

The “Best Catalyst” for Water Oxidation Depends on the Oxidation Method Employed: A Case Study of Manganese Oxides

Ravi Pokhrel, McKenna K. Goetz, Sarah E. Shaner,[†] Xiaoxia Wu, and Shannon S. Stahl*

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

S Supporting Information

ABSTRACT: Manganese oxides are a highly promising class of water-oxidation catalysts (WOCs), but the optimal MnO_x formulation or polymorph is not clear from previous reports in the literature. A complication not limited to MnO_x -based WOCs is that such catalysts are routinely evaluated by different methods, ranging from the use of a chemical oxidant such as Ce^{4+} , photoactive mediators such as $[\text{Ru}(\text{bpy})_3]^{2+}$, or electrochemical techniques. Here, we report a systematic study of nine crystalline MnO_x materials as WOCs and show that the identity of the “best” catalyst changes, depending on the oxidation method used to probe the catalytic activity.

Catalytic water oxidation is the focus of widespread investigation owing to the importance of this process in the conversion of solar energy into chemical fuels via photovoltaic water electrolysis^{1a,b} or integrated photoelectrochemical solar cells.^{1b–d,2} The highly efficient Mn_4CaO_5 cluster in the oxygen-evolving complex of photosystem II³ has contributed to significant contemporary interest in molecular⁴ and solid-state⁵ manganese oxide (MnO_x)-based water-oxidation catalysts (WOCs) as alternatives to precious metal catalysts. In connection with our own interest in metal-oxide-based WOCs,⁶ we were drawn to solid-state MnO_x materials, which exist in at least 30 different naturally occurring crystal forms.⁷ These oxides have an extensive history as catalysts for water oxidation,^{5a,b,8} but a survey of these early reports, together with results of the many recent studies, reveal a lack of convergence concerning the identity of the most effective MnO_x -based WOC. In some cases, the presence of Mn^{III} is claimed to be crucial (e.g., as in Mn_2O_3), owing to the distorted coordination geometry and enhanced reactivity of the d^4 ion.^{5f,h} But, in other cases, MnO_2 -based oxides (i.e., containing Mn^{IV}) have been implicated as the most active catalysts.^{5c–e,g} In an effort to gain insight into the apparent discrepancies, we have examined the catalytic activity of nine different crystalline MnO_x materials under different conditions. The identity of the “best” catalyst is found to depend on the oxidation method and the reaction conditions used to assess the catalytic activity. These results have important implications for the field of solar-energy conversion and the ongoing search for improved catalysts.

The catalytic activity of homogeneous and heterogeneous WOCs is routinely tested by one of a number of different methods. Three of the most common include (1) use of a chemical oxidant such as ceric ammonium nitrate (CAN), (2) use of a photochemical oxidant, typically $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/$

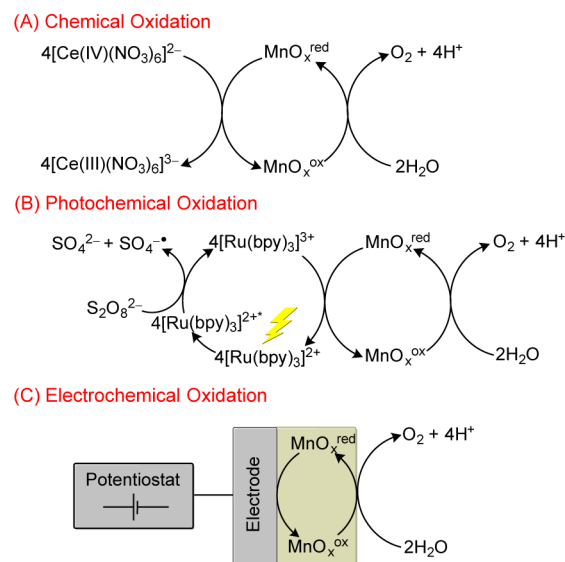


Figure 1. Three methods routinely used in evaluating water-oxidation activities of homogeneous and heterogeneous WOCs illustrated here with manganese oxide (MnO_x) catalysts: (A) chemical oxidation using CAN; (B) photochemical oxidation using $[\text{Ru}(\text{bpy})_3]^{2+}$, $\text{S}_2\text{O}_8^{2-}$, and light; and (C) electrochemical oxidation.

light, or (3) use of electrochemical methods (Figure 1).⁹ Each of these techniques is widely used, but individual reports in the literature generally feature only one of these methods, with an implicit assumption that the “best” catalyst is independent of the method employed. The lack of convergence on the optimal MnO_x catalyst identity prompted us to consider whether the uncertainties could reflect the nature of the oxidation assay. In order to probe this issue, we sought a self-consistent set of diverse MnO_x samples that could be compared by each of the three techniques identified in Figure 1.

We selected nine unique crystalline MnO_x samples for comparison (Figure 2). Six of the nine crystalline polymorphs have unique MnO_2 structures, while the other three structures consist of Mn_2O_3 , Mn_3O_4 , and LiMn_2O_4 (Figure 2). Previously reported synthetic procedures were followed, with slight modifications when needed to ensure structural homogeneity of the samples (see Supporting Information (SI) for details). Powder X-ray diffraction (pXRD) patterns of the synthesized MnO_x samples confirmed their identity and purity (Figure S1), and the oxides were further characterized by Brunauer, Emmett,

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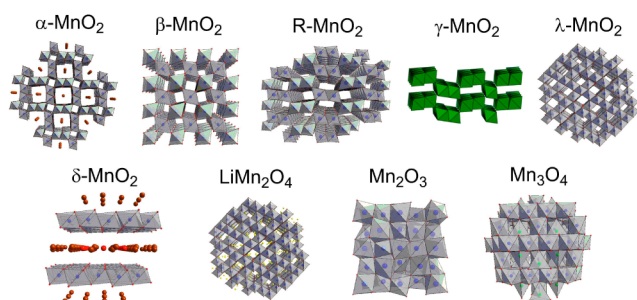


Figure 2. Structural representation of nine crystalline MnO_x materials used in this study: α - MnO_2 , β - MnO_2 , R-MnO_2 , γ - MnO_2 , λ - MnO_2 , δ - MnO_2 , LiMn_2O_4 , Mn_2O_3 , and Mn_3O_4 . The structural representation for γ - MnO_2 is taken from ref 10 with permission because the unit cell parameters of γ - MnO_2 are not available in structural databases. All other structures were created from the unit cell parameters obtained from the Inorganic Crystal Structure Database (<https://icsd.fiz-karlsruhe.de/>).

and Teller (BET) N_2 adsorption–desorption measurements, scanning electron microscopy, and transmission electron microscopy (Table S1, Figures S2 and S3).

Each of the MnO_x samples was analyzed initially by using the chemical and photochemical assays illustrated in Figure 1A and 1B. Cerium(IV) in CAN is a one-electron oxidant and has a standard potential, E° , of about 1.7 V vs NHE,^{11,12} providing substantial driving force to promote water oxidation. The simplicity of monitoring evolved O_2 using a Clark-type O_2 -sensing electrode or an optical fluorescence-quenching O_2 sensor has made the use of CAN popular in evaluating the water-oxidation activities of many homogeneous and heterogeneous WOCs.¹³ However, CAN is only stable in acidic media, and other chemical or photochemical oxidants have to be used to evaluate activities of WOCs at higher pH, especially when the WOCs are not stable in acid. At near-neutral pH, chemical oxidants such as potassium peroxydisulfate (Oxone) and sodium periodate have been used.^{9a,14} However, both of these oxidants are two-electron oxidants and potential oxo-transfer reagents, which complicates the interpretation of water oxidation activity. Another approach compatible with near-neutral pH employs the one-electron oxidant, $[\text{Ru}(\text{bpy})_3]^{3+}$, which has an E° of 1.26 V vs NHE.¹⁵ $[\text{Ru}(\text{bpy})_3]^{3+}$ is generated in situ by visible-light excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ followed by oxidative quenching by persulfate.

A 0.2 M solution of CAN, with a measured pH of ~ 0.8 , was used to drive water-oxidation catalysis by the MnO_x powder samples (Figure 3A), and the rates of water oxidation were monitored with a Clark electrode. The initial rates of O_2 evolution were used to obtain turnover frequencies (TOFs) for O_2 evolution in units of $\text{mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$ for all of the MnO_x samples (Figure 3B). γ - MnO_2 had the highest TOF of 0.41, followed by 0.22 for δ - MnO_2 , 0.17 for Mn_3O_4 , and 0.06 for Mn_2O_3 . All other MnO_x were either inactive or had $\text{TOF} < 0.015 \text{ mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$.

MnO_x -catalyzed O_2 -evolution rates were then probed at pH 8 using the $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/\text{light}$ photochemical oxidation method, again using a Clark electrode (Figure 3C). The resulting TOFs for O_2 evolution (Figure 3D) showed that Mn_2O_3 exhibits the highest TOF of 2.7 $\text{mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$, followed by 1.6 for Mn_3O_4 , 0.78 for γ - MnO_2 , and 0.46 for δ - MnO_2 . All other MnO_x had $\text{TOF} < 0.2 \text{ mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$.

Although CAN and $[\text{Ru}(\text{bpy})_3]^{3+}$ are used at very different pH values, their E° values correspond to similar “overpotentials” for water oxidation: 530 and 502 mV at pH 1 and 8, respectively. In

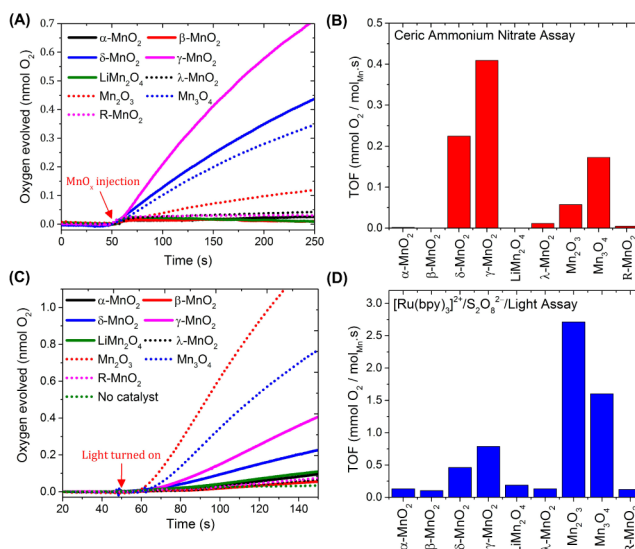


Figure 3. (A) O_2 -evolution measurements with CAN. (B) TOFs for water oxidation driven by CAN. (C) O_2 -evolution measurements with $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/\text{light}$. (D) TOFs for water oxidation driven by $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/\text{light}$. Standard deviations of $\pm 0.025 \text{ mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$ were observed for Figure 3B, and $\pm 0.20 \text{ mmol O}_2/(\text{mol}_{\text{Mn}}\cdot\text{s})$, on the basis of duplicate experiments.

spite of this similarity, the relative activities of the different MnO_x materials differ dramatically. γ - MnO_2 and δ - MnO_2 are the best catalysts when water oxidation is driven by CAN at pH 1, whereas Mn_2O_3 and Mn_3O_4 are the best catalysts when water oxidation is driven by a $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/\text{light}$ assay. A number of recent studies have described CAN-driven water oxidation with MnO_x -based catalysts under acidic conditions, but these have predominantly focused on Ca-containing Mn-oxides, so benchmarks to the present materials are not available.^{5c,16} Our photochemical oxidation data, however, largely align with the results of Dismukes et al., who recently showed that Mn_2O_3 and Mn_3O_4 catalysts exhibit the highest and second-highest activity for water oxidation, respectively, among a series of Mn-based oxides using a $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}/\text{light}$ -based assay.^{5f} Other studies have shown that MnO_2 -based materials are active for water oxidation under comparable conditions (consistent with the activity we observe for δ - and γ - MnO_2), but comparisons with Mn_2O_3 and Mn_3O_4 were not made in these cases.^{5d,e}

Electrochemical water oxidation provides a means to assess catalyst performance at different pH values, thereby allowing the effect of reaction conditions to be evaluated without changing the oxidation method. All of the MnO_x samples were tested for their performance as electrocatalysts for water oxidation in acidic, neutral, and alkaline pH. For a direct comparison with the CAN assay, a solution of 0.1 M HNO_3 was used as an acidic electrolyte (pH 1). Catalytic activities were assessed by using linear sweep voltammetry (LSV) in order to minimize complications associated with the long-term instability of these materials under acidic conditions. The current densities achieved during LSV show that Mn_2O_3 , γ - MnO_2 , and α - MnO_2 exhibit significant electrocatalytic activity at pH 1 (Figure 4A and 4B). The data are quite different from the trends observed with the same MnO_x samples using CAN as the oxidant (cf. Figure 3A and 3B). Previous reports have suggested that some MnO_x materials, for example, α - MnO_2 and β - MnO_2 , are stable under acidic conditions,^{5e,8d} but all of the oxides tested here proved to be highly unstable during electrolysis at pH 1 (Figure S4).

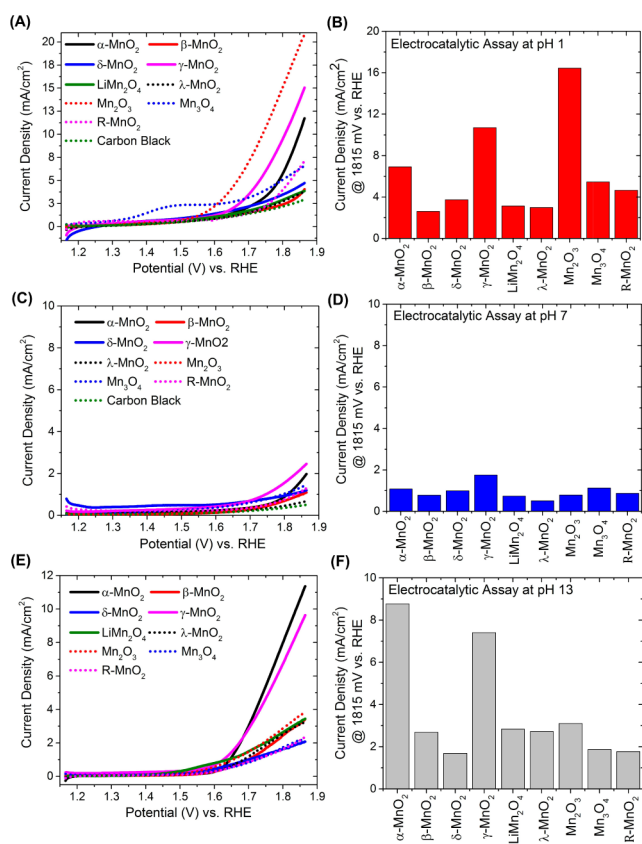


Figure 4. (A) LSV at a scan rate of 5 mV/s in 0.1 M HNO₃, pH 1. (B) Current densities at 1815 mV vs RHE in 0.1 M HNO₃, pH 1. (C) LSV at a scan rate of 5 mV/s in 0.1 M sodium phosphate, pH 7 (Note: LSV trace of LiMn₂O₄ has been omitted from this figure due to a large precatalytic oxidation feature which makes the figure hard to read. It is separately reported in the SI as Figure S7). (D) Current densities at 1815 mV vs RHE in 0.1 M sodium phosphate, pH 7. (E) LSV at a scan rate of 5 mV/s in 0.1 M NaOH pH 13. (F) Current densities at 1815 mV vs RHE in 0.1 M NaOH, pH 13. Note: Changes in catalytic activity during electrolysis under some of the reaction conditions (especially acidic; see SI) prompted us to use LSV scans as the best approximation of the intrinsic activity of the different MnO_x (pre)catalysts.

Electrocatalytic water oxidation was also tested at pH 7 in sodium phosphate buffer. Under these conditions, γ -MnO₂ showed the highest activity on the basis of LSV experiments (Figure 4C and 4D), albeit with considerably lower activity than that observed under acidic and basic conditions. The low activity of MnO_x catalysts at neutral pH has been noted previously and attributed to the disproportionation of Mn^{III} ions at this pH;¹⁷ however, the low conductivity of the pH 7 sodium phosphate electrolyte relative to sodium hydroxide and nitric acid also probably contributes to these observations.¹⁸ Electrolysis data for γ -MnO₂, δ -MnO₂, and Mn₃O₄ at pH 7 showed that the activities of these oxides initially increases during the initial several minutes of electrolysis, followed by a steady decrease over longer time periods (Figure S5). This behavior is attributed to structural reorganization of active oxide surface sites during the electrolysis.¹⁷

The same MnO_x samples were tested for electrocatalytic water oxidation using LSV at pH 13, in 0.1 M NaOH. Under these conditions, α -MnO₂ and γ -MnO₂ exhibited the highest catalytic activity (Figures 4E, 4F, and S6). All other MnO_x performed relatively similarly with substantially lower activities. As observed for the electrolyses performed at neutral pH, some of the oxides,

such as α -MnO₂ and β -MnO₂, showed an initial increase in activity during the course of water electrolysis (Figure S6). Overall, the MnO_x catalysts showed significantly improved stability under alkaline conditions.

Electrochemical water oxidation with MnO_x-based catalysts has been the focus of considerable investigation,^{5b,g,17,19} but most prior studies have focused on a limited set of catalysts and/or conditions. For example, β -MnO₂, Mn₂O₃, Mn₃O₄, γ -MnOOH, and δ -MnO₂ have been studied independently under alkaline conditions.^{5b,19a,d,20} A recent study by Suib and co-workers, however, provides an important benchmark for the results described here. They studied four different MnO_x-based catalysts for water oxidation at pH 13 (α -MnO₂, β -MnO₂, and δ -MnO₂, and an amorphous manganese oxide) and observed the highest activity and stability for α -MnO₂.^{5b} This outcome aligns well with our observations (Figure 4F), which also show that γ -MnO₂ exhibits activity comparable to α -MnO₂.

Efforts have been made to correlate the water-oxidation activity of MnO_x-based catalysts with the presence of Mn^{III} and its e_g¹ occupancy.^{5f,h} This correlation seems to hold for the [Ru(bpy)₃]²⁺/S₂O₈²⁻/light assay, where Mn₂O₃ and Mn₃O₄ feature the highest fraction of Mn^{III} and are the most active catalysts. However, a similar correlation is not evident in the CAN or the electrocatalytic water oxidation assays. With CAN as the oxidant, Mn^{IV}-based oxides (γ -MnO₂ and δ -MnO₂) exhibit higher activity than Mn₂O₃ and Mn₃O₄. And, at neutral and alkaline pH, at least two MnO₂ polymorphs (α -MnO₂ and γ -MnO₂) exhibit higher activity than Mn₂O₃ and Mn₃O₄.

To our knowledge, this study provides the first critical assessment of the three commonly used oxidation methods in Figure 1 with respect to their influence on the activity of water oxidation catalysts. The data clearly show that the relative activity of different catalysts is not an intrinsic property of the materials, but that the catalytic performance can vary widely and depends strongly on the oxidation method employed. At a minimum, these observations suggest claims of “best” or “most active” in reference to water oxidation catalysts need to be properly qualified to account for the assay method employed. Perhaps more importantly, the results indicate that efforts to identify an optimal catalyst should account for the end application and the nature of catalyst integration within an ultimate device.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional discussion on structure and characterization of MnO_x samples, additional electrochemical experiments, experimental procedures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.Sb05093.

■ AUTHOR INFORMATION

✉ Corresponding Author

*stahl@chem.wisc.edu

📍 Present Address

†Department of Chemistry, Benedictine University, Lisle, Illinois 60532.

📝 Notes

The authors declare no competing financial interest.

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