a structural distortion induced by incorporation of molybdenum into the lattice (Figure S7). In line with the PXRD data, HRTEM images further provided direct evidence of structural distortions in the [222] direction (Figure 3a-h).

HRTEM images (Figure 3a) show the well-ordered atomic structure in $\alpha\text{-Mn}_2\text{O}_3$ (Figure 3a inset, 3c yellow lines) with coherent planes of atoms. The fast Fourier transform (FFT) of the HRTEM image shown in Figure 3d reveals peaks from the [222] projection plane arising from the cubic structure and corresponding Miller indices hkl (yellow arrows in Figure 3d). The normalized and background-subtracted surface plot obtained from images of $\alpha\text{-Mn}_2\text{O}_3$ (Figure 3e) shows high-intensity and well-localized manganese atoms in the $\alpha\text{-Mn}_2\text{O}_3$ lattice. In contrast, HRTEM images of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ show structural defects and misalignment in the atomic planes (Figure 3b inset, 3f yellow lines). The FFT of the HRTEM image (Figure 3g) shows that the $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ lattice ($Ia\bar{3}$) is preserved, but the presence of Mo dopant atoms in the lattice gives rise to some diffuse scattering appearing in the FFT spectra (red arrow in Figure 3g), which indicates structural distortions in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$.

Diffuse scattering in electron diffraction can be induced by disorder or some less ordered atomic positions. Practically, this effect can be visible in the background around strong Bragg spots in diffraction patterns of crystals or in the FFT view in electron diffraction.⁵⁴ The normalized and background-subtracted surface plot extracted from images of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ (Figure 3h) shows lower intensity than that of $\alpha\text{-Mn}_2\text{O}_3$, thus revealing more local structural dispersion of the Mn atomic planes in the $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ lattice, which agrees with Fourier transform Mn K-edge EXAFS spectra of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ (see Figure 5). Based on previous reports, Mn_2O_3 is one of the most active crystalline manganese oxides in water oxidation.^{50,55} In the following, we investigate in detail the role of Mo-induced structural distortions in the optimization of its catalytic activity.

Spectroscopic Analyses of Mo-induced Structural Distortions in $\alpha\text{-Mn}_2\text{O}_3$.

The activity of Mn_2O_3 is attributed to the presence of Jahn–Teller distorted edge-sharing octahedra occupied by Mn^{3+} (d^4) centers with significantly elongated Mn–O bonds.¹² Due to the asymmetric occupation of e_g^* orbitals, the bonding energy is decreased and the Mn^{3+} –O octahedra are activated to participate in the OER.^{56–62} Layered manganese oxides, such as birnessite materials, show extended structural disorder due to a high number of Mn vacancies in the edge-sharing MnO_6 octahedra and intrinsic distorted structures within the layers.¹⁷ Similar to the Jahn–Teller effect in Mn_2O_3 , these Mn vacancies induce weaker and more flexible Mn–O bonds, which can be associated with higher water oxidation activity.⁶¹ The survey XPS spectrum of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ is shown in Figure S14. The characteristic binding energies of Mn (2s, 2p, 3s, 3p), Mo (3p, 3d, 4s, 4p, 4d), O (1s, 2s, 2p), and C 1s were observed. The Mo 3d XPS spectrum of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ shows spin–orbit splitting with Mo 3d_{5/2}–3d_{3/2} components (Figure 4a). The asymmetric shape of the Mo 3d peaks suggests a mixed valence state $\text{Mo}^{4+}/\text{Mo}^{6+}$ in the $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ lattice. Both Mo 3d_{3/2} and Mo 3d_{5/2} core levels can be deconvoluted into two peaks. The main couple of peaks at ~231.6 eV and 234.7 eV with a splitting of 3.1 eV are assigned to the Mo^{4+} species, while the minor couple of peaks at ~232.6 and 235.8 eV with a splitting of 3.3 eV are attributed to the Mo^{6+} oxidation state.^{63,64}

Figure 3. HRTEM images of (a) α - Mn_2O_3 and (b) $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. Magnified images of (c) α - Mn_2O_3 and (f) $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ along the $[222]$ zone axis. Fast Fourier transform (FFT) pattern extracted from HRTEM images of (d) α - Mn_2O_3 and (g) $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. Normalized surface plot extracted from HRTEM images of (e) α - Mn_2O_3 and (h) $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$.

Analysis of the Mo binding energy and intensity revealed that the Mo valence states are mainly Mo^{4+} with a minor amount of Mo^{6+} . Annealing in protective nitrogen atmosphere at 400 °C in the presence of NH_4^+ residues in the carbonate precursor, which arises from the ammonium heptamolybdate and ammonium sulfate additives during the synthesis procedure, induces a partial reduction of Mo^{6+} centers (Figure S15, reaction 1). CHN elemental analysis showed the presence of a considerable amount of nitrogen (1.25 wt %) in the carbonate precursor (Table S3). While annealing in air during the second step of the synthesis, Mn^{2+} species are oxidized to Mn^{3+} ($E_{\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}}^\circ = 1.56 \text{ V}$,⁶⁵ Figure S15, reaction 2). In the case of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$, the molybdenum content is much lower than the manganese content and Mn^{2+} oxidation to Mn^{3+} can induce further reduction of molybdenum ions ($E_{\text{Mo}^{6+} \rightarrow \text{Mo}^{4+}}^\circ = -0.818 \text{ V}$).⁶⁵ Reduction of Mo^{6+} to Mo^{4+} through Mn centers has been reported in previous studies.^{66,67} During annealing in air, Mn^{2+} is oxidized to Mn^{3+} , which leads to weakly bonded lattice oxygen and relatively long Mn–O bonds, which could reduce Mo^{6+} to Mo^{4+} by electron transfer due to charge compensation and random potentials around Mo ions into the Mn sublattice.^{46,49,68} Furthermore, oxygen vacancies could assist the reduction of Mo^{6+} to Mo^{4+} through the surface oxygen vacancy mechanism $\text{Mo}^{6+} + \text{O}^{2-} \rightarrow \text{Mo}^{4+} + \frac{1}{2} \text{O}_2$. This charge-compensation mechanism has been formerly reported for

Mo oxides,^{68,69} and it has been shown that the intensity of the vibrational frequencies involving Mo^{4+} species is slightly increased. This agrees with the slight increase of the intensity of the IR bands of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ (Figure S12). Whereas moderate oxygen vacancy concentrations could effectively enhance the catalytic activity, due to the high lattice oxygen mobility arising from vacancy sites, extremely high oxygen vacancy concentrations lead to a decrease of the activity.⁷⁰ For the simplest charge transfer mechanism, oxygen vacancies react with OH^- species from the electrolyte. Once the OER potential is reached, the electrode surface reacts with the generated charge carriers to produce oxygen, while the H_2O molecules form new oxygen vacancies in the course of a reaction cycle.⁷¹ For higher concentration levels of oxygen vacancies, Mo–Mn oxides are reduced to stable phases exhibiting cations with only low oxidation states.⁷² While we did not measure the oxygen vacancy concentration directly, the formation of low concentrations of catalytically active oxygen vacancies is energetically more favorable at our experimental conditions. Moreover, HRTEM images and PXRD patterns of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ (Figures 3, S3 and S6 and Table S1) show that Mo doping does not change the phase of the α - Mn_2O_3 host lattice. Hence, since the level of Mo doping is quite low, those results indicate that the concentration of oxygen vacancies in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ is just slightly higher than that of the α -

Mn₂O₃ host lattice. However, this slight increase of oxygen vacancies can further boost electron transfer between the Mn₂O₃:2.64%Mo surface and water molecules. While being aware of the above oxygen vacancy mechanisms, we here place a stronger focus on the correlation between the catalytic activity and the local structural distortions induced by Mo doping into the α -Mn₂O₃ matrix. As a control experiment, pure ammonium molybdate tetrahydrate (AHM) was heated in a protective nitrogen flow (60 mL min⁻¹) at 400 °C (12 °C min⁻¹) for 8 h (Figure S15, reaction 3). PXRD results (Figure S16) showed that after heating in nitrogen, AHM is indeed converted into reduced molybdenum oxide species (AHM-N₂) containing Mo₄O₁₁. From the Mn2p binding energy region it is difficult to distinguish the Mn oxidation state. In the Mn 2p binding energy region (Figure 4b), two main peaks, Mn 2p_{3/2} and Mn 2p_{1/2}, are observed, with binding energies of 640.7 and 652.4 eV, respectively, resulting in a spin-orbit coupling with a splitting of ~11.74 eV. However, the asymmetric shape of the Mn2p_{3/2} band in Figure

4b has been reported to arise from mixed Mn³⁺ and Mn⁴⁺ ions in the crystal lattice.⁷³ The Mn 3s binding energy is a more accurate probe to estimate the valence state of Mn ions in manganese oxide structures.^{74–76} The splitting of the 3s core level in transition-metal compounds arises from the exchange coupling between the 3s hole and the 3d electrons. The amplitude of the energy gap [$\Delta E(3s)$] corresponds to $(2S+1)$, where S is the local spin of the 3d electrons in the ground state.⁷⁶ The reported $\Delta E(3s)$ ranges for MnO, Mn₂O₃, and MnO₂ are >6.0, ~5.4–5.7, and ~4.1–4.5 eV, respectively, which agree with our calculated $\Delta E(3s)$ values for reference manganese oxides (Figures 4c and S17). The $\Delta E(3s)$ of the photoelectron peaks increases almost linearly as the Mn oxidation state decreases.⁷⁷

Figure 4. XPS spectra displaying the Mo3d (a) and Mn2p (b) binding energies of Mn₂O₃:2.64%Mo. The peak areas for Mo⁴⁺3d_{5/2}, Mo⁴⁺3d_{3/2}, Mo⁶⁺3d_{5/2} and Mo⁶⁺3d_{3/2} were calculated as 52.68%, 35.09%, 7.34% and 4.39% respectively. (c) Mn3s binding energy of Mn₂O₃:2.64%Mo in comparison with MnO, Mn₂O₃ and MnO₂ references. Deconvoluted XPS spectra of the O1s core level in α -Mn₂O₃ (d) and Mn₂O₃:2.64%Mo (e) samples.

As shown in Figure 4c, the Mn 3s splitting for Mn₂O₃:2.64%Mo is slightly higher than that of α -Mn₂O₃, indicating that the average oxidation state (AOS) of its Mn centers is slightly lower than for Mn₂O₃. From the linear fitting of $\Delta E(3s)$, an AOS of 2.8+ was calculated for Mn₂O₃:2.64%Mo (Figure S17). As reported in previous studies, manganese-based WOCs with the average oxidation state of manganese between 2.5 and 2.8 are highly active due to the presence of mixed valent species within a disordered structure.^{12,78,79} The O 1s peak in α -Mn₂O₃ and Mn₂O₃:2.64%Mo samples displayed the presence of Mn–O–Mn as expected for manganese oxides and a small peak assigned to Mn–OH bonding (Figures 4d,e).⁷² Additionally, the corresponding O 1s binding energy and intensities indicated that Mn₂O₃:2.64%Mo exposes more hydroxide species on the surface, which are likely to increase the surface affinity for water adsorption and therefore its water oxidation activity.

To determine the AOS of Mn in the as-synthesized α -Mn₂O₃ and Mn₂O₃:2.64%Mo mixed oxides, we analysed X-ray absorption near edge structure (XANES) spectra. Figure 5a shows XANES spectra of α -Mn₂O₃, and Mn₂O₃:2.64%Mo and those of reference oxides. The AOS of Mn was estimated from the linear dependence of the Mn K-edge position at the energy corresponding to a $\mu(E)$ -value of 0.5 of the normalized XANES spectra.⁸⁰ Thus, from the absorption edge energy position of reference compounds Mn²⁺O, Mn⁴⁺O₂ and Mn^{2.67+}O₄, the AOSs of Mn for as-synthesized α -Mn₂O₃ and Mn₂O₃:2.64%Mo mixed oxides were calculated to be 3+ and 2.8+, respectively (the inset in Figure 5a). The Mn K-edge absorption edge of Mn₂O₃:2.64%Mo is slightly shifted to a lower energy by 0.35 eV (Figure 5a), i.e., Mo doping into the α -Mn₂O₃ lattice induced a decrease in the AOS of Mn ions, which agrees with the XPS results from the Mn 3s binding energy (Figures 4c and S17). The slight decrease in the relative white line intensity at

≈ 6556.82 eV in the XANES spectra further suggests a small structural disorder induced by Mo doping and shows that the density of unoccupied d-states and the AOS of Mn in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ are slightly different from those of $\alpha\text{-Mn}_2\text{O}_3$.

To better understand the atomic short-range order of the as-synthesized $\alpha\text{-Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ mixed oxides, we analysed their EXAFS spectra. Figure 5b shows fitting of the Fourier transform $\text{FT}[k^3\chi(k)]$ spectra of the measured Mn K-edge EXAFS spectra $k^3\chi(k)$ of $\alpha\text{-Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. Calculated main values for interatomic distances, atomic coordination numbers (N), and Debye–Waller factors (σ^2) are given in Table S4. The $\text{FT}[k^3\chi(k)]$ spectra of as-synthesized $\alpha\text{-Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ show two prominent peaks arising from single backscattering from neighboring O ions at $r \approx 1.46$ Å with Mn^{3+} in an octahedral oxygen coordination environment and Mn atoms at $r \approx 2.70$ Å with Mn–Mn pairs of edge-sharing $\{\text{MnO}_6\}$ octahedra. The lower intensity peak at $r \approx 3.51\text{--}3.58$ Å in $\text{FT}[k^3\chi(k)]$ corresponds to Mn–Mn pairs of corner-sharing $\{\text{MnO}_6\}$ octahedra. Remarkably, while the relative amplitude of the first Mn–O coordination shell in the $\text{FT}[k^3\chi(k)]$ spectra at $r \approx 1.46$ Å is slightly different for $\alpha\text{-Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$, the relative magnitude of the second Mn–Mn(–Mo) coordination shell in the $\text{FT}[k^3\chi(k)]$ spectra of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ is lower when compared with that of $\alpha\text{-Mn}_2\text{O}_3$ (Figure 5b). The amplitude decay in $\text{FT}[k^3\chi(k)]$ is correlated with a decrease of the coordination number (N) or an increase in the mean-square disorder σ^2 . Here, static structural disorder σ^2 emerges upon Mo doping, which induced crystal defects due to slightly different interatomic distances in the Mn–Mn(–Mo) coordination shell, which is directly evident from the HRTEM data (Figure 3). As shown in Figure 5b and Table S4, the atomic coordination number N for the Mn–O coordination shell in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ is slightly lower than that of $\alpha\text{-Mn}_2\text{O}_3$, while N values for the Mn–Mn(–Mo) coordination shell are the same. However, the mean-square disorder parameter σ^2 increases steadily for $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. These findings agree with the results from HRTEM imaging in which $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ shows a disordered structure due to the local structural dispersion of Mn atoms (Figure 3). Our analytical results in their entirety suggest that substitution of Mn^{3+} with molybdenum by annealing in a protective nitrogen atmosphere at 400 °C coupled with vacancy generation results in a distorted structure. The effect of this structural modification on the oxygen evolution performance is investigated in the following.

Figure 5. (a) Mn K-edge X-ray absorption near edge structure (XANES) spectra of $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ and reference oxides used for energy calibration ($\text{Mn}^{\text{II}}\text{O}$, $\alpha\text{-Mn}^{\text{III}}_2\text{O}_3$, $\beta\text{-Mn}^{\text{IV}}_2\text{O}_7$, and Mn_2O_3). Inset at the top: a shift in the Mn absorption edge at 0.5 normalized intensity. Inset at the bottom: Mn oxide linear calibration used to quantify the main Mn oxidation state. (b) Fitting of the Fourier transform EXAFS spectra $\text{FT}[k^3\chi(k)]$ of $\alpha\text{-Mn}_2\text{O}_3$ and $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$.

Enhanced Water Oxidation Performance of Mo-Doped $\alpha\text{-Mn}_2\text{O}_3$

Oxidant-driven water oxidation experiments were conducted with all catalysts (10 mg, Figure 6a) in a deoxygenated aqueous solution of 0.11 M cerium ammonium nitrate (CAN). The activity was normalized to the Brunauer–Emmett–Teller (BET) surface area, catalyst mass, and the Mn content (Table S5 and Figure S18). Among the synthesized series, $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ was found to exhibit very good activity with a maximum TOF of $585 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ ($19.1 \text{ mmol O}_2 \text{ h}^{-1} \text{ g Cat.}^{-1}$), which is higher than that of birnessite,⁵⁰ one of the most active Mn-based catalysts, and exceeds the activity of pure $\alpha\text{-Mn}_2\text{O}_3$ by 15 times. Furthermore, the normalized TOF per Mn content for $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$ ($1.5 \text{ mmol O}_2 \text{ h}^{-1} \text{ mmol Mn}^{-1}$) is higher than that for $\text{K}_{0.11}\text{Ca}_{0.22}\text{MnO}_{2.03} \cdot 0.7\text{H}_2\text{O}$ (Todorokite) and comparable with that for birnessite ($\text{Ca}_{0.21}\text{MnO}_{2.16} \cdot 1.3\text{H}_2\text{O}$) structures⁵⁰ (Table S6). Further comparisons with Mn oxide catalysts in the presence of CAN are given in Table S6. As a control experiment, a mixture of $\alpha\text{-Mn}_2\text{O}_3$ and MoO_3 was applied under the same reaction conditions with the same Mo/Mn ratio as in $\text{Mn}_2\text{O}_3:2.64\%\text{Mo}$. Mechanical mixing was found to exhibit only a negative effect on the water oxidation activity of $\alpha\text{-Mn}_2\text{O}_3$ (Figure 6a). As previously reported,⁷⁸ treatment of layered manganese oxides with reductive agents leads to a 25-fold TOF increase in water oxidation activity. In the present case, the coexistence of $\text{Mo}^{4+}/\text{Mo}^{6+}$ within the manganese oxide lattice can recover the

manganese water-oxidizing active sites.⁷⁸ Hence, it can be concluded that incorporation of Mo centers into the host lattice along with the structural distortion revealed in HRTEM analyses has a significant effect on the water oxidation activity of pristine α - Mn_2O_3 . A photocatalytic water oxidation reaction for α - Mn_2O_3 and Mn_2O_3 :2.64%Mo was performed in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ as a two-electron acceptor and tris(2,2'-bipyridyl)dichloro-ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$; bpy = 2,2' bipyridine) as a photosensitizer in borate buffer (pH 8.5) as shown in Figure 6b. The generated dissolved oxygen was quantified with a Clark electrode. The maximum TOF of O_2 evolution for Mn_2O_3 :2.64%Mo was calculated as $1.5 \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$, which is significantly higher than that of α - Mn_2O_3 ($0.77 \mu\text{mol O}_2 \text{ m}^{-2} \text{ s}^{-1}$), and previously reported values for Mn-based photocatalytic water-oxidizing catalysts (see Table S7 for comparisons with related manganese oxides as tentative references). In a separate experiment, the oxygen was measured in the headspace and analyzed quantitatively by GC (for more details, cf. the experimental part). The amounts of generated oxygen for α - Mn_2O_3 and Mn_2O_3 :2.64%Mo were determined as 3 and 5.3 μmol , respectively, which is in line with Clark electrode results.

Figure 6. (a) Dissolved oxygen concentrations of catalysts (10 mg) measured with a luminescent dissolved oxygen (LDO) electrode in deoxygenated aqueous solutions containing 0.11 M CAN as an oxidant. (b) Dissolved oxygen concentrations of catalysts (1 mg) measured with a Clark electrode in borate buffer (pH 8.5) using $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) as a two-electron acceptor and $\text{Ru}(\text{bpy})_3^{2+}$ (1 mM) as a photosensitizer, under blue light-emitting device (LED) illumination ($\lambda = 460 \text{ nm}$).

This electrochemical performance of Mn_2O_3 :2.64%Mo is better than that of thick layers of Mn_2O_3 electrodes earlier reported with higher catalyst loading,⁸¹ and it seems to be slightly higher than some reported values for Co-doped MnO_2 ,⁸² CoNi-doped Mn_xO_y ,⁸³ and Fe/Co/Ni-doped hollandite-type Mn oxides.⁸⁴ However, since comparison of the electrocatalytic performance between two different materials requires the full standardization of the reaction parameters, catalyst loadings, electrode preparation, electrolyte, potential and electrochemical setup, directly comparing the performance of Mn_2O_3 :2.64%Mo with that of Fe/Co/Ni-doped Mn oxides reported in the literature is ambiguous because those electrodes were synthesized and tested under different electrochemical conditions. To confirm the catalytic onset potential of Mn_2O_3 :2.64%Mo obtained from the LSV analyses, we carried out a multistep amperometry measurement. The increase in current density along with increasing potential is negligible below 1.53 V, and the sharp increase in the current density starts between 1.53 and 1.58 V (Figure 7b). Therefore, it is reasonable to define 1.53 V as the onset potential for Mn_2O_3 :2.64%Mo. The overpotential (η)/current density (j)

HRTEM imaging of the postcatalytic material did not show any decomposition or amorphization after photocatalytic and chemical water oxidation reactions, indicating that Mn_2O_3 :2.64%Mo maintains a good postcatalytic structural integrity (Figure S19). However, STEM-EDX analyses showed that, after the catalytic reaction, Mn_2O_3 :2.64%Mo particles are covered by ruthenium or cerium oxides, which decreases the postcatalytic accuracy of EDX elemental analysis of manganese, molybdenum, and oxygen (Figures S20 and S21).

Electrocatalytic measurements were performed in alkaline 1.0 M KOH electrolyte using linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} (Figure 7a). The potentials are reported vs a reversible hydrogen electrode (RHE). As shown in Figure 7a, the onset potential for Mn_2O_3 :2.64%Mo was 1.53 V and the overpotential (η) was 300 mV. The current density of 10 mA cm^{-2} was obtained at 1.79 V ($\eta = 570 \text{ mV}$, without any iR compensation) which is only 20 mV above a benchmark RuO_2 electrode and compares well with the reported active Mn-based OER catalysts (Table S8).

curve, extracted from multistep amperometry in the overpotential range of 1.53–1.83 V vs RHE (Figure 7c), shows that the recorded current density of Mn_2O_3 :2.64%Mo is much higher than that of the α - Mn_2O_3 reference. Figure 7d shows multistep amperometry data for Mn_2O_3 :2.64%Mo with the voltage increasing from 1.43 to 2.03 V (500 mV cm^{-2} per 300 s). After the onset potential window of 1.53 V, all subsequent steps present high and stable current, reflecting the excellent mass transport and conductivity properties as well as the mechanical stability of Mn_2O_3 :2.64%Mo electrodes.

Developing economical, nontoxic and abundant Mn–Mo-based electrocatalysts and electrodes that can persist in seawater oxidation, without chlorine evolution, could address the drinking water crisis.^{85,86} We therefore performed water oxidation using simulated alkaline seawater⁸⁶ (1.0 M KOH + 0.5 M NaCl) with Mn_2O_3 :2.64%Mo as the OER catalyst. As the Mn_2O_3 :2.64%Mo compound oxidizes water with low overpotential, we exclusively observed water oxidation because chloride oxidation in alkaline pH occurs at higher potentials. The amount of generated oxygen was

recorded with a LDO sensor (Figure S22a,b). The Faradaic efficiency⁸⁷ was calculated as 91%, which shows that the electrode has a high selectivity toward OER in simulated alkaline seawater.

XANES and EXAFS analyses after 100 cyclic voltammetry (CV) cycles showed that the Mn K-edge absorption edge of postcatalytic Mn₂O₃:2.64%Mo is slightly shifted by 0.2 eV (Figure S23a), suggesting that the Mn species in the catalyst were slightly oxidized after OER. The low white line intensity (6556.8 eV) in the XANES spectrum and the lower amplitude of the Mn–O coordination shell (at $r \approx 1.46$ Å) in the FT $|k^3\chi(k)|$ spectrum (Figure S23b) suggest a small induced structural disorder in the {MnO₆} coordination octahedra after OER. Furthermore, postcatalytic SEM-EDX investigations of the electrode surface after 100 CV cycles (Figure S23d-g) and after multi-potential-step chronoamperometry (Figure S24a-f) showed stable surface morphologies with a homogeneous distribution of molybdenum, manganese, and oxygen species. Tafel slopes showing linear behaviors were extracted in the overpotential range of 0.29–0.44 V. The slope obtained for Mn₂O₃:2.64%Mo (75 mV dec⁻¹) is lower than the one obtained for the α -Mn₂O₃ (109 mV dec⁻¹) which is consistent with its high activity (Figure 7e). The increase in the apparent Tafel slope value for α -Mn₂O₃ could be ascribed to a change in the reaction mechanism.^{88,89} To evaluate the durability of the Mn₂O₃:2.64%Mo catalyst for water oxidation, controlled-potential electrolysis was carried out at 1.62 V vs RHE in 1.0 M KOH. For this purpose, we used a double jacketed 1 L electrochemical cell to reduce the pH drop issue and connected it to a water circulator (at 25 °C) for constant temperature during the long-term electrolysis. As shown in Figure 7f, a stable current density (~ 2.3 mA cm⁻²) much higher than for pure α -Mn₂O₃ (~ 0.5 mA cm⁻²) was obtained for 30 h (Figure 7f). No obvious activity loss was observed during 30 h of the stability test.

Key Parameters for High WOC Activity of Mn₂O₃:2.64%Mo

The catalytic OER activity of Mn₂O₃:2.64%Mo outperforms the activities of most of the previously reported Mn-based OER catalysts (Table S8) and is comparable with that of relevant noble-metal-free catalysts such as of iron, cobalt, and nickel (Table S9). We linked the remarkably enhanced catalytic activity of Mn₂O₃:2.64%Mo to its higher electrical conductivity compared to α -Mn₂O₃ using electrochemical impedance spectroscopy (EIS). EIS for Mn₂O₃:2.64%Mo and α -Mn₂O₃ electrodes was carried out in a three-electrode configuration in 1.0 M KOH at 1.63 V vs RHE. The electrodes were prepared by a spray method with PEO-containing ink, which was used as well for the above voltammetry and amperometry studies. A coated electrode equivalent electrical circuit was used to fit the EIS data.⁶⁰ The fitting parameters of the equivalent circuit elements are shown in Table S10, where R_s is the electrolyte resistivity and R_{film} and CPE_{film} are describing the film characteristics. R_{ct} attributes to the charge transfer resistivity of the

OER reaction on the electrode surface, and CPE_{dl} is the constant phase element of a double layer to model the double layer between the electrode surface and electrolyte as an imperfect capacitor (Table S10). From CPE analysis (see SI for details), the double-layer capacitances C_{dl} of the electrodes were calculated as 0.167 $\mu\text{F cm}^{-2}$ and 311 $\mu\text{F cm}^{-2}$ for α -Mn₂O₃ and Mn₂O₃:2.64%Mo, respectively.⁹⁰⁻⁹³ Since C_{dl} is proportional to the surface area of the electrodes^{94,95}, the ratio of C_{dl} can be regarded as the ratio of the electrochemical surface areas. Therefore, these results clearly show that the catalytically active surface area of Mn₂O₃:2.64%Mo is much higher than that of α -Mn₂O₃ for the OER at the applied potential of 1.63 V vs RHE. The Nyquist plots of both electrodes show a semicircle in the frequency range of 0.1–50 kHz (Figure 7g). The diameter of the semicircle in the Nyquist diagram for Mn₂O₃:2.64%Mo decreases dramatically in comparison with α -Mn₂O₃ showing lower R_{ct} , which corresponds to decreased resistivity to the electrochemical OER that is taking place on the electrode surface. The R_{ct} of Mn₂O₃:2.64%Mo in 1.0 M KOH at 1.63 V applied potential vs RHE is estimated to be 2339 $\Omega \text{ cm}^{-2}$. This is clearly much lower than R_{ct} for α -Mn₂O₃ (38308 $\Omega \text{ cm}^{-2}$) which shows that Mo doping into the α -Mn₂O₃ lattice facilitates the electron transfer during OER (Table S10). R_{ct} can be estimated by reading the Bode plot when the impedance is plotted with logarithmic frequency and y-axis is the absolute value of the impedance ($|Z|$).⁹⁶ This is evident from the Bode plots (Figure 7h), where Mn₂O₃:2.64%Mo shows a lower $\log|Z|$ value than α -Mn₂O₃ which is related to lower R_{ct} for Mn₂O₃:2.64%Mo.⁹⁷ We thus conclude that the OER performance of α -Mn₂O₃ is limited by its high resistance to the OER in the applied potential window, while the superior low R_{ct} of Mn₂O₃:2.64%Mo leads to better water oxidation activity, in agreement with its lower Tafel slope (Figure 7e). To further demonstrate the productive effect of Mo on the OER activity of α -Mn₂O₃, we examined the EIS of Mn₂O₃:2.64%Mo and α -Mn₂O₃ electrodes in 0.1 M KPi at pH 7 in Nafion (see Experimental Section for details) and compared it with published EIS data for the α -Mn₂O₃ system.⁶⁰ The Nyquist plots of both electrodes show a semicircle in the frequency range of 0.1–50 kHz (Figure S25a) that is mainly correlated to charge transfer resistance (R_{ct}) in the manganese oxide catalysts. A coated electrode equivalent electrical circuit was used to fit the EIS data, and the R_{ct} of Mn₂O₃:2.64%Mo at 1.4 V applied potential (vs Ag/AgCl) was estimated as 362 $\Omega \text{ cm}^{-2}$, i.e. lower than that of α -Mn₂O₃ (747 $\Omega \text{ cm}^{-2}$). The calculated value for α -Mn₂O₃ is in line with reported values.⁶⁰ In addition, this is evident from the Bode plots (Figure S25b), where Mn₂O₃:2.64%Mo shows the lower charge transfer resistivity of the OER reaction on the electrode surface than α -Mn₂O₃. These results demonstrate that the enhanced activity of Mn₂O₃:2.64%Mo is not related to the electrode preparation methods or the additive materials that have been used in the spraying method.

Figure 7. (a) LSV curves at 5 mV/s scan rate of FTO/Mn₂O₃:2.64%Mo and FTO/α-Mn₂O₃ in 1.0 M KOH solution compared with RuO₂ and FTO. (b) Multi-potential-step chronoamperometry in 1.0 M KOH solution with a potential step of 0.05 V. (c) Overpotential (η)/current density (j) extracted from multistep amperometry in the range of 0.5 to 0.8 V. (d) Multi-potential-step chronoamperometry in 1.0 M KOH solution with a potential step of 0.05 V amperometry in the potential range of 1.43 to 2.03 V. (e) Tafel plot derived from the corresponding polarization (LSV) curves. (f) Bulk electrolysis with Mn₂O₃:2.64%Mo and α-Mn₂O₃ in KOH 1.0 M at 1.64 V vs. RHE. (g) Nyquist and (h) Bode plots of Mn₂O₃:2.64%Mo and α-Mn₂O₃ in 1.0 M KOH at 1.63 V vs. RHE applied potential in the frequency range of 0.1 Hz–50 kHz.

Conclusions

Bixbyite-type molybdenum-doped manganese oxides were synthesized as highly active all-round water oxidation catalysts in chemical, electrochemical, and photochemical assays. Monitoring of the synthetic optimization process by applying a wide range of analytical techniques showed that molybdenum doping could stabilize an average Mn oxidation state of +2.8 in the bixbyite structure at lower calcination temperatures than required for the formation of pure α-Mn₂O₃. Mn³⁺ is stabilized in the bixbyite lattice at lower temperatures by the presence of molybdenum dopants. HRTEM analysis provided direct evidence of structural distortions in the vicinity of the Mo centers of the most active water oxidation catalyst among the series, Mn₂O₃:2.64%Mo. Their role in the observed high water oxidation activity was further investigated with XPS and XANES. Results of both methods confirm the partial reduction of Mn³⁺ centers in the bixbyite lattice in the course of Mo doping. Furthermore, EXAFS data underscore the induced structural distortion in the Mn–O and Mn–Mn coordination shells, which are a key parameter in the high water oxidation activity of Mn₂O₃:2.64%Mo. The catalytic OER activity of Mn₂O₃:2.64%Mo outperforms the activities of most of the previously reported Mn-based OER catalysts and is comparable with that of important noble-metal-free catalysts such

as cobalt and nickel. The chemical water oxidation activity of Mn₂O₃:2.64%Mo in CAN media with a TOF of 585 μmol O₂ m⁻² h⁻¹ is 15 times higher compared to pure α-Mn₂O₃ oxide. Likewise, photochemical water oxidation performance of the Mn₂O₃:2.64%Mo/[Ru(bpy)₃]²⁺/S₂O₈²⁻ system resulted in an enhanced TOF of 1.5 μmol O₂ m⁻² s⁻¹.

In addition, Mn₂O₃:2.64%Mo displayed a current density of 10 mA cm⁻¹ at 1.79 V (η = 570 mV), i.e. only 20 mV above RuO₂ as a noble metal benchmark, while providing long-term stability and high conductivity. Electrochemical impedance spectroscopy (EIS) showed a higher catalytically active surface area for Mn₂O₃:2.64%Mo and the charge transfer resistance of Mn₂O₃:2.64%Mo (R_{ct} = 2339 Ω cm⁻²) is much lower compared to pristine α-Mn₂O₃ (R_{ct} = 38308 Ω cm⁻²).

This study of highly active Mo/Mn oxides demonstrates how highly efficient and low-cost catalysts for artificial photosynthesis can be designed through fine-tuning the structural interactions of abundant elements with biological relevance and geochemical compatibility. Our strategy of selective dopant-induced structural distortions for optimization of the catalytic activity will enable new catalytic discoveries through economical doping strategies to exploit the inexhaustible variety of cost-effective transition-metal oxides.

Experimental Section

Materials and Methods

All reagents and solvents were purchased from commercial sources and were used without further purification ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ $\geq 99\%$ from Fluka analytical (09880-100G), $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ 99% from Sigma-Aldrich (769509-250G), NH_4HCO_3 $\geq 99\%$ from Sigma-Aldrich (A6141-500G), $(\text{NH}_4)_2\text{SO}_4$ $\geq 99\%$ from Sigma-Aldrich (A4418-100G), $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_6\text{Ru}\cdot 6\text{H}_2\text{O}$ 99.95% from Sigma-Aldrich (544981-1G), $\text{Na}_2\text{S}_2\text{O}_8$ $\geq 99\%$ from Sigma-Aldrich (71890-500G), $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ $\geq 99.99\%$ from Sigma-Aldrich (229547), TritonTM X-100 laboratory grade from Sigma-Aldrich (X100-100ML), poly(ethylene oxide) from Sigma-Aldrich (372781-250G). Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed using FEI TALOS F200X and Zeiss Supra 50 VP instruments, respectively. X-ray photoelectron spectroscopy (XPS) was conducted on selected samples using a Physical Electronics (PHI) Quantum 2000 X-ray photoelectron spectrometer featuring monochromatic Al K_α radiation, generated from an electron beam operated at 15 kV and 32.3 W. The energy scale of the instrument was calibrated using Au and Cu reference samples. The samples were pressed onto indium foil patches, mounted onto a sample plate, and then introduced into the spectrometer. The analysis was conducted at 1×10^{-6} Pa, with an electron take-off angle of 45° and a pass energy of 23.50 eV for all samples. Charge compensation during the measurement was achieved using a low-energy electron source. The spectra were analyzed using the CasaXPS software, and the data were fitted using a Shirley background function.

X-ray absorption spectroscopy (XAS) at the Mn K-edge on solid powder samples of $\alpha\text{-Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3\cdot 2.64\%\text{Mo}$, and references (MnO , MnO_2 , Mn_2O_3 , and Mn_3O_4) dispersed in cellulose was performed at the European Synchrotron Radiation Facility (ESRF), Swiss-Norwegian Beamline BM31, Grenoble-France. The storage ring was run in top-up mode, at an average current of 400 mA. The X-ray beam was collimated using a Si-coated mirror, and the energy was scanned using a double crystal Si[111] monochromator. Measurements were performed using a three-ionization chamber configuration in transmission mode employing a 13-element Ge detector. For energy calibration, the spectrum of a metal Mn foil was measured simultaneously at the second ionization chamber. The measured k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra $k^3\chi(k)$ were extracted by standard data reduction, absorption edge energy calibration and background subtraction as implemented in ATHENA.⁹⁸ The spectra were reduced into the range $\Delta k \approx 3\text{--}12 \text{ \AA}^{-1}$ and Fourier transform to $\text{FT}[k^3\chi(k)]$ into the real-space interval $\Delta R \approx 0\text{--}6 \text{ \AA}$. To calculate main values for interatomic distances, coordination numbers and Debye-Waller factors σ^2 nonlinear least-squares fitting of the $\text{FT}[k^3\chi(k)]$ spectra was carried out with ARTEMIS⁹⁸ using an atomic cluster of Mn_2O_3 (PDF 01-071-0636), generated by ATOMS⁹⁸ as implemented in IFEFFIT.⁹⁸ Amplitude and phases shifts for single-multiple scattering paths were calculated using FEFF6.⁹⁹ Powder X-ray diffraction patterns (PXRD) were recorded on an STOE STADI P diffractometer in transmission mode using Mo $K_{\alpha 1}$ radiation in a flat-plate sample holder with Ge monochromator and a position-sensitive microstrip solid-state detector (MYTHEN 1K).

Synthesis of $\text{MnCO}_3\cdot 2.64\%\text{Mo}$

For the synthesis of $\text{MnCO}_3\cdot 2.64\%\text{Mo}$, manganese nitrate tetrahydrate [2 mmol $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, 0.502 g] and ammonium molybdate tetrahydrate [0.143 mmol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 0.176 g] were dissolved in water (16 mL). This solution was mixed slowly with a solution of ammonium sulfate (8.3 mmol, 1.1 g) in water (16 mL) and stirred for 2 h. A third solution of ammonium bicarbonate (8.3

mmol, 0.66 g) in water (16 mL) was then added slowly to the above mixture and stirred for 4 h. The obtained light-yellow precipitate was collected by centrifugation, washed thoroughly with distilled water and absolute ethanol, and dried at 60°C for 12 h. For other molar ratios $\text{MnCO}_3\cdot 1.72\%\text{Mo}$, $\text{MnCO}_3\cdot 32.23\%\text{Mo}$ and $\text{MnCO}_3\cdot 49.67\%\text{Mo}$ the synthesis procedures were the same, except that the molar ratio of ammonium molybdate tetrahydrate was 0.0715, 0.286, and 0.572 mmol for $\text{MnCO}_3\cdot 1.72\%\text{Mo}$, $\text{MnCO}_3\cdot 32.23\%\text{Mo}$ and $\text{MnCO}_3\cdot 49.67\%\text{Mo}$, respectively.

Synthesis of $\text{Mn}_2\text{O}_3\cdot 2.64\%\text{Mo}$

For synthesis of $\text{Mn}_2\text{O}_3\cdot 2.64\%\text{Mo}$, the carbonate precursor $\text{MnCO}_3\cdot 2.64\%\text{Mo}$ was heated in a tubular furnace with a nitrogen flow of 60 mL min^{-1} at 400°C ($12^\circ\text{C min}^{-1}$) for 8 h and kept there for an additional 12 h, followed by cooling naturally to RT. Afterwards, the resulting material was calcined in an air atmosphere at 400°C ($12^\circ\text{C min}^{-1}$) for 24 h. For the synthesis of other molar ratios ($\text{Mn}_2\text{O}_3\cdot 1.72\%\text{Mo}$, $\text{Mn}_2\text{O}_3\cdot 32.23\%\text{Mo}$ and $\text{Mn}_2\text{O}_3\cdot 49.67\%\text{Mo}$) the calcination procedures were performed in the same way.

Chemical Water Oxidation

Chemical water oxidation experiments were performed in the presence of Ce(IV) using an HQ40D portable dissolved oxygen meter connected to an oxygen monitor with a digital readout at 25°C . In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in an air-tight reactor. After establishing a constant baseline reading, we replaced water in the reactor with a Ce(IV) solution. In the absence of the catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, the catalyst was added as a powder, and the oxygen evolution was recorded with the oxygen meter under stirring. The formation of oxygen was monitored, and the oxygen formation rates per surface area were obtained from linear data fitting using the initial data points that have a linear behavior.

Photochemical Water Oxidation

The deaerated reaction solutions were prepared in a 10 mL glass vial as follows: 9.5 mg $\text{Na}_2\text{S}_2\text{O}_8$ (5 mM) was added to 8 mL of a buffered solution, pH 8.5 borate buffer (80 mM), containing completely dissolved 6 mg $[\text{Ru}(\text{bpy})_3]\text{Cl}_2\cdot 6\text{H}_2\text{O}$ (1 mM) and catalyst (1 mg). Glass vials with the above solutions were sealed with a combination of a rubber septum [poly(tetrafluoroethylene)—PTFE] and an aluminum crimp cap, followed by deaeration through purging with helium (purity 6.0) for 15 min.

The O_2 evolution of the above catalytic solutions was measured independently with a Clark electrode. For measurements, an Oxygen sensor (OX-N) Clark electrode (Unisense) was inserted into the deaerated solution through the rubber septum, followed by irradiation with a 470 nm high flux LED light (26.1 mW cm^{-2} , Rhopoint Components Ltd) after a constant signal of the Clark electrode was obtained under a stirring rate of 1000 rpm. O_2 evolution was monitored with the SensorTrace software (Unisense) applying a frequency of one data point per sec. The calibration of the Clark electrode was performed according to the procedure provided by the Unisense user manual with a sodium ascorbate solution (2 g of sodium ascorbate in 100 mL of 0.1 M NaOH solution) as the zero calibration solution and aerated water as the aerated calibration solution (for details, cf. the Unisense user manual). For GC measurements, the deaerated solution was irradiated with a LED light source for 30 min under a stirring rate of 1000 rpm, and a 200 μL gas sample was taken with a gas-tight microliter syringe (Hamilton 1825RN) and transferred to the GC injection port. After pushing the syringe bar to the 100 μL mark, 100 μL of the gas sample was

quickly injected into the GC (Agilent Technologies 7820A) equipped with a thermal conductivity detector (Varian). O₂ and N₂ were separated by passing the sample through a 3 m × 2 mm packed 5 Å molecular sieve 13X 80-100 column with a helium carrier gas (purity 6.0). Quantification of O₂ evolution was carried out with a good linear GC calibration curve obtained from measuring a series of volumes (50–500 µL) of pure O₂ vs the peak area of each O₂ signal. Contamination of air was corrected by subtracting the half peak area of N₂ from the peak area of O₂ (due to the similar GC response to O₂ and N₂, the peak area of the contaminating O₂ basically equals 1/3 of the N₂ peak area).

Electrochemical Water Oxidation

Electrochemical experiments were performed using a SP-150 Potentiostat (Bio-Logic Science Instrument) with a three-electrode setup, in which a fluorine-doped tin oxide-coated glass slides (FTO, 7 Ω sq⁻¹, Sigma-Aldrich) worked as a working electrode, an Ag|AgCl|KCl 3 M served as a reference electrode, and a platinum rod served as auxiliary electrodes. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) in 1.0 M H₂SO₄ solution at 1 mV s⁻¹ scan rate (more details in Figure S26). Previous reports showed that the use of platinum as counter electrode and its dissolution in the reaction medium led to the redeposition of Pt on the reduction half-cell, which can significantly improve the catalytic activity in reduction phenomena such as hydrogen evolution reaction and oxygen reduction reaction.¹⁰⁰⁻¹⁰³ In this work, as a control experiment, the negligible activity of a platinum rod auxiliary electrode in OER was examined and considered as blank measurement (Figure S27a). The SEM-EDX mapping of the postcatalytic working electrode did not show any redeposition of Pt species on the FTO surface (Figure S27b). Electrodes for voltammetry, electrochemical impedance spectroscopy (EIS), and amperometry measurements were prepared by the modified spraying PEO-containing ink method.¹⁰⁴ Metal oxide powders (100 mg) were suspended in a mixture of distilled water (1 mL), acetylacetone (0.1 mL), Triton X-100 (0.1 mL), and PEO (30 mg). Next, the suspension was stirred slowly for 12 h. Afterward, 1.2 mL of the PEO-ink was mixed with 50 mL of H₂O and filled into a 150 mL sprayer. For the spraying process, the FTO electrode substrates were heated on a hot plate to 300 °C and then sprayed for 20 min with the suspension using a gentle and continuous stream of compressed air. The electrodes were then annealed at 100 °C for 60 min and subsequently calcined at 400 °C for 12 h. The final amount of the loaded catalyst on the FTO surface was determined as 1 mg cm⁻² by averaging from five electrodes. For comparison, a RuO₂-modified electrode was also prepared in the same way. For the Nafion/catalyst electrode for EIS studies in a phosphate buffer to be prepared, 7.2 mg of the obtained metal oxide powders was dispersed in 100 µL of H₂O and sonicated for 15 min. A total of 40 µL of the suspension was dropcast on the conductive side of FTO glass (1 cm²) and kept at 80 °C for 15 min. Afterward, 10 µL of 1% Nafion (ethanol solution) was dropcast on the deposited layer and dried at 50 °C for 15 min to evaporate the solvent. Ruthenium(IV) oxide, 99.9% trace metal basis (Sigma-Aldrich product no.: 238058) was used for this study. SEM-EDX images with morphology and elemental mapping information have been added to the supporting information (Figure S28). All values are reported without considering any iR compensation. All chemical, photochemical, and electrochemical measurements were repeated at least three times, starting with a freshly fabricated electrode at each measurement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

PXRD patterns, TGA and DTG analyses, Rietveld refinement data, SEM images, EDX patterns, HRTEM images, STEM-EDX analyses, HAADF-STEM-EDX mapping, XPS spectra, CHN analyses, XAS fitting data, BET-TOF analyses, additional OER activities, EIS analyses, and LSV data (PDF).

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Notes

The authors declare no conflict of interest.

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