Parameterization of Water Electrooxidation Catalyzed by Metal Oxides Using Fourier Transformed Alternating Current Voltammetry

Shannon A. Bonke, Alan M. Bond, Leone Spiccia,* and Alexandr N. Simonov*†

School of Chemistry and the ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Victoria 3800, Australia

Supporting Information

ABSTRACT: Detection and quantification of redox transformations involved in water oxidation electrocatalysis is often not possible using conventional techniques. Herein, use of large amplitude Fourier transformed ac voltammetry and comprehensive analysis of the higher harmonics has enabled us to access the redox processes responsible for catalysis. An examination of the voltammetric data for water oxidation in borate buffered solutions (pH 9.2) at electrodes functionalized with systematically varied low loadings of cobalt (CoOₓ), manganese (MnOₓ), and nickel oxides (NiOₓ) has been undertaken, and extensive experiment-simulation comparisons have been introduced for the first time. Analysis shows that a single redox process controls the rate of catalysis for Co and Mn oxides, while two electron transfer events contribute in the Ni case. We apply a "molecular catalysis" model that couples a redox transformation of a surface-confined species (effective reversible potential, $E_{\text{red}}^{\text{eff}}$) to a catalytic reaction with a substrate in solution (pseudo-first-order rate constant, $k_1$), accounts for the important role of a Brønsted base, and mimics the experimental behavior. The analysis revealed that $E_{\text{red}}^{\text{eff}}$ values for CoOₓ, MnOₓ, and NiOₓ lie within the range 1.9–2.1 V vs reversible hydrogen electrode, and $k_1$ varies from $2 \times 10^3$ to $4 \times 10^4$ s⁻¹. The $E_{\text{red}}^{\text{eff}}$ values are much higher than reported for any water electrooxidation catalyst before. The $E_{\text{red}}^{\text{eff}}$ values provide a guide for in situ spectroscopic characterization of the active states involved in catalysis by metal oxides.

INTRODUCTION

The development of efficient chemical technologies needs to be underpinned by a detailed quantitative understanding of reaction mechanisms. One crucial technology receiving considerable attention nowadays is electrocatalytic water decomposition, as it would generate a clean and “infinite” fuel, namely, molecular hydrogen.¹–³ The overall process includes cathodic hydrogen evolution and anodic oxygen evolution half-cell reactions, occurring under catalytic conditions.⁴ The current view is that even for the most active catalytic materials, water oxidation (or the oxygen evolution reaction, OER) is still substantially less efficient than water reduction (the hydrogen evolution reaction).⁵,⁶ This inefficiency has led to extensive searches for new catalysts, the recent focus being on materials derived from abundant elements that function efficiently in near-neutral or alkaline solutions. Catalysts addressing these requirements include Coₓ⁷–¹¹ Niₓ¹²–¹⁴ and Mnₓ¹⁵–²⁴ oxides/oxyhydroxides (CoOₓ, NiOₓ, and MnOₓ, respectively, and MOₓ in general).

Linking these electrocatalysts together are structural similarities, with each composed of edge-sharing octahedral metal centers in a layered metal oxide arrangement.¹³,¹⁵,¹⁷,²⁴–³² These similarities have led to proposals that catalysis may be following a similar mechanism in each case.³,³⁵ Hence, CoOₓ, NiOₓ, and MnOₓ are the focus of the mechanistic study herein. Conveniently, facile oxidative electrodeposition methods are available to fabricate the MOₓ-based water oxidation anodes.²,¹²,¹³,¹⁶,¹⁸,³⁴,³⁵

A substantial body of research on the mechanism of formation and catalytic function of electrodeposited metal oxides has been published in recent years, particularly for CoOₓ. In these studies, CoOₓ deposited from phosphate buffer is often denoted Co–P, or Co–B, for the borate equivalent,⁷,⁸,³⁴ to reflect the importance of the buffer in catalyst function, or more simply CoCat.⁵,¹¹ The Brønsted base is vital for efficient proton abstraction at each of four electron-transfer steps of water oxidation,⁵,³⁶,³⁷ and mass-transport of base can limit the catalysis rather than the intrinsic reaction rates. Comprehensive electrochemical¹¹,³⁶–³⁹ and spectroscopic²⁷,²⁹,⁴⁰ studies of CoOₓ-catalyzed water electrooxidation have provided information on the rate-limiting steps. For example, Nocera and colleagues have proposed that proton-coupled [CoⅢ–OH]/[CoⅡ=O] electron transfer followed by slow oxygen–oxygen bond formation are the critical processes.³⁶

More generalized insights into the mechanism of water oxidation have been provided through detailed density functional theory (DFT) calculations.³¹–⁴⁴ Examination of
the water oxidation energetics indicates that key intermediates in the process (OH, O, and OOH) are bound either too strongly or too weakly on all metal oxide surfaces. An implication of this is a significant intrinsic overpotential for water electrooxidation, which appears to be impossible to avoid for monometallic MOx systems.

The mechanistic complexity of water electrooxidation is a main impediment to parametrization of the electron transfer and chemical transformation steps in this reaction. Nevertheless, several important contributions seeking to quantify the thermodynamics and kinetics have been reported recently. Ahn and Bard used scanning electrochemical microscopy to estimate apparent rate constants for the interaction of water with electrodeposited cobalt oxide.45 Savéant and co-workers introduced fast scan rate dc cyclic voltammetry to study water electrooxidation catalyzed by CoOx and outlined the relevant theory,46 while Dau and colleagues employed electrochemical impedance spectroscopy (EIS) to probe the kinetics of the MnOx-catalyzed reaction.32

The present work aims to further advance the parameterization of the water oxidation mechanism via comparisons of experimental and simulated higher order harmonic data derived from Fourier transformed (FT) ac voltammetry. Advantages provided by the use of ac voltammetry for quantitative analysis of mechanisms where an electron transfer process is coupled to a chemical reaction47 and in avoiding background current have been recently reported with surface confined processes.48,49 To avoid the complicated electron/proton transport issues associated with thick catalyst films,11,37,39,46 we have used very low surface concentrations of CoOx, NiOx, and MnOx immobilized on a low background electrode material.

## SECTIONAL EXPERIMENT

### Materials

Reagent or analytical grade chemicals were used as received from commercial suppliers. Fluorine doped tin oxide (FTO) coated glass with a sheet resistance of 8 Ω square−1 was purchased from Dyesol (TEC8 Glass Plates). Reverse osmosis purified water (resistivity 1 MΩ cm at 25 °C) was used to prepare all aqueous solutions. Borate buffer was prepared by alkalization of a freshly prepared aqueous boric acid solution with fresh 1 M NaOH.

### Deposition Solutions

A 10 mM aqueous solution of [CoEDTA]2− was prepared as described previously,10 and diluted with borate buffer (1:10) prior to the experiments. A λmax at 467 nm (ε = 12 M−1 cm−1) was determined by UV−vis spectrophotometry (Lambda 950, PerkinElmer), consistent with literature.50 The synthesis of [Ni(NH3)6]Cl2 followed a published method32 (λmax = 568 nm (ε = 0.2 M−1 cm−1)), in agreement with literature.29 Aqueous solutions (0.5 mM) were prepared each day and diluted with borate buffer (1:50) to prepare the deposition solution. A stock solution of [Mn(OH)2]12− (10 mM, aqueous) was prepared from Mn(CH3COO)2·4H2O diluted with borate buffer (1:20) and used in deposition experiments.

### Electrochemical Procedures

dc Experiments were performed with a Bio-Logic VSP electrochemical workstation. Custom built instrumentation was used for the ac measurements.7 All ac voltammetric experiments were undertaken with amplitude of ΔE = 0.08 V, which provides an adequate level of nonlinearity to allow higher order harmonics to be detected, and at the same time, does not induce very significant ohmic losses and broadening.25 The frequency of f = 9.02 Hz provides a sufficient level of kinetic sensitivity due to the relatively slow rates of the probed electron-transfer events (vide infra). Control experiments undertaken with f = 22.02 and 89.00 Hz did not provide enhanced ac current in higher order harmonics, which also confirms that 9.02 Hz was sufficient for analysis.

All experiments were undertaken in a three electrode configuration. Ag/AgCl|3 M NaCl (BAS) with a salt bridge was employed as the reference electrode, but potentials are reported versus the reversible hydrogen electrode (RHE;ERHE/V = −0.21 − 0.059pH/V vs Ag/AgCl). A custom-made electrode positioner was used to maintain a constant distance between the working and reference electrodes, and the resistance between them (R) was quantified by EIS. The auxiliary electrode (high surface area Ti wire) was isolated from the test solution by a PTFE coated stirring bar. Prior to switching solutions to different cations, the cells were cleansed with hot aqua regia (HCl:HN03, 3:1 vol.) and rinsed thoroughly with water.

The FTO glass used as a working electrode substrate was received as 100 × 100 mm sheets and laser-engraved (Universal Laser Systems, VLS3.50) to define the electroactive area (0.16 cm2). The glass was then cut into rectangles (10 × 30 mm), and subjected to cleaning procedures (vide infra). Electrical connection was achieved by soldering a wire to the FTO electrode. The electroactive area was finally defined by polyimide (Kapton) tape to give the configuration shown in Figure S1. Functionalization of FTO was performed by spontaneous adsorption of the MOx precursor for the lowest loadings, voltammetrically for medium loadings and potentiostatically for the highest loadings.

### Treatment of FTO Electrodes

Examination of water electrooxidation necessitates the use of an electrode substrate with negligible catalytic activity at up to ca. 2 V vs RHE. FTO subjected to standard cleaning procedures, e.g., 20 min ultrasonifications in surfactant (Hellmanex), water and ethanol (96%), displayed unwanted water oxidation activity (Figure S2a), presumably due to traces of transition metal(s). To produce less catalytically active FTO (magenta traces in Figure S2a), the electrodes were placed in HNO3(aq) (18 wt %) and refluxed for 60 min or immersed in hot aqua regia for 10 min. Subsequently, the glass pieces were rinsed thoroughly under a stream of water. The water oxidation capacity could be further suppressed permanently by a single scan of the potential from 1.05 to −0.25 V vs RHE (teal trace in Figure S2a).

### Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Quantification of metal content of the deposited films was achieved by ICP-MS analysis (NeXION 350D, PerkinElmer) of solutions obtained by dissolving MOx in refluxing 4 M HNO3(aq) (CoOx) or hot aqua regia (NiOx, MnOx) for 40–60 min, and resting for ca. 16 h at ambient temperature. The values measured from three unused FTO electrodes were taken as a baseline. The samples were spiked with Sc internal standard, and a second internal standard of Y ions was plumbed into the sample inlet to allow correction for the instrumental drift. Raw analyte counts were standardized by means of a calibration curve constructed using commercially available stock solutions. No Fe contamination on the electrodes was detected. The extremely low dissolved metal ion concentrations were often at the limit of detection, which imposes a degree of uncertainty on some of the results.

### THEORY

All simulations were undertaken with the DigiElch 7.F software.44 The generally accepted water electrooxidation mechanism involves four proton-coupled electron transfer events,42,43 whose modeling is challenging and requires several simplifying assumptions. The Butler−Volmer electron-transfer kinetics formalism, with charge-transfer coefficients arbitrarily set to 0.50, was used to avoid overparameterization and ensuing uncertainties.55,56 Use of Marcus−Hush theory could be more appropriate, but the required reorganization energies are not known.

Previous kinetic studies on water electrooxidation employed a so-called “molecular catalysis” model.32,45,46 Therein, water oxidation is proposed to occur via a chemical redox reaction
between a substrate and a surface-confined catalyst when the latter reaches a sufficiently high oxidation state through application of a potential. By assuming that the rate-determining step in the 4-electron and 4-proton sequence is much slower than other three, the key reactions can be simplified to

\[ \text{OH} \xrightarrow{M^{2+}} + B^− \xrightarrow{M^{2+}} \text{M}^{2+} + BH + e^- \quad (1) \]

\[ [\text{H}_n\text{O}^\text{m}_\text{m}] + \text{M}^{2+} \xrightarrow{k_{\text{cat}}} [\text{H}_{n+1}\text{O}^\text{m+1}_\text{m}] + \text{M}^{2+} \quad (2) \]

where \([\text{OH}^\text{m}_\text{m}] \) and \([\text{M}^{2+}] \) are the catalyst species in inactive and active (oxidized) state; \(B^− \) and \( BH \) are conjugate base of the buffer and its protonated form, respectively; \([\text{H}_n\text{O}^\text{m}_\text{m}] \) and \([\text{H}_{n+1}\text{O}^\text{m+1}_\text{m}] \) represent the reduced and oxidized states of the substrate at the rate-determining step.

In our analysis, the overpotential-determining process is assumed to occur first in the 4-electron transfer sequence, and the remaining three faster electron transfer steps are replaced with a hypothetical 3-electron process. This was necessary to facilitate simulations within the confines of the software package. The concentration of water is very high and can be assumed to remain constant at the electrode surface at all times. However, the process can still run into a mass-transport controlled regime, since each oxidation step requires withdrawal of a proton by a base (eq 1). This was demonstrated previously, and confirmed to apply here (Figure S3). Thus, the reaction was assumed to be controlled by mass-transport of \(B^− \), while the \(\text{H}_2\text{O} \) concentration was incorporated into relevant rate constants. Application of these assumptions leads to the simplified "molecular catalysis" electrode model given in Table 1. The full set of parameters needed for simulation of this model is shown in Figure S4.

### RESULTS AND DISCUSSION

Activity as a Function of Catalyst Loading. In this study, mechanistic aspects of water electrooxidation catalyzed by non-noble transition metal oxides have been probed using very low catalyst loadings on an FTO surface. For the cobalt oxides, \([\text{Co(EDTA)}]^2− \) was used as a precursor for oxidative electrodeposition of \(\text{CoO}_x \). The strong chelating ligand slows the deposition and prevents the formation of large amounts of \(\text{CoO}_x \), but does not induce fundamental changes in the structure of the catalyst. Dilute \([\text{Ni(NH}_3)_6]^2\text{Cl}_2 \) and \(\text{Mn(CH}_3\text{COO})_2 \) solutions (0.01–0.1 mM) were used to functionalize the electrodes with nickel and manganese oxides, respectively. The use of \([\text{Ni(NH}_3)_6]^2\text{Cl}_2 \) as a precursor decelerates \(\text{NiO}_x \) deposition as needed to control the catalyst loadings for our experiments. Spontaneous adsorption of metal cations onto FTO from these solutions produced an appreciable enhancement in water electrooxidation activity and this approach was used to prepare electrodes with very low \(\text{NiO}_x \) or \(\text{MnO}_x \) surface concentrations.

Figure 1 exemplifies cyclic voltammograms obtained with an FTO electrode modified with two different loadings for each type of a catalyst. Water electrooxidation is manifested by a steep increase in current density at potentials more positive than ca. 1.75 V with a small level of hysteresis detected under the conditions employed. As expected, an increase in the amount of catalyst enhances the water electrooxidation capacity of the electrode.

Prior to the catalytic process, the voltammogram for each metal oxide exhibits a fingerprint response (insets in Figure 1) derived from redox transformations of Co, Ni, or Mn oxides. These processes provide a reliable in situ method for quantifying the surface concentration of electroactive \(\text{MoO}_x \) species (\(\text{Γ} \) /mol cm\(^{-2}\)). This is essential as the ultralow loadings necessary for this study preclude visualization of catalytic species using microscopy or quantitative detection by X-ray based techniques. In the analysis that follows, the number of electrons corresponding to the processes shown in insets to Figure 1 was assumed to be unity in each case. On this basis, \(\Gamma = Q_{\text{cat}} \times F \times A^{-1} \), where \(Q_{\text{cat}} \) / C is the charge associated with a...
First potential cycles are shown for CoO compared with the background response from the FTO electrode. However, substantial and persistent degradation was found for the FTO catalyst, data for two samples having different loadings are compared with the background response from the FTO electrode (gray).

For selected samples, the amount of deposited metal was determined by ICP-MS (Table S2). Comparison of thus selected for comparisons of the catalytic current, inset. Previously, 100% electrochemical activity was reported for electrodeposited NiO (a, wine squares), MnO (b, purple triangles), and NiO (c, blue rhombuses). Data were extracted from dc components of FT ac voltammograms measured in borate buffer (0.1 M, pH 9.2). Green and red symbols refer to theoretical predictions based on the model in Table 1 and parameters in Table 2 for Γ ranges (a) 3–11 (×), 100–110 (+), and (c) 5–10 pmol cm−2. Data sets (1) and (2) in (b) were obtained with pretreated FTO supports that slightly differed in water oxidation activity (see text). Expanded versions of the low Γ regions are shown in insets. Lines are guides to an eye.

An OER overpotential of ca. η = 0.62 V (1.853 V vs RHE) was selected for comparisons of the catalytic current, j_oER, to limit interference from background water-oxidation catalyzed by the FTO substrate and ohmic losses.

At low CoO coverage (Γ < 10 pmol cm−2), the enhancement in water oxidation current density exceeds that predicted from a linear activity-loading dependence (see inset to Figure 2a). Since data in Figure 2 are not corrected for IR drop, a linear relationship between the intrinsic activity of the electrode and Γ would result in a dependence of the kind derived from theoretical simulations (vide infra and Figure 2). This indicates a notable increase in the specific metal-weighted catalytic activity, k_oER/A nmol−1 = j_oERΓ−1. At higher loadings, the j_oER vs Γ dependence trends downward as expected if k_oER is not strongly dependent on Γ, in agreement with reports for much thicker catalyst films.11,39,59

For MnO, k_oER increases substantially over the whole catalyst loading range examined, but is highly sensitive to the properties of the FTO support (cf. data sets 1 and 2 in Figure 2b).
Dependence 1 of $j_{0.62V}$ vs $\Gamma$ results from the use of pretreated FTO electrodes with essentially no water oxidation activity at $\eta = 0.62 V$ ($j_{0.62V} \lesssim 1 \mu A \, cm^{-2}$) prior to deposition of MnO$_x$. Dependence 2 was obtained with FTO supports pretreated in the same manner but that were slightly more active with $j_{0.62V}$ of ca. 3–5 $\mu A \, cm^{-2}$ before functionalization with MnO$_x$.

For the NiO$_x$ electrocatalysts with extremely low loadings ($\Gamma$ below a few pmol $cm^{-2}$), the water oxidation current densities rise dramatically with essentially undetectable increases in the amount of Ni (inset to Figure 2c). In this ultralow $\Gamma$ range, NiO$_x$ substantially outperforms CoO$_x$ and especially MnO$_x$ in terms of $j_{0.62V}$. However, higher surface concentrations of NiO$_x$ produce lower enhancements in catalytic activity (Figure 2c), with $j_{0.62V}$ decreasing from 2 to 0.1 A nmol$^{-1}$ when $\Gamma$ is increased from 5 to 300 pmol cm$^{-2}$. Once $\Gamma$ exceeds 1000 pmol cm$^{-2}$, the activity vs loading dependence for NiO$_x$ is close to linear. The incorporation of trace Fe into NiO$_x$ to form FeNiO$_x$ has been shown to significantly enhance the water oxidation catalytic activity.$^{60}$ Although such a process cannot be absolutely excluded herein, our control measurements with blank FTO (continuous cycling of the potential from 1.15 to 2.15 V; chronoamperometry at 1.8 V) did not show any indication of Fe being deposited, namely, no unexpected enhancement of the electrooxidation current on the time scale of our measurements.

The pronounced increase in the specific water oxidation activity at low catalyst loadings can be attributed to the crucial importance of multivalent metal centers (ensembles) in sustaining this reaction efficiently. Indeed, the involvement of at least two adjacent metal atoms in the oxide structure is postulated in proposed mechanisms for the OER.$^{3,32,36,37,46,61}$ An enhanced relative contribution of catalyst dissolution to the apparent increase in $j_{0.62V}$ may apply for low loadings of the MnO$_x$ catalyst. Importantly, there was no detectable loss of catalytic activity observed for CoO$_x$ and NiO$_x$.

**ac Voltammetric Studies: Qualitative Mechanistic Observations.** Interpretations of how redox transformations of heterogeneous MO$_x$ catalysts contribute to water electrooxidation, based on dc methodology, has been the subject of debate.$^{17,46,64}$ FT ac voltammetric analyses have provided some qualitative mechanistic insights.$^{48,65}$ The results of the more comprehensive FT ac voltammetric study described herein resolve ambiguities in the assignment of electron transfer processes coupled to the catalytic reaction, which are obscured in dc voltammetry. Detailed experiment-simulation comparisons are now introduced for the first time.

ac Voltammetric data obtained for the CoO$_x$, MnO$_x$ and NiO$_x$ electrocatalysts in borate buffered solutions at pH 9.2 are displayed in Figures 3 and 4. The most useful information is available from the ac harmonics resolved from the total current (Figure 3a) using the FT–band filtering–inverse FT sequence of operations.$^{53}$ The aperiodic component of an FT ac voltammogram is analogous to a dc voltammogram, and is dominated by the featureless water oxidation current (Figure 3b). However, in the ac harmonics, the contribution from catalytic water oxidation is minimal and the underlying redox transformations become directly accessible (cf. Figure 3b and c,d).

For the CoO$_x$-functionalized electrodes, the dc component displays the process noted above, now designated as process I, which precedes the catalytic wave (Figure 3b). This is the only observable feature prior to water oxidation, and it is attributed to a Co$^{II/III}$ transition.$^{64}$ In contrast, the fundamental ac harmonic exhibits two well-defined processes, process I and process II, that strongly differ in their intensity and dependence on $\Gamma$ (Figure 3c).

Variations in the CoO$_x$ catalyst loading do not significantly affect the potential where process I is found (ca. 1.4–1.5 V), but influence the current intensity in the fundamental harmonic (Figure 3c). The electron transfer rate for this process is so slow that it is essentially indistinguishable from background in the fourth harmonic (Figure 3d). The substantially faster process II gives well-defined higher order harmonic signals that shift to more negative potentials and are enhanced by increases in $\Gamma$ and water oxidation dc current density (Figures 3c,d and 5a). Such behavior and the asymmetric shape of the harmonics for process II are consistent with the coupling of
Thus, process II is coupled to a rate-limiting chemical step and is accessible only at potentials where the catalytic current is significant, while the involvement of process I in efficient water oxidation catalysis is negligible.

Interpretation of the ac voltammetric data for MnO
x-catalyzed water oxidation is more complicated. At low Γ, there is only one clearly distinguishable and again very slow redox process prior to the onset of water electrooxidation, process Ia, at ca. 1.3 V (Figure 4a). The potential for this process is not positive enough and the rate too slow to catalyze water oxidation. When Γ is above ca. 100 pmol cm
−2, process Ib emerges in the FT ac voltammograms at ca. 1.5–1.6 V (Figure 4a). The electron transfer rate for process Ib is faster than that for process Ia, as deduced from the higher current magnitude and shape of the ac harmonics (exemplified in fourth harmonics by circles over the curves in Figure 4a). However, since there is no pronounced dependence of the position of process Ib on the catalyst loading and water electrooxidation rate, this redox transformation is again not regarded as being directly involved in catalysis. Finally, at even more positive potentials, the catalytically important process II was detected for electrodes functionalized with MnO
x and a dependence on Γ similar to that for CoO
x was observed (Figures 4a and 5). Therefore, MnO
x-catalyzed water oxidation is predominantly governed by the kinetics of process II and coupled chemical transformation(s).

The ac voltammetric data for the NiO
x-based anodes is even more complex. At higher Γ, the dc components reveal a well-defined process at ca. 1.5 V (Figure 4b), which is prior to the catalytic wave. The corresponding fundamental ac harmonic shows two peaks (Figure 4b), implying contribution from two types of redox active species. Additionally, there are substantial differences in the ac response on the positive and negative potential sweep (Figure 4b and S8). These observations combined with the large peak-to-peak separation in dc voltammetry confirm that processes Ia are coupled to a structural rearrangement, such as a phase change, rather than water oxidation, since the potential is not positive enough and is independent of the catalyst loading. Higher Γ results in the
emergence of process Ib at ca. 1.65–1.7 V in the ac harmonics (Figure 4b), as for MnO₂. Process II is also observed for NiOₓ though in this case its behavior is clearly more complicated.

When examining the relationship between the catalytic current density and the position of process II in the 4th harmonic, the NiOₓ data can be subdivided into three regions each corresponding to different catalyst loadings (Figure 5c). At very low Γ, process II moves to more negative potentials as the NiOₓ loading is increased and there is a concomitant improvement in catalytic activity (Figure 5c, filled rhombuses). Once Γ reaches a level allowing both process Ia and Ib to be detectable, process II is only weakly dependent on the Ni concentration/activity in the higher order ac components.

Specifically, in the 4th harmonic, process II shows only a minor negative shift in potential as j_{0,62V} increases from 0.05 to 0.2 mA cm⁻² (Figure 5c, empty rhombuses). For CoOₓ and MnO₂, a shift of ca. 0.1 V was observed for comparable increases in j_{0,62V}. When the NiOₓ Γ is further increased, process Ib and II merge in the higher harmonics (Figure 4b: 4th), giving rise to highly scattered data (Figure 5c, struck-through rhombuses). Thus, at very low NiOₓ surface concentrations, water oxidation catalysis is mainly coupled to process II, as for CoOₓ and MnO₂. However, at intermediate NiOₓ loadings (5–500 pmol cm⁻²), a contribution to catalysis from process Ib cannot be excluded. At Γ above ca. 500 pmol cm⁻², process II shows a notable negative shift, but overlaps with process Ib and becomes unresolved. However, the response for process II can still be monitored in the fundamental harmonic over all loadings and it consistently shifts to less positive potentials as Γ increases (Figure 4b: 1st). In summary, FT ac voltammetric analysis indicates that water electro-oxidation catalyzed by CoOₓ, MnO₂, and to a major extent by NiOₓ occurs via a similar mechanism. On a qualitative level, process II and coupled chemical transformation(s) control the overall reaction rate. Interestingly, closely related FT ac voltammetric data are obtained for nonfunctionalized FTO (Figures S2b and S9), indicating that the reaction mechanism is also the same. It is also important to note that Co, Mn and Ni oxides undergo redox transformations at positive potentials prior to process II (Figures 4 and S5), which suggests that the catalytically relevant state of their surface is formed through oxidation and accompanying processes.

**Experiment-Simulation Comparisons by FT ac Voltammetry.** The “molecular catalysis” model used for simulations is summarized in Table 1. Three parameters need to be determined from comparisons of theoretical and experimental data: the effective reversible potential (E_{cat}^{0}) and the heterogeneous electron transfer rate constant (k_{cat}^{0}) for reaction 3, and the forward rate constant for reaction 4 (k'). Quantitative analysis of a mechanism coupling an electron transfer process to a chemical reaction is among the most challenging problems in contemporary electrochemistry. Indeed, essentially indistinguishable dc voltammetric curves can be simulated using the model in Table 1 and an infinite number of combinations of the E_{cat}^{0}, k_{cat}^{0}, and k' parameters. From this perspective, FT ac voltammetry affords important advantages as shown previously, and below.

Application of the model in Table 1 resulted in excellent agreement between ac voltammetric experimental data and simulations (Figures 6 and S10) when using the parameters summarized in Tables 2 and S3. Importantly, the simulated ac harmonic components were very sensitive to variation in the values of E_{cat}^{0}, k_{cat}^{0}, and especially k' (Figure S11). The derived values of E_{cat}^{0}, k_{cat}^{0}, and k' allow the CoOₓ, NiOₓ, and MnO₂ catalysts to be compared quantitatively.

Hysteresis in the dc component and corresponding positive shift in the ac signals upon reversing the scan direction (Figures 3, 6, and S12) was essentially impossible to mimic. Our modeling suggests that this hysteresis is not due to depletion of base near the electrode surface. Even at very low water oxidation current densities, when mass-transport limitations are negligible, stirring the solution does not eliminate the hysteresis (Figure S13a). We conclude that the electro-catalytic activity of CoOₓ and NiOₓ changes with the applied potential, but the catalyst is returned to its previous state during the reverse voltammetric sweep, i.e., this change is reversible (Figure S13b). The scan direction hysteresis is least pronounced for the lowest loadings of CoOₓ and NiOₓ (cf. data in Tables 2 and S3).

At high Γ, unrealistically low k_{cat}^{0} and k' would be required to fit the positive sweep, i.e., values that would not allow the experimentally observed peak currents in dc voltammetry (Figure S3) to be reached. Similarly, no acceptable fit for the positive sweep could be achieved for MnO₂ at high Γ (Table S3). On this basis, it can be argued that the voltammetric data obtained during the backward (negative) sweep...
The similarity of oxidation in solution are similar. Our analysis suggests that the parameters derived from best respective observed $j_{o.62} \text{V vs } \Gamma$ and $j_{o.62} \text{V vs } E_{\text{cat}}^{\text{0th}}$ data (Figure 2a; Figure S1, Table 2). Successful modeling of the data at higher $\Gamma$ required higher $k^f$ and $k^r_{\text{cat}}$ values (Table 2). An increase in $k^f$ at higher catalyst concentrations is consistent with an "ensemble effect", reflecting the critical importance of multatomic active sites. A similar, but less pronounced effect of $\Gamma$ on the $k^f$ and $k^r_{\text{cat}}$ values was found for MnO$_x$. Deterioration of the NiO$_x$ specific activity as the loading increases is also reflected in a lowering of $k^f$ and $k^r_{\text{cat}}$ values (Table 2). A plausible reason for the deceleration in $k^r_{\text{cat}}$ is bulk structural rearrangement that occurs upon oxidation/reduction of the thicker nickel oxide layers.$^{31,63,68}$

The values of $k^f$ for CoO$_x$, NiO$_x$, and MnO$_x$ are of the same order of magnitude and fall within the $4 \times 10^{10}$ to $8 \times 10^{10}$ M$^{-1}$ s$^{-1}$ range. Previous works aimed at parametrizing the catalytic reaction between the oxidized, active state of CoO$_x$, NiO$_x$, and MnO$_x$, and H$_2$O used a pseudo-first-order rate constant, $k^f_1$/s$^{-1}$. Thus, comparisons with our results can be made by multiplying the second order rate constant, $k^f_1$, by the concentration of base to give $k^f_{\text{cat}}$. The lower limits for $k^f_1$ $\geq 2$ s$^{-1}$ and $\geq 112.5$ s$^{-1}$ reported by the groups of Bard$^{46}$ and Savéant,$^{46}$ respectively, are consistent with the values of $k^f_{\text{cat}}$ (17500 s$^{-1}$) derived from our analysis of the CoO$_x$ ac voltammetric data (Table 2). For MnO$_x$, $k^f_{\text{cat}}$ determined herein is ca 4000 s$^{-1}$,

good water oxidation catalysts with comparable activity. If one considers a “heterogeneous catalysis” model (Table S2), similar $E_{\text{cat}}^{\text{0th}}$ values reflect a similar strength of adsorption of the substrate on the catalyst surface.

The dependence of the CoO$_x$ catalyst properties on $\Gamma$ is reflected by the need to employ catalyst loading dependent [$E_{\text{cat}}^{\text{0th}}$, $k^f$, $k^r_{\text{cat}}$, $k^f_1$] parameter combinations to fit the experimentally observed $j_{o.62} \text{V vs } \Gamma$ and $j_{o.62} \text{V vs } E_{\text{cat}}^{\text{0th}}$ data (Figure 2a; Figure S1, Table 2). Successful modeling of the data at higher $\Gamma$ required higher $k^f$ and $k^r_{\text{cat}}$ values (Table 2). An increase in $k^f$ at higher catalyst concentrations is consistent with an "ensemble effect", reflecting the critical importance of multatomic active sites. A similar, but less pronounced effect of $\Gamma$ on the $k^f$ and $k^r_{\text{cat}}$ values was found for MnO$_x$. Deterioration of the NiO$_x$ specific activity as the loading increases is also reflected in a lowering of $k^f$ and $k^r_{\text{cat}}$ values (Table 2). A plausible reason for the deceleration in $k^r_{\text{cat}}$ is bulk structural rearrangement that occurs upon oxidation/reduction of the thicker nickel oxide layers.$^{31,63,68}$

The values of $k^f$ for CoO$_x$, NiO$_x$, and MnO$_x$ are of the same order of magnitude and fall within the $4 \times 10^{10}$ to $8 \times 10^{10}$ M$^{-1}$ s$^{-1}$ range. Previous works aimed at parametrizing the catalytic reaction between the oxidized, active state of CoO$_x$, NiO$_x$, and MnO$_x$, and H$_2$O used a pseudo-first-order rate constant, $k^f_1$/s$^{-1}$. Thus, comparisons with our results can be made by multiplying the second order rate constant, $k^f_1$, by the concentration of base to give $k^f_{\text{cat}}$. The lower limits for $k^f_1$ $\geq 2$ s$^{-1}$ and $\geq 112.5$ s$^{-1}$ reported by the groups of Bard$^{46}$ and Savéant,$^{46}$ respectively, are consistent with the values of $k^f_{\text{cat}}$ (17500 s$^{-1}$) derived from our analysis of the CoO$_x$ ac voltammetric data (Table 2). For MnO$_x$, $k^f_{\text{cat}}$ determined herein is ca 4000 s$^{-1}$,

provides a better reflection of the catalytic properties relevant to water electrooxidation.

Several important conclusions can be drawn on the basis of the parameters derived from fitting simulations to experimental data (Table 2). The effective reversible potentials for the CoO$_x$, NiO$_x$, and MnO$_x$ redox transformations coupled to substrate oxidation in solution are similar. Our analysis suggests that $E_{\text{cat}}^{\text{0th}}$ lies in the 1.9—2.1 V vs RHE potential range and is not strongly dependent on $\Gamma$. This agrees with the lower limit for $E_{\text{cat}}^{\text{0th}}$ value for CoO$_x$ of >1.92 vs RHE reported by the group of Savéant.$^{46}$ The similarity of $E_{\text{cat}}^{\text{0th}}$ for CoO$_x$, NiO$_x$, and MnO$_x$ provides one fundamental explanation for each being

The values of $k^f_1$ for CoO$_x$, NiO$_x$, and MnO$_x$ are of the same order of magnitude and fall within the $4 \times 10^{10}$ to $8 \times 10^{10}$ M$^{-1}$ s$^{-1}$ range. Previous works aimed at parametrizing the catalytic reaction between the oxidized, active state of CoO$_x$, NiO$_x$, and MnO$_x$, and H$_2$O used a pseudo-first-order rate constant, $k^f_1$/s$^{-1}$. Thus, comparisons with our results can be made by multiplying the second order rate constant, $k^f_1$, by the concentration of base to give $k^f_{\text{cat}}$. The lower limits for $k^f_1$ $\geq 2$ s$^{-1}$ and $\geq 112.5$ s$^{-1}$ reported by the groups of Bard$^{46}$ and Savéant,$^{46}$ respectively, are consistent with the values of $k^f_{\text{cat}}$ (17500 s$^{-1}$) derived from our analysis of the CoO$_x$ ac voltammetric data (Table 2). For MnO$_x$, $k^f_{\text{cat}}$ determined herein is ca 4000 s$^{-1}$,
which is in agreement with a lower limit of 100 s⁻¹ reported by Dau and colleagues and notably higher than $k_{\text{f}}^0 = 500$ s⁻¹ for the Mn₄CaO₅ complex of Photosystem-II.³²,⁶⁹

Considering other influential catalysts, molecular Ru complexes have been studied in great detail.⁷⁰ The $k_{\text{f}}^0$ rate constants of 0.00075 and 0.0014 s⁻¹ for Ru monomers ([Ru²⁺(tpy) (bpm) (OH₂)]²⁻, [Ru²⁺(tpy) (bpy) (OH₂)]²⁺) and 0.002 s⁻¹ for the "blue dimer" (ciscis-[(bpy)₂(H₂O)RuᴵᴵᴵO-Ruᴵᴵᴵ(OH₃)(bpy)₂]⁴⁺) were reported. Values of $k_{\text{f}}^0$ ranging from 0.00014 to 0.00078 s⁻¹ for bpy)²⁺),⁷² were reported. Values of $k_{\text{f}}^0$ ranging from 0.00014 to 0.00078 s⁻¹ were determined for a series of other Ru monomers and dimers,⁷³ while values up to 0.014 s⁻¹ have been reported for the [Ruᴵᴵᴵ(bpp) (trpy)(H₂O)]³⁻ dimer.⁷⁴ All are several orders of magnitude lower than $k_{\text{f}}^0$ for the more efficient heterogeneous systems examined in this and other studies.

Another important outcome of our work is the exceptionally high specific catalytic activity of nickel oxides at ultralow loadings that substantially surpasses that of CoO and MnO₂ (Table 2). In particular, at the lowest voltammetrically detectable Γ of ca. 1 pmol cm⁻², $k_{\text{f}}^0$ and $k_{\text{f}}^0_{\text{cat}}$ for the NiO₂-modified electrodes are an order of magnitude higher than those for CoOₓ with loadings below 50 pmol cm⁻². One strategy to exploit this property of NiO₂ is to immobilize the catalyst on a very high-surface area support to avoid the formation of dense nickel oxide layers since they exhibit notably lower specific activity.

**CONCLUSIONS**

Systematic examination of water electrooxidation catalyzed by low amounts of cobalt, manganese and nickel oxides using FT ac voltammetry enables unique mechanistic insights and quantification of key reaction parameters. The experimental data are reliably mimicked by the "molecular catalysis" model and the $E_{\text{ac}}^0$, $k_{\text{f}}^0_{\text{cat}}$ and $k_{\text{f}}^0$ parameters have been derived via extensive experiment-simulation comparisons. Estimates of the pseudo-first order $k_{\text{f}}^0$ provided by our analysis are substantially higher than values reported previously for similar and other water oxidation catalysts. This suggests that FT ac voltammetry offers improvements in sensitivity executable in quantitative kinetic studies of this complex reaction. The unprecedentedly high specific catalytic activity of NiO₂ at very low loadings (<2 pmol cm⁻²), as reflected by high $k_{\text{f}}^0$ and $k_{\text{f}}^0_{\text{cat}}$ could be of applied significance.

Quantitative FT ac voltammetric studies can significantly improve our understanding of mechanistic aspects of water electrooxidation. The parameterized electrode model of the reaction introduced here for the first time provides a guide for in situ spectrosocopic studies to assist in identification of true active states of metal-oxide-based electrocatalysts, and indicates that experiments at very positive applied potential (1.9–2.1 V vs RHE) are desirable. Information derived from these experiments is indispensable for the design and benchmarking of improved catalytic materials for this critically important process.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10304.

Photographs of electrodes; ac voltammetry and dc voltammetric peak current data for FTO; DigiElch 7.0F parameters; modeling of two noninteracting water oxidation catalysts; “heterogeneous catalysis” model; similarity of predictions of the “molecular” and “heterogeneous” catalysis models; ICP-MS data; dc voltammetry for MnO₂; higher harmonics of FT ac voltammogram for NiO₂; $j_{\text{ac}}$ vs $E_{\text{ac}}^0$ plot for FTO; experiment-simulation comparisons for NiO₂ influence of $k_{\text{f}}^0_{\text{cat}}$ and $k_{\text{f}}^0$ on simulated FT ac voltammograms; experiment-simulation comparisons for CoO₂; “molecular catalysis” model parameters derived from the forward voltammetric sweep data; effect of stirring and multiple cycling on dc voltammetry for water oxidation (PDF)

**AUTHOR INFORMATION**

*Corresponding Authors
leone.spiccia@monash.edu
alexandr.simohon@monash.edu

**ORCID**
Alexandr N. Simonov: 0000-0003-3063-6539

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