

Opinion

# Measurements of Dioxygen Formation in Catalytic Electrochemical Water Splitting

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**Abstract:** Water oxidation is a multielectron complex reaction that produces molecular oxygen as the final product. The article addresses the lack of confirmation of oxygen product formation in electrochemical oxygen evolution reaction (OER) studies, despite the extensive research conducted on catalysts for water splitting. It critically evaluates the trend observed in many studies that solely rely on electrochemical methods for OER quantification without confirming the oxygen product via complementary analytical techniques. The omission of measuring evolved oxygen gas leaves a crucial gap in the quantification of the OER process and raises concerns about the validity and accuracy of reported results. Analytical techniques, such as gas chromatography, Rotating Ring-Disk Electrode (RRDE), fluorescence oxygen probes, Clark electrode, and volumetry are critically analyzed and described to ensure the reliability and credibility of voltammetry and bulk electrolysis to provide a more accurate assessment of the OER process.

**Keywords:** electrochemical catalysis; water oxidation; quantification of dioxygen yield

## 1. Introduction

The conversion of solar light to chemical energy is considered to be the ultimate solution in quickly accommodating the demand for energy by human civilization. Water splitting into oxygen and hydrogen powered by the Sun is a sustainable source of energy. The electrolysis of water is one of the most promising ways to generate hydrogen. Water splitting consists of two half-reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Both processes proceed only in the presence of catalysts. There have been numerous articles published in this and other journals on the investigation of electrochemical oxygen evolution reaction (OER) using a vast array of catalysts. While these articles contribute to the understanding of OER, it is important to critically evaluate the trend observed in many of these studies—the lack of measurement and confirmation of oxygen product formation during the electrochemical OER. One of the recently published papers [1] triggered the writing of this review. We checked all the publications in *Catalysts* in 2022–2023 related to water electrolysis and we were surprised by the number of papers claiming a high catalytic activity of their materials without confirming dioxygen formation in electrolysis [1–10]. This journal is not an exception. A similar trend was found in other journals. By examining this collective lack of confirmation, we can better understand the potential limitations and uncertainties associated with the published OER studies. The studies mentioned above [1–10] have focused on evaluating OER performance using electrochemical methods, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), or chronoamperometry. However, the omission of measuring the evolved oxygen gas, either directly or indirectly, leaves a crucial gap in the quantification of the OER process. The lack of confirmation regarding oxygen formation raises concerns about the validity and accuracy of the reported results. While electrochemical techniques provide valuable information about current densities, overpotentials, and Faradaic efficiencies, they cannot directly



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measure the oxygen gas evolution. Relying solely on electrochemical measurements for OER quantification may lead to potential misinterpretation of the data and compromise the reliability of the conclusions drawn from these studies [1–10]. Complementary analytical techniques are necessary to ensure the validity of the electrochemical results. A comprehensive understanding of the OER process requires a multi-faceted characterization approach that encompasses both electrochemical measurements and direct confirmation of oxygen product formation. Neglecting complementary analytical techniques, such as mass spectrometry, gas chromatography, or other spectroscopic methods, limits the ability to fully evaluate the performance of OER catalysts and may overlook important aspects of the reaction mechanism and kinetics. To ensure robust conclusions and a comprehensive understanding of OER, it is crucial to incorporate analytical techniques that directly confirm the evolved gases. This cross-validation of electrochemical measurements with direct oxygen product quantification can enhance the reliability and credibility of the reported results. By including these additional analyses, researchers can validate the electrochemical data and provide a more accurate assessment of the OER process.

Water splitting is a mature field in chemistry and the current state of the art requires that all papers claiming water oxidation must include not only the confirmation of oxygen formation but the measurements of Faradaic efficiency of OER. The same is valid for HER, but this process is not the subject of the present article.

## 2. Discussion

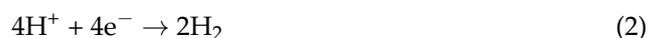
### 2.1. Problems in Electrochemical Water Oxidation Studies

A half-cell multi-electron water oxidation process releases four electrons and four protons to form each molecule of oxygen (O<sub>2</sub>) as shown below:



A suitable buffer solution is needed to maintain the pH of the electrochemical solution during water oxidation. When performing catalytic water oxidation, the authors [11,12] either did not use buffer at all at pH 7, or used the wrong buffers, e.g., 0.5 M acetate “buffer” to maintain pH 7, phosphate at pH 7. Moreover, the buffer itself may not be innocent in OER but may be a part of a catalytic system [11,12]. The highly acidic or basic solutions are self-buffered, but high concentrations of electrolytes may considerably affect the dynamics of electrochemical processes. Therefore, the maintenance of pH and possible effect of electrolyte must be always taken into account.

Water oxidation is a half-reaction (Equation (1)) of water splitting. The second half-reaction is water/proton reduction to H<sub>2</sub>, Equation (2),



To avoid cross reactions in an electrochemical cell, water electrolysis should be carried out in two-compartmented cells separated by a membrane with a good proton conductivity. Since two hydrogen molecules are formed per one molecule of oxygen, the difference in gas pressure between the two compartments increases. This creates substantial problems in keeping the cell air-free.

During the electrochemical oxygen evolution reaction (OER), several side reactions can occur alongside the desired oxygen generation. These side reactions can impact the overall efficiency and performance of the OER process. Here are some common side reactions that may occur during electrochemical OER:

1. Hydrogen Oxidation Reaction (HOR) is a common side reaction if electrolysis is performed in one compartment cell. Hydrogen may also diffuse through a membrane such as a glass frit.
2. Catalytic oxidation of electrolyte or buffer ions. For instance, chloride anions from an electrolyte or acetate anions from acetate buffer are prone to oxidation.
3. Catalytic oxidation of an organic ligand of a catalyst of OER or an electron transfer catalyst.

4. Catalytic oxidation of anode material (such as graphite).
5. Surface passivation can hinder the transport of reactants and products, leading to decreased catalytic activity and increased overpotentials.

It is important to minimize these side reactions during electrochemical OER to enhance the selectivity and efficiency of oxygen generation. Catalyst design, optimization of operating conditions, electrode and membrane selection, and electrolyte composition are among the factors that can be tailored to mitigate the occurrence of these side reactions and improve the overall performance of the OER system.

These side reactions may significantly affect the data of electrochemical studies of catalytic activity of materials. They may mimic the effect of oxygen formation and lead to wrong interpretation of results. The shift of overpotential and increased current density can be seen in voltammetry, and the increased and stable current density at lower potentials can be observed in bulk electrolysis. As a result, the Faradaic efficiency and Turnover Frequency are commonly calculated based on wrong interpretation of results.

### 2.2. Visual Observation of Gas Formation

Water oxidation generates oxygen which has a low solubility in water and can form gas bubbles on the electrode surface. A catalyst which allows the achievement of the current density  $I = 10 \text{ mA/cm}^2$  in bulk electrolysis is commonly considered as highly active [13,14]. At such current density and 100% Faradaic efficiency, the flux of  $\text{O}_2$  in  $\text{mol/s.cm}^2$  from the electrode is  $I/4F$ , where  $F$  is the Faraday constant. The diffusion length of  $\text{O}_2$  is  $L = 2(D \times \tau)^{1/2}$ , where  $D \approx 2 \times 10^{-5} \text{ cm}^2/\text{s}$  is the diffusion coefficient of  $\text{O}_2$  in water at room temperature and  $\tau$  is the reaction time. Thus, in bulk electrolysis without stirring during time  $\tau$  the average concentration of  $\text{O}_2$  in a diffusion layer with a thickness  $D$  will be  $(1 \times 10^3) \cdot I \cdot \tau / 8F \cdot (D \cdot \tau)^{1/2} \approx (1 \times 10^{-4}) \cdot (\tau)^{1/2} \text{ M}$ . The solubility of  $\text{O}_2$  (1 atm) is approximately 1 mM. After an electrolysis time of approximately 100 s, the concentration of  $\text{O}_2$  in the diffusion layer will be around 1 mM, which is close to the solubility of  $\text{O}_2$ . Therefore, if at current density  $10 \text{ mA/cm}^2$  the bubbles are not formed in several minutes of electrolysis, this indicates that the Faradaic yield of  $\text{O}_2$  formation is very low. However, it should be kept in mind that water oxidation forms four protons near the anode. The pH of NaOH/KOH solutions in the diffusion layer is a critical and non-trivial parameter for electrocatalysis [15]. The diffusion coefficient of protons in water is  $D \approx 9.3 \times 10^{-5} \text{ cm}^2/\text{s}$  and the estimated average concentration of  $\text{H}^+$  in a diffusion layer will be around 2 mM. This will decrease the solution pH even in the presence of buffer. The deviation of pH from optimal may significantly affect the measured catalytic activity. If bubbles are not quickly removed from the electrode, its surface area decreases affecting the current density. To avoid all these complications, the solutions must be very efficiently stirred. Thus, the stirring rate is one of the key parameters of electrochemical water oxidation. Under efficient stirring, all generated  $\text{O}_2$  will escape into the headspace of the electrochemical cell.

### 2.3. Gas Chromatography (GC)

Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) are the ultimate methods to prove and to quantify  $\text{O}_2$  formation. These simple techniques are commonly used in homogeneous catalytic water oxidation by sacrificial electron acceptors (oxidants). In brief, the reaction vessel closed with a rubber septum is purged with Ar and the sample of gas is withdrawn from the gas space by a gas-tight syringe and injected into GS equipped with a thermos-conductivity detector (TCD). If Ar is used as a carrier gas, then oxygen and nitrogen peaks are commonly seen. The leak of air into the reaction vessel results in the appearance of nitrogen peaks and in an increase of oxygen peaks. Then, the amount of oxygen formed in the reaction can be corrected by a difference between the observed oxygen and oxygen from air calculated from nitrogen peaks. It is very important that the amount of oxygen from the reaction should be at least 3–4 times higher than the oxygen from air. We attempted to use this technique to quantify the oxygen yield for electrochemical water oxidation but failed despite all our efforts. The main problem is

the reaction stoichiometry, since two hydrogen molecules are formed per one molecule of oxygen. This results in a building up of different gas pressures in the headspaces of cathodic and anodic compartments. If a glass frit is used as a membrane, a higher pressure in the cathodic compartment induces the transfer of catholyte to anolyte.

#### 2.4. Volumetric Measurements of Dioxygen Yield

To minimize the problem of different increase of pressure in anodic and cathodic compartments, Das et al. [16,17] designed an electrochemical cell to collect the generated oxygen and to measure its volume. This cell (two electrode configuration) resembles a double-jacked vessel in which the inner anodic chamber is connected to the outer cathodic chamber with a small hole to manage and maintain ionic transport. No membrane is used as a separator. The inner chamber has a closed volumetric tube on the top filled with electrolyte solution. The gas produced at the anode is collected in the headspace of the volumetric flask, and H<sub>2</sub> produced at the counter electrode forms a thin layer around the outer surface of the inner compartment (upper part). The accumulated O<sub>2</sub> gas displaces some electrolyte solution into the external tube to balance out the pressure. Importantly, the saturation of electrolyte solutions by pure oxygen gas is crucial for precise measurements. The gas in the headspace of the volumetric tube contains 24 mm Hg of water vapor gas at 25 °C, which should be taken into consideration while converting the volume to moles. GC analysis shows the absence of nitrogen. This setup does not allow us to carry out the electrolysis at constant potential but can be further improved. The possible sources of errors are changes of barometric atmospheric pressure and room temperature.

#### 2.5. Use of Fluorescence Probe

In 2008, Kannan and Nocera [12] used an Ocean Optics (recently rebranded to Ocean Insight) oxygen sensor system for the quantitative detection of O<sub>2</sub> in electrochemical water oxidation catalyzed by a Co/phosphate system. The electrolysis was performed in a custom-built two compartment gas-tight electrochemical cell. This classical work created the obligatory norm for publications in electrocatalytic water oxidation, namely *the quantitative detection of O<sub>2</sub>*.

This method has been precisely described by Nocera et al. in their publications [12,18]. The use of oxygen fluorescence sensor systems is rather simple, and their costs are not prohibitively high. The probe can be placed either in the headspace or in the solution. If the probe is in the headspace, the amount of O<sub>2</sub> in the solution should be added to measured total amount of O<sub>2</sub> in the headspace. This might create an experimental error of around 3%. Importantly, in this case the tip of the sensor should remain dry (not covered by a thin layer of water). If a probe is used to quantify O<sub>2</sub> in solutions containing potential fluorescence material or is exposed to bright light, the tip of the sensor must be coated by a thin non-transparent film, such as black silicon. Of course, the probe can only be used in strictly air-tight set-ups.

The measurement of O<sub>2</sub> formation in photo-assisted electrochemical systems requires the use of special cells with optical windows. Here, use was made of the method reported by Hill et al. [18], which was used in the studies of stabilization of polyoxometalate water oxidation catalysts on hematite by atomic layer deposition. In this work, [19] [Ru<sup>IV</sup><sub>4</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>}(γ-SiW<sub>10</sub>O<sub>34</sub>)<sub>2</sub>]<sup>10-</sup> (Ru<sub>4</sub>Si<sub>2</sub>) was supported on hematite photoelectrodes and then protected by ALD Al<sub>2</sub>O<sub>3</sub>. Oxygen measurements were performed in a 3-compartment cell made of a commercial 40 mm × 10 mm quartz cuvette (Science Outlet), with a custom-made Teflon lid. The lid had 4 holes for counter, reference, working electrode and a FOXY Forspor oxygen probe (Ocean Optics). Solutions of 240 mM borate buffer, pH 8.3 and 0.1 M KNO<sub>3</sub>, were purged with Argon (Ar) gas for 30 min before each use. The Pt-wire counter electrode was placed in a glass tube with a Nafion proton membrane tip. The tubes with a counter electrode, reference and working electrodes were inserted through the holes in a Teflon lid and secured with melted paraffin and vacuum grease. The reference electrode was 1.0 M KCl Ag/AgCl. The Ar-purged solution was added into the cell purged

with Ar through an open hole in the lid until the solution overflowed to get rid of the head space and the last open hole was sealed with grease. As described elsewhere, the homemade “argon box” was fabricated from melted paraffin around the electrochemical cell. The windows for light were cut in front of the paraffin block. This cell was placed into the “argon box” with the upper part of the cell continuously purged with Ar. The oxygen probe was placed close to the working electrode with the remaining oxygen level dissolved in a solution serving as the baseline. The solution was stirred by a magnetic bar. The controlled experiments showed that there was no O<sub>2</sub> leak from air inside the cell. The electrode was illuminated by a beam of light with a diameter of approximately 5 mm. The Faradaic yields were calculated from the charge passed through the working electrode and the total amount of formed oxygen. This method is not applicable for measurement of large O<sub>2</sub> yields. At a concentration of oxygen higher than its solubility the bubbles of O<sub>2</sub> gas are formed in the cell. This limit can be increased if a smaller working electrode (or light beam) is used. In addition, the O<sub>2</sub> probe should be calibrated using correct values of Henry’s coefficients,  $[O_2]_{\text{gas}}/[O_2]_{\text{solution}}$ , since this ratio depends on electrolyte concentrations.

#### 2.6. Pseudo-Clark Generator/Collector Set-Up

This method has been developed by Mallouk et al. [20] to quantify the O<sub>2</sub> yield in photoelectrochemical water splitting. The setup includes 4 electrodes (two working, reference, and counter) connected to a bipotentiostat, which applies two different potentials to two working electrodes. The first working electrode was a photoanode (generator) illuminated from the back side. The second electrode was a platinized FTO film (detector) separated by a spacer (1–3 mm) from the working surface of the first electrode. The collector efficiency (~60%) was calibrated using two working Pt electrodes. The first electrode generated O<sub>2</sub> by oxidizing water, while the second reduced O<sub>2</sub> back to water. We successfully used this method with minor modifications [21].

#### 2.7. Stirring of Solutions during Electrochemical Experiments [22]

A bulk movement of the solution near the electrode strongly affects values of current in electrochemical experiments. Therefore, solutions are not stirred in such popular electroanalytical techniques as cyclic voltammetry or chronoamperometry. Unfortunately, the influence of convection in unstirred solution can only be ignored for a time scale less than approximately 30 s. For a longer time scale the effect of convection is inevitable. Therefore, the use of hydrodynamic voltammetry such as rotating disk electrodes instead of cyclic voltammetry is strongly recommended. For the same reason, the values of data obtained by chronoamperometry are very questionable.

#### 2.8. Rotating Ring-Disk-Electrode (RRDE)

The rotating ring-disk-electrode is popular and widely used in hydrodynamic voltammetry for the measurement of O<sub>2</sub> in electrochemical systems [22–24]. It allows the quantification of the amount of oxygen evolved, providing valuable insights into the kinetics and mechanisms of the OER. The RRDE consists of two concentric electrodes: a central disk electrode and a surrounding ring electrode. The disk electrode is used for the electrochemical generation of the OER, while the ring electrode is inert and serves as a collector for the evolved oxygen. The disk electrode is usually made of a material that catalyzes the oxygen reaction of interest. The method has numerous complications and is recommended for use by professional electrochemists.

### 3. Conclusions

The quantification of oxygen production during electrochemical water oxidation is crucial for understanding and evaluating the performance of OER catalysts. Relying solely on electrochemical methods for OER quantification without complementary analytical techniques compromises the reliability and accuracy of the reported results. This article emphasizes the need for researchers to incorporate direct confirmation of evolved oxygen.

By validating the electrochemical data with direct oxygen product quantification, the reliability and credibility of the reported results can be enhanced.

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