MnO$_x$/IrO$_x$ as Selective Oxygen Evolution Electrocatalyst in Acidic Chloride Solution

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ABSTRACT: The oxygen evolution reaction (OER) and chlorine evolution reaction (CER) are electrochemical processes with high relevance to water splitting for (solar) energy conversion and industrial production of commodity chemicals, respectively. Carrying out the two reactions separately is challenging, since the catalytic intermediates are linked by scaling relations. Optimizing the efficiency of OER over CER in acidic media has proven especially difficult. In this regard, we have investigated the OER versus CER selectivity of manganese oxide (MnO$_x$), a known OER catalyst. Thin films (~5–20 nm) of MnO$_x$ were electrodeposited on glassy carbon-supported hydrous iridium oxide (IrO$_x$/GC) in aqueous chloride solutions of pH ~0.9. Using rotating ring–disk electrode voltammetry and online electrochemical mass spectrometry, it was found that deposition of MnO$_x$ onto IrO$_x$ decreases the CER selectivity of the system in the presence of 30 mM Cl$^-$ from 86% to less than 7%, making it a highly OER-selective catalyst. Detailed studies of the CER mechanism and ex-situ structure studies using SEM, TEM, and XPS suggest that the MnO$_x$ film is in fact not a catalytically active phase, but functions as a permeable overlayer that disfavors the transport of chloride ions.

1. INTRODUCTION

A “hydrogen economy” could allow pollution-free capture and utilization of solar power as an alternative to inherently limited fossil fuels. Bockris first envisioned the hydrogen economy in the 1970s as the direct electrochemical splitting of seawater into H$_2$ and O$_2$, driven by nuclear or solar power in desert areas near sea coasts, where the influx of solar energy is high and reliable. Use of seawater would offer the benefit of having no competition with fresh water resources and could also serve as a source of very pure fresh water originating from the eventual reverse reaction in a fuel cell. Despite enormous research efforts, large-scale energy storage by means of water electrolysis has not been realized yet. In large part, this is because the oxygen evolution reaction (OER), the desired reaction and OER is a detrimental side reaction. Inherent to O$_2$, toxic Cl$_2$ cannot be easily disposed of.

The competition between OER and CER is not only relevant to saline water splitting for solar energy conversion, in the energy intensive chlor-alkali process, CER is in fact the desired reaction and OER is a detrimental side reaction.
established that catalyst materials that show a proficiency toward oxidation of water also tend to catalyze the oxidation of chloride, implying that the two reactions have a similar active site or partially shared reaction pathways.\textsuperscript{18–20} In recent computational work studying the presumed mechanisms of OER and CER, indeed a scaling relation has been observed between the binding energetics of the OER and CER intermediates, implying that catalysts that bind oxygen-bound intermediates strongly also bind chloride-bound intermediates strongly.\textsuperscript{21–23} In a related fashion, OER is usually accompanied by catalyst degradation, a major problem for the durability of practical electrolysers.\textsuperscript{24–26} For pure metal oxides, the OER activity and extent of catalyst degradation during OER have been directly correlated,\textsuperscript{25,27} implying an additional “scaling relation” between activity and degradation. However, it is also known that OER activity and catalyst degradation can be decoupled, such as by mixing with appropriate heterometal oxides.\textsuperscript{28,29} On the other hand, CER does not seem to correlate strongly with catalyst degradation.\textsuperscript{30–32} Unraveling the intricacies of CER versus OER selectivity is expected to lead to “cross-linked” insights in both reactions and to aid the development of better catalytic materials for both.

The majority of research concerning competition between OER and CER has been performed in light of the chlor-alkali industry, focusing on selective CER in acidic solutions on mixed metal oxides based on RuO\textsubscript{2} and IrO\textsubscript{2}, stabilized by TiO\textsubscript{2} (so-called dimensionally stable anodes, DSAs).\textsuperscript{33,34} Anodes that are highly OER selective in acid are very rare, due to the favorable kinetics of the CER and the OER versus CER scaling relation described above. A notable exception is manganese oxide (MnO\textsubscript{x}), an OER-active material that has received significant interest in recent years.\textsuperscript{35–38} Initially reported by Bennet,\textsuperscript{39} anodes based on MnO\textsubscript{x} show a strong tendency to selectively evolve oxygen from acidic saline water. Hashimoto et al. studied a series of Mn-based mixed metal oxides (MMO) deposited on an IrO\textsubscript{x}/Ti substrate and showed that such anodes often exhibit nearly 100% selectivity toward OER, under a variety of experimental conditions, for many hours of sustained operation.\textsuperscript{30–43} Besides its high reported OER selectivity, MnO\textsubscript{x} is also one of the few nonprecious metal-based catalysts that has been reported to be moderately stable in acid under OER conditions.\textsuperscript{44} This stability is in strong contrast with other 3d metal oxides such as CoO\textsubscript{x} and Ni/Fe-based oxyhydroxides, materials that show very high OER activity in alkaline pH, but are unstable and inactive in acid.\textsuperscript{45–50}

Inspired by Bockris’ vision of a hydrogen economy based on saline water splitting plants near desert coasts, we became interested in the origin of the exceptional OER selectivity of the MnO\textsubscript{x}-based materials studied by Hashimoto and co-workers. To our knowledge, the mechanism by which MnO\textsubscript{x} “breaks the scaling” between OER and CER was never thoroughly investigated. In part, we believe this was due to the difficulty of reliably measuring OER versus CER activity in situ, for which no fast, practical method existed. We have recently developed a rotating ring–disk electrode (RRDE) method with a platinum ring electrode for chlorine detection, which allows rapid and precise CER activity measurement in acidic media.\textsuperscript{51} Using this method, we reported CER behavior on amorphous IrO\textsubscript{2}, a material that is considered one of the most active and stable acidic OER catalysts.\textsuperscript{52} In the present study, we use the RRDE method to study thin films of MnO\textsubscript{x} on IrO\textsubscript{2} with respect to their OER and CER selectivity during cycling voltammetry and amperometry. Product species are also studied using online electrochemical mass spectrometry (OLEMS) measurements in combination with isotopic labeling. To gain more insight in the nature of the MnO\textsubscript{x} film, ex-situ studies of the catalyst were performed using bulk X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron microscopy (XPS). In this way, we aim to shed more light on the mechanism by which MnO\textsubscript{x}-based anodes selectively evolve oxygen and how selectivity between OER and CER may be better controlled.

2. EXPERIMENTAL SECTION

All experimental protocols and details can be found in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Deconvolution of Chlorine Evolution Rates during Parallel OER and CER by Means of an RRDE.

For the quantification of CER rates during electrocatalyst operation, we make use of an RRDE setup with a Pt ring electrode, with the potential of the ring fixed at $E_{\text{Ring}} = 0.95 \text{ V}$.\textsuperscript{51} This enables the quantitative measurement of Cl\textsubscript{2} at the ring via the reduction of Cl\textsubscript{2} back to Cl\textsuperscript{−}, provided that the solution pH is below 1, to prevent hydrolysis of Cl\textsubscript{2} into hypochlorous acid, and the concentration of chloride is above 15 mM, to prevent interference of oxide formation on the ring.\textsuperscript{52} Under these conditions, the collection factor for Cl\textsubscript{2} (N\textsubscript{f}) was reproducible within 2% and virtually identical to that of the Fe[CN]\textsubscript{6}\textsuperscript{3−}/Fe[CN]\textsubscript{6}\textsuperscript{4−} redox couple ($N_f = 0.244$; see also the Supporting Information). CER currents on the disk ($i_{\text{CER}}$) can then be determined by

$$i_{\text{CER}} = \frac{i_{\text{Ring}}}{N_f}$$

(3)

The main advantage of this method is its speed and flexibility in measuring CER activity during catalyst operation, which takes place on the disk electrode. Since the IrO\textsubscript{x}/GC catalyst under study can be considered stable under the present conditions,\textsuperscript{53} OER is the sole remaining reaction, and direct quantification of the OER current ($i_{\text{OER}}$) is possible via

$$i_{\text{OER}} = i_{\text{Disk}} - i_{\text{CER}} = i_{\text{Disk}} - \frac{i_{\text{Ring}}}{N_f}$$

(4)

where $i_{\text{Disk}}$ equals the disk current, corrected for (pseudo)-capacitance by taking the average of forward and backward scans. Following the determination of $i_{\text{OER}}$ and $i_{\text{CER}}$, the selectivities toward CER ($\epsilon_{\text{CER}}$) and OER ($\epsilon_{\text{OER}}$) are calculated from

$$\epsilon_{\text{CER}} = 1 - \epsilon_{\text{OER}} = \frac{1}{2\epsilon_{\text{CER}}} = \frac{1 + 4\epsilon_{\text{OER}}}{2\epsilon_{\text{CER}} + 1}$$

(5)

Figure 1 illustrates how the RRDE method is implemented, comparing disk and ring currents for chloride concentrations of [Cl\textsuperscript{−}] = 0 mM and [Cl\textsuperscript{−}] = 30 mM. By observing the ring current, the onset of CER can be located at around 1.42 V, meaning it proceeds with negligible overpotential at pH = 0.88. We can then compare $i_{\text{Disk}}$ in the absence of Cl\textsuperscript{−}, which is equal to “pure” OER current, and $i_{\text{OER}}$ in the presence of 30 mM KCl, as calculated from eq 4. As was reported previously,\textsuperscript{51} OER is not strongly affected by either the presence of Cl\textsuperscript{−} or...
parallel CER under the used conditions. Furthermore, selectivity toward CER is approximately 86% near 1.55 V.

Although a chloride concentration of 30 mM is far removed from realistic seawater concentrations, which typically exceed 0.5 M, the use of such concentrations would compromise the ability to carry out fundamental CER studies, due to increasing experimental noise levels and interference of gas bubbles in the RRDE setup. In consideration of our previous study, where we observed no obvious changes in CER behavior for Cl− concentrations up to 100 mM,51 we believe a concentration of 30 mM chloride constitutes an optimal system for study.

3.2. Effect of MnOx Deposition on Chlorine Evolution.
In acidic media, deposition of MnOx can proceed via the overall reaction

$$2\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_x + 4\text{H}^+ + 2\text{e}^-$$

$$E_{\text{MnO}_x/\text{Mn}^{2+}}^0 = (1.23 - 0.059\text{pH}) \text{V vs RHE}$$ (6)

To form MnOx films on IrOx and study their effect on CER selectivity, we resorted to growing MnOx thin films in situ by “spiking” the working solution with 0.6 mM MnSO4. This small but significant concentration of Mn2+ ions prevents the net dissolution of the acid-unstable MnOx films during experiments.34,52 Despite obvious disadvantages, such as lack of precise control over film thickness during scanning, this method allows the growth and study of thin MnOx films of variable thickness in an identical system, without the severe uncertainty of the film’s integrity (and problems concerning buildup of dissolved Mn2+ in the solution, in the case of repeated externally grown MnOx films). It is thus possible to measure how CER kinetics depend on MnOx film growth.

Figure 2 shows CVs from 1.1−1.55 V of an IrOx/GC electrode, in the presence of 30 mM KCl and 0.6 mM MnSO4, under a 1500 rpm rotation rate. Compared to a Mn2+-free solution, MnOx deposition manifests itself as a superimposed current with a slow onset near 1.37 V (see Figure S4 for a close-up). To grow MnOx films of variable thickness and to test their effect on CER activity, we first conditioned the disk electrode at $E_{\text{Disk}} = 1.48$ V, while rotating at 1500 rpm. The conditioning potential was chosen such that it was more positive than $E_{\text{MnO}_x/\text{Mn}^{2+}}^0$ (approximately 1.13 V at pH = 0.88), but not too far into the mixed OER/CER region as to prevent excessive gas formation during deposition. Immediately after conditioning, the electrode was scanned up to a positive potential limit of $E = 1.55$ V. At the same time, the ring was kept at $E_{\text{Ring}} = 0.95$ V; analogous to results described in Section 3.1, the ring is assumed to act as a selective probe for chlorine. Formation of Cl2 can be seen in both the forward and reverse sweep. During the reverse scan, complete cathodic dissolution of the MnOx films appears as a reduction wave from approximately 1.450 to 1.15 V. Dissolution of the film effectively “resets” the working electrode, and the charge under the reduction peak (described as $Q_{\text{MnO}_x}$) allows to approximate the thickness of the film that was originally present in the forward scan. Repeated scanning without preconditioning led to overlapping CVs, with reproducible peak currents, ring currents, and cathodic MnOx dissolution peaks, showing that the original system is restored every time after traversing the negative potential limit of 1.10 V (see Figure S5). A Mn2+ concentration of 0.6 mM was purposefully tested as optimum: lower concentrations led to impractically long deposition times, and higher [Mn2+] (>1 mM) often resulted in films that were too thick to completely dissolve after returning to 1.10 V. This was evident from a remaining brown-red glow on the electrode surface and significant but slowly subsiding negative current when the potential was kept at 1.10 V. Thicker films also occasionally led to mechanical instability in the form of brown MnOx flakes peeling off the electrode during rotation. Keeping [Mn2+] as low as possible also reduced the extent of continuous (uncontrolled) MnOx deposition current during scanning and allowed a more accurate comparison of $i_{\text{OER}}$ and $i_{\text{CER}}$, as will be discussed below.

Figure 3 displays the measured disk and ring currents for $E_{\text{Disk}} = 1.55$ V as a function of $Q_{\text{MnO}_x}$, the charge determined from the MnOx dissolution wave in the corresponding reverse
sweeps. We chose the potential of 1.55 V for quantitative analysis, since this is the point of potential reversal and as such contains minimal current contributions from (pseudo-)capacitive processes. To be able to compare directly, ring currents \( i_{\text{Ring}} \) are corrected for \( N_f \) to obtain \( i'_{\text{Ring}} \). The distinction between \( i_{\text{Ring}}' \) and \( i_{\text{CER}} \) will be discussed shortly.

The deposition of MnOx has a profound effect on both \( i_{\text{Disk}} \) and \( i_{\text{Ring}}' \) but the most interesting aspect is the selectivity: \( i_{\text{Ring}}' \) is impacted very differently than \( i_{\text{Disk}} \). As \( Q_{\text{MnOx}} \) varies within 0–2 mC, a proportional decrease in both \( i_{\text{Disk}} \) and \( i_{\text{Ring}}' \) can be seen, leading to an approximately constant ratio \( i_{\text{Ring}}'/i_{\text{Disk}} \) (Figure 3). For \( Q_{\text{MnOx}} > 2 \) mC, the ratio \( i_{\text{Ring}}'/i_{\text{Disk}} \) shows a sudden drop. We also observe a change in shape of the MnOx reduction wave as \( Q_{\text{MnOx}} \) increases above 2 mC: below 2 mC, a single, broad reduction peak is observed, which transforms into two peaks for \( Q_{\text{MnOx}} > 2 \) mC, with peak potentials shifting continuously more negative as the reduction charge increases (see also Figure S6 and Figure S7). The appearance of separate peaks may be due to proton diffusion becoming the limiting factor during film reductive dissolution.

Unfortunately, the quantification of \( i_{\text{OER}} \) and \( i_{\text{CER}} \) in the presence of Mn\(^{3+}\) is obfuscated by Mn-related redox processes, in contrast to the measurements on MnO\(_x\)-free IrO\(_x\) in Section 3.1, where it was assumed that OER and CER were the sole reactions. There are two reasons for this: first, \( i_{\text{Disk}} \) after subtraction of \( i_{\text{Ring}}' \) is no longer “pure” OER current but the sum of OER and MnO\(_x\) deposition current. Second, close inspection of the ring currents (Figure S4) suggests reduction of a species that appears at a potential slightly more negative than the onset potential of CER. We ascribe this additional current to the reduction of solution-phase Mn\(^{3+}\). This species originates from the disk and is a generally accepted intermediate during acidic MnO\(_x\) deposition. Ring currents can thus no longer be ascribed solely to CER (\( i_{\text{Ring}}' \neq i_{\text{CER}} \)). To take these two sources of error into account, we use the following correction. The diffusion-limited current density of MnO\(_x\) deposition \( (i_{\text{Disk}}) \) is estimated at 140 \( \mu \)A using the Levich equation (see the Supporting Information).

This value serves as an “upper limit” of the MnO\(_x\) deposition current during OER and CER. Likewise, the maximum ring current originating from Mn\(^{3+}\) reduction can be estimated at 70 \( \mu \)A, representing an upper limit of ring current falsely attributed to CER. For \( Q_{\text{MnOx}} < 2 \) mC, where \( i_{\text{Ring}}' > 1800 \mu \)A, we assume this error to be negligible, but at \( Q_{\text{MnOx}} > 4 \) mC, the remaining ring current approaches 30 \( \mu \)A. In this regime, the ring current may not be unambiguously assigned to CER, and the real CER current could be significantly lower.

To still make an estimation of OER versus CER selectivity, we assume the worst-case scenario in terms of OER selectivity: this translates to (i) assuming that MnO\(_x\) deposits with diffusion-limited current densities at all potentials, allowing the calculation of the minimum OER current after ring current subtraction, and (ii) assuming that the \( N_f \)-corrected ring current \( i_{\text{Ring}}' \) originates only from CER, irrespective of \( Q_{\text{MnOx}} \) leading to the maximum possible CER current. In other words, eq 3 applies, like the case for the “blank” IrO\(_x\) catalyst: 

\[
\epsilon_{\text{OER}} \approx i_{\text{Disk}} - i_{\text{CER}} - \frac{1}{i_{\text{Disk}}} = i_{\text{Disk}} - i_{\text{Ring}}' = -140 \mu \text{A}
\]

(7)

Figure 4 displays the calculated currents and selectivities toward OER and CER as a function of \( Q_{\text{MnOx}} \). As already suggested by the ratio \( i_{\text{Ring}}'/i_{\text{Disk}} \) in Figure 3, \( \epsilon_{\text{OER}} \) rises sharply at the expense of \( \epsilon_{\text{CER}} \) beyond a MnO\(_x\) reduction charge of 2 mC. We will refer to the reduction charge of the MnO\(_x\) film at which there is a strong shift of selectivity from CER toward OER as the “critical MnO\(_x\) charge”. Figure 4 shows that modification of IrO\(_x\) by growth of a thick MnO\(_x\) film makes it >90% OER selective with a moderate (45%) drop in activity.

The dependence of CER kinetics on MnO\(_x\) deposition can be studied by making Tafel plots based on measured ring currents (Figure S5), especially at high ring currents where the
error from Mn\textsuperscript{3+} reduction is negligible. On “bare” IrO\textsubscript{x} as well as during the initial stages of MnO\textsubscript{x} film growth (Q\textsubscript{MnO\textsubscript{x}} < 2 mC), CER Tafel slopes range within 40–45 mV/dec, suggesting a rate-limiting second electron transfer step controlling the CER mechanism, in correspondence with previous literature\textsuperscript{19,25}. The Tafel curves in this regime show good linearity, as determined from R\textsuperscript{2}-values in the inset of Figure 5. As Q\textsubscript{MnO\textsubscript{x}} increases beyond the critical charge, Tafel slopes increase to ca. 120 mV/dec. This value agrees remarkably well with a mechanism where the first electron transfer step becomes rate-determining, suggesting that the apparent kinetics of the reaction change. However, a pronounced departure from linearity is also apparent (Figure 5 inset), suggesting that the measured Tafel slopes become clouded by additional effects. Above all, we expect the error from Mn\textsuperscript{3+} reduction to be high here, and the measured Tafel slope may well be related to the solution phase oxidation of Mn\textsuperscript{2+} to Mn\textsuperscript{3+} on the disk (assuming a symmetry factor α of nearly 1/2).

To gain more insight in the sudden change in CER activity, we recorded ring–disk amperometry curves to study the potential-dependent deposition behavior of MnO\textsubscript{x} on IrO\textsubscript{x} (Figure 6). The ring currents in the lower panel were normalized versus their initial value (i\textsubscript{Rng,0}), to compare the relative decrease in CER for different potentials. An increase in E\textsubscript{Disk} has a 2-fold effect: (i) i\textsubscript{Disk} increases strongly, which is due to a rise in CER current (top panel), and (ii) CER rates start declining earlier (lower panel). It was previously postulated that MnO\textsubscript{x} deposition proceeds through a progressive electrochemical nucleation and growth mechanism, in which the current contribution from the growth of existing nuclei is larger than current from the formation of new nuclei.\textsuperscript{88–90} Our own findings suggest that MnO\textsubscript{x} deposition at 1.45 V on amorphous IrO\textsubscript{x} near pH = 1 is kinetically controlled and proceeds via a similar mechanism, since the deposition current shows an induction time followed by a peak (Figure S9). The observed drop in CER activity would then coincide with the moment where the exclusion zones of the individual MnO\textsubscript{x} nuclei intertwine and the full coverage of the IrO\textsubscript{x} surface by MnO\textsubscript{x} rapidly increases.

To corroborate the RRDE findings, we measured the competition of CER versus OER on IrO\textsubscript{x} and the effect of MnO\textsubscript{x} deposition using OLEMS. Since the use of a stationary electrode is required in the OLEMS setup, we used a stirrer bar at ~600 rpm to enhance mass transport of chloride and Mn\textsuperscript{2+} and reduce the effects of transient broadening of the diffusion layer. Despite this, mass transport to the surface was significantly lower than in the RRDE setup. To ensure a strong enough Cl\textsubscript{2} mass signal in the OLEMS and to reach MnO\textsubscript{x} film growth comparable to the RRDE experiments, a relatively high concentration of chloride (80 mM) and MnSO\textsubscript{4} (1.2 mM) was used. In Figure 7A, cyclic voltammetry was performed on an IrO\textsubscript{x}/GC electrode with a significant amount of MnO\textsubscript{x} predeposited at 1.460 V, after which three cycles were carried out in the potential region of mixed CER, OER, and MnO\textsubscript{x} deposition. The initial forward sweep starting from 1.460 V shows a relatively low maximum current, and the backward sweep shows a wave where the preformed MnO\textsubscript{x} layer is reductively removed. In scans 2 and 3, the IrO\textsubscript{x} electrode was scanned into the CER/OER region again, such that the electrode was free of preformed MnO\textsubscript{x}. Mass signals m/z 32 and m/z 70 (corresponding to O\textsubscript{2} and Cl\textsubscript{2}, respectively) were collected in the mass spectrometer during the scans. Both species have peaks in the mixed OER/CER region as expected, but there are major differences between the three cycles. The rate of Cl\textsubscript{2} formation is clearly suppressed during the first cycle, then strongly increases in cycles 2 and 3. The O\textsubscript{2} mass signal in the first scan shows significant trailing and is also higher than in scans 2 and 3. Comparison of results from scan 1 and scan 2 suggests that the emergence of CER activity is coupled to a decrease in OER activity. This appears to contradict the previous results from the RRDE method that OER and CER are independent. However, we want to note that the amount of chloride produced in cycles 2 and 3 was rather high, which was necessary to obtain a sizable m/z 70 signal, as the majority of produced Cl\textsubscript{2} dissociates and recombines in the ionization chamber to form HCl\textsuperscript{+}, mass signal m/z 36.\textsuperscript{61} It is thus highly likely that the collection efficiency of O\textsubscript{2} was affected by the vigorous chlorine evolution near the electrode surface. Nonetheless, we believe the most important result of the OLEMS measurements is the strong suppression of chlorine evolution in the first cycle, meaning that on an IrO\textsubscript{x}/MnO\textsubscript{x} electrode, O\textsubscript{2} is formed highly selectively.
In Figure 7C, current versus time curves were recorded at 1.50 V to investigate the effect of transient MnOx deposition, along with changes in O2 and Cl2 mass signals (Figure 7D). In the current profile, the semisteady current declines abruptly after ∼100 s, converging to a current of around 200 μA. The abrupt decline is reminiscent of results in Figure 6 and correlates with a selective decrease in the Cl2 signal.

3.3. Structure of the MnOx/IrOx Film. The results in the previous sections show that during mixed OER and CER on an IrOx electrode covered by a MnOx film, there is a decrease in oxidation current coupled to strongly enhanced selectivity of OER over CER with an increase of the coverage by the MnOx film, as well as a change in the apparent CER Tafel slope. Besides the origin of this selectivity shift, a relevant question concerns the degree to which MnOx is catalytically active under these conditions. OLEMS measurements on a MnOx/GC sample in an acidic solution, without IrOx present, showed no detectable activity for OER or CER (Figure S11), in accordance with previous literature. However, it has been reported that the crystal phase and oxide stoichiometry of MnOx as well as the existence of metal-support interactions can greatly affect the OER performance.62−65 We thus wanted to study the structure of the deposited materials.

For structural studies, films were grown hydrodynamically in ClO4− solutions in the presence of 20 mM Cl−, allowing use of the ring electrode to monitor the rate of chlorine evolution during deposition. An amount of MnOx was deposited such that the CER rate was approximately 50% of the initial value (Figure S12). The nature of the MnOx films in the following studies should thus be close to films corresponding to the critical MnOx charge of 2 mC discussed earlier. MnOx films grown in ClO4− and HSO4− electrolytes showed identical morphologies in SEM and likewise behavior of εCER versus QMnOx, suggesting that adsorption of HSO4− inhibits MnOx deposition but does not alter its mechanism (Figure S10).

Figure 8A shows a SEM micrograph of a representative IrOx/GC film, with a morphology corresponding well to previous reports.66−69 The GC surface is covered by a thin layer of nanoparticulate IrOx, as was revealed by drying-induced cracks of the film (see Figure S14B). We also occasionally observed mesoporous clusters of IrOx particles with diameters of 50−150 nm (Figure 8B). The clusters generally occupied less than 4% of the GC electrode surface, as estimated from SEM images of a large section of the electrode. Figure 8C and D show SEM micrographs of MnOx/IrOx/GC samples, the films grown in the presence of 20 mM Cl− and representing ”50% CER activity”: compared to MnOx-free conditions. A porous structure of thin intertwined sheets is visible on top of the IrOx particles and layer, which is composed of MnOx, as verified via energy-dispersive X-ray spectroscopy (EDS) analysis. From the SEM micrographs, the MnOx sheet thickness is within 8−10 nm (Figure S14A). MnOx deposited on GC in the absence of IrOx forms a similar structure (Figure S14C). The MnOx morphologies resemble earlier SEM results of δ-MnO2 (Birnessite), a poorly crystalline polymorph of MnO6 octahedra arranged as sheets (see also Figure S14D for micrographs of MnOx formed during extended deposition times).70−73 However, we cannot draw conclusions about the MnOx structure on the basis of SEM morphology alone.

Figure 7. OLEMS measurements of an IrOx/GC disk electrode in 0.5 M KH2PO4, 80 mM KCl, and 1.2 mM MnSO4 (pH = 0.89). (A) CVs of the electrode after preconditioning for 450 s at 1.46 V, followed by three scans. Scan rate: 5 mV s−1. (C) Amperometry at 1.500 V for 600 s. (B and D) Corresponding OLEMS mass signals over time. Solution is saturated with Ar. A stirrer bar at ∼600 rpm was employed to increase mass transport.

Figure 8. SEM micrographs of representative electrodes used in this study. (A and B) IrOx/GC electrode, deposited according to the procedure described by Nakagawa et al. (C and D) MnOx/IrOx/GC electrode; MnOx was deposited onto IrOx/GC as described in the text.
We attempted to take XRD spectra of IrO$_x$ and the combined Mn/Ir oxide, using samples as-deposited on GC (see Figure S13). Besides the GC background, no diffraction peaks were observed, suggesting that the IrO$_x$ and MnO$_x$ are amorphous. Previous studies of hydrated IrO$_x$ colloids, as well as MnO$_x$ deposited at constant potential, also reported amorphous structures.$^{62,69,74,75}$ We must note that the films may be too thin to lead to sufficient signal in the diffractometer, although an attempt was made to compare the diffraction patterns to a small quantity of highly crystalline RuO$_2$. Alternatively, IrO$_x$ nanoparticles were precipitated and isolated from acidified colloid solutions. Even when scanning such bulk samples, we could not observe XRD peaks.

To obtain more structural information on the MnO$_x$/IrO$_x$ samples, we performed TEM measurements along with EDS and selected-area electron diffraction (SAED). Figure 9 shows bright-field TEM micrographs of a MnO$_x$/IrO$_x$ film that was carefully scraped off the GC electrode. IrO$_x$ nanoparticles with a diameter of 2−4 nm as well as occasionally larger particles were visible (Figure 9A and B), similar to results from Zhao et al.$^{66}$ Like the SEM results, a veinly MnO$_x$ deposit could be seen (verified by EDS); the ~8 nm thick sheets were visible in the microscope (Figure 9D). Despite the much higher diffraction cross-section in comparison with XRD, most SAED experiments led to diffuse patterns. We could sporadically obtain better defined radial profiles, roughly corresponding to rutile-IrO$_2$ (Figure 9C).$^{67}$ In the microscope, a rare instance of a crystallite that was also properly oriented showed a $d$-spacing of 3.18 Å, corresponding to the rutile IrO$_2$ (110) plane.$^8$ We also generated SAED patterns at higher beam accelerating voltages of 200 keV (Figure S17), the result of which showed sporadic rutile-related diffractions from IrO$_2$ and $\beta$-MnO$_2$. Unfortunately, significant contributions from metallic Ir (and possibly Mn) were also present, likely due to beam radiation damage.$^{79}$

To probe the electronic structure and the extent of interaction between the two oxides, we performed ex-situ XPS on a representative MnO$_x$/IrO$_x$/GC film, as well as on single oxide reference samples termed MnO$_x$/GC and IrO$_x$/GC. Core-level Ir 4f scans were performed, as this peak is considered a reliable probe for determining the average Ir oxidation state.$^{78,80,81}$ The magnitude of the Mn 3s peak multiplet splitting serves a similar function in Mn.$^{82,83}$ Additional narrow spectra of the O 1s and Cl 2p peaks are shown in the Supporting Information (Figure S19 and Figure S20).

Figure 9. TEM micrographs of a MnO$_x$/IrO$_x$ film that was grown identically to the films used for SEM in Figure 8, then carefully scraped off the GC support for imaging. (A) Sheets of amorphous IrO$_x$ particles, having diameters in the range of 2−4 nm. (B) Larger IrO$_x$ particles (diameter ~60 nm) within the film. (C) SAED pattern of the area shown in B. Diffuse diffraction rings corresponding to rutile IrO$_2$ are visible. The also present MnO$_x$ does not generate a clear contribution to the pattern. (D) Intertwined MnO$_x$ sheets perpendicular to the beam direction, as also seen in SEM micrographs.

Figure 10. Core-level XPS scans of the Ir 4f (left) and Mn 3s (right) spectral peaks, on an absolute intensity scale. Both elements were scanned in samples of their MnO$_x$/GC single oxides (top panels) and the mixed MnO$_x$/IrO$_x$/GC sample (lower panels). Note the difference in scale in the lower left-hand panel, illustrating the relatively low intensity of the Ir 4f signal.
(Figure S18). Most of the signal originates from the MnOx overlayer, as was also verified from the appearance of a large O 1s contribution at 529.9 eV, and by comparing Mn:Ir ratios determined from XPS and amperometry deposition data (Table S1). We could nonetheless still observe the Ir 4f peak, with a peak fitting-derived binding energy of approximately 62.5 eV (see Figure 10), a shift of +0.1 eV relative to IrOx/GC. The signal intensity was too weak for a more elaborate peak deconvolution. A relevant question is whether the Ir sites contributing to the weak Ir 4f peak are covered by MnOx, which was suggested by the SEM measurements. The reductive charge Qmed of grown MnOx films corresponds to a layer roughly 10 nm thick, approaching the limit for the detection depth of XPS. The weak Ir 4f peak in the sample shows a strong prevalence of inelastic scattering in the form of tailing at higher binding energies and a rise in background scattering that is disproportionately higher than the IrOx/GC reference (Figure S21). We thus assume that the weak XPS Ir 4f peaks originate from subsurface Ir and that this Ir must be in intimate contact with the MnOx layer. The Mn 3s peak splitting in MnOx/IrOx/GC is 5.2 eV, a difference of +0.1 eV with respect to the MnOx/GC reference sample. This shift may indicate a lowering of the average oxidation state, but the shift is small and negligible within the margins of experimental error (±0.1 eV).

Summarizing our structural studies, we find that the formed MnOx and IrOx are amorphous and probably form non-stoichiometric oxides. The MnOx catalyst without IrOx showed no activity in OLEMS, and we could also see no evidence of a strong interaction between Mn and Ir from the almost identical Ir 4f binding energies and Mn 3s multiplet splitting in XPS.

This makes it doubtful whether the close proximity of and interaction with IrOx could somehow activate MnOx for OER.

3.4. Isotopically Labeled OLEMS Measurements and OER Studies on an RDE. Given the lack of electronic interaction between MnOx and IrOx suggested by the detailed characterization described in the previous section, we undertook isotopically labeled OLEMS measurements to further probe the origin of the OER/CER selectivity of the MnOx/IrOx/GC electrode. We also looked more closely into the OER behavior of the selective catalyst using RDE experiments.

In Figure 11A and B, we performed isotopic labeling experiments on MnOx/IrOx/GC in an attempt to determine the origin of the oxygen produced by the catalyst. This is made possible by the tendency of oxygen of the IrOx lattice to participate in the OER mechanism. First, the IrOx lattice oxygen was partially exchanged with the 18O isotope by performing OER in a 0.1 M KH2SO4 solution of “marked water” (H216O). MnOx was then grown in “regular water” at 1.45 V (a potential just before the OER onset), and OLEMS measurements were performed on this Mn16Ox/Ir18Ox/GC electrode. By observing changes in the ratio of mass/charge signals 34 and 32,77 we were able to determine whether the oxygen formed originated from MnOx (leading to 18O2) and no enrichment in the m/z 34 signal) or Ir19Ox (partially producing 18O16O and changing the 34/32 ratio). At this point, 18O2 can also be formed; unfortunately, the mass charge ratio of this species (m/z 36) coincides with that of HCl, a species formed in the ionization chamber, and as such this signal is ambiguous. As can be seen in Figure 11B, the catalyst shows an enrichment of 18O during OER in the first scan. The produced oxygen thus at least partially originates from the subsurface IrOx layer. The
Side-View (C) Showing the Isotopic Labeling Experiment in Figure 11A and B, despite the existence of a MnOx layer. 

we interpret as chloride being unable to penetrate the MnOx containing solution) and neither did MnOx/IrOx/GC, which what was previously assumed (at least implicitly), our results or OER at pH very little electronic interaction between MnOx and IrOx, it is S11). Combined with the XPS measurements that indicate agreement with previous literature.39,40 However, contrary to MnOx/GC in the absence of IrOx is not active for either CER or OER at pH ~0.9, even at high potentials of 1.8 V (Figure S11). Combined with the XPS measurements that indicate very little electronic interaction between MnOx and IrOx, it is therefore highly unlikely that MnOx “takes over” OER and CER catalysis from IrOx when it is deposited. Another feature that strongly disfavors MnOx being the active catalyst is the OER ability seen in Figure 11C. The MnOx/IrOx/GC electrode displayed an OER current of nearly 5 mA at this stage seems to solely inhibit CER, whereas OER remains relatively unaffected, suggesting that at this point the film growth is intrinsically different from its initial deposition stage.

When “fully grown”, the amorphous MnOx film still seems to allow transport of H2O, H+, and O2 between IrOx and the electrolyte. The decreased selectivity versus CER can thus be explained on the basis of concentration overpotentials, in line with recent reports on electrolytically at “buried interfaces” by Takanabe et al.94 and Esposito et al.95,96 The slow transport of chloride through the MnOx phase means that near the buried IrOx interface both the chloride diffusion coefficient and concentration gradient are lowered. This leads to a significant increase of the diffusion layer thickness and an effective increase in the CER overpotential. We further verified the anion-deflecting behavior of MnOx by performing OER using a MnOx/IrOx/GC catalyst in the presence of bromide ions (Figure S22). In a fashion analogous to Section 3.1, we used the Pt ring as a probe for bromine reduction. We found that the blocking of the bromine evolution reaction is strongly coupled to the presence of the MnOx film. Lastly, the effect of MnOx deposition on CER selectivity was verified using a Pt disk electrode as CER catalyst (Figure S23). A MnOx/Pt electrode evolved insignificant amounts of Cl2, whereas the OER onset could be seen near 1.7 V, which is reminiscent of the previously reported OER onset on bare Pt.97

IrOx was also present in the MnOx-based seawater anodes by Hashimoto et al., for which thick heterometal-doped MnOx,

**3.5. General Discussion on the Origin of the OER/CER Selectivity.** From the above results, we conclude that a MnOx film facilitates the selective formation of O2 over Cl2 in agreement with previous literature. However, contrary to what was previously assumed (at least implicitly), our results show that MnOx is not actually a catalytically active phase. This conclusion is in fact in agreement with previous literature: MnOx is generally not very active for OER in strongly acidic media (pH < 1) and certainly cannot be expected to show significant activity within the potential window employed in this work.97,44,60,68,69 From the OLEMS results, it is clear that MnOx/GC in the absence of IrOx is not active for either CER or OER at pH ~0.9, even at high potentials of 1.8 V (Figure S11). Combined with the XPS measurements that indicate very little electronic interaction between MnOx and IrOx, it is therefore highly unlikely that MnOx “takes over” OER and CER catalysis from IrOx when it is deposited. Another feature that strongly disfavors MnOx being the active catalyst is the OER ability seen in Figure 11C. The MnOx/IrOx/GC electrode displayed an OER current of nearly 5 mA at this stage seems to solely inhibit CER, whereas OER remains relatively unaffected, suggesting that at this point the film growth is intrinsically different from its initial deposition stage.

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coatings were grown on Ti-supported IrOx (IrOx/Ti). The IrOx was added with the intention of preventing the formation of insulating TiO2 during electrode operation. We believe the OER-selective Mn,M(1−y)Ox/IrOx/Ti anodes operate in a similar fashion to our MnO2/IrOx/GC catalyst under study and that the IrOx layer may have been crucial for the relatively low polarization resistance during the galvanostatic experiments. The OER selectivity effect of different dopants may have been due to modified MnOx film stability or morphology under the strongly oxidizing operating conditions.

Application of selective blockage of chloride in seawater electrolysis was recently demonstrated by Ravichandran et al.98 An analogous case of selectivity induced by a catalytically inert film is likely at hand in the industrial chloride process, where Cr(OH)3-coated cathodes are used for selective hydrogen evolution.13,99,100 The H2-selectivity of the chromium film has been suggested to stem from the selective blocking of dissolved ClO−anions and oxygen. Interestingly, MnOx has been recently suggested as a promising alternative to the use of Cr(VI) for the selective hydrogen evolution.101

4. CONCLUSION

In this work, we have investigated the unusual OER over CER selectivity of MnOx-based anodes in the context of hydrogen production from acidic saline water electrolysis. Deposition of a thin MnOx film onto glassy carbon-supported IrOx moderately decreases the catalytic activity and strongly shifts the product selectivity from Cl2 toward O2 once a critical MnOx film charge Q_mdox, of approximately 2 mC (10 mC cm−2) is reached. The MnOx deposit is catalytically inactive and instead seems to function as a diffusion barrier that prevents Cl− from reacting on the IrOx catalyst underneath, while still facilitating the transport of water, protons, and O2 between IrOx and the electrolyte, necessary for OER activity. The results of this work fit in an emerging trend of using diffusion barriers to affect selectivity. This may be a promising approach in practical brine electrolysis, in contrast to finding an OER catalyst that breaks the intrinsic scaling between selectivity and activity.

ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05382.

Detailed information regarding used chemicals and experimental procedures; supplementary electrochemical and structural data (PDF)

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Notes
The authors declare no competing financial interest.

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