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Trace anodic migration of iridium and titanium ions and subsequent cathodic selectivity degradation in acid electrolysis systems.

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Summary:

The oxygen evolution reaction in acidic electrolyzers requires the presence of stable catalysts and current collectors at the anode. IrO₂ catalysts and Ti current collectors are among the best in this regard. We show evidence of iridium and titanium corrosion and subsequent membrane crossover in long-term experiments of proton-exchange membrane electrolyzers for H₂O₂ production. The accumulation of trace iridium at the cathode was linked to degraded performance and increased cathodic current from hydrogen evolution. Detection of trace metal content at the cathode electrodes was enabled by prompt-gamma ray activation analysis and neutron activation analysis. These findings are not just relevant for H₂O₂ electrolyzers but to any system using iridium-based anode catalysts, including CO₂ electroreduction.

1. Introduction

Electrocatalysis plays a central role in clean energy conversion, enabling a number of sustainable processes.[1] This includes the production of industrial chemicals which has an energy demand that is projected to grow 40 percent from 2016-2040 and today is mainly based of fossil resources.[2] Specifically, decentralized electrochemical devices have potential to contribute to a sustainable future by synthesizing chemical commodities onsite via electrolysis.[3,4] These chemical commodities include ammonia, hydrogen, reduced carbon-based compounds and hydrogen peroxide. Proton-exchange membrane (PEM) electrolyzers are generally considered advantageous for decentralized production owing to operation at higher current densities and better stability towards load-cycling and shutdown as compared to alkaline electrolyzers. IrO₂

catalysts are commonly used at the anode of proton-exchange membrane (PEM) electrolyzers for the oxygen evolution reaction, and understanding the consequences of their degradation is of critical importance to the advancement of these technologies. [5–8]

Figure 1. A schematic of the two-electrode set-up of electrolyzer for H₂O₂ production used to study performance degradation. Deionized water is flowed through both the cathode and anode chambers at 0.2 ml/s each. Oxygen gas is flowed through the cathode chamber at 0.3 l/min. The oxygen evolution reaction (OER) is catalyzed by IrO_x in the anode chamber. The oxygen reduction reactions (ORR) are catalyzed in the cathode chamber yielding H₂O₂ and H₂O.

While IrO₂ is an exceptionally stable catalyst in acid, it can still corrode in the highly oxidizing environment of a PEM electrolyzer anode.[9–12] In addition, titanium is commonly used as a current collector in PEM systems and is also susceptible to corrosion.[13–16] It has been further shown that the resulting metals ions from corrosion have migrated into the Nafion polymer of membrane electrode assemblies (MEA).[17–20] Trace contaminants can degrade the electrochemical selectivity of oxygen reduction reaction (ORR) electrodes.[21,22] Specifically, it has long been understood that iridium can reduce H₂O₂ via ORR on the cathode.[26] Therefore, the migration and subsequent contamination of iridium to an H₂O₂-producing electrode would result in degraded performance and show evidence to a novel degradation phenomenon that is undesirable to any electrolyzer system selectively producing chemicals other than H₂.

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H₂O₂ is an environmentally-friendly oxidant that can be electrochemically produced.[27] Production of H₂O₂ by electrolysis of oxygen from air and water using proton-exchange membrane (PEM) systems has been suggested via the two-electron ORR process selectively catalyzed on the cathode gas diffusion layer (GDL).[3,28–30] Such a PEM system has the advantage of needing just water, air, and electricity at ambient conditions for H₂O₂ synthesis (Figure 1) without any need for consumables. The presence of trace iridium and titanium contaminants on the cathode is speculated to be a cause of degradation to H₂O₂ selectivity. It is therefore an important diagnostic to understand the level of crossover of metallic ions through the proton-exchange membrane. The literature on PEM reactor degradation mechanisms is focused on H₂ electrolysis and H₂ fuel cells, where this iridium contamination would be irrelevant in similarly active Pt-based cathodes.[19,22,31] Here we present the trace contamination of electrochemically active iridium on ORR cathodes in H₂O₂ PEM-electrolyzers (Figure 1), which is a general problem for any PEM electrolyzer system not producing H₂ and is especially relevant in the field of CO₂ electroreduction. [23–25]

Trace amounts of contaminant metals at the ORR catalyst remains a challenge to detect and quantify.[21] Commonly-used surface characterization techniques, such as XPS and EDX, have limited sensitivity. Measuring the hydrogen evolution reaction (HER) of the system would, in principle, give an indirect measurement of the undesirable iridium contaminants present, in the case where iridium is more active for HER than the cathode catalyst.[32] Inductively coupled plasma-mass spectrometry (ICP-MS) can measure trace metals in the low ppb range but is limited to dissolved samples. The accuracy of ICP-MS analysis of solid samples is thus limited by the pretreatment process.[21] Prompt gamma-ray activation analysis (PGAA) and neutron activation analysis (NAA) are highly-sensitive, non-destructive quantitative analytical techniques. NAA has been used for the determination of iridium in geological samples in the ppb to ppt range,[33] while PGAA is unique for the analysis of light elements, i.e., the elements in nafion. Thus their combination (in-beam activation analysis) is suitable for the determination of iridium and titanium in organic matrices. Using ICP-MS, HER I-V, and PGAA/NAA, we investigate the trace metal anodic corrosion and subsequent nafion membrane migration and crossover in long-term, ambient-temperature experiments of H₂O₂ PEM electrolyzers with varying degrees of degrading performance.

2. Results and Discussion

2.1 Confirmation of Iridium and Titanium crossover via ICP-MS analysis

Iridium and titanium crossover was initially investigated by analyzing the metal content of the cathodic effluent via ICP-MS. In order for the detected iridium and titanium in the cathode effluent to be representative of anodic crossover, components containing these metals were not used in the cathode chamber (refer to Figure 1). Specifically, niobium substituted the titanium as the cathode current collector. The metal content of the cathode effluent in operation would therefore be a measure of the anodic

crossover rate of iridium and titanium. Cathode effluent flow was collected over two minutes and its mass was measured to determine a flow rate. These same samples were analyzed with ICP-MS (details are included in the supplementary information). Samples were collected at least 48 hours after rampup to avoid the elevated signals from the galvanic steps.[34] Figure 2A-B summarizes these results, showing that metal crossover is correlated with ORR current density. ORR current density was controlled by setting the potential at 1.84 V_{set-point} or 2.20 V_{set-point} ('■' data points' at 87 mA/cm² and 230 mA/cm² respectively). It has been established that higher potential and currents results in more iridium dissolution in cyclic voltammetry experiments.[34][35] It is therefore presumed that higher dissolution is occurring in the 2.20 V_{set-point} experiments compared to 1.84 V_{set-point} experiments. In addition, higher current densities translates to a larger flux of protons and water through the nafion membrane which could result in more metal species crossing over. In contrast to the short CV dissolution experiments that have been established, we observe metal crossover in a PEM electrolysis cell held at a constant potentials with consistent currents over longer periods of time.

Figure 2. Metal content of the cathodic effluent as a function of varying ORR current densities. The rate of iridium (A) and titanium (B) species that crossover and result in the cathodic effluent was expressed in terms of 'metal contaminant flow (ng h⁻¹)' which is determined by the product of the cathodic flow rate and the metal content (g h⁻¹)*(ppb) = (ng h⁻¹). Cathodic flow rate is determined by mass collected over two minutes and metal content of cathodic effluent was determined via ICP-MS. All setups used a niobium cathode current collector. The ■ are hotpressed setups with the 1.84 V_{set-point} at 87 mA/cm² and the 2.20 V_{set-point} at 230 mA/cm². The ▼ are non-hotpressed GDL setups that were later used for PGAA/NAA. Lines are added to guide the eye.

2.2 Confirmation of Iridium contamination via HER

Following that iridium does pass through the membrane and exits the electrolysis cell with the cathodic effluent water, the next step is to establish to which degree iridium would redeposit to the cathode electrode as the system's performance degrades during operation. Given that the HER activity of iridium is higher than the cathode catalyst, an increasing amount of electrochemically active iridium present on the cathode should lead to a higher HER current. We therefore measure HER activity of the electrodes after operating at different ORR currents over the same amount of time.

The characterization of a degrading system's loss of H_2O_2 selectivity with an increasing HER current density was investigated in two parallel experiments operated for 975 hours without any significant ORR current density loss (Figure S1). The loss of electrochemical H_2O_2 selectivity is represented as normalized faradaic efficiency. Normalized faradaic efficiency (NFE) is the ratio of an experiment's final faradaic efficiency divided by its initial faradaic efficiency. The HER current density was measured by switching the cathodic gas input to N_2 , effectively eliminating ORR activity. HER current densities were measured across a range of potentials (1.65-2.05 V_{setpoint}) that were corrected for ohmic drop based on high-frequency resistance (HFR) measurements and the interpolated value at 1.95 $V_{\text{HFR-corrected}}$ was used to compare HER current densities between two different set-ups (refer to supplementary information for more details). The two parallel experiments were run for 975 h at 1.84 V_{setpoint} and 2.20 V_{setpoint} resulting in a passed total ORR charge of 5.10×10^4 coulombs and 1.28×10^5 coulombs, respectively (Figure 3). The system subject to more ORR charge had lower NFE, and more HER current density. This suggests that electrochemically HER active iridium contaminants are accumulating on the cathode GDL during operation, and they are contributing to the H_2O_2 selectivity loss over time.

Figure 3. The hydrogen evolution reaction (HER) current density at the interpolated 1.95 $V_{\text{HFR-corrected}}$ and normalized faradaic efficiency of two experiments subject to differing amounts of ORR charge over a 975 h period. HER current density was measured by switching the cathodic input gas to N_2 and measuring current in .05 V increments from 1.65-2.05 V_{setpoint} and corrected for ohmic drop.

Higher HER current density after operating at higher ORR current densities leaves the question if accumulating iridium contaminants are the actual cause, since these trace amounts cannot be detected by XPS or EDX (Figure S5-8). In addition, it is unclear whether accumulating titanium contaminants are present and facilitating the degradation of NFE.

The quantification of trace iridium and titanium contaminants that have accumulated on the cathode catalyst GDL samples with varying levels of degradation was investigated. Six cathode GDL samples with different degrees of degradation were prepared for the PGAA/NAA experiment in order to quantify the iridium and titanium content of the cathode GDL (Table 1). Samples 1 and 2 were stopped after 48 (± 2) hours of operation to control for any effects during the ramp-up and initial operation. Samples 1 and 2 were used as backgrounds to isolate the degradation from when the initial H_2O_2 faradaic efficiencies are measured, where effectively zero degradation has occurred. Sample 3 was the low current density experiment where some NFE degradation and HER current density increase was expected. Sample 3 could be compared to the high current density experiments operating for similar lengths of time. Sample 4 and 5 were the high current density experiments where significant NFE degradation and HER current density increase were expected. Given that samples 4 and 5 had similar HFR measurements (Table S1), it is assumed that the difference in ORR current density was due to the complications of the assembly of the non-hot pressed cathode, where proper electrochemical contact isn't ensured without the heat-pressing procedure. Metallic content of cathodic effluent of samples 3-5 are summarized by the '▼ data points' in Figure 2. In addition, a blank sample, which was not used in any system, was used as a background for the analysis. Further details of these six samples are described in Table S1 and with ORR current profiles depicted in Figure S2 (see supplementary info).

Table 1. The six samples that were prepared for PGAA/NAA analysis

Sample Name	Net ORR charge ($\text{A} \cdot \text{s} \cdot \text{cm}^{-2}$)	Voltage set-point ($V_{\text{set-point}}$) ^[b]	Average ORR current density ($\text{mA} \cdot \text{cm}^{-2}$) ^[c]	Time (h)
Blank ^[a]	-	-	-	-
Sample 1	5.4×10^3	1.84	32	46
Sample 2	5.5×10^3	1.84	32	48
Sample 3	4.0×10^4	1.84	34	323
Sample 4	8.5×10^4	2.20	79	352
Sample 5	1.05×10^5	2.20	97	326

[a] The blank sample was not included in any set-up.

2.2 Confirmation of trace Iridium and titanium contamination via PGAA/NAA

Non-hot pressed cathode assemblies were necessary in order to ensure the integrity of the GDL and catalyst layer for analysis, and a cathodic niobium current collector was used to ensure that the titanium detected via PGAA would best represent the titanium crossover from the anode side. The samples (150-200 mg, 30x30x0.2 mm) were irradiated in the cold neutron beam of the PGAA facility with the flux of $3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ for 8–10 h. During the irradiations, the prompt gamma spectra were acquired using a high-purity germanium detector.[36] The activated samples were then counted off-beam. The spectra were evaluated as described in Ref.[37] The elements detected in samples 1-5 are summarized in Table S2 (included in the supplementary information).

Figure 4. Iridium content (■) of cathode samples determined by neutron activation analysis (NAA) and normalized faradaic efficiency (⊠) of the cathode samples as a function of the coulombs the samples are subject to. Lines are added to guide the eye.

Figure 5. Average metal crossover rates of iridium (A) and titanium (B) as a function of the ORR charge the samples are subject to. Metal crossover rate resulting in the cathode effluent was determined by ICP-MS. Metal crossover rate resulting in the GDL cathode was determined by dividing the metal content determined by PGAA/NAA with the experiment times of around 300 hours. The metal content of the initial ramp-up 5000-coulomb samples were subtracted from GDL samples to correct for any bias during ramp-up of the experiment.

The samples subjected to higher ORR charge exhibited lower normalized faradaic efficiency for H_2O_2 and higher iridium content quantified by PGAA/NAA (Figure 4). While, sample 4 and sample 5 were intended to be replicates, the lower ORR current in sample 4 is likely due to the poorer electrochemical contact of the cathode, and still provides useful data. Neither the ORR charge nor the normalized faradaic efficiency appeared to be linked to the titanium content determined by PGAA (Figure S3). This can also be observed in the inconsistencies from the non-hotpressed samples in Figure 2. This suggests that titanium species are neither facilitating HER nor H_2O_2 degradation.

Additionally, a comparison between the metal crossover contaminants in the cathode GDL and cathode effluent was made. Across all ORR charges values, more than 99% of the iridium adheres to the cathode GDL rather than flowing out with the cathodic effluent (Figure 5A). In contrast, the titanium adherence to the cathode GDL and the titanium flowing out with the cathodic effluent are within the same order of magnitude. This rationalizes the noise in the ICP-MS measurements and suggests that ICP-MS might not be suitable in most cases for diagnosing iridium crossover that adheres to the cathode GDL.

Figure 6. Hydrogen evolution reaction (HER) current density at the interpolated $1.95V_{\text{HFR-corrected}}$ as a function of the iridium content of the GDL cathodes detected by neutron activation analysis (NAA). A line is added to guide the eye. The data point with zero grams of iridium is represented by the average of six cathode GDL's from a similar batch to the blank sample analysed in the PGAA/NAA experiment. HER current density was measured by switching the cathodic input gas to N_2 and measuring current in .05 V increments from 1.65-2.05 V_{setpoint} and corrected for ohmic drop.

After PGAA/NAA measurements, the cathode GDL samples were hot-pressed into new MEA's to assess performances and perform HER I-V curves to evaluate the electrochemical activity of the iridium contaminants. HER I-V curves were measured between 1.65-2.05 V_{setpoint} (see Figure S4). Figure 6 shows that the samples with higher iridium content have higher HER current densities at $1.95 V_{\text{HFR-corrected}}$. It should be noted that the HER current densities cannot account for all of the degraded H_2O_2 current density that results in a loss of normalized faradaic efficiency. Given that the HFR of the degraded samples was higher (Table S2), it could be possible that metals trapped inside the membrane are facilitating HER. These metals potentially trapped in the membrane would not have been represented in the HER measurements because a new membrane and iridium anode was used. It should also be noted that the degraded performances remained constant after replacing the iridium anode (Table S1). This suggests that this degradation phenomena observed is purely in the cathode.

Iridium dissolution has been extensively established in literature with stability benchmarks being made.[38,39] There has been a large focus on stability in conjunction with activity. However, the trace dissolutions accumulating on the cathode is one of the leading causes of degradations. Rather than short-term cyclic voltometry experiments, long-term chronoamptometry experiments between 100-200 mA/cm^2 focusing on mitigating this trace dissolution and crossover should be explored. Specifically, optimizing a form of iridium catalyst for these relatively lower current conditions where significant loss OER performance would likely not be detected. Another solution could be the modification of the nafion membrane to block metal crossover.[40] This is assuming that this blocked metal accumulation in the membrane does not introduce another problem entirely.

It is emphasized that the total current of these experiments remains mostly constant despite gaining HER current, and losing NFE. This suggests that the source of the lower NFE might be a chemical catalyst facilitating H_2O_2 degradation, such as a Fenton's reagent. Other speculations include the iridium ions depositing in a way that would alter two 2-electron sites into a 4-electron site or H_2O_2 oxidizing the carbon GDL, affecting its functionality. One source of error in these measurements includes the assembly of the MEA and prototype because it cannot be guaranteed that the iridium contaminants return to electrochemical contact. In future experiments, HER I-V measurements should be performed prior to the PGAA/NAA measurements, in the same MEA and two-electrode set-up.

3. Conclusion

In conclusion, iridium and titanium crossover and subsequent cathode contamination has been quantified both in the effluent and in the cathode GDL using ICP-MS and PGAA and NAA, respectively. The rate at which this trace iridium accumulates on the cathode is current density dependent, and linked to the performance degradation of the system. Furthermore, HER current density confirms that at least a portion of these iridium contaminants are electrochemically active. Since HER is a highly undesirable side reaction when the cathode is used for chemical production other than hydrogen, this is a general problem. Electrochemically active iridium contaminants are especially relevant in the field of CO_2 electroreduction, where less-active catalysts are operating at very negative overpotentials, resulting in the undesirable competition of HER. [23–25]

Experimental Section

The experimental section is provided in full detail of the supplementary section.

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Keywords: Electrochemistry • Electrolysis • Oxygen evolution • PEM • PGAA

Data Availability

The processed data to reproduce these findings are included in the supplementary information. The raw data to reproduce these finding cannot be shared at this time due to legal reasons and technical limitations.

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Graphical Abstract

Context and Scale

Decentralized electrochemical devices using proton-exchange membranes (PEM) can sustainably synthesize industrial chemical commodities onsite via electrolysis. IrO_2 catalysts are commonly used in PEM electrolyzers, and understanding the consequences of their inevitable corrosion is of critical importance to the advancement of these technologies. Specifically, the iridium ions migrating across the PEM and subsequently contaminating the working electrode is a fundamental degradation mechanism for the selective electrochemical production of chemicals other than H_2 . Previous literature on degradation mechanisms in PEM devices is focused on H_2 electrolysis and H_2 fuel cells, where this contamination would be irrelevant.

We report the trace anodic metal crossover through the proton exchange membrane and the subsequent accumulation on the oxygen reduction reaction cathode in H_2O_2 electrolyzers. The trace iridium contaminants were detected in electrode samples of varying degradation with neutron activation analysis and prompt gamma ray analysis (NAA/PGAA). The electrochemical activity of these iridium contaminants was determined by measuring the hydrogen evolution reaction. The trace electrochemically active iridium contaminants was linked to a loss in H_2O_2 selectivity. This undesirable phenomena is applicable to similar systems that are selectively electrochemically producing chemicals, including CO_2 electroreduction.