

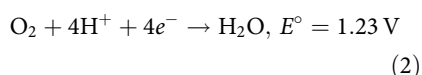
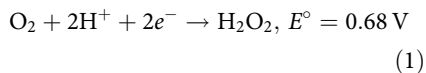
OXYGEN REDUCTION REACTION

Recommended practice to report selectivity in electrochemical synthesis of H₂O₂

Two different types of H₂O₂ selectivity are reported for the electrochemical synthesis of H₂O₂: molar fraction selectivity and Faradaic selectivity. Here we revisit their definitions and discuss the best way to report H₂O₂ selectivity, which can help to avoid misunderstandings or unfair performance comparisons in this growing field.

Chuan Xia, Jung Yoon (Timothy) Kim and Haotian Wang

Hydrogen peroxide (H₂O₂), as one of the most important basic chemicals in the world, is widely used in chemical synthesis, bleaching, wastewater treatment, disinfection, and so on¹. Until today, more than 95% of global H₂O₂ production came from the well-established anthraquinone process, which was developed in 1939 by Riedl and Pfeleiderer² and later scaled-up in chemical plants in 1953. However, this synthesis process has a large carbon footprint, as well as organic waste. Additionally, centralized H₂O₂ production requires transportation and storage of unstable and hazardous bulk H₂O₂ solutions. Electrochemical H₂O₂ synthesis from oxygen reduction or water oxidation, with energy input from renewable electricity, offers a green and sustainable route for on-site H₂O₂ generation^{3–6}. However, the challenge here is to develop highly selective catalysts that can direct the reaction pathway towards the desired product. In the oxygen reduction reaction (ORR), for example, O₂ molecules can be electrochemically reduced to either H₂O₂ via a 2e[−] pathway, or H₂O via a 4e[−] pathway:



As most ORR studies over the past decades have focused on developing 4e[−] catalysts for fuel cell applications, the H₂O₂ pathway has long been treated as the side reaction to be avoided until a recent surge of interest, especially over the past two years, in searching for selective 2e[−]-ORR catalysts (Fig. 1).

The first reported catalyst that was purposely developed for selective H₂O₂ generation via ORR was reported by Traube in 1887 using a Hg–Au catalyst⁷.

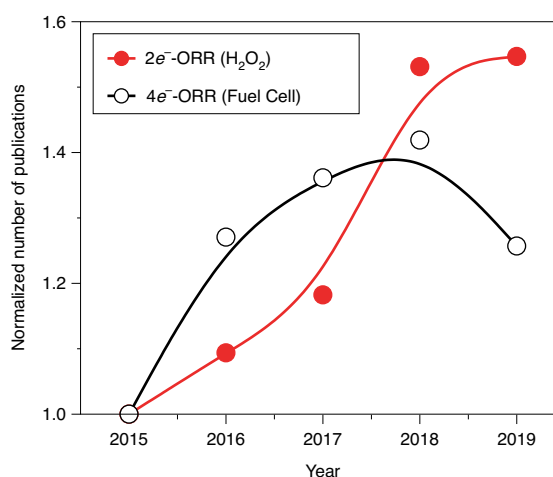


Fig. 1 | Trends of 2e[−]-ORR and 4e[−]-ORR publications in recent years. The normalized number of 2e[−]-ORR and 4e[−]-ORR publications per year over the past five years, with the publication numbers in 2015 normalized as 1. While the publication numbers for both reactions have continued to grow over the years, the past two years show a clear surge in H₂O₂ interest compared to traditional 4e[−]-ORR. The counts were obtained from Web of Science.

Many more classes of materials, including metal alloys, carbon, single-atom catalysts, and so on, were discovered in recent years to show extraordinary H₂O₂ selectivity^{1,4,5,8}. As an exponential increase in the number of reports on H₂O₂ catalysts is expected, a standard and normative way to report H₂O₂ selectivity will help researchers to have fair comparisons of different catalysts, and tremendously benefit the healthy development of the field. However, we noticed that different types of H₂O₂ selectivity are reported depending on the quantification techniques used, which could cause confusion for researchers, particularly for those coming from different research backgrounds. One type of H₂O₂ selectivity is reported as molar fraction, which is widely used in rotating ring-disc electrode (RRDE) measurements⁴, and the other one is reported as Faradaic efficiency, which typically comes from either titration

or spectroscopic quantification methods^{8,9}. While these two types of selectivity have completely different definitions and report different data sets (Fig. 2), which will be discussed in detail in the following section, the worrying part is that they are sometimes used interchangeably, especially in recent publications, suggesting that confusion exists in the growing research community. Therefore, we consider it the right time to revisit the definition of H₂O₂ selectivity and discuss the most reasonable way to report it, which could serve as a standard for fair comparisons, and help to avoid any confusions or mistakes in future reports on the electrochemical synthesis of H₂O₂.

H₂O₂ selectivity quantification

The RRDE is one of the most common setups for quantifying catalysts' H₂O₂ selectivity^{4,10,11}. Electrochemically generated H₂O₂ on the disc electrode is flushed to a

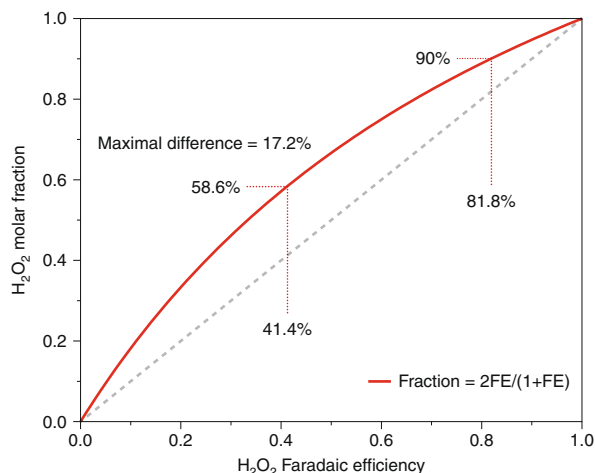
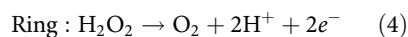
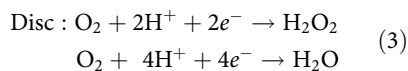


Fig. 2 | The relationship between the two types of selectivity. The difference between H_2O_2 molar fraction selectivity and Faradaic efficiency (FE) selectivity under the same performance dataset can reach a maximal of 17.2%.

Pt ring, where it is partially oxidized, according to the following reactions¹²:



By measuring the Pt ring current and its collection efficiency, the H_2O_2 generation current on the disc can be obtained and used to calculate its selectivity. In 1959, Alexander Frumkin et al. published their initial findings on a theoretical description of solution flow at the RRDE¹³, and then introduced this technique to the electrochemistry community. Since then, RRDE setup has been extensively used in ORR studies, especially in H_2/O_2 fuel cell catalysis where H_2O_2 is an undesired by-product¹⁴. As the purpose of using the RRDE in 4e^- -ORR is to quantify how much H_2O_2 was produced during the ORR, H_2O_2 selectivity was conventionally defined as the molar fraction of ORR products based on the following equation:

$$\begin{aligned} X_{\text{H}_2\text{O}_2} &= \frac{n(\text{H}_2\text{O}_2)}{n(\text{H}_2\text{O}_2) + n(\text{H}_2\text{O})} \\ &= \frac{\frac{I_R}{N}/2F}{\frac{I_R}{N}/2F + (I_D - \frac{I_R}{N})/4F} \\ &= \frac{2I_R/N}{I_D + I_R/N} \end{aligned} \quad (5)$$

where I_R , I_D , N and F are the ring current, disc current, collection efficiency of the setup and Faraday constant, respectively. Obviously, the molar fraction of H_2O_2 is quite different from its corresponding Faradaic efficiency. The Faradaic efficiency of H_2O_2 is defined as the amount of

current (charge) producing H_2O_2 versus the total current (charge) invested, which are typically used in H-cell or flow-cell measurements. After a certain number of charges pass through the electrochemical cell, generated H_2O_2 can be quantified by titration or spectroscopic methods, followed by calculation of the H_2O_2 Faradaic efficiency.

Inconsistent H_2O_2 selectivity

Due to the different testing methodologies, researchers typically report H_2O_2 molar fraction as the selectivity in the RRDE test, and report H_2O_2 Faradaic efficiency as the selectivity in H-cell or flow cell tests. While these two types of selectivity have their clear definitions, confusion sometimes kicks in, particularly in reports where the RRDE test was used as the standard test for catalysts' H_2O_2 selectivity followed by applying the catalysts onto gas diffusion layer electrodes in cells for bulk electrolysis. More importantly, due to inconsistency, H_2O_2 selectivity comparison in the field may not be standardized. We found that the molar fraction selectivity can be up to 17.2% higher than that of Faradaic selectivity using the same dataset (Fig. 2). As Faradaic efficiency can be calculated as $\frac{I_R/N}{I_D} \times 100\%$ in the RRDE system, the relationship between molar fraction and Faradaic efficiency (FE) can be derived as:

$$\text{Molar fraction} = \frac{2FE}{1 + FE} \quad (6)$$

As shown in Fig. 2, the molar fraction selectivity is always higher than Faradaic efficiency, except at 0% and 100%. Under a typical benchmark molar fraction

selectivity of 90%, its actual Faradaic selectivity is only about 81.8%. This big difference needs urgent emphasis in the field to avoid any unfair comparisons between molar fraction selectivity and Faradaic selectivity, or any mixed use of these two measures of selectivity.

Molar fraction or Faradaic efficiency

As we now have a clear image of the big gap between these two types of selectivity, a natural question would be: what is the best way for researchers to report H_2O_2 selectivity in the field of electrochemical synthesis of H_2O_2 ? This is obviously an open question to the whole community, and could have different answers. But here we would like to initiate this discussion by providing some of our own thinking and arguments. Our recommendation is that, to avoid any confusions in the future and to make literature comparison easy, it would be more meaningful to directly report Faradaic efficiency as H_2O_2 selectivity, instead of the molar fraction, no matter what experimental setup is used. This is based on the following three points:

Firstly, using molar fraction as H_2O_2 selectivity only holds in cases where only H_2O_2 and H_2O are produced, without any other by-products. This will become invalid if there are other side reactions. For example, in acidic ORR to H_2O_2 , there are catalysts that may need large overpotentials — even more negative than the reversible hydrogen electrode — to drive the reaction¹⁵. In some other cases, large polarizations are needed to deliver industrially relevant currents^{3,16}. Under these negative potentials, the hydrogen evolution reaction becomes a possible side reaction that needs to be taken into consideration. Another example would be the side reactions in catalysts, such as the well-known oxidized carbon catalysts, where surface oxygen can slowly get reduced under large overpotentials³.

Secondly, for electrosynthesis of H_2O_2 where electricity input is considered one of the most important operational costs, it makes more practical sense to focus on the current efficiency, namely Faradaic efficiency. This is also widely used in other electrosynthesis areas, including CO_2 reduction, N_2 reduction, methane oxidation, hydrogen evolution, and many other organic electrochemical reactions, where the product selectivity is generally equivalent to its Faraday efficiency^{17,18}. It would also help researchers coming from these areas to avoid possible confusions or mistakes.

Thirdly, reporting H_2O_2 Faradaic efficiency in 2e^- -ORR could easily be integrated with water oxidation to H_2O_2 , where molar fraction selectivity has never

been used due to many possible side reactions (OH radical, O₃, catalyst oxidation, and so on)^{6,9}.

We hope that our suggestions will help researchers to normalize catalytic performance while limiting the possibility of false-positive results. We believe that this practice should ultimately lead to a better picture of the intrinsic catalytic properties of new H₂O₂ electrocatalysts. In future studies, more practical electrochemical systems for H₂O₂ generation — such as flow cell reactors or membrane electrode assembly — will become crucial for the applicability of 2e⁻-ORR catalysts on larger scales. However, as RRDE testing has been and will still be a prominent method of evaluating 2e⁻-ORR catalytic performances, it is important to unify how ORR selectivity in RRDE and other electrochemical methods is presented in scientific reports. While we believe the two different types of selectivity need to be unified, we are also open to other suggestions. At least, H₂O₂

selectivity needs to be explained more explicitly in research papers. □

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Author contributions

The project was conceptualized by C.X. and H.W., and supervised by H.W.; C.X. and H.W. wrote the manuscript with input from J.K.

Competing interests

The authors declare no competing interests.