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Best practices for hydrogen peroxide (photo)electrosynthesis

Yaovi Holade,^{1*} Srabanti Ghosh^{2,3} & Teko W. Napporn⁴

¹*University of Montpellier, CNRS, ENSCM, Montpellier, France. Email: yaovi.holade@umontpellier.fr*

²*Energy Materials & Devices Division, CSIR - Central Glass and Ceramic Research Institute, Kolkata, India*

³*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, Uttar Pradesh, India*

⁴*University of Poitiers, IC2MP UMR 7285 CNRS, Poitiers Cedex 9, France*

Green synthesis of hydrogen peroxide (H₂O₂) with a sunlight driven process or a renewable energy powered electrochemical route is essential to its decentralized production and sustainable end-use. Here, we discuss how to develop a fairer basis for performance evaluation of the (photo)electro synthesis.

(Photo)electrocatalytic oxidation of water (WOR) and reduction of O₂ (ORR) with two-electron transfer are emerging synthetic technologies for access to more sustainable H₂O₂.¹⁻³ However, reporting on the performance of new (photo)electrocatalysts or reactor designs is not straightforward, partly due to the complex nature of ORR/WOR and the oxidation of organic matters by H₂O₂, e.g. ionomer/membrane, molecular (photo)electrocatalysts, organic electrolytes, etc. Here, we identify the common problems associated with performance measurement in H₂O₂ (photo)electrosynthesis. We then recommend best practices for achieving standardization in the (photo)electrochemical production of such an important chemical.

Common problems in reporting performance

H₂O₂ can be (photo)electro-synthesized by the selective two-electron transfer ORR (O₂ + 2H⁺ + 2e⁻ → H₂O₂, E°(O₂/H₂O₂) = 0.70 V_{RHE}) and WOR (2H₂O → H₂O₂ + 2H⁺ + 2e⁻, E°(H₂O₂/H₂O) = 1.76 V_{RHE}).^{4,5} The first problem is selectivity evaluation since, for each scenario, at least two reaction products are possible.⁵ This is further compounded in that industrially relevant currents⁸ inevitably push ORR into HER (hydrogen evolution) region or that WOR interferes with (photo)electrocatalysts transformation while the solar energy decomposes H₂O₂.⁵ The inconsistency in H₂O₂ performance indicators results from the difference in experimental methodology either the rotating ring-disk electrode (RRDE, Fig. 1a) or (photo)electrolysis (Fig. 1b–1c). The “Faradaic efficiency” or “current efficiency” given by Equation (1) when H₂O₂ is quantified by titration or spectrometric calibration^{5,7,8} is often confused with RRDE measurements reporting the “molar fraction selectivity” given by Equation (2) (*I*_{ring}: ring current; *I*_{disk}: disk current; *N*: collection efficiency).^{9,10}

$$FE(\%) = H_2O_2(\%)_{redox} = \frac{H_2O_2(mol) \times 2 \times 96485(C\ mol^{-1})}{Total\ charge\ passed\ (C)} \times 100 \quad (\text{Equation 1})$$

$$H_2O_2(\%)_{RRDE} = \frac{200}{1 + \left| \frac{N \times I_{disk}}{I_{ring}} \right|} \quad (\text{Equation 2})$$

We note errors for the formula of $H_2O_2(\%)_{RRDE}$ and/or number of electrons, incorrect in ref.¹¹ (correct in ref.²), ignoring that I_{ring} (electrooxidation current) and I_{disk} (electroreduction current) have opposite signs. Because FE can be expressed by Equation (3), Equation (4) indicates that when RRDE reports 90%, the actual FE is 82%, which can bias decision-making.⁹

$$FE(\%) = \frac{|I_{ring}|}{N \times |I_{disk}|} \times 100 \quad \text{Equation (3)}$$

$$H_2O_2(\%)_{RRDE} = \frac{200 \times FE(\%)}{100 + FE(\%)} \quad \text{Equation (4)}$$

An ignored issue is the (photo-electro)chemical stability of the membrane, which often separates anodic and cathodic compartments (Fig. 1b–c). H_2/O_2 fuel cells require “minimum H_2O_2 from incomplete ORR”¹⁴ because H_2O_2 produces highly oxidizing radicals that attack the membrane/ionomer, intensified by transition metals species within electrolytes and catalytic materials.^{5,6} This problem is exacerbated in alkaline electrolytes, as the predominant form of the hydroperoxide anion HO_2^- ($pK_a(H_2O_2/HO_2^-) = 11.75$) can either accumulate in anionic membranes or cross them to concentrate in the counter compartment where it can degrade, leading to underestimation or release of exasperating radical species. The lack of specification of membrane characteristics is common, particularly when acid membranes are used in alkaline electrolytes, posing challenges for comparing different studies. The stability problem is compounded with photoanodes, whose bandgap allows the generation of oxidizing radicals that degrade organic matter, while solar energy (UV irradiation) decomposes H_2O_2 .⁵ Another issue associated with solar devices is the overrating and discrepancy in the solar-to-chemical conversion efficiency because of the non-uniform spatial illumination and the mismatch between the irradiated area and the photoelectrocatalytic area depending on the distance between the light source and the working electrode, and the electrolyte composition.^{5,12}

Comparing data on H_2O_2 productivity is challenging due to the multiplicity of metrics, either gravimetric ($mg_{H_2O_2} kg^{-1}_{cat} h^{-1}$, $mg_{H_2O_2} kg^{-1}_{cat} s^{-1}$, $mol_{H_2O_2} kg^{-1}_{cat} s^{-1}$, $mol_{H_2O_2} kg^{-1}_{cat} h^{-1}$) or surface ($mg_{H_2O_2} cm^{-2}_{geo} h^{-1}$, $mg_{H_2O_2} cm^{-2}_{geo} s^{-1}$, $mol_{H_2O_2} cm^{-2}_{geo} s^{-1}$, $mol_{H_2O_2} cm^{-2}_{geo} h^{-1}$) basis. The complexity is further heightened for porous electrodes,¹⁶ where overestimation occurs because the effective geometric surface exceeds that derived from simple dimensions (such as width and length). Indeed, RRDE induces very little bias on the electrode surface; however, for (photo)electrolyzers, porous (photo)electrodes are frequently employed, yet the surface directly participating in the reaction remains unspecified due to undisclosed substrate characteristics.

Another parameter often undisclosed is the electrolyte volume in the working electrode compartment (Fig. 1b), which is problematic because the ratio between this volume and the working electrode area affects the H₂O₂ production rate. Additional issues with three-electrode setups are the choice of electrodes (working, counter and reference), which leads to problems of contamination, durability and comparison of electrode potential values. While the ohmic-drop correction for the voltage/electrode potential is relevant for assessing intrinsic activity, some claimed (photo)electrocatalysts displaying low overpotentials after ohmic-drop correction cannot be implemented because of low energy efficiency^{3,6} and are often overlooked. Hence, solely reporting ohmic-drop data without accounting for the ohmic resistance is inadequate. Furthermore, there is often no mention of (photo)electrochemical cell temperature control, despite considerable variations in ambient temperatures across different locations and seasons, and the thermal decomposition of H₂O₂ in photoelectrocatalysis, wherein the electrolyte is generally cooled in an ice bath (273–278 K).

Fig. 1 | Illustration of a typical experimental step-up for H₂O₂ (photo)electrosynthesis by H₂O oxidation and/or O₂ reduction. a, Three-electrode single-compartment cell. b, Three-electrode H-type batch cell. c, Flow-field electrolysis cell (two-/three-electrode).

Recommended practices

Here, we recommend a set of practices to help the community standardize the evaluation of H₂O₂ photo-electrosynthesis performance so that the researchers can better understand, reproduce, reference, and emulate results for future research.

All experimental details should be fully transparent. Like in CO₂ research,¹⁴ H₂O₂ photo-electrosynthesis should be evaluated and reported comprehensively using a matrix of figures of merit: Faradaic efficiency, productivity, electrode potential/cell voltage, current density (geometric and electrochemically active surface area (ECSA) when possible) and stability. We recommend that, after specifying the catalyst loading (except for bulk (photo)electrodes) and the (photo)electrode area, the H₂O₂ productivity be reported on a gravimetric ($\text{mol}_{\text{H}_2\text{O}_2} \text{g}^{-1}_{\text{cat}} \text{h}^{-1}$) and surface ($\text{mol}_{\text{H}_2\text{O}_2} \text{cm}^{-2}_{\text{geo}} \text{h}^{-1}$) basis, and ultimately mass-surface ($\text{mol}_{\text{H}_2\text{O}_2} \text{g}^{-1}_{\text{cat}} \text{cm}^{-2}_{\text{geo}} \text{h}^{-1}$) to avoid any overestimation resulting from the use of ultra-small (photo)electrode area or mass of catalyst. All the characteristics for three-dimensional electrodes should be disclosed, where overestimation occurs because the effective geometric

surface exceeds that derived from simple dimensions (width and length).¹³ Even if H₂O₂ can be further concentrated/diluted depending on the intended application,⁶ the output concentration in mg L⁻¹ and wt% should be reported. We recommend using the RRDE for fast tracks (Fig. 1a), followed by bulk (photo)electrolysis (Fig. 1b–c). While H-type cells can be fluidic, they do not necessarily offer a superior understanding of mass transport phenomena. The energy consumption (kWh per kg (H₂O₂))¹ and electricity(solar)-to-H₂O₂ efficiency (theoretical cell voltage per experimental one)³ should be reported (ideally corrected by FE) because, under the industrial current density, HER interferes with ORR. Hence, we recommend reporting both the ohmic-drop corrected and uncorrected cell voltages/electrode potentials, with explicit indication of the manner of correction (resistance and methodology).

To avoid errors in the electroanalytical formulas associated with the RRDE method,¹¹ we recommend using absolute values for current when expressing H₂O₂ molar fraction selectivity by (Equation 2) and the electrons transferred by (Equation 5).

$$n_{RRDE} = \frac{4}{1 + \left| \frac{I_{ring}}{N \times I_{disk}} \right|} \quad (\text{Equation 5})$$

Measurement of the collection efficiency (N , fraction of the species produced at the disk that reach the ring to react) should be carried out in degassed electrolyte with stable species such as K₃[Fe(CN)₆].¹⁰ During durability studies by RRDE measurements, we recommend renewing the electrolyte because the accumulated species (H₂O₂ for ORR and O₂ for WOR) biases the ring current. Since there is no consensus on the electroanalytical equations for using RRDE in WOR, we suggest relying on bulk electrolysis followed by UV-vis assays to quantify H₂O₂. For WOR, the carbonate-bicarbonate electrolyte appears as the best electrolyte^{3,8} and ¹⁸O isotope measurements can provide mechanistic insights.³ For H₂O₂ productivity and FE, we recommend UV-visible method, for establishing H₂O₂ calibrations based on the reaction of H₂O₂ with other substrates (cerium, oxalate or permanganate),^{1,2,4,7,10} which can detect concentrations of few μg L⁻¹ (ppm) particularly for photoelectrocatalysis.

When claiming a high FE, productivity and corresponding current density and stability should be reported together. Stability should be evaluated under practical H₂O₂ productivity with current densities of 0.1–0.5 A cm⁻² (1–50 mA cm⁻² for photoelectrocatalysis) for hundreds of hours to accelerate aging.⁶ For such experiments, the water content is likely to change due to hydrated ions transfer across the membrane, consumption or evaporation,^{12,14} hence, we recommend measuring the volume to minimize the over/underestimation of the efficiency. We

recommend evaluating the total organic content (TOC) to interrogate the durability of membrane-based processes in such an oxidizing/irradiation environment. Adequate stability evaluation, irrespective of the ion-conductive separator (membrane, glass frit, etc.) used to allow ion transfer and electron flow barriers, should rely on TOC evolution and corrosion species during (photo)electrolysis for tens to hundreds of hours. Although employing a proton-exchange membrane in alkaline electrolytes can concentrate HO_2^- by eliminating crossovers, long-term stability must be demonstrated under a relevant current density. Whereas diaphragms would result in high electrical resistance and H_2O_2 crossover, separator-less alternative (photo)electrolyzers require selective catalysts for paired electrosynthesis through 2e-ORR//2e-WOR.^{1,3}

For photoelectrochemical devices, we recommend 1 SUN (AM 1.5) solar simulator following proper calibration,^{2,12} noting that H_2O_2 decomposes under UV irradiation.⁵ The choice of materials for photoelectrochemical reactors is constrained by the need for efficient light transmission and reflection, mainly quartz and fused silica, so, the corrosion species should be monitored. During light irradiation, some energy is converted into heat, and heat exchange is vital to preserving the desired temperature. Hence, we recommend (photo)electrochemical cells with built-in temperature control temperatures. Arguably, for cells without built-in temperature control, measuring and reporting the temperature during the experiment is a solution. The irradiated area, the distance between the light source and the working area, and specific performance metrics (incident photon-to-current efficiency (IPCE), other parameters in ref.⁵) should be disclosed.

Mercury-containing reference electrodes (calomel/silver-silver chloride is not stable in alkaline electrolytes) being discouraged for environmental reasons, we recommend commercial/homemade reversible hydrogen electrode (RHE). The RHE stability should be checked regularly and can be gauged through platinum voltammetry in H_2 -saturated electrolyte between -0.1 and 0.1 V versus RHE, which is the calibration methodology whatever reference electrode is used before converting electrode potentials to RHE. We advise against employing Nernst calculations due to the potential drift commonly associated with junction potentials. When air is the O_2 source, it should be purified before reaching alkaline and neutral electrolytes to avoid carbonation, which can be detrimental to the stability of the (photo)electrolysis system. A base trap, i.e., bubbling the air into an alkaline solution should suffice to capture CO_2 by an acid–base reaction. An acidic trap could be added in series to neutralize any traces of base in the CO_2 stream that might change the pH for non-alkaline electrolytes. Aqueous traps should be renewed periodically depending on the duration of the experiments.

H₂O₂ productivity being possibly better in alkaline electrolytes,^{2,3,8} which could be understood analogously to organic compounds; since catalytic activity would be optimal for a pH close to the compound's p*K*_a,¹⁵ glass cells should be avoided (corrosion issues), prioritizing Teflon or Kel-F[®] materials. For photoelectrocatalysis, the light absorption of materials and electrolytes should be evaluated.

Despite the remarkable performance of (photo)electrochemical membrane-based reactors, we suggest that future reports include a discussion of membrane stability as well as the aforementioned precautions to ensure achievable sustainability.

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Competing interests

The authors declare no competing interests