A review on recent developments in electrochemical hydrogen peroxide synthesis with a critical assessment of perspectives and strategies

Sengeni Anantharaj, Sudhagar Pitchaimuthu, Suguru Noda

PII: S0001-8686(20)30600-X

DOI: https://doi.org/10.1016/j.cis.2020.102331

Reference: CIS 102331

To appear in: *Advances in Colloid and Interface Science*

Revised date: 16 November 2020

Please cite this article as: S. Anantharaj, S. Pitchaimuthu and S. Noda, A review on recent developments in electrochemical hydrogen peroxide synthesis with a critical assessment of perspectives and strategies, *Advances in Colloid and Interface Science* (2020), https://doi.org/10.1016/j.cis.2020.102331

A Review on Recent Developments in Electrochemical Hydrogen Peroxide Synthesis with a Critical Assessment of Perspectives and Strategies

Sengeni Anantharaj[1,*] anantharaj1402@gmail.com**, Sudhagar Pitchaimuthu**[2,*] S.Pitchaimuthu@swansea.ac.uk**, and Suguru Noda**[1,3,*] w.iac19088@kurenai.waseda.jp noda@waseda.jp

[1]Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

[2]Multi-functional Photocatalyst and Coatings Group, SPECIFIC, Materials Research Center, College of Engineering, Swansea University (Bay Campus), Swansea SA1 8EN, Wales, United Kingdom

[3]Waseda Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

[*]Corresponding authors.

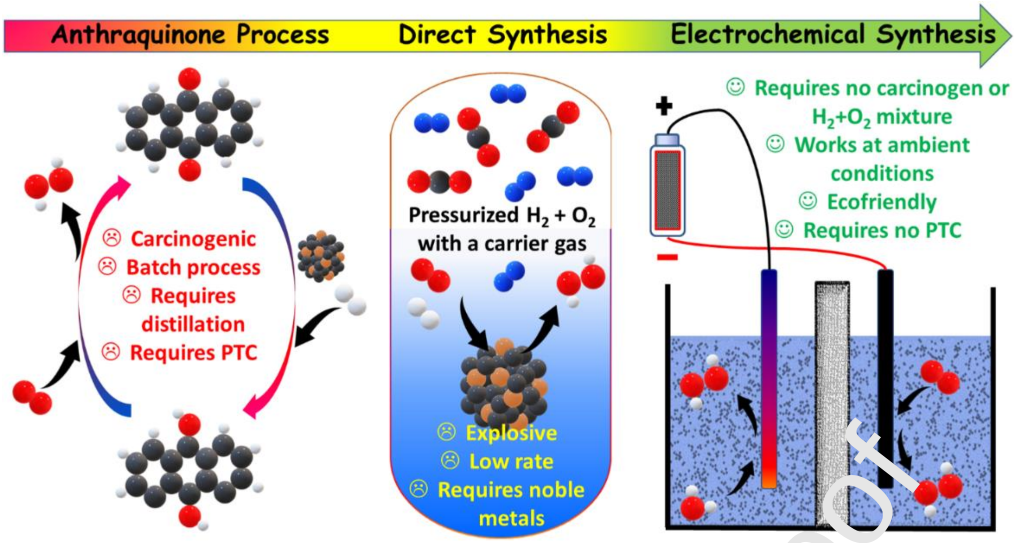
ABSTRACT

Electrochemical hydrogen peroxide synthesis using two-electron oxygen electrochemistry is an intriguing alternative to currently dominating environmentally unfriendly and potentially hazardous anthraquinone process and noble metals catalysed direct synthesis. Electrocatalytic two-electron oxygen reduction reaction (ORR) and water oxidation reaction (WOR) are the source of electrochemical hydrogen peroxide generation. Various electrocatalysts have been used for the same and were characterized using several electroanalytical, chemical, spectroscopic and chromatographic tools. Though there have been a few reviews summarizing the recent developments in this field, none of them have unified the approaches in catalysts' design, criticized the ambiguities and flaws in the methods of evaluation, and emphasized the role of electrolyte engineering. Hence, we dedicated this review to discuss the recent trends in the catalysts' design, performance optimization, evaluation perspectives and their appropriateness and opportunities with electrolyte engineering. In addition, particularized discussions on fundamental oxygen electrochemistry, additional methods for precise screening, and the role of solution chemistry of synthesized hydrogen peroxide are also presented. Thus, this review discloses the state-of-the-art in an unpresented view highlighting the challenges, opportunities, and alternative perspectives.

Keywords: H_2O_2 generation; Electrocatalysis, Oxygen reduction reaction; Water oxidation reaction; Electrochemical synthesis.

INTRODUCTION

Electrochemical hydrogen peroxide synthesis has become one of the efficient and easier ways of generating the greener oxidizing agent (i.e. H_2O_2) in an environmentally friendly manner [1]. Hydrogen peroxide is a universal oxidizing agent which is used as oxidant, disinfectant, bleaching agent, and as a fuel depending on the site of application. Fuel-cells, industrial bleaching, waste-water treatment, pulp bleaching, fine synthesis of organic molecules, and medical equipment cleansing are few of several applications that it has found [2,3]. Hydrogen peroxide is eco-friendly as it releases water as the by-product upon use whereas bleaching agents such as oxychlorides release toxic chlorine gas and also increase the salt content of the medium in the overall process [4,5]. Hence, it has been given a greater attention in the recent past. Despite being the greenest oxidizing agent of all, its global production is still dominated by the anthraquinone process which was developed back a century [6,7]. Anthraquinone process is a multi-step process that requires hydrogenation of anthraquinone over a metal catalyst surface which is generally Ni or Pd, separation of hydroquinone, oxidation of hydroquinone with air, phase transfer of produced hydrogen peroxide to water, distillation of hydrogen peroxide transferred to aqueous phase for concentrating, and the recovery of regenerated anthraquinone. Since anthraquinone process is a multi-step process, hydrogen peroxide is usually produced in batches with very high concentration (~80%). This concentrated solution is then diluted at the site of use depending on the application which is a dangerous process and require extreme precautions. Moreover, transporting such highly concentrated solutions of hydrogen peroxide was also witnessed to be detrimental as there was an incident of explosion [8]. Realizing the demerits of anthraquinone process, researchers came up with the direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen gases over metallic catalyst surfaces [9–12]. Though this method offers a single-step synthesis with no requirements for phase transfer and distillation, the potentially explosive combination of molecular hydrogen and oxygen gases in a wide range of composition makes it still a hazardous method. This issue is usually avoided introducing an inert gas in the reaction medium. Due to these pitfalls of anthraquinone process and direct synthesis, researchers are now focusing on the decentralization of hydrogen peroxide production from these processes. One of the efficient ways to do is going for electrochemical synthesis as it is relatively safer, faster, and easier to handle with [1]. Electrochemically, hydrogen peroxide can be synthesized by both partial oxygen reduction reaction (ORR) and partial water oxidation reaction (WOR) [3,13]. Major complexity in electrochemical synthesis of hydrogen peroxide is achieving the two-electron selectivity. Even though electrochemical synthesis has several advantages over both anthraquinone process and the direct synthesis (**Scheme 1**).



Scheme 1: Graphical depiction of fundamental functions in anthraquinone process, the direct synthesis, and electrochemical synthesis with associated demerits and merits.

Unlike anthraquinone process, electrochemical synthesis can be carried out continuously with no requirements for phase transfer catalysts (PTC), distillation, and use of a carcinogen. Unlike the direct synthesis, electrochemical synthesis require either water or only dioxygen molecule as a starting material and uses protons and electrons generated in situ via electrolysis at the counter electrode to form hydrogen peroxide [14,15]. Hence, electrochemical synthesis of hydrogen peroxide is far superior to both anthraquinone process and the direct synthesis. Electrocatalysts of different kinds have been reported to perform two-electron ORR avoiding four-electron path to the complete reduction of O_2 to water with selectivity as high as 100%. These catalysts include heteroatom (N, S, O, and F) containing carbons [15–20], metal complexes with N-donors in carbon matrices (M-N-C catalysts) [18,21–23], metals and their alloys [24–26], Similarly, partial water oxidation is also performed with oxidized/oxygen containing carbons[27,28] and metal oxides of very poor selectivity towards four-electron water oxidation [29–32]. Number of catalysts developed for two-electron ORR is quite larger in number than that of two-electron

WOR [1,13]. Owing to the superiority of electrochemical synthesis of hydrogen peroxide, it has become very frequent to see new catalysts appearing in the literature. Recent reviews appeared in literature had either focused only on two-electron ORR[13] or a complete evolution of the field from the beginning while emphasizing the future directions [1,3]. In contrast, this review critically analyses the strategies used in catalysts' design, perspectives of evaluation and associated ambiguities, and proposes the key changes that are to be adopted for further developments while emphasizing the future direction of growth in an unpresented view. Different practices followed by different groups of researchers in assessing the performance of H_2O_2 evolving electrocatalysts lay difficulties in unifying and benchmarking activity trends. Hence, a significant part of this review is dedicated to critique the ambiguities in screening methods and propose alternative quantification methods with an elaborated note on oxygen electrochemistry. In addition, the necessity of electrolyte engineering in improving H_2O_2 productivity which was never talked by any review is discussed here. Finally, we have identified the strategies used in catalysts' design for both two-electron ORR and two-electron WOR and unified them all under a few simple principles which helped us predicting other prospective elements in the periodic table capable of forming H_2O_2 selective catalysts. Therefore, this review assists the researchers by providing a rational guide to use the evaluation techniques appropriately while familiarizing them with the recent strategies employed in catalyst's design targeting two-electron oxygen electrochemistry in a viewpoint never presented earlier.

EVALUATION PERSPECTIVES

In general, electrocatalysts are screened for their activity, stability and selectivity. These characteristics of a catalyst must be satisfied in order to qualify it for sustainable full-cell operations [33,34]. Activity of an electrocatalyst is determined by the overpotential at a defined current density (or at onset) in general which is a thermodynamic parameter. The same is true in electrochemical synthesis of hydrogen peroxide too. In two-electron WOR, the onset overpotential is calculated subtracting the equilibrium potential of hydrogen peroxide evolution from water (1.76 V vs. reversible hydrogen electrode (RHE)) from the potential at which the catalyst under study delivers 0.2 mA cm^{-2} [30]. In contrast, such onset overpotential is given relatively less importance in two-electron ORR. In fact, any catalyst that has larger overpotential for ORR than the equilibrium potential (0.70 V vs. RHE) of hydrogen peroxide formation from dioxygen (i.e. two-electron ORR) is considered to be a good catalyst [13]. The approach followed in two-electron WOR allows us to take energy-efficiency of an electrocatalyst into consideration whereas the approach used in two-electron ORR does not. Stability is one of three important characteristics of an electrocatalyst which primarily testifies its suitability for long-term operations and it is examined in the same way for both two-electron ORR and two-electron WOR catalysts unlike the different conventions followed in activity determination. In general, chronoamperometry or chronopotentiometry is carried out at a fixed potential/current where the selectivity of the catalyst is higher for several hours to days of operation and the stability of the catalyst under study is expressed in terms of percentage loss (in chronoamperometry) or increase in overpotential (in chronopotentiometry) of activity [35]. Above both activity and stability, selectivity of an electrocatalyst is given a greater significance in both two-electron WOR and two-electron ORR as there is a thermodynamic competition between four-electron and two-electron paths [1]. By definition, four-electron path of ORR and WOR is said to occur at a relatively lower equilibrium potential (1.23 V vs. RHE). This equilibrium potential of four-electron oxygen electrocatalysis is 0.53 V cathodic to two-electron WOR and 0.53 V anodic to two-electron ORR which implies that there is a very high probability for four-electron path while comparing the desired two-electron paths of ORR and WOR. Because of this reason, almost all electrocatalysts developed so far have been carefully designed and engineered to suppress the four-electron paths. In general, the best catalysts that are selective for two-electron ORR and WOR are poor for four-electron ORR and WOR which are desired for energy-efficient fuel cell and water electrolysis operations [36,37]. Selectivity is usually determined in terms of Faradaic efficiency (FE) which is determined by different methods such as rotating ring disk electrode (RRDE) [13], gas chromatography [27,29,32], titration [1,25], and even by instant test strips [29,30,32]. The RRDE method has so far been used only for two-electron ORR. In this method, equation (1) is used to determine the FE [13].

$$\mathrm{FE}\ (\%) = [i_R / (N_{CL} \times i_D)] \times 100 \qquad (1)$$

where, i_R and i_D are ring and disk currents, respectively. N_{CL} represents the collection efficiency of the RRDE which can be obtained from the average of ratio of i_R and i_D acquired at 100, 400, 900, 1600, and 2500 rpm with a known redox couple (such as Ferro-Ferri) involving single electron transfer [38,39]. In typical quantification of hydrogen peroxide produced from two-electron ORR by RRDE method, a rotation rate of 1600 rpm is chosen for acquiring polarization curves in the potential region of 0.05 to 1.00 V vs. RHE at the disk electrode while maintaining a constant potential of 1.2 V vs. RHE at the ring electrode. Then, from ring and disk currents and from the calculated N_{CL}, FE is calculated. Recently, the potential dependent disk current corresponding to hydrogen peroxide formation is also calculated using the ring current and N_{CL} [13,24,25]. Compared to all other methods of quantification of produced hydrogen peroxide, RRDE method is handier and quicker and does not require sufficient saturation of electrolyte with the synthesized H_2O_2. Other mentioned methods such as chromatography, titration, and H_2O_2 test strips uses the equation (2) to calculate FE [13].

$$\text{FE (\%)} = \text{Experimentally quantified } H_2O_2 \text{ (mol)} / \text{Calculated } H_2O_2 \text{ (mol)} \times 100 \qquad (2)$$

These methods require the electrolyte solution under screening to get saturated with the electrochemically generated hydrogen peroxide sufficiently before analysis. Hence, usually, potentiostatic electrolysis for a period of 5 to 10 min is performed every time before quantification at all desired potentials.[30] In this way, these methods are disadvantageous to that of RRDE method where the later can quantify electrochemically generated hydrogen peroxide simultaneously at the ring while keeping the potential at the ring constant. However, chromatography, titration, and H_2O_2 test strips have their own merits as they show the actual concentration of hydrogen peroxide in solution after significant time of electrolysis and under no externally induced or forced mass transfer. The rotation rate set at RRDE method induces a forced mass transfer (convectional) of synthesized hydrogen peroxide and influence the selectivity to a greater extent. As far as two-electron ORR half-cell studies are concerned, the RRDE method is superior but not the precise one reflecting the actual rate and selectivity. On the other hand, chromatography, titration, and H_2O_2 test strips are more reliable when it comes to full-cell studies (such as flow-cell, proton exchange membrane fuel cell (PEMFC), gas diffusion electrode (GDE), etc.) [16,40-44]. In titration method, the electrogenerated H_2O_2 is titrated against the standardized acidified permanganate solution which could easily oxidize H_2O_2 and the end point of which is indicated by a persisting pale pink colour as a result of added excess permanganate [45]. This is the cheapest method of all which do not require sophisticated instruments (RRDE, gas chromatography, and spectrophotometers). The chemical reaction that involves in the titrimetric quantification of H_2O_2 is given in equation (3) [3].

$$5H_2O_2 + 6H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O + 5O_2\uparrow \qquad (3)$$

Other than these, RRDE method is also sometimes used to calculate the O_2 efficiency as another way to show the selectivity for H_2O_2 evolution in ORR which uses equation (4) [13].

$$O_2 \text{ efficiency } (\%) = (2 \times i_R/N_{CL}) / (i_D + i_R/N_{CL}) \times 100 \qquad (4)$$

However, in our view, it is convenient to show FE in percentage calculated using equation (1). Besides, a few group of researchers use the Koutecký–Levich (K-L) plot for determining the number of electron transferred in ORR which also can qualitatively reveal the selectivity of an electrocatalyst [6,46]. These are the methods that have so far been used to determine the selectivity. Though it is important that the given electrocatalyst should have exclusive selectivity for two-electron ORR or WOR, the activity and stability must not be neglected in the meantime. Tafel analysis and TOF determination must also be given equal importance to that of selectivity.

Ambiguities in Evaluation Methods

From the above discussions, it is quite clear that the selectivity of a H_2O_2 evolving catalyst is determined using various methods by different group of researchers. This basically makes it difficult to come up with a rational comparison of performances studied electrocatalysts. In two-electron ORR, a majority of people uses RRDE method whereas a few are using titration/chromatography method. On the other hand, RRDE is not used in two-electron WOR. Similarly, in two-electron ORR, the overpotential is not given much significance whereas people who work on two-electron WOR consider the potential at which the catalyst under study delivers 0.2 mA cm^{-2} as onset potential [29,30]. Despite being a concurrent, handier, and faster method of quantification, RRDE suffers from the fact that it is not revealing the selectivity of the catalyst under study in a standard condition (i.e. no externally induced/forced mass transfer). Because of this, a catalyst's performance is always overestimated when the selectivity is determined using RRDE method. The very first experimental evidence showing the differences in the FE determined using RRDE and titration for Au/C, Ag/C and Pt-Hg/C was shown by Yang and co-workers (**Figure 1**) [13].

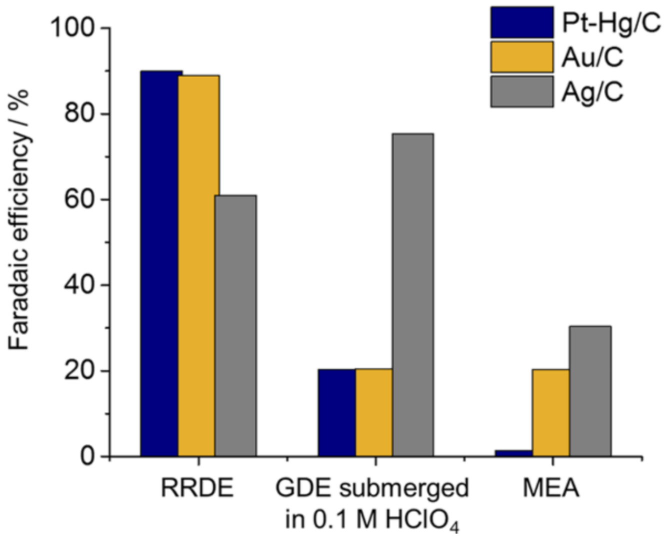


Figure 1: Faradaic Efficiency of Pt-Hg/C (dark blue), Au/C (ocher), and Ag/C (grey) two-electron ORR catalysts determined in 0.1 M $HClO_4$ with RRDE, gas diffusion electrode (GDE) submerged and membrane electrode assembly (MEA) setups. Titration method was used to quantify H_2O_2 in GDE submerged and MEA cell set ups. Reproduced with permission from ref. 13 (Copyright 2018, American Chemical Society).

Clearly, the RRDE method overestimates the selectivity (for Au/C and Pt-Hg/C) as it was measured under externally forced mass transfer condition. Besides, their experiment also showed the influence of design of electrochemical cell on the selectivity. This indicates us that there most certainly exists an ambiguity in selectivity determination. The effect of design of cell and the mesoscopic structure of catalyst/electrode interface could also cause ambiguities in selectivity determination of two-electron WOR too. The key issues with the evaluation perspectives in two-electron ORR and two-electron WOR are listed below.

- Though the same H_2O_2 is synthesized and quantified in both two-electron ORR and two-electron WOR, the methods used are totally different and thereby questioning the reliability.
- In two-electron ORR, RRDE is the mainly used technique for the quantification which provides no information on real-time productivity and saturation of H_2O_2.
- In two-electron WOR, permanganate titration or the test strip reader take too much time within which further chemical, thermal, photo, and electrochemical decomposition of synthesized H_2O_2 is highly feasible thereby undervaluing the actual Faradaic efficiency of respective electrocatalysts.
- Irrespective of the electrochemical path used for H_2O_2 electrosynthesis, most of the studies were carried out with conventional three-electrode cell in which the oxidation/reduction of H_2O_2 at the counter electrode is not given any significance.
- Major proportion of interest is given mainly to the selectivity than activity and stability which are also crucial in assessing the rate of production of H_2O_2.
- Tafel analysis is key component in all sort of electrocatalysis research which is not used as effectively as it is used in water electrolyser and fuel-cell characterizations.
- Mesoscopic effect of electrode and cell are not given any significance albeit these effects could largely affect activity, selectivity, and stability of the catalysts under study.

Other Ways of Precisely Assessing H_2O_2 Evolving Catalysts

It is comprehended from above discussion that it is hard to come up with a standard set of evaluation perspectives for electrochemical hydrogen peroxide evolution either via two-electron ORR or two-electron WOR. However, following modifications in the standard protocols of evaluation could be adapted to make the data more insightful and truly reflecting the intrinsic activity. The very first modification that we suggest is the use of RRDE method for both two-electron ORR and WOR. Undoubtedly, the selectivity measured using RRDE is not of standard conditions but of externally forced mass transfer conditions. Even then, most of the well-established two-electron ORR catalysts have only been evaluated using RRDE. Therefore, it is inevitable at this stage and we propose the use of RRDE for two-electron WOR too. In this case, potential of WOR catalyst modified disk electrode can be swept from 1.60 to 2.60 V vs. RHE (or even as high as 3.20 V vs. RHE as reported in a few recent reports) while maintaining a constant potential of 1.20 V vs. RHE at the ring electrode. Doing this, two-electron WOR catalysts' selectivity can also be determined concurrently as done for two-electron ORR catalysts. Even though there is a huge possibility that anodically produced H_2O_2 may also get oxidized at the disk electrode (the potential of which is being swept) at high anodic potentials, the oxidation of H_2O_2 at Pt ring electrode at 1.20 V vs. RHE would still be kinetically more facile than the catalyst coated over the disk electrode which is designed exclusively for two-electron WOR. However, the Pt ring in a commonly used RRDE set up has its own disadvantages such as self-oxidation at 1.2 V vs. RHE causing changes in kinetics of H_2O_2 electrooxidation and associated collection efficiency, ability to disproportionate electrosytnhesized H_2O_2 chemically, and slow kinetics of H_2O_2 electrooxidation at Pt surfaces. Hence, if a RRDE with a Pt ring is to be used, we recommend the following procedure to be followed. 1) Using a potential a little lesser than the self-oxidation potential of Pt but higher than the oxidation potential of H_2O_2 (i.e., lower than 1.2 V and higher than 0.7 V vs. RHE), 2) Using the highest possible rotation rate so as to avoid the diffusion limitation issue to avoid the chemical disproportionation of H_2O_2 on Pt surface, and 3) Making the measurements as quickly as possible without exposing Pt to the electrolyte for a much longer time to avoid the deactivation of Pt. Instead, a RRDE set up with a gold or silver ring can be an optimal choice which do not possess such issues. Otherwise, the quantification methods used under standard conditions (such as chromatography, H_2O_2 test strips, and titration) should also be used for two-electron ORR. As stated earlier, titration method utilizes the redox reaction (equation 3) between acidic permanganate and hydrogen peroxide in which the generally oxidizing H_2O_2 becomes a reducing agent as the reduction potential of acidified permanganate is much higher than that of H_2O_2. In this method, the endpoint is determined from the pale pink colour imparted by the excess permanganate added to the analyte (with unknown H_2O_2) which means that the concentration determined from this endpoint is always slightly higher than the actual concentration of H_2O_2 in the analyte. Moreover, there are higher chances for human error while manually adding titrant from the burette which would further cause additional errors in endpoint determination. To overcome this, we propose the use of conductometry/potentiometry titration from which the endpoint could precisely be obtained from the change in conductivity/potential with respect to the addition of titrant to the analyte. Besides, one can also opt one of many H_2O_2 sensors available in the market (such as H_2O_2 test strips) or could make one on their own with a little knowledge from photochemical or electrochemical or photoelectrochemical detection of H_2O_2 using a variety of catalysts reported in literature which could detect in nano molar concentrations.

So far, we have discussed the alternate methods of determination of selectivity. On the other hand, high activity is also important for rapid and bulk production of H_2O_2. Activity is measured by overpotential at defined current density (or at onset of H_2O_2 evolution). This is a very loosely followed evaluation parameter in this field and we even found that no significance was given in a few works to such activity markers. As in other electrocatalytic reactions (such as complete ORR and OER), no assumption on fixed current density can be made (to measure overpotential) as we are not sure that the observed current is either of H_2O_2 evolution or of the formation of H_2O/O_2 or the combination thereof. Hence, it is suggested that the onset overpotential can be preferably used. In addition, the rate of production of H_2O_2 can be determined from the quantification results as turnover frequency (TOF) which could also be used as another activity marker.

As we are more concerned about the selectivity, we could also make use of extensive Tafel analysis to shed light on the mechanism which in turn can be used to highlight the selectivity qualitatively in a given region of overpotential [47,48]. In HER and OER electrocatalysis, the Tafel slope is used to judge the mechanism by which the catalyst under study perform the desired reaction. Typically, the experimental conditions of H_2O_2 evolution (both two-electron ORR and two-electron WOR) are much similar to that of HER and OER. To corroborate the mechanism of HER/OER, the Tafel slope is used to predict the number of electrons transferred in the rate determining step (RDS). If the Tafel slopes are 120, 90, 60, and 30 mV dec^{-1} and the charge transfer coefficient is assumed to be 0.5, the corresponding number of electrons transferred in the RDS is one, two, three, and four, respectively [49]. If one acquires the Tafel plot from the kinetic current for a wide range of overpotentials, they can predict the number of electrons transferred in RDS, mechanism and the selectivity (qualitatively). Obtaining Tafel slope in a wide range of overpotentials could also reveal change in mechanisms which can be used to correlate the trend in FE determined by other methods. Tafel plots of different stainless steel 304 (SS-304) foils treated chemically for different time of reaction and IrO_2 modified SS-304 (**Figure 2**) revealing the change in mechanism of OER in 1.0 M KOH is an example how such an extensive Tafel analysis can also be used in H_2O_2 evolution too to predict the mechanism and selectivity [50].

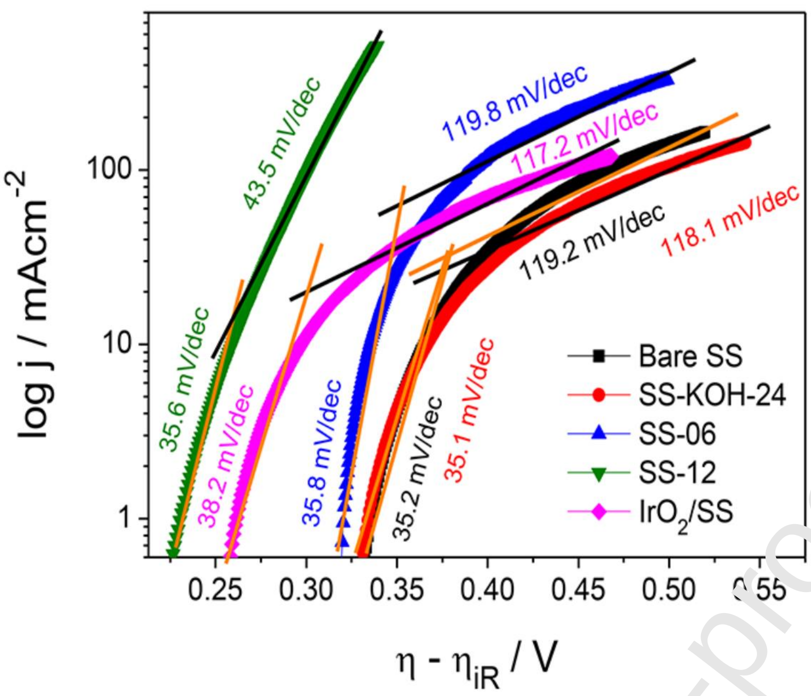


Figure 2: Tafel plots of SS-304 treated in different conditions and of IrO$_2$ modified SS-304 showing change Tafel slopes which in turn indicates the change in mechanism of OER. Reproduced with permission from ref. 50 (Copyright 2017, American Chemical Society).

However, this method is applicable only to two-electron WOR as two-electron ORR is limited by mass transfer after a certain overpotential. However, still one could get to know the mechanism of ORR from the Tafel plot derived out of mass-transport influence corrected kinetic currents [51,52]. Recently studied two-electron WOR catalysts are also polarized as high as 3.20 V vs. RHE within which the equilibrium potential of hydroxyl radical formation via water oxidation falls at 2.73 V vs. RHE. This means that there is a fair chance for the preferable formation of hydroxyl radical over hydrogen peroxide. In general, a few two-electron WOR catalysts showed decreased FE after 2.70 V vs. RHE. Such changes in reaction cannot be understood just from FE measurements whereas an extensive Tafel analysis can. We believe that the above discussed additional methods of precisely assessing the activity and selectivity of H_2O_2 evolving electrocatalysts will extensively be used in future works.

OXYGEN ELECTROCHEMISTRY

Electrochemical transformation of oxygen and its compounds is the most important reaction process without which the realization of clean energy generation, storage, sustainable energy technology, and hydrogen economy are nowhere near in the future [53,54]. Efficiency of fuel cells depends largely on the performance of the cathode catalyst performing four-electron ORR [51,52,55]. Similarly, energy efficiency of hydrogen generation from water through electrolysis is determined almost exclusively by the four-electron WOR (otherwise familiar OER) which is complex and involves in O–O bond forming reaction [56–58]. Amount of electrical energy stored in a metal-air battery on the other hand depends largely on the efficiency of bi-functional activity of the catalyst material used as an air-electrode. This air-electrode must perform both complete four-electron ORR and four-electron WOR in order to have high cell-voltage and subsequent high power density [59–62]. Other than these, environmental pollution treatment processes such as electrochemical bleaching (electro Fenton process) in the presence of a co-catalyst which will form the highly reactive hydroxyl radicals is also involving in electrochemical transformation of oxygen and oxygen containing small molecules (H_2O_2 and water) [63–65]. An excellent review focussing on various energy conversion reactions that utilize the electrochemical transformation of oxygen and its species was written by Katsounaros and co-workers[53] which can be referred for further grasping of the significance of oxygen electrochemistry in a broader sense. Just like the above said areas of energy research and their dependence on oxygen electrochemistry, electrochemical hydrogen peroxide synthesis also gets benefitted by it. In this case, as we introduced earlier, it is the two-electron and two-proton path in both ORR and WOR.

Electrochemical Oxidation of Water

Water is one of the most-abundant sources for hydrogen on earther and hence, a tremendous attention is being paid on its electrolysis to generate hydrogen. Beyond just hydrogen generation, water also offers other potential and value-added products that find important industrial applications which include hydrogen peroxide. Equations (5 – 8) shows the ways by which water can be electrochemically oxidized depending on the number of electrons and protons transferred.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E = 1.229 \text{ V vs. RHE} \qquad (5)$$

$$2H_2O \rightarrow HO_2^{\cdot} + 3H^+ + 3e^- \qquad E = 1.655 \text{ V vs. RHE} \qquad (6)$$

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \qquad E = 1.760 \text{ V vs. RHE} \qquad (7)$$

$$H_2O \rightarrow HO^{\cdot} + H^+ + e^- \qquad E = 2.730 \text{ V vs. RHE} \qquad (8)$$

Hence, controlled electrochemical oxidation of water may benefit us with hydroperoxyl radical (the anion of it is called superoxide), hydrogen peroxide, and hydroxyl radical. However, in practice, the formation of hydroperoxyl radical through three-electron water oxidation has never been succeeded before as four-electron and three-electron paths are almost concurrent and indistinguishable. Fortunately, one-electron reduction of oxygen offers a safe path to form hydroperoxyl radicals and superoxide ions which is very commonly observed in biological systems. A classic example is the production of superoxide anion by protonated nicotinamide adenine dinucleotide (NADH) in response to invading pathogens in human body via one-electron reduction of dioxygen molecule [66–68]. This hydroperoxyl radical or superoxide anion acts as rather a strong reducing agent than a oxidizing agent. In fact, the order of oxidizing capability of these reactive oxygen species goes as hydroxyl radical > hydrogen peroxide > hydroperoxyl radical > dioxygen. Hence, in principle, depending the target materials which require oxidation/reduction one can simply control the formation of desired reactive oxygen species (ROS) formation by monitoring the potential. However, it is not that simple in practice because of the kinetic competition between four-electron oxidation of water and other paths. In addition, the four-electron mechanism is the thermodynamically favored path with the lowest equilibrium potential (1.229 V vs. RHE).

Electrochemical Reduction of Dioxygen

Electrochemical reduction of dioxygen is an equally thoroughly explored area of energy conversion electrocatalysis owing to its importance in determining the cell voltage and power density of fuel cells and metal-air batteries [51,52,69]. Besides, it is also vastly studied for the generation of hydroxyl radical and hydrogen peroxide. As far as hydrogen peroxide synthesis via oxygen reduction is concerned, it is advantageous as one can achieve exclusive selectivity [1,13]. However, the mass transfer limitation, need for continuous oxygen supply, and low-current production lowers its significance greatly. Equations (9 – 12) show the different ROS that can be formed via controlled reduction of dioxygen molecule.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E = 1.229 \text{ V vs. RHE} \qquad (9)$$

$$\frac{3}{2}O_2 + 3H^+ + 3e^- \rightarrow 3HO^{\cdot} \qquad E = 0.803 \text{ V vs. RHE} \qquad (10)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E = 0.700 \text{ V vs. RHE} \qquad (11)$$

$$O_2 + H^+ + e^- \rightarrow HO_2^{\cdot} \qquad E = 0.330 \text{ V vs. RHE} \qquad (12)$$

These reactions and the corresponding equilibrium potentials are important in designing catalysts considering the energies of interactions of intermediate species. In our case, it is the two-electron path for both ORR and WOR. Hence, while designing an electrocatalysts one always has to be cautious in suppressing the thermodynamically favoured four-electron path at lower overpotentials and other possible (three- and single-electron) paths at high overpotentials to ensure high rate and exclusive selectivity. So far, every two-electron ORR and two-electron WOR catalysts reported in literature had strategically avoided the four-electron path by making them poor catalysts for complete ORR and OER which are discussed in forthcoming sections. Such catalysts had always begun ORR and WOR beyond the equilibrium potential of two-electron paths (0.700 and 1.760 V vs. RHE, respectively for ORR and WOR).

Effect of Single- and Three-Electron Paths in H_2O_2 Synthesis

Change in the selectivity of H_2O_2 evolving catalysts at relatively higher overpotential is an understudied phenomenon in this area of research. Apparently, several, two-electron ORR and two-electron WOR electrocatalysts had exhibited lowering in the H_2O_2 Faradaic efficiency. In most of the cases where H_2O_2 was synthesized via two-electron water oxidation, the reason for such a lowering was attributed to the shift in equilibrium caused towards the starting material (H_2O) with the increasing product (H_2O_2) concentration according to Le Chatelier's principle which seems to be true as no relationship between such a lowering in selectivity and equilibrium potentials of other possible paths of oxygen electrochemistry discussed above [32].

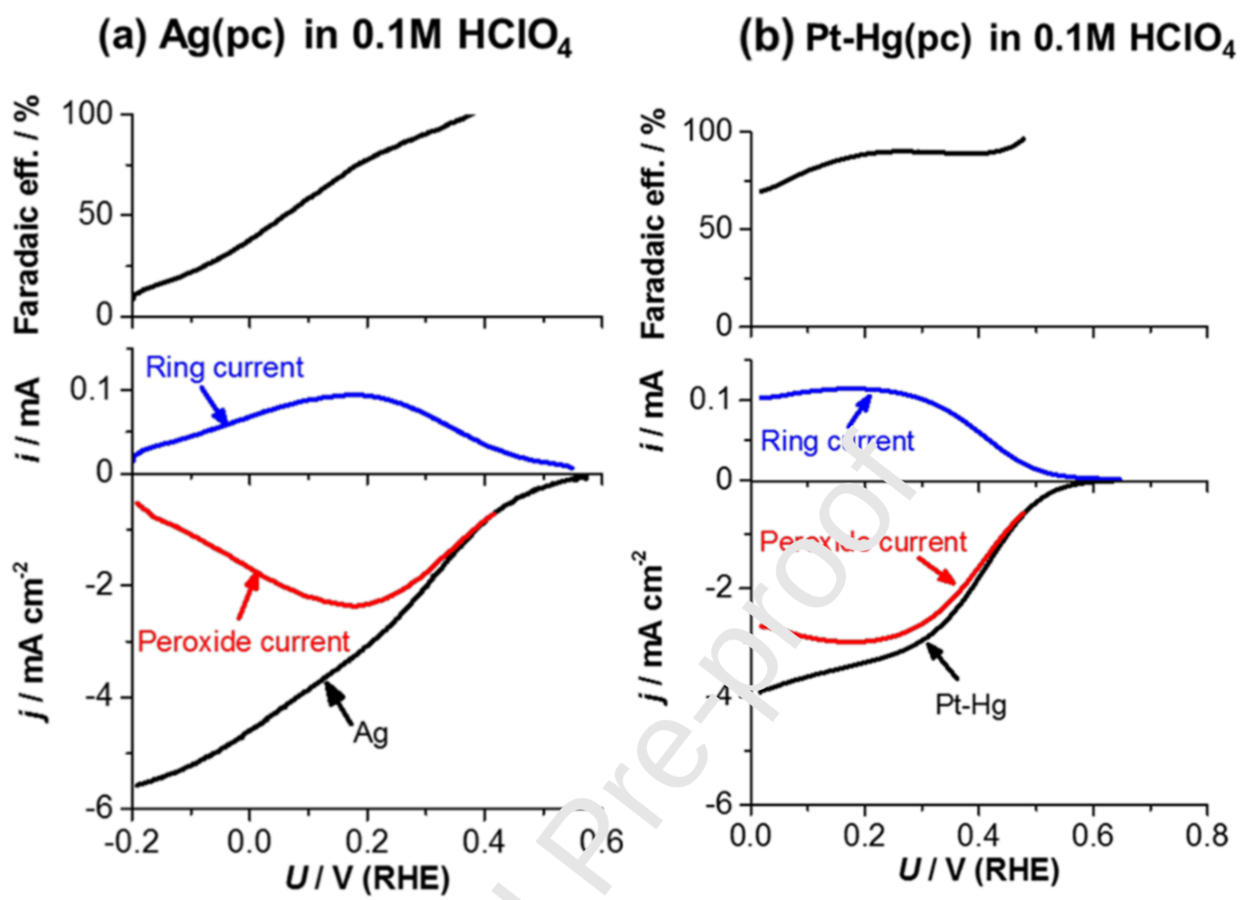


Figure 3: ORR LSVs of Ag (a) and Pt-Hg (b) catalysts in 0.1 M $HClO_4$ showing gradual lowering in FE, peroxide current (red), and ring current corresponding the oxidation of H_2O_2 formed at the disk of RRDE assembly at U < 0.3 V vs. RHE (the equilibrium potential of hydroperoxide radical formation via single-electron ORR). Reproduced (a) with permission from ref. 13 (Copyright 2018, American Chemical Society) and (b) from ref. 24 (Copyright 2013, Nature Publishing Group).

Another possible reason is that at high overpotentials, these materials which are poor in performing four-electron oxidation might have become active for it due to the probable changes that occur in the work function of the surface. Beyond these reasons, lowering in selectivity of two-electron path could also be attributed to the emergence of single-electron path. However, such a justification was never made in any reports wherever such a lowering is observed and the potential at which the lowering witnessed was closer to the equilibrium potentials of single-electron paths in ORR and WOR.

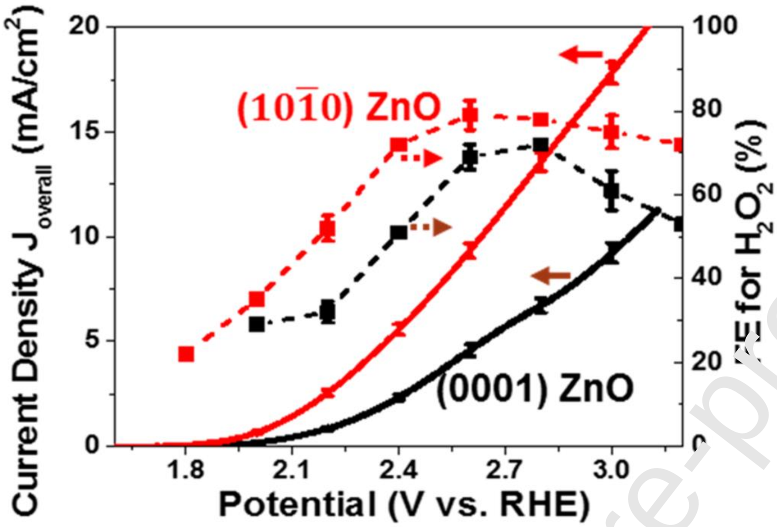


Figure 4: WOR LSVs of different facets of ZnO in 2.0 M $KHCO_3$ showing a gradual lowering in FE beyond 2.73 V vs. RHE (the equilibrium potential of formation of hydroxyl radical via single-electron WOR). Reproduced with permission from ref. 29 (Copyright 2019, American Chemical Society).

A cautious survey of such studies where lowering of selectivity witnessed at higher overpotentials corresponding to single-electron path are discussed here. Yang and co-workers[13] and Siahrostami and co-workers[24] witnessed such a lowering in selectivity for Ag and Pt-Hg two-electron ORR catalysts in 0.1 M perchloric acid (**Figure 3**a-b). As we can see from Figure 3a-b that at U < 0.3 V vs. RHE (the equilibrium potential for the formation of hydroperoxyl radical via ORR), the peroxide current (red) and the corresponding peroxide oxidation current at ring electrode (blue) began decreasing gradually. Meanwhile, a concurrent lowering in the FE was also evidenced. However, such a potential dependent selectivity change with these same catalysts are observed only in 0.1 M perchloric acid but not in 0.1 M potassium hydroxide. This further indicates that solution pH will have huge role in determining the efficiency of a given electrocatalyst in H_2O_2 synthesis via two-electron ORR. Similarly, a recent work by Kelly and co-workers[29] demonstrated that the different phases of ZnO two-electron WOR catalysts (in 2.0 M $KHCO_3$) suffered lowering selectivity just above 2.7 V vs. RHE which is the equilibrium potential for the formation of hydroxyl radical via single-electron WOR (**Figure 4**). These studies are showing an unhighlighted phenomenon of selectivity change at higher overpotentials which could be detrimental when high rate production of H_2O_2 is aimed. Again, such a change in selectivity can be reflected via an extended Tafel analysis covering a larger range of overpotentials discussed in the previous section. It is also expected that just like the detection of H_2O_2 via electrochemical oxidation and titrimetric reduction, methods and techniques should be developed to detect and quantify the hydroperoxyl radical/superoxide anion and hydroxyl radical formed as a result of change in selectivity via single-electron ORR and single-electron WOR. This could lead to the development of a brand new and an exciting area of research involving single-electron electro activation of water and dioxygen with potential applications elsewhere. To conclude this section, the merits and demerits of both two-electron ORR and two-electron WOR are described briefly in **Table 1**.

Table 1: Merits and demerits of two-electron ORR and two-electron WOR in H_2O_2 electrosynthesis.

Two-electron ORR	
Merits	Demerits
• Requires less overpotential • Mostly deliver 100% Faradaic	• Further electroreduction of H_2O_2 at high overptoentials

efficiency • Easily quantified with RRDE • Number of known catalysts is greater than that of two-electron WOR	• Influence of three-electron ORR after 0.3 V vs. RHE in the cathodic region • Use of mercury is unavoidable in known metallic catalysts with 100% Faradaic efficiency. • Faradaic efficiency is determined instantaneously using RRDE and hence, cannot reflect other key issues such as rate of production, saturation, stability of synthesized H_2O_2 in solution. • It lacks from low productivity as a consequence of low current density limited by the diffusion of O_2. • Requires continuous bubbling of O_2 for interruption less H_2O_2 production.
Two-electron WOR	
Merits	Demerits
• High productivity as a result of high current activity • No bubbling of O_2 is required • Faradaic efficiency is determined using relatively precise methods after	• Further electrooxidation of H_2O_2 • Hydroxyl radical formation after 2.7 V vs. RHE • Poor Faradic efficiency as a result of competing four-electron OER

sufficient saturation. • Loss of H_2O_2 is accounted in general by relating with the chemical and electrochemical decomposition paths • Simultaneous evolution of O_2 enhances the diffusion of H_2O_2 away from the electrode surface • Does not require sophisticated analytic tools such as RRDE.	• Number of known catalysts is very low when compared to that of two-electron ORR • No standard procedure of quantification of H_2O_2 is followed • Higher probability of further electrooxidation as a result of low rate of H_2O_2 diffusion

BONDING AND ENERGIES OF INTERACTIONS

Bonding of catalytic site to the electroactive species and the energies of interactions of intermediate species with the electrocatalytic site are crucial in determining activity. In that sense, H_2O_2 evolving catalysts are no exception. It was introduced earlier that the catalyst development for controlled ORR is quite mature but not so for controlled WOR to produce H_2O_2. However, there is a few first principle studies that evaluated the activity trend of various ORR catalysts (metals, alloys, and M-N-C) and various metal oxide WOR catalysts. Such theoretically predicted activity trend is discussed here.

Trends in Two-Electron ORR

In determining the activity trend of any given set of electrocatalysts, constructing a Sabatier volcano plot is the primary step [70]. To do this, calculated limiting overpotential is plotted against the adsorption of energy of an intermediate species, the formation of which is likely to be the rate determining step (RDS). In ORR, formation of metal hydroperoxide intermediate (M-

OOH) is considered to be the RDS and hence, the adsorption free energy of *OOH is plotted with the limiting potential for determining the activity trend.

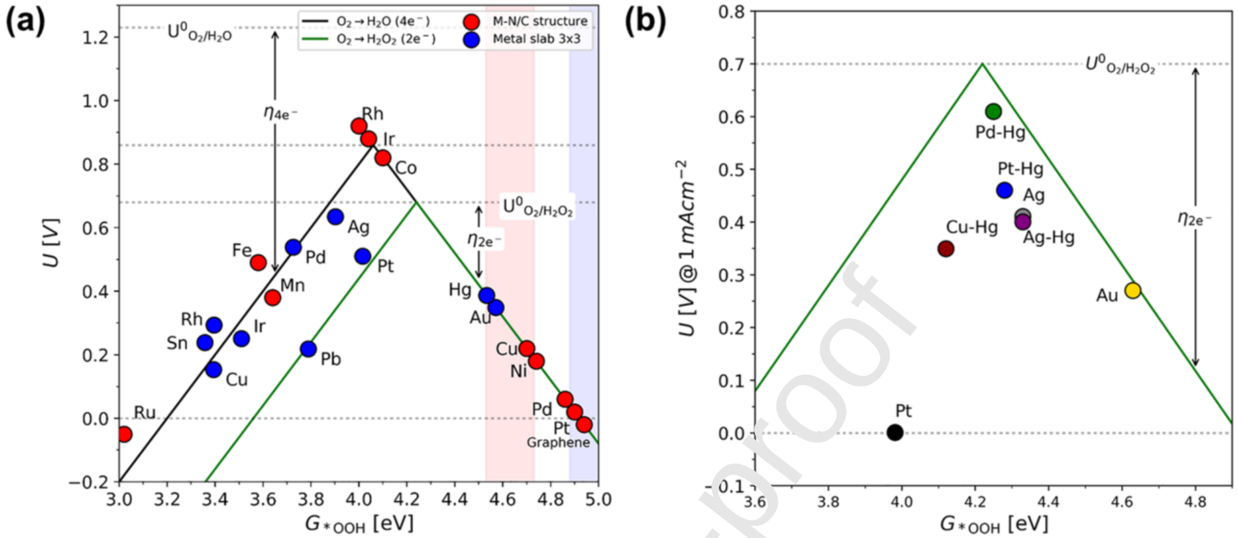


Figure 5: (a) Two- and four-electron Sabatier ORR volcano plots of various metals. (b) Two-electron ORR Sabatier volcano plot for Hg alloys of Pd, Pt, Au and Cu in comparison with pristine Au and Pt surfaces. Reproduced (a) with permission from ref. 71 (Copyright 2012 American Chemical Society) and (b) from ref. 25 (Copyright 2014 American Chemical Society).

Following this, Viswanathan and co-workers[71] reported the two-electron and four-electron ORR activity trends for a range of metal catalysts (**Figure 5**a). This study showed that no catalyst in which the reduction of *OOH to H_2O_2 is limited by the strong adsorption of *OOH can perform two-electron ORR as the potential for four-electron ORR is always more positive (black line). Conversely, the right-leg of both four-electron path and two-electron path in ORR overlaps suggesting equal probability for the formation of H_2O_2 and H_2O with the catalysts sitting on the right leg of the volcano having weak binding energy towards *OOH adsorption. This clearly shows that the electronic effects of these metals do not favour H_2O_2 formation. However, this electronic effect was successfully manipulated by alloying these poorly active two-electron ORR catalysts with inert metal host such as Hg (Figure 5b) [25]. Such a change directed towards two-election ORR is purely a geometrical effect and not of electronic effect. This is the well-known strategy of making isolated catalysts in a matrix of inert material which either be a metal like Hg or an extended covalent network like graphitic carbons and graphene derivatives. This topic is detailed in the forthcoming sections.

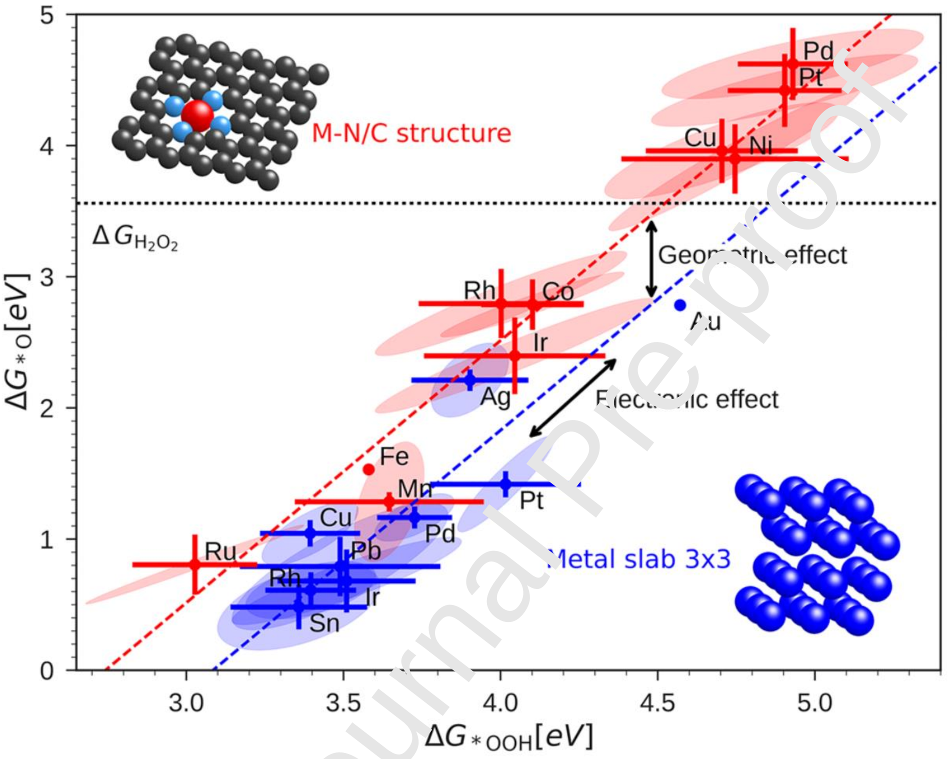


Figure 6: Plot of *O adsorption free energy against *OOH adsorption free energy of various metals and M-N/C catalysts studied for two-electron ORR. Reproduced with permission from ref. 13 (Copyright 2018, American Chemical Society).

Irrespective of the RDS, considering the very high tendency (thermodynamically favoured) for four-electron ORR, it is also important to ensure that the formation of *O is suppressed in order to have high selectivity. This can be achieved only by isolating the catalytic sites from other sites by placing them far away in an inert matrix like Hg or graphitic carbon because the preferred *O adsorption sites are the hollow and bridge sites and the existence of which can be eliminated via such an isolation. When the catalytic sites are geometrically isolated from one another, the probable existence of hollow and bridging sites becomes very low and the adsorption of *OOH will always occur on atop site which is the only catalytic site favouring two-electron ORR. However, such geometrical isolation also destabilizes *OOH adsorption but increases the selectivity leading to overall enhancement in H_2O_2 production rate. This effect was shown by Yang and co-workers[13] for a range of metal and M-N-C ORR catalysts by plotting the respective adsorption free energy of *O against the adsorption free energy of *OOH (**Figure 6**). According to Figure 6, M-N-C (M=Cu, Ni, Pt, and Pd) that sit above the horizontal line indicating the optimal adsorption free energy for *O could perform better in H_2O_2 synthesis via two-electron ORR.

Trends in Two-Electron WOR

Just like the activity trends predicted for ORR catalysts from first principle calculations, activity and selectivity trends for WOR catalysts can also be predicted using Sabatier volcano plot which is obtained by plotting limiting potentials (where all elementary steps are in thermoneutral state) against the adsorption free energy of *OH which is believed to be the RDS of water oxidation. For a WOR catalyst to be highly selective for H_2O_2 evolution instead of O_2 evolution, adsorbed *O and hydroxyl radicals in solution must be less stable than H_2O_2 in solution and adsorbed *OH, respectively. In general, with two-electron WOR catalysts that bind oxygen intermediates too strongly, the oxidation of *OH to H_2O_2 is the RDS whereas with WOR catalysts that bind oxygen intermediates too weakly, formation of adsorbed *OH from water is the RDS. Since *OH is involved in RDS of both strongly binding and weakly binding WOR catalysts, a conventional Sabatier volcano plot can be constructed by plotting theoretically calculated limiting potentials against the adsorption free energy of *OH. This means that a highly active two-electron WOR catalyst will sit on the top (when WOR U_L is in negative values) or at the valley (when WOR U_L is in positive values) of the Sabatier volcano plot.

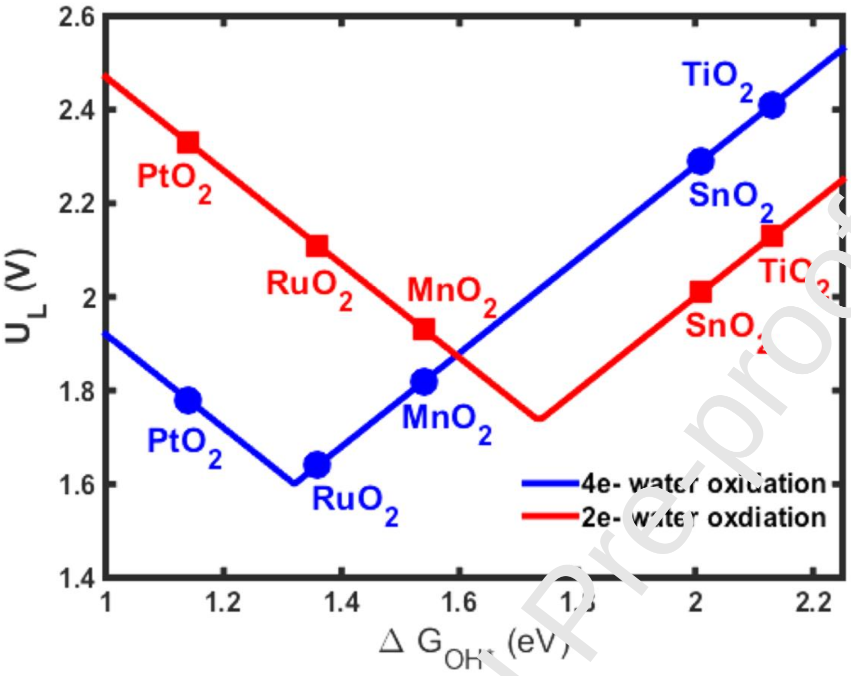


Figure 7: Sabatier volcano plot of four- and two-electron water oxidation reactions for a few metal oxide catalysts. Reproduced with permission from ref. 72 (Copyright 2015, American Chemical Society).

Such a volcano plot for both four-electron and two-electron WOR was first predicted by Viswanathan and co-workers[72] (**Figure 7**) that included PtO_2, RuO_2, MnO_2, SnO_2, and TiO_2. Following this, the volcano plot of two-electron WOR metal oxide catalysts is being updated frequently by the works of Siahrostami and co-workers [29–32]. **Figure 8** is the volcano plot of two-electron WOR catalysts reported till date in which we can find that ZnO (00–10) sits at the top of the plot with the most optimal binding energy for *OH adsorption while maintaining high selectivity for H_2O_2 evolution. Besides, WOR catalysts that bind oxygen strongly and WOR catalysts that bind oxygen weakly require huge overpotentials. However, their selectivity was relatively better. In order to have a wide potential window of evolving H_2O_2 via water oxidation, an ideal catalyst would have supressed selectivity towards O_2 and hydroxyl radical evolution (four- and single-electron oxidations, respectively).

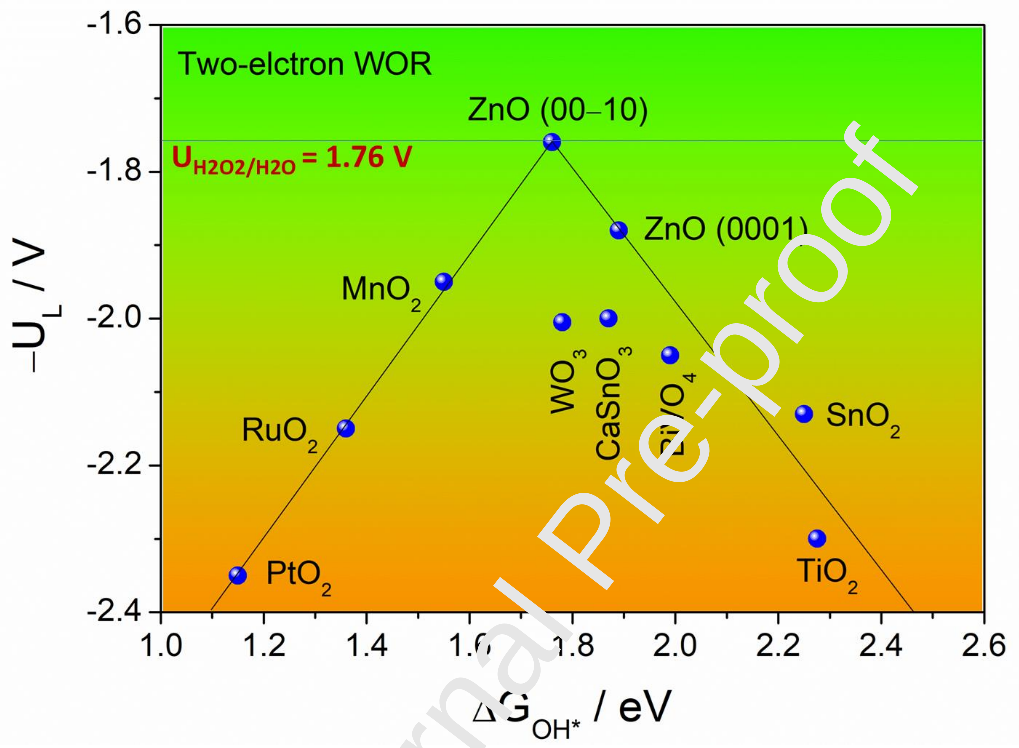


Figure 8: Two-electron WOR volcano plot for reported H_2O_2 evolving catalysts. The corresponding data were taken from the works of Viswanathan and co-workers[72] and Siahrostami and co-workers.[29–32]

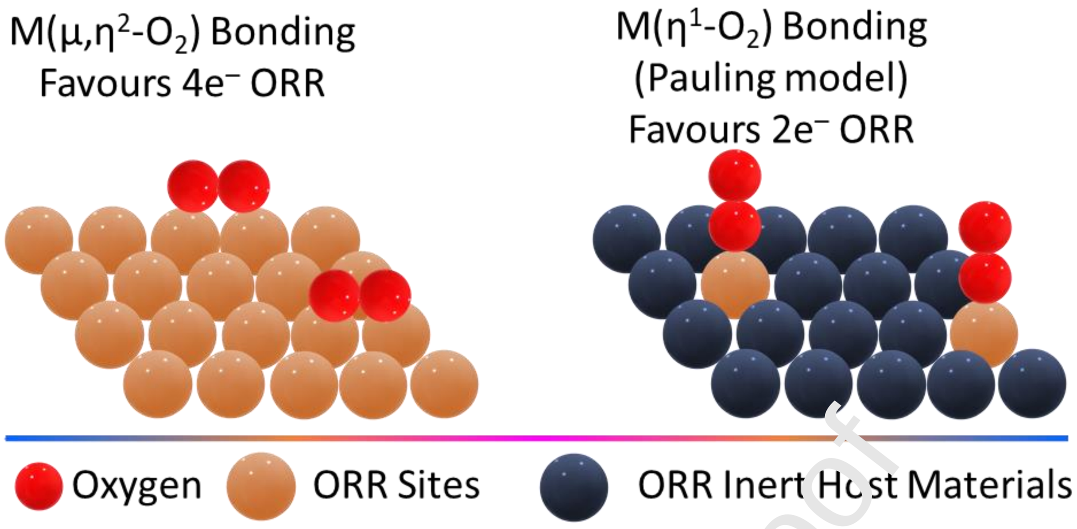
A similar two-electron WOR volcano plot for carbon based catalysts was reported by Xia and co-workers[28] who examined the effect of extent of oxidation of these carbon catalysts on the selectivity of two-electron WOR. One thing that is common with all these catalysts is that they all are poor catalyst for thermodynamically favoured four-electron WOR. As far as two-electron WOR is concerned, the number of catalysts developed is relatively low and it is expected explode in numbers in near future. At this point, it is also emphasized that the trends witnessed with volcano plots are not be taken as a sole indicator of superior activity. Rate of the reaction under study and the environment also do matter a lot. This means that a catalyst that occupy the atop position could show low selectivity and productivity and *vise-versa*.

TRENDS IN CATALYSTS' DESIGN

Above discussed activity trends, evaluation perspectives and associated ambiguities, corresponding electrochemical transformations of oxygen will help us understanding the trends in catalysts' design. In this section, we have chosen only the seminal discoveries of the field which fetched significant advancement to the field to a newer level. A detailed summary of two-electron ORR catalysts and two-electron WOR catalysts that have so far been reported can be found elsewhere [1,3,13,73].

Trends in Designing Two-Electron ORR Catalysts

As stated earlier, two-electron ORR is quite saturated in terms of catalysts' development and the reported catalysts can be classified basically into four types as metals and their alloys, heteroatoms (N. F, and O) doped carbons, metal oxides, and M-N-C structures. With all these catalysts, the selectivity for two-electron ORR is achieved following a single principle of having isolated ORR sites. Alloying, complexing with macromolecular chelating agents and partial masking are three important strategies employed in achieving ORR catalytic site isolation. When we have such isolated ORR catalytic sites, the formation metal hydroperoxide intermediate is facilitated as the only possible mode of bonding is via Pauling model ($M(\eta^1-O_2)$ in which breaking of O–O bond is highly unlikely to occur. This selective mode of binding achieved by catalytic site isolation is actually the most important phenomenon governing H_2O_2 selectivity. **Scheme 2** depicts different modes of O_2 binding when we closely packed and isolated ORR sites.



Scheme 2: Graphical sketch showing H_2O_2 evolution facilitating Pauling model of O_2 binding with isolated ORR sites.

Strategy of Alloying

Isolation of ORR active catalysts in an inert host was first shown by alloying. Pt is known for its superior four-electron ORR activity in both acid and alkali. Interestingly, when this Pt is alloyed with ORR inactive materials such as Hg and Au, it performed two-electron ORR very selectively. Siahrostami and co-workers[24] began this strategy by alloying Pt with Hg that showed excellent selectivity for H_2O_2 synthesis around 0.45 V vs. RHE in 0.1 M $HClO_4$. Later, Verdaguer-Casadevall and co-workers[25] had extended this strategy to alloy Ag, Pd, and Cu with Hg and found similar enhancement in selectivity towards H_2O_2 synthesis in 0.1 M $HClO_4$ saturated with O_2. An interesting finding in this study was that Pd-Hg demanded even lower overpotential than Pt-Hg whereas Cu-Hg and Ag-Hg that demanded relatively higher overpotential delivered ~100% selectivity (**Figure 9**a-b). This implies that an ideal catalyst is the one that could have both low overpotential and high selectivity. Pizzutilo and co-workers[74] later examined the role of Au content (ORR inactive host) in ORR active Pd catalysts by varying their stoichiometric composition in the same O_2-saturated 0.1 M $HClO_4$ solution. As anticipated, higher proportion of Pd led to four-electron ORR whereas higher Au content favoured two-electron ORR. Having known that alloying an ORR active catalyst with an inert host at nanoscale was highly fruitful in improving H_2O_2 selectivity, much attention was later paid in designing single-atom catalysts (SAC) in which the total content of ORR active catalysts is several times lower than the ones in alloyed catalysts.

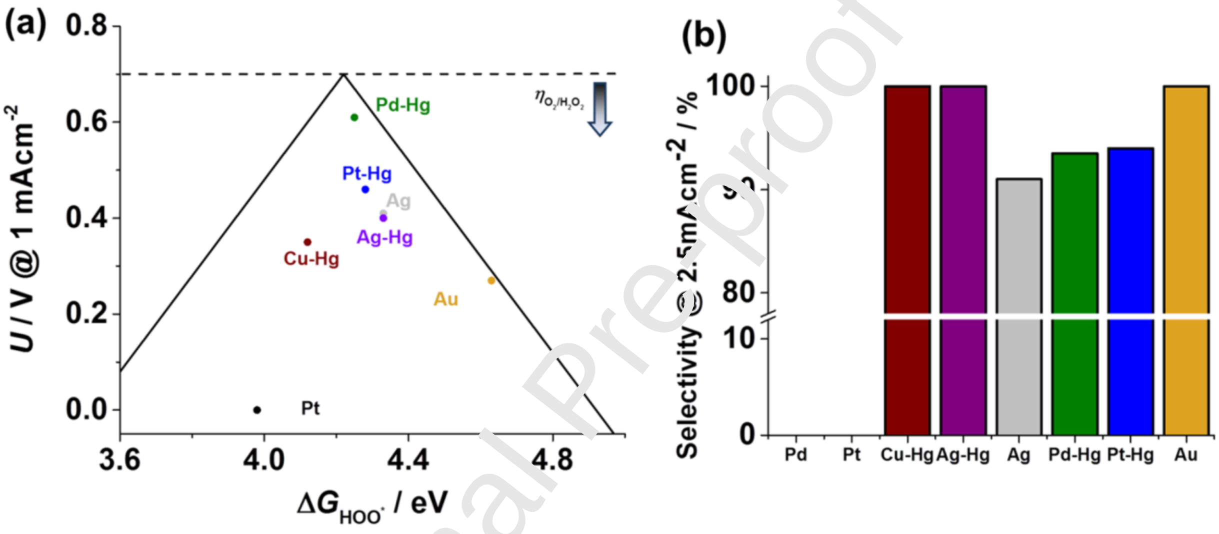


Figure 9: (a) Two-electron ORR volcano plot of Ag, Pt, Pd, and Cu catalysts alloyed with Hg. (b) Plot showing the selectivity of the same at 2.5 mA cm^{-2}. Reproduced with permission from ref. 25 (Copyright 2014, American Chemical Society).

This strategy was first shown by Jirkovsky and co-workers[75] to be effective for Au-Pd systems in which Pd is the ORR active component while Au was serving the purpose of being an inactive host in Ar-saturated 0.1 M $HClO_4$. Their results suggested that an optimum catalyst with high H_2O_2 selectivity can be obtained when the fraction of Pd is close to 0.1. Further advancements was brought out by Choi and co-workers[76] in an effort to isolate Pt SAC with a completely different inert host which was 17% sulphur containing zeolite templated 3D graphene structures in 0.1 M $HClO_4$. By this method, selectivity close to 95% was achieved. However, overpotential was much higher than the earlier studies. Meanwhile, Yang and co-workers[77] made an interesting Pt SAC-inert host couple taking TiN as the ORR inert host which has never been used before but failed to compete with the earlier reports in terms of selectivity in 0.1 M $HClO_4$ saturated with O_2. In fact, the best selectivity achieved with this catalyst was realized at a very high overpotential (600 mV). Having realized that the inert host could have an effect on H_2O_2 selectivity, the same group extended this strategy by taking TiC as an additional ORR inert host and achieved a better selectivity [78] with the same electrolytic medium. However, the issue of high overpotential was never overcome by such a change in host material from TiN to TiC. An interesting SAC of Ni with graphene (ORR inert) host has very recently been reported by Song and co-workers[46] that achieved selectivity as high as 94% with a very low overpotential (100 mV) in 0.1 M KOH in which usually the produced H_2O_2 is less stable. Hence, this finding is one among those important studies that lifted the strategy of isolating ORR catalysts with an inert host from noble metals to a non-noble metal (Ni).

Strategy of Chelating

Isolating ORR catalysts as SAC is easy to achieve when we have precise control over the number of atoms dispersed in a localized space. All the previously mentioned SACs had actually consisted a cluster of atoms rather than a truly single atom. Truly single atom containing catalysts were actually the M-N-C structures in which a single metal centre is surrounded usually by a tetradentate N-containing chelating macromolecules which include porphyrin and phthalocyanine [16,23,79–83]. These complexes of porphyrin and phthalocyanine are actually having a single atom of ORR catalysts that are well isolated form another atom of the same thereby enabling the Pauling model O_2 bonding that favours two-electron ORR.

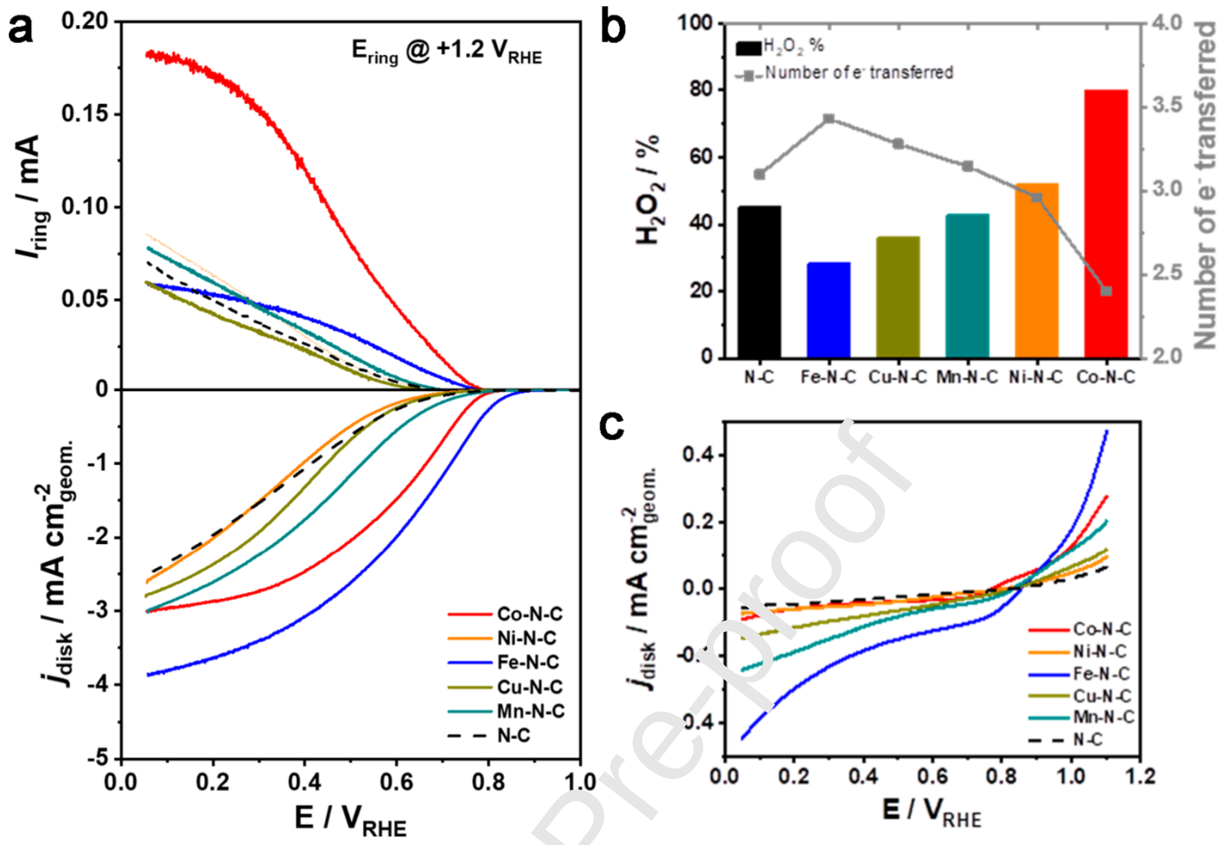


Figure 10: (a) ORR LSVs acquired with RRDE for Co, Ni, Fe, Cu, and Mn based M-N-C catalysts in comparison with N-C with their respective H_2O_2 oxidation current (@1.2 V vs. RHE) detected at the ring electrode. (b) Plot showing H_2O_2 selectivity and number of electron transfer involved in ORR. (c) H_2O_2 reduction LSVs of all studied catalysts in N_2 purged 0.5 H_2SO_4 containing 1 mM H_2O_2. Reproduced with permission from ref. 21 (Copyright 2019, American Chemical Society).

However, not all M-N-C catalysts are selective for two-electron ORR, many M-N-C catalysts have previously been reported to be highly active for four-electron ORR too [84]. Only Mn and Co based M-N-C catalysts have been reported to be selective for H_2O_2 synthesis via ORR so far and it is still elusive what makes other M-N-C based SACs efficient in four-electron ORR. Besides just M-N-C structures, their composites with other nanostructured carbon materials were also reported bring out better stability. However, the selectivity enhancement brought up in these cases may actually be due to added carbon than the M-N-C structures. Between Mn and Co based M-N-C catalysts, Co based M-N-C catalysts showed better selectivity. An extended comparison of two-electron ORR activity was recently reported by Sun and co-workers[21] who designed M-N-C structures taking Co, Mn, Ni, Fe, and Cu in N_2-saturated 0.5 M H_2SO_4. In this study, they found an excellent two-electron selectivity with Co-N-C single site catalyst Fe-N-C showed the lowest selectivity which is a well-known four-electron ORR catalyst (**Figure 10**a-c). The isolation strategies discussed above have so far been centred around only a very few ORR catalysts and it is expected that the same strategies can also be extended to other metals (Se, Ru, Ir, Rh, Nb, and Ce) that were reported for two-electron ORR in the recent past [63,85,86].

Strategy of Heteroatom Doping

Heteroatoms (O, N, B, S, and F) doped carbonaceous catalysts are the ones with the highest number of studies for two-electron ORR. A closer examination will reveal that these catalysts were also able to achieve such selectivity for two-electron ORR activity by the strategy of isolation. With these catalysts, heteroatoms in the continuum of sp^2 carbon networks usually be partially polarized (negatively except for B-doped carbon) and acts as electron reservoir for the initial adsorption of O_2 for further electrochemical reduction. When we have such isolated heteroatoms in the relatively ORR inactive carbon networks, they prefer attaching to O_2 molecule via the end-on Pauling model facilitating H_2O_2 synthesis. An extensive summary of developments of these catalysts were earlier given by the reviews by Perry and co-workers[1] and Siahrostami and co-workers [13]. Besides just heteroatom doping, modification with other molecules such as anthraquinone and its derivatives and polymers of aniline and tetrafluoro ethylene were also shown to improve the selectivity of these catalysts [63,85–88]. In this category, an interesting report was made by Chen and co-workers[89] who made isolated islands of boron nitride (BN) in a *sp*^{2} carbon matrix. This catalyst performed ORR with 90% selectivity for H_2O_2 in the low overpotential region which got lowered gradually with the increasing overpotential in O_2-saturated 0.1 M KOH.

Strategy of Partially Masking Catalytic Sites

In contrast to the above discussed ways of isolating ORR catalytic sites, partial masking differs by having a layer of an ORR inert coating (*sp*^{2} carbon networks) with sufficient number of pores over a large surface of an ORR catalyst. Choi and co-workers[90] reported this interesting strategy with Pt catalyst in which they increased the time of coating of amorphous carbon on Pt particles and found that catalysts coated extensively with amorphous carbon for over three and four hours showed selectivity as high as ~50% in oxygenated 1.0 M $HClO_4$. **Figure 11a-b** shows the advantageous end-on (Pauling model) O_2 bonding with partially masked Pt particles over the one with no coating. Though this method is shown to be effective in bringing up selectivity change with Pt, the observed selectivity is not as high as the ones achieved with alloying, chelating, and heteroatom doping. Hence, one may even think of coalescing all these four ways of isolating ORR catalytic sites in different combinations which may improve selectivity and activity towards H_2O_2 synthesis via ORR. Irrespective of the type of the catalysts used, two-electron ORR has always been achieved following a single principle of catalyst site's isolation which forbade other modes of O_2 bonding that would have led to complete (four-electron) ORR. However, further in situ/operando studies are required to reveal the actual role of having an ORR inert host and isolating ORR active sites which will be invaluable to further improve the selectivity of these ORR catalysts for H_2O_2 synthesis via controlled ORR.

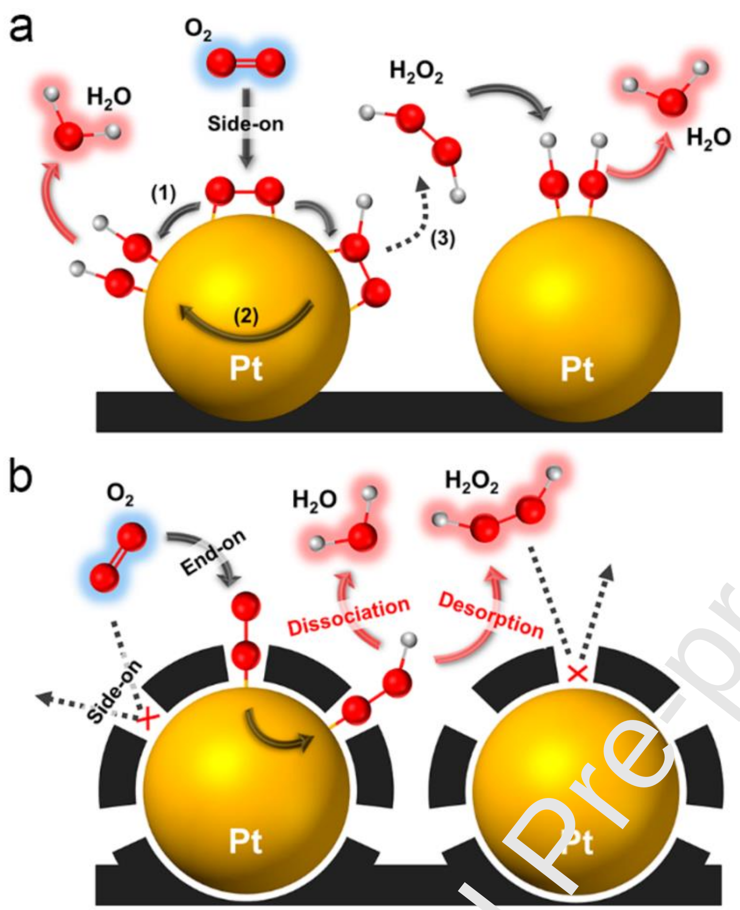


Figure 11: (a) Graphical sketch showing side-on bonding mode favoured by uncoated Pt particles leading to four-electron ORR. (b) Graphical sketch showing end-on bonding mode favoured by partially masked (amorphous carbon coated) Pt particles leading to H_2O_2 synthesis. Reproduced with permission from ref. 90 (Copyright 2014, American Chemical Society).

Trends in Designing Two-Electron WOR Catalysts

Two-electron WOR is even a handier way of producing H_2O_2 electrochemically as it does not require continuous purging of O_2 gas like two-electron ORR. The major issue with this path is the competition from the thermodynamically favoured OER (four-electron WOR). In addition, a highly oxidizing operational potential at the working electrode surface could easily lead to further oxidation of synthesized H_2O_2 if it stays for a sufficiently large time at or near the interface within the inner and outer Helmholtz planes and to some extent in the diffusion layer. Just like ORR, OER is also favoured by closely packed catalysts which can evolve O_2 molecule in a way analogous to four-membered decycloaddition reaction. However, even with single metal atom containing molecular catalysts, OER was preferably shown to be active rather than two-electron WOR [34]. This implies that one cannot simply make an OER active catalyst into two-electron active WOR catalyst just by isolating the catalytic sites which were found to be effective in switching the selectivity of well-known ORR catalysts in the favour of H_2O_2 synthesis. Hence, the first condition to make a selective catalyst for anodic H_2O_2 synthesis via two-electron WOR is finding a catalyst that does not begin water oxidation below the equilibrium potential of two-electron WOR (1.76 V vs. RHE). Obviously, this condition rules out all the well-known OER electrocatalysts of metals Ru, Ir, Ni, Fe, Co, and Mn and combination thereof [91]. Hence, people have so far been paying attention to the oxides of metals (Sn, Ti, V, W, Zn, Ca, and Bi) and combination thereof which are known for their poor OER activity [29–32]. Besides, carbonaceous catalysts with various degrees of oxidation are also shown to be highly selective for H_2O_2 evolution via two-electron WOR. This implies that the only strategy followed to design a H_2O_2 evolving anode catalyst is sticking with metals or elements known for their poor OER activity. The very first anode catalyst reported for H_2O_2 production was oxidized conducting carbon by Ando and Tanaka[27] with a PEMFC set up which were earlier used only for the production of H_2O_2 via two-electron ORR in 0.1 M NaOH. Since then, no significant improvement was witnessed with carbonaceous two-electron WOR catalysts until a very recent report by Xia and co-workers[28] who coated various carbon catalysts with hydrophobic polymers that helped confining in situ generated O_2 gas that in turn regulated the WOR to be highly selective for H_2O_2 evolution from water in 1.0 M Na_2CO_3 solution. An interesting result of this study was the gradual lowering in overall water oxidation current and gradual increase in H_2O_2 selectivity with the increasing hydrophobic polymer (PTFE) coating (**Figure 12**a-b). This is different from all those earlier studies on anodic H_2O_2 synthesis. We expect that other carbonaceous catalysts such as the ones containing different heteroatoms could also be preferable candidates for two-electron WOR.

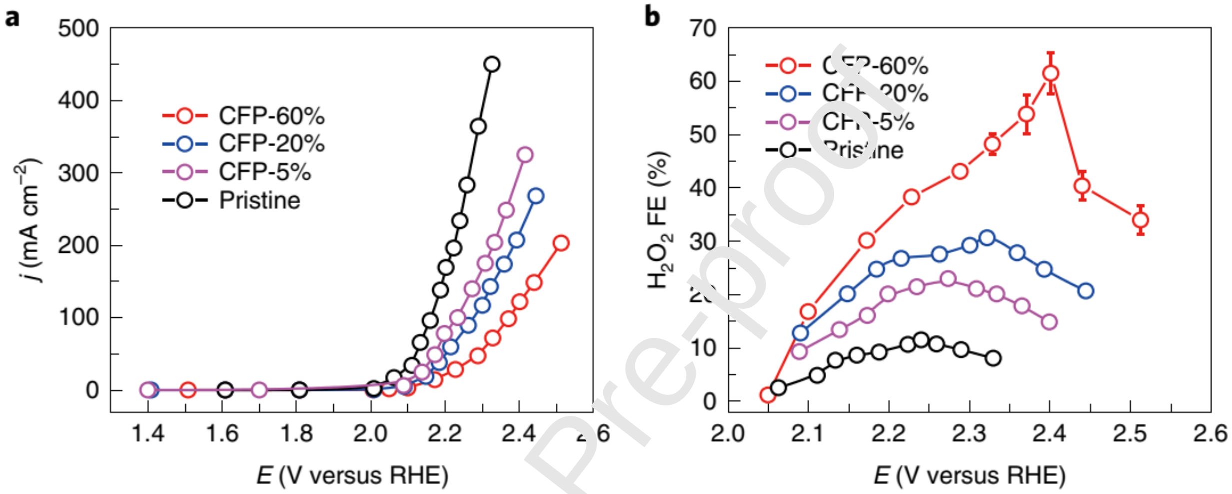


Figure 12: (a) LSVs of carbon fibre paper (CFP) with different percentages of PTFE coating. (b) Plot of Faradaic Efficiency (for H_2O_2) against various potentials. Reproduced with permission from ref. 28 (Copyright 2020, Nature Publishing Group).

Besides carbonaceous catalysts, oxides of metals known for poor OER activity have been shown to be highly selective for anodic H_2O_2 evolution from water which include TiO_2, SnO_2, WO_3, $BiVO_4$, $CaSnO_3$ and ZnO. All these catalysts have basically one thing in common that they do not begin water oxidation reaction before 1.76 V vs. RHE thereby favouring H_2O_2 evolution. Among them, ZnO has been reported to have the lowest onset potential with highest selectivity of 80% for H_2O_2 evolution from water at 3.0 V vs. RHE (**Figure 13**) [29]. $BiVO_4$ reported earlier just as an electrocatalyst by Shi and co-workers[32] was then made into an efficient photoanode via Gd-doping by Baek and co-workers[31] that fetched high selectivity and high rate of production of H_2O_2 from water in 2.0 M $KHCO_3$. This opened up a new avenue of making several photoanodes for H_2O_2 synthesis via two-electron WOR. Beyond the metals reported as oxides for two-electron WOR, other prospective metals which may possess good selectivity for anodic H_2O_2 evolution from water include Nb, Mo, Zr, Cu, Cd, Te, Sb, Ta, Re, and In. We expect that oxides of these metals in combination with alkaline earths and other reported catalysts would be reported in the near future as these are also falling in the category of metals that do not begin water oxidation below 1.76 V vs. RHE in mildly acidic to mildly basic solutions.

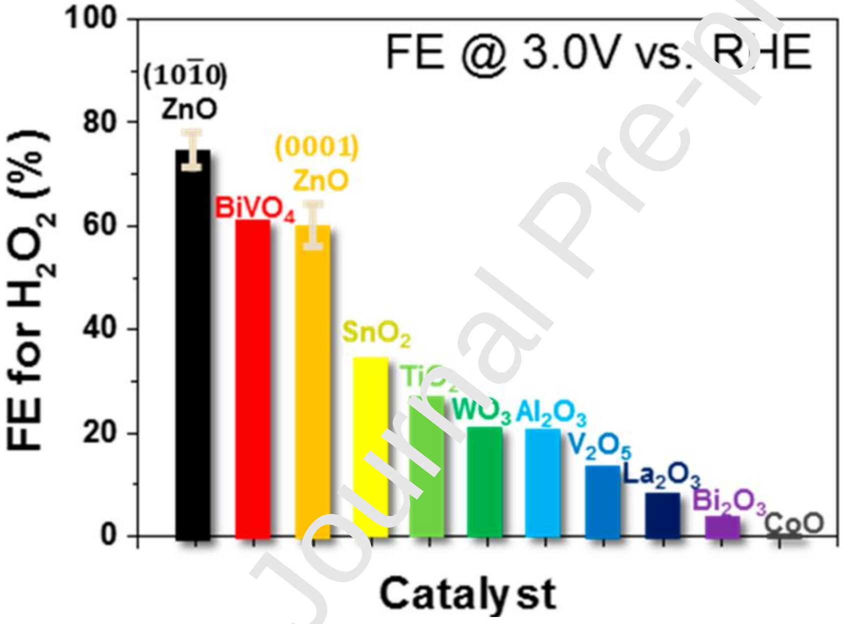


Figure 13: Bar diagram of various reported two-electron WOR catalysts with their respective Faradaic Efficiencies (in %) at 3.0 V vs. RHE. Reproduced with permission from ref. 29 (Copyright 2019, American Chemical Society).

However, it is not mandatory to be sticking around this principle as the theoretical study of Viswanathan and co-workers[72] discussed earlier predicted H_2O_2 evolution beyond certain potentials with RuO_2 and MnO_2 that are known for OER (Figure 8) too. Hence, we believe that a highly selective catalyst can also be obtained from those known for OER by applying appropriate overpotential with precise tuning of energy of intermediate species' interactions which in turn is to be done by rational catalyst design. Besides bonding and energy of interaction of intermediates, other mesoscopic characteristics such as electrode material morphology, dimension of electrode, externally forced mass transfer and efficient simultaneous removal of synthesized H_2O_2 could further improve the overall performance of H_2O_2 production via both two-electron ORR and two-electron WOR.

SOLUTION CHEMISTRY OF HYDROGEN PEROXIDE AND ITS SIGNIFICANCE IN PRODUCTIVITY ENHANCEMENT

Perceiving the solution chemistry of synthesized H_2O_2 is important in order to improve the production rate via any of the stated method which is true for the electrochemical synthesis too. Stability of synthesized hydrogen peroxide in solution is a crucial factor that determines the practical applicability of any method by which it is being produced. Hence, it is important to understand the ways in which H_2O_2 can be decomposed.

Decomposition Pathways for Electrosynthesized H_2O_2.

In both two-electron ORR and two-electron WOR, the synthesized H_2O_2 under no influence of externally induced mass transfer (i.e., diffusion is the only mechanism by which mass transfer occurs) gets accumulated near the electrode surface when compared to the bulk of the solution. This increases the chances of further oxidation (in WOR) or reduction (in ORR) as shown below.

$$H_2O_2 + \rightarrow O_2 + 2H^+ + 2e^- \qquad E = 0.68\ \text{V vs. RHE} \qquad (13)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E = 1.76\ \text{V vs. RHE} \qquad (14)$$

As can be noted from the above equations, the oxidation potential of H_2O_2 (equation 13) is much lower than the oxidation potential of water to form H_2O_2 (equation 7) and the reduction potential of H_2O_2 (equation 14) is much higher than the reduction potential of O_2 to form H_2O_2 (equation 11). This shows why the instant transport of H_2O_2 from around the electrode surface once it is formed is necessary. This implies that the selectivity of an electrocatalyst for H_2O_2 synthesis is not only depending on its intrinsic activity but also on how efficiently the synthesized H_2O_2 is taken away from the vicinity of the electrode-electrolyte interface. Whenever there is an externally induced mass transfer (such as RRDE, GDE, PEMFC, and flow-cell assemblies), the selectivity has always measured to be higher than the one determined under static conditions (i.e., when diffusion is the only mass transport mechanism). Moreover, synthesized H_2O_2 can undergo decomposition via reactions with various electrochemically generated reactive oxygen species which were summarized earlier by Perry and co-workers [1]. Hence, one should also be mindful of their working potential as hydroxyl radical can be formed at 2.73 V vs. RHE via water oxidation and superoxide can be formed at 0.33 V vs. RHE via oxygen reduction which are potential oxidizing and reducing agents, respectively and could easily lead to the dissociation of synthesized H_2O_2 while lowering the selectivity of the electrode material under study.

Besides, H_2O_2 does easily undergo disproportionate decomposition (equation 15) producing water and oxygen and the rate of which increases with increasing solution pH and temperature.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (15)$$

A relatively stable solution of H_2O_2 is obtained by diluting with acid below room temperature. Hence, continuous or frequent withdrawal of electrolyte solution when the concentration of H_2O_2 reaches the critical level that pushes the chemical decomposition should avoid this issue.

Similarly, white light having a significant portion of blue light spectrum (300 – 450 nm) had been found to induce the homolysis of O–O bond in H_2O_2 via σ → σ* electronic excitation producing highly oxidizing hydroxyl radical which can oxidize H_2O_2 in solution. Though a few two-electron WOR catalysts were shown to get benefitted from photoactivation, care must be taken to avoid photo-induced homolysis of electrosynthesized H_2O_2 to improve productivity and selectivity.

Electrolyte Engineering: A Way of Improving H_2O_2 Productivity

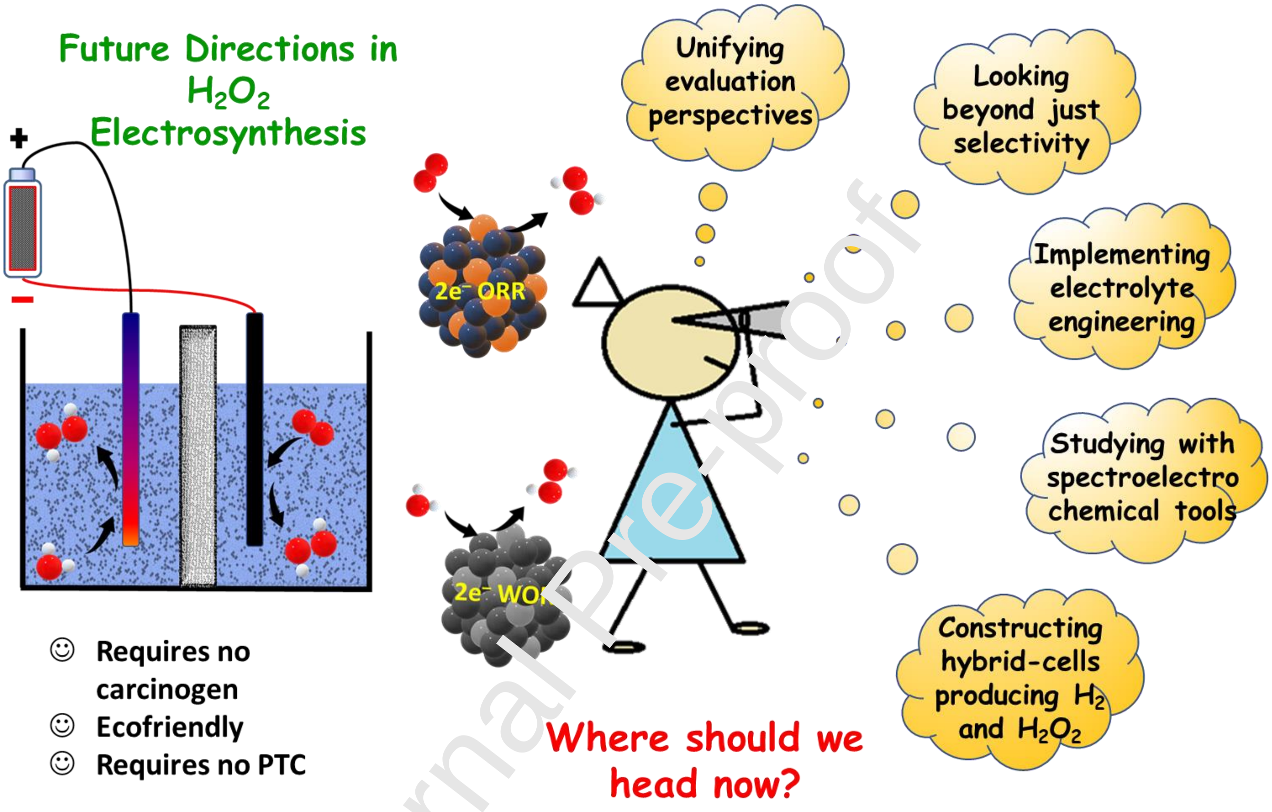
The preceding discussion has made it clear that it is not just the activity and selectivity of the catalyst under study determining the overall productivity but also the stabilization and efficient and timely removal of electrosynthesized H_2O_2. While effective removal of electrosynthesized H_2O_2 from the vicinity of electrode electrolyte interface can be achieved via stirring the solution, rotating the electrode, purging gas, flowing electrolyte, and frequent withdrawal of electrolyte solution enriched with electrosynthesized H_2O_2, the stability of it has to be achieved by engineering the electrolyte solution. Electrolyte engineering is a famous term in electrolysis of neutral and near-neutral waters where electrolyte composition is altered to enhance the catalytic activity of the material [34,92]. On the other hand, engineering electrolyte could also assist stabilizing the electrosynthesized H_2O_2. Thus, it would prevent H_2O_2 from decomposing via spontaneous chemical disproportionation which is favoured by a high negative enthalpy change ($\Delta H = -2884.5$ kJ mol^{-1}) and increase in entropy ($\Delta S = 70.5$ J mol^{-1} K^{-1}). As it has just been mentioned that pH of the solution impacts the stability of H_2O_2 to greater extent and an acidic environment is relatively ideal, having acidic buffers is the first choice that one has to make in engineering electrolyte solutions. However, not every practical application of H_2O_2 requires an acidic solution. Medical disinfection needs a solution of H_2O_2 with neutral or near-neutral pH and paper pulp bleaching requires it as a basic solution. This advocates the need for improving the stability of electrosynthesized H_2O_2 in an electrolyte of desired pH. One way to do this is adding H_2O_2 stabilizing additives such as anions of a few p-block elements such as Si, Al, Ge, and Sn [93,94]. However, it is also essential to ensure that the addition of such redox inert anions do not alter the pH of the solution by using buffered electrolytes. Moreover, charged ROS produced along with the desired H_2O_2 evolving reaction could lead its decomposition. Hence, introducing a radical scavenger which can scavenge both the oxidizing ones (such as hydroxyl radical) and reducing ones (such as superoxide) can improve the overall H_2O_2 productivity. Prospective scavengers include S and Se [95–97]. Even though engineering electrolyte is a promising way to improve practical concentration of electrosynthesized H_2O_2 beyond chemical and electrochemical decompositions, it has never been applied in any study and it is expected that it would become an irresistible strategy in improving H_2O_2 productivity via both two-electron ORR and two-electron WOR.

FUTURE DIRECTION

Electrochemical synthesis of hydrogen peroxide has so far been centralized around at cathodic partial reduction of dioxygen molecule by 90% with a range of catalysts from noble metals and their alloys to molecular M-N-C complexes. The partial reduction of O_2 (two-electron ORR) has been accomplished following a single principle of isolating ORR catalytic sites in an ORR inert host material which has obviously been paying off. However, as ORR is a mass transport limited reaction irrespective of how cathodic is the applied potential from the reversible potential of two-electron ORR (0.68 V vs. RHE), the amount of H_2O_2 produced is limited by the diffusion of O_2 which has so far been eliminated to a significant extent from affecting the selectivity by employing RRDE. However, in real large-scale operations such as the GDE or

PEMFC assemblies, the selectivity appears to have been lowered significantly than the one measured with RRDE assembly. This apparently tells us that not every two-electron ORR catalysts could actually be believed for their claimed selectivity. Besides, the mass transport limitation with two-electron ORR actually makes it a slow method of H_2O_2 production. On the other hand, we have two-electron WOR which is not limited by diffusion and capable of producing relatively larger quantity of H_2O_2 but suffers from poor selectivity. The maximum selectivity achieved in two-electron WOR so far is ~80% with ZnO by Siahrostami and co-workers [29]. This apparently implies that water oxidation could actually be the future of large scale electrosynthesis of H_2O_2 just from water with no requirement of purging O_2 all the time during the synthesis provided that the selectivity issue is addressed in the near future. Unfortunately, the quantity of catalysts reported for two-electron WOR is nowhere near to the total number of catalysts reported for two-electron ORR. This explicitly implies the need for increasing the attention on anodic H_2O_2 synthesis. Electrosynthesis of hydrogen peroxide is indeed would be the friendliest method of all provided that the electric potential supplied is from renewables. Stating that and witnessing increasing number of photoactivated electrocatalysts performing two-electron WOR, we believe that photoelectrochemical water oxidation reactors could be the choice of green H_2O_2 synthesizer.

Besides deciding between two-electron ORR and two-electron WOR, finding a generalized method of selectivity determination is an utmost priority in this field as it could overwhelm or underrate an electrocatalyst for its performance depending on the method by which its selectivity is determined. It is now understood that externally induced mass transfer could impart a great change in selectivity as it greatly enhances the transport of H_2O_2 away from the electrode surface once it has been formed. However, the relatively handier RRDE method may have earlier stated issues in two-electron WOR. Hence, permanganate titration and H_2O_2 test strips are being used widely which actually do in some ways reflect the actual performance as there is no externally induced mass transfer. However, with RRDE in two-electron ORR, the selectivity is determined simultaneously as H_2O_2 is produced. In the case of two-electron WOR, before quantifying produced H_2O_2, a relatively larger time is required (usually 5 to 10 min of electrolysis at a fixed potential). These humongous differences in the time of selectivity determination between two-electron ORR and two-electron WOR make it unfair to compare the performances. Hence, a generalized method should be developed. Beyond production and quantification, stabilization of synthesized H_2O_2 has to be improved which could be done with the ways suggested in the penultimate section. An important issue with the electrosynthesized H_2O_2 is that the electrolytic medium is not always neutral. It is mostly acidic with two-electron ORR and mildly alkaline with two-electron WOR. This makes the synthesized H_2O_2 inapplicable in many fields of its practical use. However, a few fields of application require H_2O_2 in an acidic environment (e.g., fuel cells and waste-water treatment) and also in an alkaline environment (e.g. paper pulp bleaching). In those cases, these solutions can be directly applied. For other purposes, a simple neutralization reaction with a base/acid solution of minimum volume (to ensure that H_2O_2 is not diluted extensively) yet with the desired concentration can be used to get the right pH for use. Key developments that we anticipate will occur in near future in this field are depicted graphically in **Scheme** 3. Further works focused on these directions will ensure both the eradication of ambiguities in evaluation and developments in catalysts' design. Several other perceptions on how this field must grow have been discussed in the earlier perspective and review by Siahrostami and co-workers[13] and Perry and co-workers [1]. Hence, it is concluded here that the two-electron WOR which is far better in productivity must be given additional attention while unifying/generalizing the ways in which selectivity is determined and ensuring that the H_2O_2 is produced in a completely greener way with the energy harvested from intermittent sources.



Scheme 3: Anticipated directions of growth in H_2O_2 electrosynthesis in the near future.

CONCLUSIONS AND OUTLOOK

Hydrogen peroxide, the greenest oxidizing agent of all having applications in various fields from industrial bleaching to medical disinfection has so far been majorly produced (by 95%) through the energy intensive anthraquinone process which pose several hazards from using a carcinogen (anthraquinones) to requiring the transport of concentrated H_2O_2 solution which is potentially explosive. On the other hand, the direct synthesis of H_2O_2 from hydrogen and oxygen gas over a noble metal surface under high pressure with carrier gases lack from poor rate and increased cost of production. Hence, electrochemical synthesis of H_2O_2 is being investigated intensively as a promising alternate capable of decentralizing the global production. In electrochemical synthesis, H_2O_2 can be obtained either by two-electron ORR or two-electron WOR which are hard to be performed with conventional catalysts that are known to perform four-electron ORR and four-electron WOR (OER) without rational catalysts design enabling H_2O_2 favouring bonding modes and energy of interactions. In the case of ORR, the two-electron selectivity has been achieved following a single principle of constructing isolated catalytic sites that favour Pauling mode of bonding O_2 (end-on) avoiding the breaking of O–O bond after the transfer of two electrons. In contrast, two-electron selectivity in WOR has so far been achieved by sticking to the materials known for their poor OER activity. These strategies did help in realizing high selectivity but the productivity remains an issue. In the case of ORR, H_2O_2 production is limited by the diffusion of O_2 and it requires continuous bubbling of O_2 (such as GDE assembly) which make it both relatively less productive and harder to handle. On the other hand, WOR is not limited by any electroactive species as water is the electroactive species present abundantly in the solution. However, the only thing that concerns the production of H_2O_2 via two-electron WOR is its relatively lower selectivity as reported by many. Unfortunately, this claim may not be true as the method of determination of selectivity in two-electron ORR and two-electron WOR are always and almost totally different. Hence, unifying/generalizing the ways in which selectivity is determined will be crucial for further developments in this field. Owing to the superiority of two-electron WOR of being mass transfer independent and high productivity, this realm of this research is expected to undergo a major transition in the near future. Besides just selectivity, improving activity (current) and stability are two other key factors that will be deciding the fate of the material in being applied to full cell operations for a prolonged period of time. Moreover, further progress in the field will largely depend on the comprehension of structure-activity/selectivity/stability relationship which can be obtained via *in situ/operando* spectroscopic tools. Having said that it is concluded here that the electrochemical synthesis of H_2O_2 is clearly an interdisciplinary area of research that requires helping hands from electrochemists, material chemists, theoretical chemists, and electrochemical engineers to enable its successful global-level commercialization in an effort of making H_2O_2 the truly greenest oxidizing agent of all in terms of both production and application.

DECLERATION OF INTEREST

Authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work is supported in part by the grant-in-aid by the Japan Society for the Promotion of Science (JSPS) (Grant number: JP19F18346). S. P would like to thank the European Regional Development Fund (ERDF), and Welsh Government for providing the Ser Cymru-II Rising Star Fellowship Grant.

Conflict of Interest and Authorship Conformation Form

Please check the following as appropriate:

- ○ ☒ All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- ○ ☒ This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
- ○ ☒ The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript

- The following authors have affiliations with organizations with direct or indirect financial interest in the subject matter discussed in the manuscript:

Author's name	Affiliation

REFERENCES

[1] Perry SC, Pangotra D, Vieira L, Csepei LI, Sieber V, Wang L, et al. Electrochemical synthesis of hydrogen peroxide from water and oxygen. Nat Rev Chem 2019;3:442–58. https://doi.org/10.1038/s41570-019-0110-6.

[2] Kornienko VL, Kolyagin GA, Kornienko G V, Parfenov VA, Ponomarenko I V. Electrosynthesis of H2O2 from O2 in a Gas-Diffusion Electrode Based on Mesostructured Carbon CMK-3. Russ J Electrochem 2018;54:258–64. https://doi.org/10.1134/S1023193518030060.

[3] Jiang Y, Ni P, Chen C, Lu Y, Yang P, Kong B, et al. Selective Electrochemical H2O2 Production through Two-Electron Oxygen Electrochemistry. Adv Energy Mater 2018;8:17–9. https://doi.org/10.1002/aenm.201801909.

[4] Wang LK, Hung Y-T, Shammas NK. Handbook of Advanced Industrial and Hazardous Wastes Treatment. CRC Press; 2009. https://doi.org/10.1017/CBO9781107415324.004.

[5] Spellman F. Handbook of water and wastewater treatment plant operations, CRC Press/Taylor & Francis; 2013, p. 923. https://doi.org/10.1016/B978-0-12-369520-8.50043-7.

[6] Murray AT, Voskian S, Schreier M, Hatton TA, Surendranath Y. Electrosynthesis of Hydrogen Peroxide by Phase-Transfer Catalysis. Joule 2019;3:2942–54.

https://doi.org/10.1016/j.joule.2019.09.019.

[7] Campos-Martin JM, Blanco-Brieva G, Fierro JLG. Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. Angew Chemie - Int Ed 2006;45:6962–84. https://doi.org/10.1002/anie.200503779.

[8] BBC NEWS | UK | England | London | M25 chaos after lorry explosion n.d. http://news.bbc.co.uk/2/hi/uk_news/england/london/4197500.stm (accessed March 28, 2020).

[9] Lunsford JH. The direct formation of H2O2 from H2 and O2 over palladium catalysts. J Catal 2003;216:455–60. https://doi.org/10.1016/S0021-9517(02)00070-2.

[10] Edwards JK, Freakley SJ, Lewis RJ, Pritchard JC, Hutchings GJ. Advances in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Catal Today 2015;248:3–9. https://doi.org/10.1016/j.cattod.2014.03.011.

[11] Lewis RJ, Ueura K, Fukuta Y, Freakley SJ, Kang L, Wang R, et al. The Direct Synthesis of H 2 O 2 Using TS-1 Supported Catalysts. ChemCatChem 2019;11:1673–80. https://doi.org/10.1002/cctc.201900100.

[12] Edwards JK, Freakley SJ, Carley AF, Kiely CJ, Hutchings GJ. Strategies for designing supported gold-palladium bimetallic catalysts for the direct synthesis of hydrogen peroxide. Acc Chem Res 2014;47:845–54. https://doi.org/10.1021/ar400177c.

[13] Yang S, Verdaguer-Casadevall A, Arnarson L, Silvioli L, Čolić V, Frydendal R, et al. Toward the Decentralized Electrochemical Production of H2O2: A Focus on the Catalysis. ACS Catal 2018;8:4064–81. https://doi.org/10.1021/acscatal.8b00217.

[14] Edwards JK, Solsona B, N EN, Carley AF, Herzing AA, Kiely CJ, et al. Synthesis Process. Science (80-) 2009;323:1037–41.

[15] Li N, An J, Zhou L, Li T, Li J, Feng C, et al. A novel carbon black graphite hybrid air-cathode for efficient hydrogen peroxide production in bioelectrochemical systems. J Power Sources 2016;306:495–502. https://doi.org/10.1016/j.jpowsour.2015.12.078.

[16] Yamanaka I, Onizawa T, Suzuki H, Hanaizumi N, Otsuka K. Electrocatalysis of heat-treated Mn-porphyrin/carbon cathode for synthesis of H2O2 acid solutions by H2/O2 fuel cell method. Chem Lett 2006;35:1330–1. https://doi.org/10.1246/cl.2006.1330.

[17] Perazzolo V, Durante C, Pilot R, Paduano A, Zheng J, Rizzi GA, et al. Nitrogen and sulfur doped mesoporous carbon as metal-free electrocatalysts for the in situ production of hydrogen peroxide. Carbon N Y 2015;95:949–63. https://doi.org/10.1016/j.carbon.2015.09.002.

[18] Suk M, Chung MW, Han MH, Oh HS, Choi CH. Selective H 2 O 2 production on surface-oxidized metal-nitrogen-carbon electrocatalysts. Catal Today 2019:0–1. https://doi.org/10.1016/j.cattod.2019.05.034.

[19] Chen S, Chen Z, Siahrostami S, Kim TR, Nordlund D, Sokaras D, et al. Defective Carbon-Based Materials for the Electrochemical Synthesis of Hydrogen Peroxide. ACS Sustain Chem Eng 2018;6:311–7. https://doi.org/10.1021/acssuschemeng.7b02517.

[20] Park J, Nabae Y, Hayakawa T, Kakimoto MA. Highly selective two-electron oxygen reduction catalyzed by mesoporous nitrogen-doped carbon. ACS Catal 2014;4:3749–54. https://doi.org/10.1021/cs5008206.

[21] Sun Y, Silvioli L, Sahraie NR, Ju W, Li J, Zitolo A, et al. Activity-Selectivity Trends in the Electrochemical Production of Hydrogen Peroxide over Single-Site Metal-Nitrogen-Carbon Catalysts. J Am Chem Soc 2019;141:12372–81. https://doi.org/10.1021/jacs.9b05576.

[22] Byeon A, Cho J, Kim JM, Chae KH, Park H-Y, Hong SW, et al. High-yield electrochemical hydrogen peroxide production from an enhanced two-electron oxygen reduction pathway by mesoporous nitrogen-doped carbon and manganese hybrid electrocatalysts. Nanoscale Horizons 2020;5:832–8. https://doi.org/10.1039/c9nh00783k.

[23] Jung E, Shin H, Lee BH, Efremov V, Lee S, Lee HS, et al. Atomic-level tuning of Co–N–C catalyst for high-performance electrochemical H2O2 production. Nat Mater 2020. https://doi.org/10.1038/s41563-019-0571-5.

[24] Siahrostami S, Verdaguer-Casadevall A, Karamad M, Deiana D, Malacrida P, Wickman B, et al. Enabling direct H2O2 production through rational electrocatalyst design. Nat Mater 2013;12:1137–43. https://doi.org/10.1038/nmat3795.

[25] Verdaguer-Casadevall A, Deiana D, Karamad M, Siahrostami S, Malacrida P, Hansen TW, et al. Trends in the electrochemical synthesis of H2O2: Enhancing activity and selectivity by electrocatalytic site engineering. Nano Lett 2014;14:1603–8. https://doi.org/10.1021/nl500037x.

[26] Sánchez-Sánchez CM, Bard AJ. Hydrogen peroxide production in the oxygen reduction reaction at different electrocatalysts as quantified by scanning electrochemical microscopy. Anal Chem 2009;81:8094–100. https://doi.org/10.1021/ac901291v.

[27] Ando Y, Tanaka T. Proposal for a new system for simultaneous production of hydrogen

and hydrogen peroxide by water electrolysis. Int J Hydrogen Energy 2004;29:1349–54. https://doi.org/10.1016/j.ijhydene.2004.02.001.

[28] Xia C, Back S, Ringe S, Jiang K, Chen F, Sun X, et al. Confined local oxygen gas promotes electrochemical water oxidation to hydrogen peroxide. Nat Catal 2020;3:125–34. https://doi.org/10.1038/s41929-019-0402-8.

[29] Kelly SR, Shi X, Back S, Vallez L, Park SY, Siahrostami S, et al. ZnO As an Active and Selective Catalyst for Electrochemical Water Oxidation to Hydrogen Peroxide. ACS Catal 2019;9:4593–9. https://doi.org/10.1021/acscatal.8b04873.

[30] Park SY, Abroshan H, Shi X, Jung HS, Siahrostami S, Zheng X. CaSnO 3 : An Electrocatalyst for Two-Electron Water Oxidation Reaction to Form H 2 O 2. ACS Energy Lett 2019;4:352–7. https://doi.org/10.1021/acsenergylett.8b02303.

[31] Baek JH, Gill TM, Abroshan H, Park S, Shi X, Nørskov J, et al. Selective and Efficient Gd-Doped BiVO4 Photoanode for Two-Electron Water Oxidation to H2O2. ACS Energy Lett 2019;4:720–8. https://doi.org/10.1021/acsenergylett.9b00277.

[32] Shi X, Siahrostami S, Li GL, Zhang Y, Chakthranont P, Studt F, et al. Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide. Nat Commun 2017;8:701–12. https://doi.org/10.1038/s41467-017-00585-6.

[33] Anantharaj S, Noda S. Amorphous Catalysts and Electrochemical Water Splitting: An Untold Story of Harmony. Small 2020;16:1905779. https://doi.org/10.1002/smll.201905779.

[34] Anantharaj S, Aravindan V. Developments and Perspectives in 3d Transition-Metal-Based

Electrocatalysts for Neutral and Near-Neutral Water Electrolysis. Adv Energy Mater 2019;2:1902666–95. https://doi.org/10.1002/aenm.201902666.

[35] Anantharaj S, Ede SR, Karthick K, Sam Sankar S, Sangeetha K, Pitchiah EK, et al. Precision and Correctness in the Evaluation of Electrocatalytic Water Splitting: Revisiting Activity Parameters with a Critical Assessment. Energy Environ Sci 2018;11:744–71. https://doi.org/10.1039/C7EE03457A.

[36] Anantharaj S, Ede SR, Sakthikumar K, Karthick K, Mishra S, Kundu S. Recent Trends and Perspectives in Electrochemical Water Splitting with an Emphasis to Sulphide, Selenide and Phosphide Catalysts of Fe, Co and Ni: A Review. ACS Catal 2016;6:8069–97. https://doi.org/10.1021/acscatal.6b02479.

[37] Anantharaj S, Kundu S, Noda S. Progress in nickel chalcogenide electrocatalyzed hydrogen evolution reaction. J Mater Chem A 2020:4174–92. https://doi.org/10.1039/c9ta14037a.

[38] Anantharaj S, Karthik PE, Kundu S. Petal-like hierarchical array of ultrathin Ni(OH)2 nanosheets decorated with Ni(OH)2 nanoburls: A highly efficient OER electrocatalyst. Catal Sci Technol 2017;7:882–93. https://doi.org/10.1039/c6cy02282k.

[39] Karthik EP, Raja AK, Kumar SS, Phani KLN, Liu Y, Guo S-X, et al. Electroless deposition of iridium oxide nanoparticles promoted by condensation of [Ir(OH)6]2- on anodized Au surface: Application to electrocatalysis of the oxygen evolution reaction. RSC Adv 2014. https://doi.org/10.1039/C4RA14392B.

[40] Otsuka K, Yamanaka I. One step synthesis of hydrogen peroxide through fuel cell reaction. Electrochim Acta 1990;35:319–22. https://doi.org/10.1016/0013-4686(90)87004-

L.

[41] Yamanaka I, Tazawa S, Murayama T, Iwasaki T, Takenaka S. Catalytic synthesis of neutral hydrogen peroxide at a CoN2Cx Cathode of a Polymer Electrolyte Membrane Fuel Cell (PEMFC). ChemSusChem 2010;3:59–62. https://doi.org/10.1002/cssc.200900246.

[42] Iwasaki T, Masuda Y, Ogihara H, Yamanaka I. Direct Synthesis of Pure H2O2 Aqueous Solution by CoTPP/Ketjen-Black Electrocatalyst and the Fuel Cell Reactor. Electrocatalysis 2018;9:236–42. https://doi.org/10.1007/s12678-017-0444-0.

[43] Yamanaka I, Murayama T. Neutral H2O2 synthesis by electrolysis of water and O2. Angew Chemie - Int Ed 2008;47:1900–2. https://doi.org/10.1002/anie.200704431.

[44] Murayama T, Yamanaka I. Electrosynthesis of neutral H2O2 solution from O 2 and water at a mixed carbon cathode using an exposed solid-polymer-electrolyte electrolysis cell. J Phys Chem C 2011;115:5792–9. https://doi.org/10.1021/jp1109702.

[45] Chen F, Wang N, Lei H, Guo D, Liu H, Zhang Z, et al. Electrocatalytic Water Oxidation by a Water-Soluble Copper(II) Complex with a Copper-Bound Carbonate Group Acting as a Potential Proton Shuttle. Inorg Chem 2017;56:13368–75. https://doi.org/10.1021/acs.inorgchem.7b02125.

[46] Song X, Li N, Zhang H, Wang L, Yan Y, Wang H, et al. Graphene-Supported Single Nickel Atom Catalyst for Highly Selective and Efficient Hydrogen Peroxide Production. ACS Appl Mater Interfaces 2020;12:17519–27. https://doi.org/10.1021/acsami.0c01278.

[47] Shinagawa T, Garcia-Esparza AT, Takanabe K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. Sci Rep

2015;5:13801–21. https://doi.org/10.1038/srep13801.

[48] Anantharaj S, Karthick K, Kundu S. NiTe2 Nanowire Outperforms Pt/C in High-Rate Hydrogen Evolution at Extreme pH Conditions. Inorg Chem 2018;57:3082–96. https://doi.org/10.1021/acs.inorgchem.7b02947.

[49] Anantharaj S, Karthik PEE, Kundu S, Pitchiah EK, Kundu S, Karthik PEE, et al. Self-assembled IrO2 nanoparticles on a DNA scaffold with enhanced catalytic and oxygen evolution reaction (OER) activities. J Mater Chem A 2015;3:24463–78. https://doi.org/10.1039/C5TA07075A.

[50] Anantharaj S, Venkatesh M, Salunke AS, Simha TVSVS V., Prabu V, Kundu S. High-Performance Oxygen Evolution Anode from Stainless Steel via Controlled Surface Oxidation and Cr Removal. ACS Sustain Chem Eng 2017;5:10072–83. https://doi.org/10.1021/acssuschemeng.7b02090.

[51] Wang B. Recent development of non-platinum catalysts for oxygen reduction reaction. J Power Sources 2005;152:1. https://doi.org/10.1016/j.jpowsour.2005.05.098.

[52] Guo S, Zhang S, Sun S. Tuning nanoparticle catalysis for the oxygen reduction reaction. Angew Chemie - Int Ed 2013;52:8526–44. https://doi.org/10.1002/anie.201207186.

[53] Katsounaros I, Cherevko S, Zeradjanin AR, Mayrhofer KJJ. Oxygen electrochemistry as a cornerstone for sustainable energy conversion. Angew Chemie - Int Ed 2014;53:102–21. https://doi.org/10.1002/anie.201306588.

[54] Siahrostami S, Li GL, Viswanathan V, Nørskov JK. One- or Two-Electron Water Oxidation, Hydroxyl Radical, or H2O2 Evolution. J Phys Chem Lett 2017;8:1157–60.

https://doi.org/10.1021/acs.jpclett.6b02924.

[55] Tiwari JN, Tiwari RN, Singh G, Kim KS. Recent progress in the development of anode and cathode catalysts for direct methanol fuel cells. Nano Energy 2013;2:553–78. https://doi.org/10.1016/j.nanoen.2013.06.009.

[56] Cheng Y, Jiang SP. Advances in electrocatalysts for oxygen evolution reaction of water electrolysis-from metal oxides to carbon nanotubes. Prog Nat Sci Mater Int 2015;25:545–53. https://doi.org/10.1016/j.pnsc.2015.11.008.

[57] Li P, Zhao R, Chen H, Wang H, Wei P, Huang H, et al. Recent Advances in the Development of Water Oxidation Electrocatalysts at Mild pH. Small 2019;15:1805103. https://doi.org/10.1002/smll.201805103.

[58] Anantharaj S, Noda S. Nickel selenides as pre-catalysts for electrochemical oxygen evolution reaction: A review. Int J Hydrogen Energy 2020;45:15763–84. https://doi.org/10.1016/j.ijhydene.2020.04.073.

[59] Tian GL, Zhao MQ, Yu D, Kong XY, Huang JQ, Zhang Q, et al. Nitrogen-doped graphene/carbon nanotube hybrids: In situ formation on bifunctional catalysts and their superior electrocatalytic activity for oxygen evolution/reduction reaction. Small 2014;10:2251–9. https://doi.org/10.1002/smll.201303715.

[60] Li B, Chen S, Tian J, Gong M, Xu H, Song L. Amorphous nickel-iron oxides/carbon nanohybrids for an efficient and durable oxygen evolution reaction. Nano Res 2017;10:3629–37. https://doi.org/10.1007/s12274-017-1572-9.

[61] Menezes PW, Indra A, Sahraie NR, Bergmann A, Strasser P, Driess M. Cobalt-

manganese-based spinels as multifunctional materials that unify catalytic water oxidation and oxygen reduction reactions. ChemSusChem 2015;8:164–7. https://doi.org/10.1002/cssc.201402699.

[62] Long X, Wang Z, Xiao S, An Y, Yang S. Transition metal based layered double hydroxides tailored for energy conversion and storage. Mater Today 2015;19:213–26. https://doi.org/10.1016/j.mattod.2015.10.006.

[63] Assumpão MHMT, Moraes A, De Souza RFB, Gaubeur I, Oliveira RTS, Antonin VS, et al. Low content cerium oxide nanoparticles on carbon for hydrogen peroxide electrosynthesis. Appl Catal A Gen 2012;411–412:1–6. https://doi.org/10.1016/j.apcata.2011.09.030.

[64] Xia G, Lu Y, Xu H. An energy-saving production of hydrogen peroxide via oxygen reduction for electro-Fenton using electrochemically modified polyacrylonitrile-based carbon fiber brush cathode. Sep Purif Technol 2015;156:553–60. https://doi.org/10.1016/j.seppur.2015.10.048.

[65] Brillas E, Boye B, Sirés I, Garrido JA, Rodríguez RM, Arias C, et al. Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode. Electrochim Acta 2004;49:4487–96. https://doi.org/10.1016/j.electacta.2004.05.006.

[66] Cao R, Walter ED, Xu W, Nasybulin EN, Bhattacharya P, Bowden ME, et al. The Mechanisms of Oxygen Reduction and Evolution Reactions in Nonaqueous Lithium-Oxygen Batteries. ChemSusChem 2014;7:2436–40. https://doi.org/10.1002/cssc.201402315.

[67] Shao MH, Liu P, Adzic RR. Superoxide anion is the intermediate in the oxygen reduction reaction on platinum electrodes. J Am Chem Soc 2006;128:7408–9. https://doi.org/10.1021/ja061246s.

[68] Rogers EI, Huang XJ, Dickinson EJF, Hardacre C, Compton RG. Investigating the mechanism and electrode kinetics of the oxygenlsuperoxide (O2IO2-) couple in various room-temperature ionic liquids at gold and platinum electrodes in the temperature range 298-318 K. J Phys Chem C 2009;113:17811–23. https://doi.org/10.1021/jp9064054.

[69] Gewirth AA, Thorum MS. Electroreduction of dioxygen for fuel-cell applications: Materials and challenges. Inorg Chem 2010;49:3557–66. https://doi.org/10.1021/ic9022486.

[70] Medford AJ, Vojvodic A, Hummelshøj JS, Voss J, Abild-Pedersen F, Studt F, et al. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. J Catal 2015;328:36–42. https://doi.org/10.1016/j.jcat.2014.12.033.

[71] Viswanathan V, Hansen HA, Rossmeisl J, Nørskov JK. Unifying the 2e - and 4e - reduction of oxygen on metal surfaces. J Phys Chem Lett 2012;3:2948–51. https://doi.org/10.1021/jz301476w.

[72] Viswanathan V, Hansen HA, Nørskov JK. Selective Electrochemical Generation of Hydrogen Peroxide from Water Oxidation. J Phys Chem Lett 2015;6:4224–8. https://doi.org/10.1021/acs.jpclett.5b02178.

[73] Ranganathan S, Sieber V. Recent advances in the direct synthesis of hydrogen peroxide using chemical catalysis—a review. Catalysts 2018;8:379–400. https://doi.org/10.3390/catal8090379.

[74] Pizzutilo E, Kasian O, Choi CH, Cherevko S, Hutchings GJ, Mayrhofer KJJ, et al. Electrocatalytic synthesis of hydrogen peroxide on Au-Pd nanoparticles: From fundamentals to continuous production. Chem Phys Lett 2017;683:436–42. https://doi.org/10.1016/j.cplett.2017.01.071.

[75] Jirkovský JS, Halasa M, Schiffrin DJ. Kinetics of electrocatalytic reduction of oxygen and hydrogen peroxide on dispersed gold nanoparticles. Phys Chem Chem Phys 2010;12:8042–52. https://doi.org/10.1039/c002416c.

[76] Choi CH, Kim M, Kwon HC, Cho SJ, Yun S, Kim HT, et al. Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. Nat Commun 2016;7:1–9. https://doi.org/10.1038/ncomms10922.

[77] Yang S, Kim J, Tak YJ, Soon A, Lee H. Single-atom catalyst of platinum supported on titanium nitride for selective electrochemical reactions. Angew Chemie - Int Ed 2016;55:2058–62. https://doi.org/10.1002/anie.201509241.

[78] Yang S, Tak YJ, Kim J, Soon A, Lee H. Support Effect in Single-Atom Platinum Catalyst for Electrochemical Oxygen Reduction. ACS Catal 2017;7:1301–7.

[79] Anson FC, Ni CL, Saveant JM. Electrocatalysis at Redox Polymer Electrodes with Separation of the Catalytic and Charge Propagation Roles. Reduction of O2 to H2O2 as Catalyzed by Cobalt(II) Tetrakis(4-N-methylpyridyl)porphyrin. J Am Chem Soc 1985;107:3442–50. https://doi.org/10.1021/ja00298a008.

[80] Yamanaka I, Onizawa T, Suzuki H, Hanaizumi N, Nishimura N, Takenaka S. Study of direct synthesis of hydrogen peroxide acid solutions at a heat-treated MnCl-porphyrin/activated carbon cathode from H 2 and O 2. J Phys Chem C 2012;116:4572–83.

https://doi.org/10.1021/jp207679e.

[81] Yamanaka I, Ichihashi R, Iwasaki T, Nishimura N, Murayama T, Ueda W, et al. Electrocatalysis of heat-treated cobalt-porphyrin/carbon for hydrogen peroxide formation. Electrochim Acta 2013;108:321–9. https://doi.org/10.1016/j.electacta.2013.06.072.

[82] Ziegelbauer JM, Olson TS, Pylypenko S, Alamgir F, Jaye C, Atanassov P, et al. Direct spectroscopic observation of the structural origin of peroxide generation from Co-based pyrolyzed porphyrins for ORR applications. J Phys Chem C 2008;112:8839–49. https://doi.org/10.1021/jp8001564.

[83] Wang YH, Pegis ML, Mayer JM, Stahl SS. Molecular Cobalt Catalysts for O2 Reduction: Low-Overpotential Production of H2O2 and Comparison with Iron-Based Catalysts. J Am Chem Soc 2017;139:16458–61. https://doi.org/10.1021/jacs.7b09089.

[84] Bezerra CWB, Zhang L, Lee K, Liu H, Marques ALB, Marques EP, et al. A review of Fe-N/C and Co-N/C catalysts for the oxygen reduction reaction. Electrochim Acta 2008;53:4937. https://doi.org/10.1016/j.electacta.2008.02.012.

[85] Bonakdarpour A, Delacote C, Yang R, Wieckowski A, Dahn JR. Loading of Se/Ru/C electrocatalyst on a rotating ring-disk electrode and the loading impact on a H2O2 release during oxygen reduction reaction. Electrochem Commun 2008;10:611–5. https://doi.org/10.1016/j.elecom.2008.02.004.

[86] Carneiro JF, Paulo MJ, Siaj M, Tavares AC, Lanza MRV. Nb2O5 nanoparticles supported on reduced graphene oxide sheets as electrocatalyst for the H2O2 electrogeneration. J Catal 2015;332:51–61. https://doi.org/10.1016/j.jcat.2015.08.027.

[87] Forti JC, Rocha RS, Lanza MRV, Bertazzoli R. Electrochemical synthesis of hydrogen peroxide on oxygen-fed graphite/PTFE electrodes modified by 2-ethylanthraquinone. J Electroanal Chem 2007;601:63–7. https://doi.org/10.1016/j.jelechem.2006.10.023.

[88] Wilson T, Zhang J, Oloman CC, Wayner DDM. Anthraquinone-2-carboxylic-allyl ester as a new electrocatalyst for dioxygen reduction to produce H2O2. Int J Electrochem Sci 2006;1:99–109. https://doi.org/10.20964/1030099.

[89] Chen S, Chen Z, Siahrostami S, Higgins D, Nordlund D, Sokaras D, et al. Designing Boron Nitride Islands in Carbon Materials for Efficient Electrochemical Synthesis of Hydrogen Peroxide. J Am Chem Soc 2018;140:7851–9. https://doi.org/10.1021/jacs.8b02798.

[90] Choi CH, Kwon HC, Yook S, Shin H, Kim H, Choi M. Hydrogen peroxide synthesis via enhanced two-electron oxygen reduction pathway on carbon-coated pt surface. J Phys Chem C 2014;118:30063–70. https://doi.org/10.1021/jp5113894.

[91] Fabbri E, Habereder A, Waltar K, Kötz R, Schmidt TJ, Kotz R, et al. Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. Catal Sci Technol 2014;4:3800–21. https://doi.org/10.1039/C4CY00669K.

[92] Shinagawa T, Ng MTK, Takanabe K. Electrolyte Engineering towards Efficient Water Splitting at Mild pH. ChemSusChem 2017;10:4155–62. https://doi.org/10.1002/cssc.201701995.

[93] Xu X, Thomson NR. An evaluation of the green chelant EDDS to enhance the stability of hydrogen peroxide in the presence of aquifer solids. Chemosphere 2007;69:755–62. https://doi.org/10.1016/j.chemosphere.2007.05.008.

[94] Watts RJ, Finn DD, Cutler LM, Schmidt JT, Teel AL. Enhanced stability of hydrogen peroxide in the presence of subsurface solids. J Contam Hydrol 2007;91:312–26. https://doi.org/10.1016/j.jconhyd.2006.11.004.

[95] Zimmerman MT, Bayse CA, Ramoutar RR, Brumaghim JL. Sulfur and selenium antioxidants: Challenging radical scavenging mechanisms and developing structure-activity relationships based on metal binding. J Inorg Biochem 2015;145:30–40. https://doi.org/10.1016/j.jinorgbio.2014.12.020.

[96] Zhao L, Zhao G, Du M, Zhao Z, Xiao L, Hu X. Effect of selenium on increasing free radical scavenging activities of polysaccharide extracts from a Se-enriched mushroom species of the genus Ganoderma. Eur Food Res Technol 2008;226:499–505. https://doi.org/10.1007/s00217-007-0562-7.

[97] Shen Q, Zhang B, Xu R, Wang Y, Ding X, Li P. Antioxidant activity in vitro of the selenium-contained protein from the Se-enriched Bifidobacterium animalis 01. Anaerobe 2010;16:380–6. https://doi.org/10.1016/j.anaerobe.2010.06.006.

Graphical abstract: This review analyzes the recent developments of electrochemical synthesis of H_2O_2 in terms of both catalysts' design and evaluation perspectives while predicting the direction of future growth.

Highlights:

- Trends in 2 electron ORR and WOR catalysts are critically analyzed.
- Ambiguities in evaluation perspectives are criticized and alternatives are proposed.
- Fundamentals of oxygen interfacial electrochemistry is elaborated to understand the trends.
- Advantages of 2 electron WOR over 2 electron ORR in H2O2 electrosynthesis is emphasized.
- Need for electrolyte engineering strategies to improve productivity and selectivity is discussed.

Biography of Corresponding Authors

Dr. Sengeni Anantharaj obtained his undergraduate and postgraduate degrees in chemistry from The Presidency College affiliated to University of Madras, Chennai in 2011 and 2013, respectively. Later, he obtained his PhD in 2018 from CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu, India. Currently, he is availing the prestigious JSPS Postdoctoral Fellowship at Waseda University since January 2019. His research interests include performance driven design of electrocatalysts, energy conversion (both fuel-forming and fuel-consuming) electrocatalysis, electroactivation, and anodization.

Dr. Sudhagar Pitchaimuthu, is a *Sêr Cymru II-Rising Star Fellow* and leads the ***Multifunctional Photocatalyst and Coating*** research group at Swansea University, UK. He graduated in Physics from Bharathiar University, India in 2009. He worked as a Research Assistant Professor during 2009-2013 with Prof. Yong Soo Kang at the Center for Next

Generation Dye-sensitized Solar Cells in Hanyang University, South Korea. He was then awarded the JSPS postdoctoral fellowship in 2013 with which he worked with Prof. Akira Fujishima at International Photocatalytic Research Center, Tokyo University of Science. His research interests are on the use of sustainable solar energy for multifunctional applications such as energy conversion devices (solar cells and solar fuel), environmental clean-up (photoelectrocatalytic water treatment, air purification, artificial CO_2 recycling) and sensors. He is a Founder and Chair for ANEH Conference Series.

Prof. Suguru Noda received his PhD in 1999 from The University of Tokyo, Japan, became an assistant professor and associate professor there, and then joined Waseda University in 2012 as a full professor. He is a chemical engineer conducting research in the field of materials processes. He is recently focusing on practical production of carbon and silicon nanomaterials such as carbon nanotubes and silicon films/nanoparticles, and applying these materials to energy and electronic devices including rechargeable batteries.