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Economic Manganese Oxide-Based Anodes for Efficient Water Oxidation: Rapid Synthesis and In Situ Transmission Electron Microscopy Monitoring

Sima Heidari^a, S. Esmael Balaghi^a, Alla S. Sologubenko^b, Greta R. Patzke^{a*}

^a Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

^b Scientific Center for Optical and Electron Microscopy (ScopeM), ETH Zurich, Otto-Stern-Weg 3, CH-8093 Zurich, Switzerland

ABSTRACT: Earth-abundant, environmentally friendly, and low-cost manganese oxide materials are excellent resources for water oxidation catalysts in clean solar fuel applications. We here introduce a convenient and low-cost method for manufacturing stable and highly efficient manganese oxide-based anodes for electrochemical water oxidation under neutral conditions. The electrodes were fabricated through thermal decomposition of acidic KMnO_4 solution. The phase transitions of the manganese oxide film during calcination and thermal decomposition of KMnO_4 were monitored with in situ heating transmission electron microscopy (TEM), in situ heating scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM/EDX), and in situ heating powder X-ray diffraction (PXRD). In depth monitoring of formation pathways and phase transformations by in situ techniques under high temperatures shed light upon the fabrication of efficient manganese oxides for energy conversion applications. After parameter optimizations, the best performing manganese oxide catalyst was applied for water electrolysis for 100 h with a stable current density of 1.0 mA cm^{-2} at an overpotential of 490 mV in neutral pH. Post operando characterizations of key oxide film properties showed no significant changes. The readily commercially available precursor enables a simple and rapid fabrication method, and the promising stability and high performance of the herein developed electrodes render them quite promising for technological water splitting systems.

KEYWORDS: *in situ heating TEM, XAS, in situ heating STEM/EDX, water oxidation, manganese oxide, electrocatalysis, low cost transition metals*

INTRODUCTION

Water electrolysis is a very promising approach for the large-scale production of clean hydrogen fuel.¹ However, the oxygen evolution reaction (OER) with its high thermodynamic potential, and the kinetic barrier is the bottleneck of this process.² In the current intense search for high performing water oxidation catalysts (WOCs), Ir and Ru oxides are the most active benchmarks.³⁻⁵ However, their high price and scarcity have triggered enormous efforts to design WOCs from abundant materials, with current special emphasis on molecular⁶⁻¹¹ and solid-state compounds¹²⁻¹⁹ of the first-row transition metal-based materials. Accordingly, NiFe-based materials, as well as Co oxides, have attracted considerable attention as WOCs under alkaline conditions.²⁰⁻²⁵ In parallel, manganese oxides have been intensely investigated for water oxidation because they offer manifold advantages:²⁶⁻³⁶ (1) Manganese is the third most abundant transition metal in the earth's crust³⁷ with a remarkably lower price than Co or Ni sources.³⁸ (2) Additionally, manganese is an environmentally friendly material with no significant toxicity. (3) The Pourbaix diagram of the

Mn/ H_2O system demonstrates that manganese oxide-based water oxidation catalysts can be used over a wide pH range including neutral or even acidic conditions, where Co-based and especially Ni-based systems suffer from corrosion.³⁹ (4) Given that usual semiconductor solar cells are unstable under highly alkaline or acidic conditions,²⁴ the stability of Mn-oxides renders them suitable catalysts for multi-junction semiconductor-based "artificial leaf" systems. (5) As the pH of seawater typically ranges between 7.5 and 8.4 (nowadays the pH of the oceans is decreasing due to anthropogenic CO_2 emissions),⁴⁰ manganese oxides are ideal candidates for large-scale seawater electrolysis. (6) Last but not least, manganese plays a unique role in natural water oxidation,⁴¹ and mechanistic insight into the water oxidizing pathways of the CaMn_4O_5 cluster in natural photosynthesis is a fascinating blueprint to optimize manganese oxides for artificial systems.^{26,42-46}

Catalysts with low electronic conductivity, such as manganese oxides, are best used as films on the surface of conductive electrodes for electrochemical water oxidation. However, efficient and low-cost methods to integrate such

catalysts on conductive electrodes remain a crucial challenge in the scale-up of water splitting systems. To date, different fabrication methods have been reported to prepare noble metal-free oxide films on electrodes, such as electrodeposition,^{24,47,48} screen-printing of a pre-synthesized oxide containing ink,⁴⁹⁻⁵¹ hydrothermal synthesis,³⁶ physical vapor deposition (PVD),⁵²⁻⁵⁴ atomic layer deposition (ALD),⁵⁵⁻⁵⁷ and calcination of pre-catalyst coatings⁵⁸. Among them, electrodeposition is most commonly used to prepare catalytically active oxide films. Although this method enables fast manufacturing, control over morphology, and uniformity of the final films remains difficult.⁵⁹⁻⁶¹ Likewise, ink printing offers manifold catalyst optimization options, but the obtained films often display insufficient mechanical stability.⁴⁹⁻⁵¹ Industrial applications of ALD and PVD techniques are limited due to slow processing time, high investment costs, and narrow choices of precursor materials.^{62,63} Concerning hydrothermal coating procedures, corrosion under extreme pH conditions, scaling problems, maintenance costs, and safety precautions are drawbacks on the industrial scale.⁶⁴ Therefore, inexpensive, predictable and fast routes to chemically and mechanically stable oxide films are crucial to commercialize water-splitting technologies.

To this end, we introduce and analyze a facile and cost-efficient method for manganese oxide-based anode production with high application potential for large scale water splitting. Manganese oxide films were conveniently fabricated through spraying an acidic solution of KMnO_4 on a hot FTO/glass substrate. We studied the thermal decomposition of KMnO_4 and phase transitions during annealing with complementary in situ heating PXRD, in situ heating STEM/EDX and in situ heating TEM techniques. Annealing

of manganese oxides exerts a key effect on all their application options in energy conversion and storage devices.⁶⁵⁻⁷¹ Therefore, insight into the thermal formation and reconstruction pathways of manganese oxides will pave the way to optimize a wide range of their general performance parameters, such as crystallinity, phase purity, true catalyst detection, stability in high-temperature catalysis, etc.

The herein reported economic manganese oxide coated electrodes were furthermore characterized with a wide range of analytical methods, such as PXRD, SEM, TEM, and XAS. Optimized electrodes displayed stability for at least 100 h under continuous operation in neutral solutions. Post-catalytic characterizations corroborated the high operational stability of the newly fabricated manganese oxide films.

RESULTS AND DISCUSSION

Preparation and characterization of MnO_x electrodes

Manganese oxide films were synthesized by thermal decomposition of an acidic solution of KMnO_4 to manganese oxide in air (SI for experimental details). The low cost and powerful oxidizing agent potassium permanganate is applied in various industrial processes, such as in water treatment,⁷² and organic synthesis⁷³. To generate films, the solution was sprayed on the surface of a hot FTO/glass substrate. As annealing has a pronounced effect on the catalytic activity of manganese oxide WOCs, the as-prepared electrodes were calcined at different temperatures (100-600 °C) and characterized with various techniques (abbreviated in the following: as- MnO_x = pristine film, calcined samples = MnO_x -100, etc. according to their annealing temperature). Figure 1 shows the XRD patterns of the samples.

Figure 1. XRD patterns of the fabricated electrodes (A), phase transitions of the as- MnO_x electrode during the heating process identified by in situ heating XRD (data were collected in air) (B), overall in situ heating XRD pattern from 30-600 °C (C), highlighted regions at 36.9-38.1°, 49-50° and 64.2-65.3° (D), birnessite structure (E), cryptomelane structure (F).

The XRD patterns of as-MnO_x, MnO_x-100, and MnO_x-200 mainly displayed peaks of the underlying FTO phase. However, some broad peaks are visible at $2\theta \sim 12.5^\circ$ and 37° (cf. arrows in Figures 1A and B). These broad peaks with d-spacing around 7.1 and 2.4 Å are related to octahedral layered manganese oxide (OL-1) (PDF: 01-073-7864) without any significant (micro)crystallinity. OL-1 is known as an analogue of the birnessite structure (Figure 1E). Birnessite is a layered manganese oxide phase consisting of edge-sharing MnO₆ octahedral units with exchangeable cations and/or water molecules located in interlayer spaces.⁷⁴ When annealing the as-prepared electrodes at 300-600 °C, sharp peaks related to a cryptomelane phase appeared in their PXRD patterns (Figure 1A). Cryptomelane displays a "molecular sieve" tunnel structure of edge-sharing MnO₆ octahedral chains (OMS-2, Figure 1F, tunnel dimension approx. 4.6×4.6 Å) stabilized with K⁺ cations.⁷⁵ The transition of birnessite into the cryptomelane phase upon annealing has been reported in previous studies.⁷⁶

Figure 1B shows the in situ XRD pattern of the as-MnO_x electrode upon annealing at 100, 200, 250, 300, 350, 400, 500, and 600 °C in air. The transition of OL-1 to OMS-2 is clearly observed at 300 °C. However, the overall in situ heating XRD patterns presented in Figure 1C shows that the phase transition starts around 270 °C. Furthermore, peaks related to the cryptomelane structure were shifted to lower angles when calcined at temperatures above 300 °C (Figure

1D). Additionally, the intensity of the represented peaks of cryptomelane structure increases with further elevating the temperature from 300 °C to 600 °C, thus illustrating an increase of crystallinity with processing temperature.

High-resolution TEM (HRTEM) images and corresponding FFT analyses of the prepared electrodes are shown in Figure 2. While TEM images displayed no specific morphological features for as-MnO_x and MnO_x-100, their FFT patterns showed three diffuse diffraction rings with d-spacings around 7, 3.4 and 2.5 Å related to the (002), (004) and (110) lattice planes of the birnessite structure (PDF: 01-073-7864). According to the TEM results, the size of crystalline areas in these layered structures is less than 10 nm; this phenomenon can explain the broad and low-intensity peaks in the PXRD patterns of these samples. After annealing the film at 200 °C, HRTEM images displayed a low crystalline phase (Figure S1) as well as spherical nanoparticles around 10 nm (Figure 2E). FFT patterns acquired from these nanoparticles showed diffraction rings, which perfectly match with the cryptomelane phase (PDF: 01-074-1451) (Figure 2F).

The crystallite size was calculated for MnO_x-300 to MnO_x-600 electrodes by applying the Debye-Scherrer equation ($D = K\lambda/\beta\cos\theta$), where D is the crystallite size, K is the Debye-Scherrer constant (0.9), λ is the source X-ray wavelength (0.15406 nm), β is the maximum peak width at half maximum (FWHM) and θ is the diffraction angle.⁷⁷

Figure 2. HRTEM micrograph of as-MnO_x (A), FFT pattern of the selected area of A (B), HRTEM micrograph of MnO_x-100 (C), FFT pattern of C (D), HRTEM micrograph of MnO_x-200 (E), FFT pattern of E (F), HRTEM micrograph of MnO_x-300 (G), FFT pattern of the selected area of G (H), HRTEM micrograph of MnO_x-400 (I), FFT pattern of the selected area of I (J), HRTEM micrograph of MnO_x-500 (K), FFT pattern of the selected area of K (L).

When applying this equation to the fabricated electrodes, the crystallite size was calculated from the (301) PXRD peak. As summarized in Table S1, with increasing the calcination temperature from 300 °C to 600 °C, the crystallite size increased, and a similar trend was also evident from TEM images of the samples (Figure 2). Mn K-edge X-ray absorption near edge structure (XANES) spectroscopy was furthermore employed to track the average oxidation state (AOS) of the Mn centers after calcination at different temperatures (Figure 3). Generally, highly active manganese oxide WOCs display mixed-valence states with Mn(III) sites.⁷⁸ The electronically degenerate antibonding electronic configuration of Mn(III) in an octahedral unit leads to Jahn–Teller elongated Mn(III)-O bonds.

Figure 3. Mn K-edge XANES spectra of the electrodes and reference oxides used for energy calibration ($\text{Mn}^{\text{II}}\text{O}$, $\alpha\text{-Mn}_2^{\text{III}}\text{O}_3$, $\beta\text{-Mn}^{\text{IV}}\text{O}_2$, and Mn_3O_4 , inset: shift of the Mn absorption edge at 0.5 normalized intensity) (A), Mn oxide linear calibration used to quantify the average Mn oxidation state (B).

Table 1. Average oxidation state of manganese centers obtained from Mn K-edge XANES spectra and crystal structure of all prepared electrodes.

Catalyst	AOS of Mn	Crystal structure
as-MnO _x	3.51	OL-1
MnO _x -100	3.34	OL-1
MnO _x -200	3.36	OL-1 + OMS-2
MnO _x -300	3.57	OMS-2
MnO _x -400	3.67	OMS-2
MnO _x -500	3.66	OMS-2
MnO _x -600	3.69	OMS-2

The structural flexibility of these disordered features notably enhances the water oxidation activity of such manganese oxides.^{79,80} The phases and manganese oxidation states of all anodes investigated in the present study are summarized in Table 1. We here used 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 to determine the AOS. MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 were used as reference materials. As shown in Figure 3 and mentioned in Table 1, the AOS of manganese was clearly influenced by the calcination temperature.

Upon annealing the film at <200 °C the AOS decreased, in line with previous reports.^{71,81} After calcination at 300 °C and further formation of the cryptomelane phase, the AOS of the MnO_x -300 film increased to 3.6, pointing to a low fraction of Mn sites with an oxidation state below 4+. Calcination of the samples at temperatures above 400 °C did not influence the AOS any more, and all the MnO_x -400, MnO_x -500, and MnO_x -600 samples showed an AOS of ~3.7.

In situ heating studies

The thermal decomposition of KMnO_4 was monitored with in situ heating TEM. Specimens were prepared with drop-casting of an acidic solution of KMnO_4 on the heating micro electro mechanical system (MEMS) membranes, where the Pt heating coil was embedded in the 400 nm thick amorphous SiN_x membrane. After the solution had dried, the specimens were ready for TEM studies (further details cf. SI). All measurements were performed each time on a new MEMS with a freshly prepared specimen. Ramp up programs are shown in Figure S3. Figure S4 shows the high angle annular dark-field (HAADF) image acquired in the STEM mode of the specimen area before heating. Irregularly shaped particles were dispersed randomly on the SiN_x membrane of the chip. Samples were annealed and analyzed at 55, 65, 70, 80, 100, 200, 250, 300, 400, 500, and 600 °C. The starting specimen clearly showed lattice parameters with spacings around 0.57 nm and 0.32 nm (Figure S4). Such spacings are present in KMnO_4 (PDF: 00-044-0268).

After heating the sample for around 30 min at 55 °C, morphological changes (Figure S5) along with significant spots and diffraction rings around 0.51, 0.30, 0.26, and 0.21 nm appeared in the FFT pattern (Figure S6A). Many of these d values correspond with both KMnO_4 (PDF: 00-044-0268) and K_2MnO_4 (PDF: 00-073-0459), with the exception of 0.51 nm, which is characteristic of K_2MnO_4 . Therefore, this new crystalline phase within an amorphous matrix might be related to K_2MnO_4 , which is a by-product in the decomposition of KMnO_4 to amorphous manganese oxide phases.⁸² At 70 °C, the sample underwent further reshaping (Figures S7D and E). As shown in Figures S7G-I, the diffraction rings and some lattice fringes of K_2MnO_4 were visible at 80 °C. TEM studies revealed that the degree of crystallinity is not similar in all the regions in the specimen. At 100 °C, with the further decomposition of the sample, some amorphous regions were detectable, which might be related to amorphous manganese oxide (Figure S6B). While annealing the sample at 200 °C, the amorphous nature prevailed, although some diffraction signals with d-spacing around 0.32 nm were still

observed in the FFT pattern (Figure S6C). They can be related to the remnant high crystalline starting material, which decomposed with annealing at 250 °C.

When the sample reached 250 °C (Figure S6D), the FFT pattern still exhibited diffraction rings related to the K_2MnO_4 phase, and no indications of conversion to other phases were detected. Figure S6E shows that the K_2MnO_4 structure transformed upon annealing at 300 °C, giving rise to new diffraction rings related to the 111, 200, and 220 reflections of MnO (PDF: 00-077-2363). However, FFT patterns still displayed K_2MnO_4 contents. Phase pure MnO was finally achieved at 400 °C (Figure S6F). FFT patterns of samples calcined at 500 and 600 °C (Figures S6G and S6H) show the formation of MnO phases with higher crystallinity. Noteworthy, in a separately performed experiment (Figure S9), we observed that, with the formation of highly crystalline K_2MnO_4 at 200 °C, the transformation into phase pure MnO only took place after further heating to 600 °C. However, less crystalline K_2MnO_4 was easily converted into MnO at temperatures around 300 °C (Figure S6E), finally yielding phase pure MnO at 400 °C (Figure S6F).

The presence of MnO as the only crystalline phase after in situ heating TEM studies raises the question as to where the excess K^+ ions are located. To this end, we further studied the chemical composition of the specimen with in situ heating STEM/EDX. In situ heating with chemical analysis was carried out at 23, 100, 250, and 600 °C. While the chemical composition of the sample slightly changed during heat treatment at 100 °C (Figure S11 and Table S3), the K/Mn ratio remarkably dropped upon annealing at 250 °C, down to zero in some areas. With the further formation of MnO at 600 °C (corresponding FFT image in Figure S12), STEM/EDX analysis revealed a ratio of 0 or 0.03 for K/Mn in different regions. The areas with a higher K/Mn ratio might be related to amorphous potassium manganese oxides. Interestingly, a low magnified STEM/EDX micrograph of the specimen revealed that a significant part of K^+ ions had migrated to the edges of the SiN_x window (Figure S13). Since these areas were thick regions, further TEM studies and phase identification of these zones were not possible.

Additionally, the thermal decomposition of $KMnO_4$ was studied with in situ heating XRD under vacuum. First, $KMnO_4$ was treated at 250 °C for 1 h, then the obtained product was examined by in situ heating XRD, aiming to investigate the formation of the MnO phase during the heat treatment. As shown in Figure S14, initially birnessite and K_2MnO_4 were the only products of the thermal decomposition of $KMnO_4$. Around 370 °C, the first signs of K_3MnO_4 were visible via a peak at $2\theta \sim 31.3^\circ$. With further heat treatment at 450 °C a well crystalline birnessite phase was obtained. At 550 °C no more K_2MnO_4 phase was present, indicating complete decomposition. Finally, at 570 °C birnessite and K_3MnO_4 were the only present phases. It worth noting that in comparison to the reference patterns reported at 25 °C, the herein investigated XRD patterns, obtained at high temperatures, are slightly shifted with sometimes different intensities. These can be related to structural disordering and lattice expansions at higher temperatures.

A comparison with the in situ heating XRD study in air (Figure 1B) shows that the transition of birnessite to cryptomelane structure does not take place under vacuum conditions (Figure S14). The result suggests the key role of the air atmosphere in the formation of the tunnel phase.

In line with previous reports, we did not find any XRD evidence for the presence of MnO in our experiment.⁸³ This result further confirms that the formation of MnO during the in situ heating TEM is strongly related to the experimental conditions.

Several factors, including thermal energy, high vacuum of the TEM column and electron beam irradiation can induce the formation of a MnO phase under in situ heating TEM conditions.⁸⁴⁻⁸⁶ This sensitivity of manganese oxides towards TEM conditions has been proposed in previous reports as well.^{87,88} At higher temperatures, the thermal energy reinforces the effects of the high vacuum and the electron beam. Therefore, all these factors (high temperature, high vacuum and electron beam) can promote the formation of a MnO phase under TEM conditions, which leads to the removal of K^+ ions from the monitored sample area. These analyses emphasize the importance of a careful result assessment when concluding on an ambient condition reaction mechanism from TEM monitoring.

Electrochemical water oxidation activity of the MnO_x electrode series

The electrochemical water oxidation activity of the annealed electrodes was assessed in sodium phosphate buffer (NaPi) with a multistep chronoamperometry technique in a standard three-electrode system. The potential of the working electrode was increased from 1.623 V (vs. RHE) to 2.073 V (vs. RHE) in 0.05 V steps, and the potential was kept constant in each step for 300 s. Reference electrochemical measurements for bare FTO clearly show its negligible activity in the water oxidation performance (Figure S16). The catalytic activity of the anodes was assessed by comparison of the corresponding steady-state current density of specific potentials, as shown in Figure 4.

The annealing temperature has a significant effect on the catalytic activity of the prepared films. As mentioned above (Table 1), calcination of the films at temperatures ≥ 300 °C leads to a change from the OL-1 structure to cryptomelane (OMS-2) and an increase in the catalytic activity.

Among the fabricated films, MnO_x -300 displayed the highest current densities, and the best onset potential (Figure S17). XAS studies showed an AOS of 3.6 for the manganese sites of MnO_x -300, and its crystallinity was lower than the samples calcined at higher temperatures.

The higher amount of disorder and mixed valence of Mn (III/IV) is most likely the reason for the superior electrocatalytic activity.⁷⁸⁻⁸⁰ Comparing the Fourier transform FT $[k^3\chi(k)]$ spectra of the normalized Mn K-edge EXAFS spectra $k^3\chi(k)$ for MnO_x -200, MnO_x -300, MnO_x -400 and MnO_x -500 (Figure S18), which are structurally similar to the MnO_x -300 electrode based on the PXRD and TEM results, the amplitude of the first prominent peaks at $r \approx 1.39$ Å is decreased.

Figure 4. Comparison of steady state current density for MnO_x electrodes.

This corresponds to the single scattering from the first O neighbours with Mn in octahedral oxygen coordination and points to a maximum of oxygen defects and structural distortions in the MnO_x-300 phase.³² In line with the EXAFS data, the PXRD and TEM results evidenced that at 200 °C to 300 °C, the main structure is changing from OL-1 to OMS-2, causing a dominant structural distortion and increasing amount of oxygen vacancies in the structure.

The high catalytic activity of OMS-2 has been reported for chemical and photochemical water oxidation reactions as well.^{89,90} The OMS-2 structure contains {Mn₄O₄} configurations at the edge of the tunnels, and these analogues to the OEC of PSII may well be responsible for the high activity of this phase.⁷⁴

At calcination temperatures ≥ 400 °C, the oxygen evolving activity of the electrodes decreased. As the AOS of manganese for all MnO_x-400, MnO_x-500, and MnO_x-600 samples is similar, this decline is most likely linked to the difference in the degree of their crystallinity. By calcinating the samples at higher temperatures, XRD patterns of the electrodes display an intensity rise accompanied by a shift to higher 2 θ values. Such shifts to higher 2 θ can be related to crystal lattice ordering due to enhanced crystallinity (Figure S19). It has been reported that highly active manganese oxides have some key factors in common, such as structural flexibility for substrate binding, high surface area, and mixed valence of Mn(III/IV). It has been further suggested that less ordered tunnelled and layered manganese oxides possess these properties.^{91,92}

The electrochemically active surface area (ECSA) of the electrodes is another key performance factor. An accessible method to quantify this parameter is estimating ECSA by measuring the double-layer capacitance C_{dl} (Figure S20).⁹³ Due to some assumptions, such as proposing an equal specific capacitance for all samples and considering the same electronic conductivity for all investigated electrodes, this method has limitations in comparing electrode surface areas.⁹⁴ In some studies, it has also been previously mentioned that determining the accurate active surface area of

the manganese oxide-based electrodes through this method is challenging.⁹⁵ Keeping the mentioned issues in mind, we considered the current density based on the geometric surface area to compare the OER activity of our catalysts. Meanwhile, the overpotential to reach a current density of 10 mA/cm² based on the geometric surface area is a widely applied method in the literature for comparing the catalytic activity of tested electrodes.⁹⁶ Additionally, the geometric surface area-based current density is commonly used in developing electrolysis systems for practical applications.⁹⁷

Subsequent experiments and characterizations were thus focused on properties of MnO_x-300, which was obtained at the optimal calcination temperature of 300 °C.

Kinetic study of MnO_x-300 electrodes

The kinetics of the water oxidation reaction on the MnO_x-300 electrode were studied by investigating Tafel plots and by studying the pH dependency of the reaction and the influence of buffer concentration. Tafel plots were constructed from steady-state current density as a function of overpotential, derived from multistep chronoamperometry measurements. To reduce the mass transfer effect, the measurements were performed in a stirred solution. As shown in Figure 5A, the Tafel slope of MnO_x-300 is around 118 mV/dec.

Figure 5. Tafel plot of a MnO_x-300 electrode in 1.0 M NaPi buffer, pH 7, iR corrected, with stirring (A), dependency of current density on the phosphate concentration, NaPi buffer, pH 7, iR corrected, $C_{buffer} = 1.0$ M, 0.6 M, 0.4 M, 0.2 M, 0.1 M, 0.05 M (B), K_{buffer} dependency on applied overpotential (C), pH dependency of the potential at a current density of 1.0 mA/cm², NaPi buffer, $C_{buffer} = 1.0$ M, pH 6.2, 6.5, 6.7, 6.9, 7.1, 7.3, 7.9 (D).

The phosphate concentration dependence of the reaction rate was studied by varying C_{buffer} from 1.0 to 0.05 M at fixed pH. To eliminate the different ionic strength effects, 85% iR corrections were applied to all measurements. Figure 5B shows the dependency of current density on phosphate concentration at the fixed potentials. While the current density is less dependent on buffer concentration at low overpotentials, this dependency increases with raising overpotentials.

At lower overpotentials with low water oxidation activity, the presence of proton accepting ions does not remarkably influence the current density.

Such a zero-order dependency of the activity on the phosphate ion concentration at low current densities has been reported previously.⁹⁸ However, at higher OER catalytic current density and further release of H⁺, basic ions can improve the OER activity.^{71,91}

The linear relationship between K_{buffer} and overpotential shows that the reaction order dependence on buffer concentration is equal to $K_{\text{buffer}} = 3.37\eta - 1.42$, i.e., the C_{buffer} dependency of the reaction rate increases at higher overpotentials (Figure 5C).

Next, we assessed the pH dependence of the catalytic activity of MnO_x-300 by measuring the potential at the current density of 1.0 mA/cm² while varying the pH of NaPi buffer from 6.2 to 7.9 (Figure 5D). A slope close to -59 mV per pH suggests an electron transfer coupled to the release of one proton. In an electrochemical reaction, the reaction order with respect to protons is defined as $-(\partial \log j / \partial \text{pH})_{E,T,P}$ (equation 1). Applying the Tafel slope and pH-dependent potential change values for MnO_x-300 leads to a pH reaction order of ~0.5, representing an inverse half-order dependence of the reaction rate on [H⁺] for the pH range 6.2 – 7.9. Such proton dependency has been previously reported for manganese oxides.^{71,98} In preceding works, it was suggested that a half-order fractional dependence on the proton concentration results from the combination of zero-order [H⁺] dependence at acidic pH and inverse first-order [H⁺] dependence at alkaline pH.⁹⁸

$$\left(\frac{\partial E}{\partial \text{pH}}\right)_{j,T,P} = - \left(\frac{\partial E}{\partial \log j}\right)_{pH,T,P} \left(\frac{\partial \log j}{\partial \text{pH}}\right)_{E,T,P} \quad \text{equation 1}$$

A Tafel slope of 120 mV dec⁻¹ illustrates a one-electron transfer step as the rate determining step (rds),⁹⁸ and it has been suggested that such a Tafel slope with an inverse half-ordered [H⁺] dependency can reflect a mixed order mechanism between a zero-order, and a first-order [H⁺] dependency mechanism.⁹⁸

Long-term stability and performance assessment

The long-term catalytic test of the MnO_x-300 electrode showed a stable current density during a water electrolysis experiment at 1.72 V (vs. RHE) for 100 h (Figure 6A). The post operando electrode was characterized with a wide range of methods, such as XRD, SEM, TEM, and XAS. All results showed high stability of the post-operando material. XRD patterns of MnO_x-300 after 100 h of continuous electrolysis in NaPi buffer at pH 7 showed no changes in comparison to fresh MnO_x-300 (Figure S22). As shown in Figure S23, HRTEM images of post-catalytic MnO_x-300 displayed the same morphology as a fresh MnO_x-300 sample and no amorphous phases were visible in HRTEM image of this sample. While surface amorphization is a common phenomenon, which occurs in many heterogeneous catalysts during the water oxidation reaction, we did not find evidence for such amorphization in the case of MnO_x-300 by HRTEM.

Figure 6. Long time chronoamperometry result of MnO_x-300 in 1.0 M NaPi buffer, pH 7, 1.72 V vs. RHE (A). Fitting of the Fourier transform EXAFS spectra $FT[k^3\chi(k)]$ of fresh MnO_x-300 and MnO_x-300 after long term water electrolysis (B).

This could be related to hypothetical, negligible amounts of the amorphous phase below the analytical limits and/or to a flexible conversion between manganese dioxide modifications as reported in previous studies.^{99,100}

Meanwhile, it remains difficult to check the entire bulk of the sample for possible minor amorphous phases by TEM. STEM/EDX mapping of the post-performance MnO_x-300 indicated the presence of phosphorous (Figure S24), which is related to the interaction of some manganese sites with phosphate ions. Manganese oxides are well known as phosphate ion adsorbers.^{101,102}

Finally, SEM images of MnO_x-300 did not display significant changes after 100 h of water electrolysis (Figure S23D). ICP analyses of the post catalytic electrolyte indicated the presence of low manganese contents, which suggests negligible metal leaking during 100 h of catalytic operation (~1% w/w of Mn).

XAS studies show negligible oxidation in the post catalytic MnO_x-300 in comparison to a fresh electrode (Figure 3B). While the AOS of manganese in the pristine electrode is 3.57, this value changes to 3.64 in the post-catalytic electrode, which suggests oxidation of only a small fraction of the surface manganese sites after long term electrolysis.

According to previous reports, post-catalytic manganese oxide WOCs often display partial oxidation of the manganese centers.^{58,71,103} Fourier-transform EXAFS spectra of

MnO_x-300 before and after long time catalysis and the fitted data are presented in Figure 6B.

Calculated fitting parameters for interatomic distances, atomic coordination numbers (N), and Debye–Waller factors (σ^2) are listed in Table S2. The FT-EXAFS spectra of the pristine MnO_x-300 and the post catalytic samples showed the characteristic features of the cryptomelane structure at ~ 1.4 Å, ~ 2.49 Å, and ~ 2.9 Å, which corresponds to the Mn–O pairs, Mn–Mn edge-sharing octahedra pairs, and Mn–Mn corner-sharing octahedra pairs, respectively.¹⁰⁴ When comparing the Fourier-transform EXAFS spectra of the two electrodes, a variation in long-range scattering paths above the range of the Mn–Mn corner-sharing octahedra, may suggest a long-range order distortion in the post-catalytic sample, possibly related to a surface amorphization. Nevertheless, when comparing with the pristine electrode, no changes in the first and second scattering paths are observed in the Fourier-transform EXAFS spectra of the post catalytic electrode, which confirms the stability of the cryptomelane core structure after 100 h of water electrolysis. The result is further backed with XRD and HRTEM analysis (Figures S22 and S23).

Concerning the performance assessment of MnO_x-300, a direct comparison with reported manganese oxide-based electrodes is difficult, because the electrochemical activity depends on a multitude of parameters (such as electrolyte concentration, catalyst loading, fabrication method...). Keeping these issues in mind, Table 2 compares key performance reports on manganese oxide electrocatalysts in pH 7 phosphate buffer.^{95,105–107}

MnO_x-300 reaches a current density of 1 mA/cm² (frequently used standard for manganese oxides) for comparable or lower overpotential than manganese oxide electrodes fabricated with more demanding techniques, while some notably lower overpotentials were reported for selected cases.

In addition to its good performance metrics, the high chemical and mechanical stability of MnO_x-300, as well as the very convenient electrode manufacturing method, highlight this material as a very promising candidate for technical processes in sought-after and desirable neutral conditions.

The catalytic activity of MnO_x-300 was also measured at a current density of 3 mA/cm² for 72 h (Figure S26). The overpotential to reach to such a current density was increased by ~ 100 mV at the end of the measurement. The XRD and SEM images did not show significant changes, which suggest the core structure of the electrode was intact (Figure S26).

We also report on the activity of the MnO_x-300 electrode at 10 mA/cm² (Figure S27). Based on chronopotentiometry measurements, the required overpotential to reach to 10 mA/cm² increases from ~ 2.1 V (vs. RHE) to ~ 2.4 V (vs. RHE) at ~ 4000 s, which is related to the somewhat lower stability of the electrode at a current density of 10 mA/cm².

Electrocatalytic activity of MnO_x-300 under alkaline conditions

To obtain further information on water oxidation activity of MnO_x-300 under alkaline conditions, the electrode was subjected to water electrolysis in 1.0 M or 0.1 M KOH electrolyte, respectively. As shown in Figure 7A, very high current densities of 3.5 mA/cm² and 12 mA/cm² were achieved for ~ 1.8 V vs RHE in 0.1 M and 1.0 M KOH, respectively. An even higher current density of 25 mA/cm² was reached at an overpotential of ~ 800 mV in 1 M KOH as an electrolyte.

We examined the water oxidation activity of the MnO_x-300 electrode at 1 M KOH at a current density of 3 mA/cm² for a longer time (~ 30 h).

Table 2. Comparison of manganese oxide catalysts for water oxidation (phosphate buffer, pH 7).

Catalyst	Overpotential (η)@1mA/cm ² (mV)	Test method for overpotential@1mA/cm ²	Long-term operation test	Electrode fabrication method	Ref.
MnO _x -300	490	CA	@ η =490 mV, 1 mA/cm ² , 100 h @3 mA/cm ² , η ~670 mV, 72 h	thermal decomposition of KMnO ₄ solution	This work
Amorphous manganese oxide	330	LSV	@ η =480 mV, 4 mA/cm ² , 1 h @ η =580 mV, 8 mA/cm ² , 20 h	electrodeposition	71
Ca-Birnessite	480	CA	@ η =480 mV, 1mA/cm ² , 2 h	screen-printing	49
β -MnO ₂	440	LSV	@ η =600 mV, 3 mA/cm ² , 1 h	redox-precipitation	50
α -Mn ₂ O ₃	370	LSV	@ η =470 mV, <0.6 mA/cm ² , 1 h	electrodeposition	105
Ca ₂ Mn ₃ O ₈	620	LSV	---	screen-printing	106
1.83[K _{0.068} Ni _{0.18} MnO ₂ ·0.8 3H ₂ O]@MnFe ₂ O ₄	500	CA	@ η =500 mV, 1 mA/cm ² , 20 h	screen-printing	107
MnO _x coated carbon fibre paper	445	CA	@ 2 mA/cm ² , η =500 mV, 24 h	redox-precipitation of KMnO ₄	95

* LSV = linear sweep voltammetry, CA = chronoamperometry

Figure 7. Steady state current density for the MnO_x-300 electrode at different potentials in alkaline conditions (A), reusability of a MnO_x-300 electrode in alkaline water electrolysis at 1.84 V (vs. RHE) ($\eta \sim 600$ mV), electrolyte: 1 M KOH, pH 14 (B).

Chronopotentiometry results showed an increase in overpotential in the initial hours of catalytic performance. At the end of the reaction the potential of the working electrode was ~ 1.72 V (vs. RHE, Figure S28). XRD and SEM characterizations of the MnO_x-300 electrode after ~ 30 h water oxidation performance at a current density of 3 mA/cm² in a 1 M KOH solution showed no changes (Figure S28), because these methods are bulk techniques and cannot probe possible low amounts of surface amorphous phases. However, ICP/MS analyses indicated some manganese leakage from the electrolyte (~ 0.5 w/w of Mn).

MnO_x-300 showed reasonable stability at 1.84 V vs RHE ($\eta \sim 600$ mV) in 1 M KOH for 2 h. Furthermore, we demonstrated the good reusability of the electrode at pH 14 for another 2 h of electrolysis (Figure 7B), where a decline of the initial current density by ca. 1 mA/cm² was observed. According to the Pourbaix diagram of manganese, manganese oxides are not thermodynamically stable in highly alkaline conditions and they can convert into MnO₄⁻ at high overpotentials.³⁹

CONCLUSIONS

Manganese oxide-based anodes with high water oxidation activity were fabricated via a convenient and low-cost spraying method of acidic KMnO₄ solutions on heated FTO substrates. The thermal decomposition pathways of the KMnO₄ precursor were studied with a wide range of in situ heating techniques, encompassing TEM, XRD, and STEM/EDX. In situ screening of thermal formation and structural evolution pathways of manganese oxides will open up new routes to fully utilize their complex structural and chemical properties for applications based on the informed structural design.

Our results furthermore show that the decomposition routes of manganese oxide materials depend to a large extent on the specific applied in situ techniques, thereby pointing out key challenges associated with the comprehensive monitoring of such precursor transformations.

The as-fabricated anodes were calcined at different temperatures, and the influence of the annealing temperature on the properties of the resulting manganese oxide films was investigated with a wide range of analytical methods, such as XRD, SEM, TEM, and XAS. Electrodes calcined at 300 °C (MnO_x-300), consisting of the OMS-2 phase, displayed the highest electrochemical water oxidation activity at pH 7 (NaPi buffer). They excelled through remarkable long-term stability over 100 h at a low overpotential of 490 mV (current density ~ 1 mA/cm²) while being accessible with minimal preparative efforts. Although Ni- and Co-based catalysts are often more active than Mn-based water oxidation catalysts, the lower cost of manganese resources in comparison to Ni and Co and the scalability of the herein reported technique render increasing the electrode size an interesting alternative strategy.

Post-catalytic ICP-MS, XRD, SEM, TEM, and XAS measurements all confirmed the high stability of this optimized manganese oxide anode during long time tests. Furthermore, MnO_x-300 electrodes offered very promising activity and reusability under alkaline water oxidation conditions. Our facile and direct route to high-performance manganese oxide electrodes starts solely from KMnO₄ and HNO₃ as inexpensive chemicals and opens up new ways for economic large scale water splitting. Moreover, our technique can be easily adapted to various substrate types and sizes and permits direct control over the catalyst loading through controlled spray rates and durations.

Additionally, the demonstrated recyclability of this anode type renders it technically attractive. As KMnO₄ is industrially produced by fusing of manganese oxides with KOH,¹⁰⁸ recycled anodes can be directly used as starting material for re-manufacturing. Even KMnO₄-containing acidic wastewater from the initial washing step before calcination can be re-used as a precursor again, thus enabling attractive cycle chemistry processes.

In conclusion, we pave new ways to leverage the global manganese resources for water splitting applications with a highly convenient fabrication strategy for manganese oxide electrodes that excels through cost-efficiency, simplicity,

highly active and stable catalysts as well as versatile electrode recycling options.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website (PDF).

Experimental details on electrode fabrication, analytical characterization, electrochemical measurements, Faradaic efficiency, SEM images of the electrodes, temperature programs of in situ heating TEM and in situ heating STEM/EDX, in situ heating TEM images and FFT patterns, in situ heating STEM/EDX maps, XRD, TEM, STEM/EDX maps of the post catalytic MnO_x -300 electrode, and long term activity of MnO_x -300 for 72 h at 3 mA/cm².

AUTHOR INFORMATION

Corresponding Author

Greta R. Patzke - Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland;

E-mail: greta.patzke@chem.uzh.ch

Notes

The authors declare no conflict of interest.

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