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Production of Hydrogen Peroxide for Drinking Water Treatment in a Proton Exchange Membrane Electrolyzer at Near-Neutral pH

Winton Li, Arman Bonakdarpour,* Előd Gyenge,*z and David P. Wilkinson,*z

Department of Chemical and Biological Engineering and the Clean Energy Research Center, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

We provide a detailed report on the electrosynthesis of H₂O₂ for drinking water treatment under near-neutral conditions using a proton exchange membrane (PEM) electrolyzer. Two novel cathode catalysts for O₂ electroreduction to H₂O₂ were investigated in the PEM electrolyzer: an inorganic cobalt (Co₃C) composite and an organic redox catalyst anthraquinone-riboflavinyl mixed with carbon (AQ-C), respectively. The impact of operational variables such as temperature, cathode carrier water flow rate, and anode configurations (aimed at mitigating carbon corrosion at the anode) were examined in single-pass and full recycle operation. Using a superficial current density of 245 mA cm⁻² and an operating temperature of 40 °C, H₂O₂ molar fluxes of 360 μmol hr⁻¹ cm⁻² and 580 μmol hr⁻¹ cm⁻² were generated at near-neutral pH with the Co-C and RF-AQ catalysts, respectively. Seventy-two hour experiments with closed loop recirculation, produced H₂O₂ concentrations of 1300 and 3000 ppm for the Co-C and AQ-C catalysts, respectively. These concentrations are adequate for advanced oxidation (UV/H₂O₂) treatment of drinking water, rendering the PEM electrolysis approach particularly suitable for on-site and on-demand production of H₂O₂.

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Hydrogen peroxide is an excellent oxidizer and is widely used in a number of applications such as waste or drinking water treatment, textile industry, pulp and paper bleaching and a number of other chemical oxidation processes. Furthermore, it is considered an environmentally-friendly oxidizer because oxygen and water are the only products of H₂O₂ decomposition. For these reasons, hydrogen peroxide, with a global market of about $2.44 billion (USD) per year, has a steady market growth trajectory for the next decade.1 At present, economic and high-volume production of hydrogen peroxide is only achieved by the anthraquinone auto-oxidation (AQAO) process (also known as the Riedl-Pflieger process) involving cyclic hydrogenation and oxidation of an alkylanthraquinone precursor, Pd-catalysts, organic solvents, and liquid-liquid extraction. The Riedl-Pflieger process requires significant energy input and in addition, produces waste chemicals that require proper disposal and/or recycling. Because of these difficulties and also the great importance of H₂O₂ in the chemical industry and water treatment sectors, research on sustainable and green methods of H₂O₂ production remains quite active. One such approach is the reduction of O₂ to H₂O₂ through an electrochemical process. Campos et al. provide a review of AQAO and alternative methods of H₂O₂ production.2

In alkaline media, various forms of carbon can produce significant amounts of hydrogen peroxide. Alkaline peroxide synthesis has been demonstrated in a number of different reactor designs such as trickle bed, fluidized bed and gas diffusion electrode designs.3 In acidic to neutral media, however, modified forms of carbon (e.g., with added metals such as cobalt) leads to lower oxygen reduction overpotentials.4,5 More recent research in this area include the work of Zhao et al. who reported high production rates and efficiency for the 2e⁻ reduction of O₂ to H₂O₂ on fluorine-doped hierarchically porous carbons at low pH (~1). As a result of fluorine doping, the electronic properties of porous carbon was tuned to facilitate the desorption of the HOO⁻ radical intermediate.4 Other recent reports of electrocatalysts for the electroreduction of oxygen to hydrogen peroxide include highly ordered mesoporous nitrogen-doped carbon6 and hierarchically-structured porous carbons.7 On the application side, Drogui and co-workers have used a RuO₂-coated titanium anode for generation of oxygen, and a carbon felt cathode for reduction of the generated O₂ to produce H₂O₂ in order to remove dissolved organic carbonaceous compounds from municipal sewage plant effluents.8 In another application, Ridruejo et al. reported on the activity of pyrite-structured nanoparticles of supported-Co₃S₄ towards production of H₂O₂ and demonstrated their effectiveness on the removal of pharmaceutical tetracaine from an acidic solution.9 Besides experimental activities, theoretical calculations are also gaining significant attention in catalyst design and identification of catalytic trends. The propensity of an electrocatalyst for reduction of O₂ to H₂O₂ can be largely gauged by the adsorption energy of the HOO⁻ intermediate in the overall reaction pathway, the strength of which should ideally be thermoneutral at the equilibrium potential (O₂/H₂O₂ = 0.7 V vs SHE) in order to yield a theoretically zero-overpotential active surface. Recently, density functional theory (DFT) techniques have been successfully used to determine, and even predict, the trends in activity and selectivity of catalysts for the direct reduction of O₂ to H₂O₂ by locating the optimum values of HOO⁻ binding energy. For example, Verdaguer-Casadevall and co-workers have identified Pt-Hg and Ag-Hg electrocatalysts with enhanced activity for the reduction of O₂ to H₂O₂.10,11 However, the practical applicability of Hg containing Pt and Ag catalysts is very limited. DFT calculations have also been used to identify electrocatalysts, such as SnO₂, which can selectively oxidize water to H₂O₂ (as opposed to O₂) by tuning the OH⁻ binding energy in order to suppress the four electron process of oxygen evolution.12

In our earlier studies, we reported on the synthesis and electrochemical characterization of novel catalysts for the 2-electron reduction of O₂ to H₂O₂ including low-cost inorganic Co-C composites and also organic redox mediators (riboflavin, anthraquinone derivatives and riboflavinyl-anthraquinone 2-carboxylate ester).13,14 The Co-C composite was successfully demonstrated in a H₂O₂ PEM fuel cell with simultaneous production of electric power and H₂O₂ at neutral pH.15 Furthermore, a number of different bifunctional cathode structures were examined to optimize the H₂O₂ production and power output.16 Although in the H₂O₂ fuel cell mode only the Co-C composite can operate, both Co-C and the organic-based redox mediator catalysts are functional in a PEM electrolyzer.

The work presented here is part of a large research initiative, the REAS/EAU WaterNet Program, a federally funded research program aimed at studying drinking water issues currently affecting...
small rural communities across Canada. The intent has been to develop cost-effective portable water treatment using H₂O₂/UV advanced oxidation and producing the hydrogen peroxide on-site and on-demand for small communities. Based on 500 liters of water required per day for each resident in a community of 500 residents, the H₂O₂/UV treatment unit would require 10 ppm (or 0.3 mM) of H₂O₂ in order to provide sufficient treatment for 250,000 liters of water at a flow rate of 100–300 l min⁻¹. Both the inorganic (cobalt-carbon composite) and the organic redox catalyst (anthraquinone-riboflavin) were evaluated using a PEM electrolyzer with 49 cm² geometric electrode area. Specifically, cell polarization and also steady-state long-term experiments were performed to study the impact of cathode water flow rate, temperature, and cathode catalyst and anode configuration on the production and stability of hydrogen peroxide. To the best of the knowledge of the authors, this is the first report on the use of an organic redox catalyst for hydrogen peroxide production in a PEM electrolyzer and, moreover, the first comparison with an inorganic composite catalyst.

Experimental Methods

Cathode and anode electrode preparation.—The cathode catalyst synthesis methods for the inorganic Co–C composite and the organic 10 wt% anthraquinone-riboflavin on carbon (AQ–C) catalysts were previously reported by our group. The catalyst inks were prepared by mixing pre-weighed amounts of Co–C (or AQ–C) powders with deionized (DI) water (18.2 MΩ cm, Barnstead E-Pure System, Thermo-Fisher), 10 wt% NaF solution (Sigma-Aldrich), and 2-propanol (Fischer-Scientific), then sonicating the mixture for 60 min. The catalyst inks were sprayed by a hand-held spray gun pressurized with compressed air (Mastercraft HVLP Air Spray Gun Set, Canadian Tire) onto a gas diffusion layer (GDL) (TGP-H060 Toray paper with 10 wt% teflon, Fuel Cell Earth LLC), while maintaining the temperature at about 80 °C using a hotplate (Corning PC-620D, Cole-Parmer Canada Company). Similar cathode loadings of about 3.6 mg cm⁻² were used for both catalysts.

Two types of anode configurations were investigated using Pt black catalyst (Platinum black standard, Johnson Matthey Company): i) (Type I) Pt-black catalyst ink sprayed onto TGP-H060 unmodified Toray carbon paper with a catalyst loading of 0.2 mgPt cm⁻², and ii) (Type II) Pt-black catalyst ink sprayed on one side of a polymer exchange membrane (Naﬁon® PFSA membrane NR-112, DuPont Naﬁon® Products) with a catalyst loading of 0.4 mgPt-black cm⁻² (identiﬁed as a half-CCM). Figure 1 shows the schematic diagram of anode types I and II. The Ti-mesh was chosen because of its superior corrosion resistance at higher potentials with respect to the carbon support.

The half-CCM was prepared by first drying a cleaned protonated Naﬁon 112 membrane using a hotpress (Dake Model 44226) at 135 °C for two minutes. After cooling, the dried membrane was secured on a hotplate (at 70 °C) using a vacuum table and Pt black anode catalyst inks were then sprayed on the membrane using a spray gun. Catalyst loading was determined by weighing the membrane before and after the spraying. Membrane electrode assemblies (MEA), were produced by hot pressing (Dake Model 44226) a sandwich of membrane with the catalyst coated GDEs at 135 °C and 7584 kPa for a period of 2.5 min.

Electrolysis cell hardware and testing equipment.—A commercially-available fuel cell hardware with an active area of 49 cm² (TP50, Tandem Technologies Ltd.) was modiﬁed in-house and was used for all the electrolysis experiments. Six K-type thermocouples (Omega Engineering Canada) were inserted into the cell hardware through the bottom endplate to the test station, and were used to monitor the temperature of the cooling water loop, the anode and cathode streams (both inlet and outlet), and the cell temperature. This hardware enabled us to readily replace the cell components without any disruption of the input feed. A standard single pass serpentine flow ﬁeld design was used for both the anode and the cathode ﬂow ﬁeld plates, and the assembled plates were in a cross-ﬂow conﬁguration. The cathode plate used was the original graphite plate provided by Tandem Technologies. The anode plate was, however, machined in-house from brass (McMaster Carr Supply Company) and was coated with 4 μm nickel and 1 μm gold (ACME Plating and Silver Shop Ltd., Vancouver, Canada) in order to provide adequate corrosion resistance at the high electrolysis potentials.

Sealing of the MEA between the ﬂow ﬁeld plates was achieved with Silicone JRTV gaskets (Dow Corning Corporation). Figure S1 and Table S1 (available online at stacks.iop.org/JES/167/044502/mmedia) show the cell hardware and details of the cell components used (see the Supplementary Electronic Information). Figure 2 shows the schematics of the experimental setup used for the experiments reported here. A 2-kW fuel cell test station (G100 Test Station with HYWARE II software, Green Light Innovation) was used to control...
the flows of cathode gas and coolant loop to the electrolysis cell. The carrier water feed (neutral DI water) to the cathode was controlled by a peristaltic pump (model 7553–80, Masterflex). The water flow rate in the anode compartment was 15 ml min\(^{-1}\) and was provided by a similar peristaltic pump. An external power supply (Xantrex XHR 20–50, AMETEK Programmable Power, Inc.) was used to provide the required electrical power for the electrolysis experiments.

**MEA conditioning and polarization measurements.**—During the electrolysis experiments the modified TP50 cell was compressed to a pressure of 827 kPa. Table I presents the employed experimental conditions, controlled and monitored by the Greenlight test station. At the beginning of the experiments first the cathode and anode DI water streams were turned on, and then an initial current density (≈ 29 mA cm\(^{-2}\)) was applied to initiate the MEA conditioning at 60 °C. The current density was slowly increased every 10–15 min up to ≈ 143 mA cm\(^{-2}\), while monitoring the cell potential. The MEA was conditioned at this higher current density for one hour.

All polarization measurements were carried out galvanostatically using eighteen different superficial current densities between 30 to 300 mA cm\(^{-2}\). Each polarization current density point was held for two minutes, during which time the voltage was approximately constant throughout, and its value was recorded at the end of the two-minute period.

**Full recycle loop experiments.**—The operating conditions for the long-term recycle tests were the same as those listed in Table 1. These experiments started with the cell operating in a single pass mode for 25 min with the cathode carrier water flow at 15 ml min\(^{-1}\) at a current density of 61 mA cm\(^{-2}\). Once sufficient product solution was accumulated in the collection reservoir in order to allow for sampling, the recycle pump was turned on with the recycle cathode carrier flow rate fixed at 15 ml min\(^{-1}\). The anode water was not recycled during the experiments and was operated in a single pass mode with a fixed flow rate of 15 ml min\(^{-1}\). The recycle experiments were conducted up to 72 h of continuous operation with samples taken periodically for analysis.

**Chemical analysis.**—Both the anode and the cathode outlet water streams were sampled. On the anode side the outlet water sample was tested for trace metal ions from possible anode corrosion. On the cathode side, samples were analyzed for H\(_2\)O\(_2\) concentration, as well as trace metal ions.

Quantitative analysis of H\(_2\)O\(_2\) concentration was performed by a modified tri-iodide/UV–VIS spectroscopy method described by Klassen et al.\(^{20}\) This method is suitable for H\(_2\)O\(_2\) concentrations of up to 10 ppm. Samples with greater H\(_2\)O\(_2\) concentrations were diluted prior to analysis. All the measurements were carried out under neutral conditions. The UV–VIS measurements were conducted with a UV–VIS spectrophotometer (UVmini-1240, Shimadzu Corp.) and were performed at least twice to ensure repeatability. Errors were within ± 0.5%.

Inductively coupled plasma—optical emission spectrometry (ICP-OES) measurements were performed using an Agilent 725 ICP-OES, equipped with an auto-sampler and radial view. The samples were prepared by mixing a 1 ml solution of the cathode (or anode) in a 2 % HNO\(_3\) solution to a final volume of 10 ml.

**Results and Discussion**

The fundamental mechanisms for the two-electron O\(_2\) reduction on either Co–C or the organic redox catalyst anthraquinone-riboflavynil (AQ–C) were discussed by us previously.\(^{16,17}\) Here the focus is exclusively on the results obtained in the PEM electrolyzer.
Table I. Standard operating conditions and the experimental variables investigated for the electrolytic generation of H\textsubscript{2}O\textsubscript{2}.

| Operating Variable                  | Value       |
|-------------------------------------|-------------|
| PEM Electrolyzer Compression [kPa(g)] | 827         |
| Anode DI Water Flow Rate [ml min\textsuperscript{-1}] | 15          |
| Cathode Relative Humidity [%]       | 100         |
| Cathode Gas Flow [ml min\textsuperscript{-1} O\textsubscript{2}] | 1000        |
| Cathode Pressure [kPa]              | 150         |
| Operating Temperature [°C]          | 20 40 60 80 |
| Cathode DI Water Flow Rate [ml min\textsuperscript{-1}] | 5 15       |

Stoichiometric factor: 58.6 @ 100 mA cm\textsuperscript{-2}
Effect of temperature on \( \text{H}_2\text{O}_2 \) production.—Figure 3 shows the impact of temperature on current efficiency, cell potential, and \( \text{H}_2\text{O}_2 \) production for the Co–C catalyst (a–c) and the AQ–C cathode catalysts (d–f), respectively. The type I anode (i.e., Pt/C) was used in these experiments. With Co–C catalyst, at current densities \( \leq 100 \text{ mA cm}^{-2} \), the \( \text{H}_2\text{O}_2 \) production rate is almost identical for all temperatures examined. As the current density increases above \( 100 \text{ mA cm}^{-2} \), however, differences among the four temperatures studied appear (Fig. 3c). The highest \( \text{H}_2\text{O}_2 \) production rate is obtained at 40 °C as well as a corresponding increase in current efficiency (Figs. 3a and 3c). Further increase of the temperature to 60 °C and 80 °C is not beneficial in terms of \( \text{H}_2\text{O}_2 \) production and current efficiency. At elevated operating temperatures the \( \text{H}_2\text{O}_2 \) decomposition rate increases more significantly with current density.

The AQ–C catalyst shows generally similar trends to the Co–C with respect to the temperature effect (Figs. 3d–3f). At either 40 °C or 60 °C the \( \text{H}_2\text{O}_2 \) production rate on AQ–C reaches a maximum of approximately 580 \( \mu \text{mol hr}^{-1} \text{cm}^{-2} \) (at 245 mA cm\(^{-2}\)) exceeding by about 21% the maximum production rate obtained using Co–C (Figs. 3f and 3c). At 40 °C and 100 mA cm\(^{-2}\) the organic redox catalyst AQ–C generated a 19% current efficiency, whereas with Co–C the current efficiency was only 10% (Figs. 3d and 3a). However, the current efficiency on AQ–C decreases at current densities higher than 100 mA cm\(^{-2}\). This indicates that the rates of the secondary reactions \( \text{H}_2\text{O}_2 \) reduction and \( \text{H}_2 \) evolution become more significant. In terms of temperature, similar to the Co–C catalyst, 40 °C is optimal, favoring higher production rate while keeping the \( \text{H}_2\text{O}_2 \) decomposition rate low.

Effect of cathode carrier water flow rate on \( \text{H}_2\text{O}_2 \) production.—Figure 4 shows the results of experiments performed with both types of catalysts at 40 °C and water flow rates of 5 and 15 ml min\(^{-1}\), respectively. In case of the AQ–C cathode catalyst, the cell performance was similar for both cathode water flow rates. For Co–C however, the higher water flow rate (i.e., shorter residence time) had a significant beneficial effect on all figures of merit: \( \text{H}_2\text{O}_2 \) production rate, cell voltage and current efficiency. This may
Electrolyzer for H$_2$O$_2$ production can be compromised by carbon CCM and Ti mesh anode (Type II) was not hot pressed. Therefore, prepared using a hot press method, whereas the MEA with a half-

catalyst coated half-membrane (half-CCM) was also used in con-

junction with Ti mesh (Type II anode, Fig. 1). Figure 5 shows a comparison of the two anode types tested: Ti-CCM and C-Pt anodes with AQ–C cathode catalyst. The cell potential using the half-CCM anode with Ti mesh is similar to that of the carbon paper GDL–Pt anode (Fig. 6b), however, the H$_2$O$_2$ production is lower (Fig. 6c). This is due to the competition between H$_2$O$_2$ generation and losses through pathways such as secondary electro-

reduction, and thermocatalytic decomposition (see next section).

Effect of the anode configuration.—The durability of the PEM electrolyzer for H$_2$O$_2$ production can be compromised by carbon corrosion at the anode (i.e., carbon paper GDL, Type I anode, Fig. 1). To address this issue an anode configuration composed of Pt catalyst coated half-membrane (half-CCM) was also used in conj-

ction with Ti mesh (Type II anode, Fig. 1). Figure 5 shows a comparison of the two anode types tested: Ti-CCM and C-Pt anodes with AQ–C cathode catalyst. The cell potential using the half-CCM anode with Ti mesh is similar to that of the carbon paper GDL–Pt anode (Fig. 6b), however, the H$_2$O$_2$ production is lower (Fig. 6c). The reason for lower H$_2$O$_2$ production with Type II anode could be attributed to the different preparation of the MEAs. The MEA with the Type I anode (i.e., containing the carbon paper GDL) was prepared using a hot press method, whereas the MEA with a half-

CCM and Ti mesh anode (Type II) was not hot pressed. Therefore, the interaction and bonding between the ionomer and the cathode catalyst layer is superior in the case of the hot pressed MEA (i.e., with Type I anode), improving the cathode catalyst layer utilization and, therefore, the H$_2$O$_2$ production rate. It should be also mentioned that further reduction of the over cell potential can be achieved using iridium oxide-based anodes. In the present work Pt-based anodes were used for direct comparison of the same cell in either electrolysis or fuel cell mode operation for peroxide generation.\(^{18,19}\)

Full recycle operation mode.—The capability to produce H$_2$O$_2$ over a longer period of time is crucial to assess the applicability of the proposed PEM electrolyzer approach for commercial operation. In order to simulate on a laboratory scale such a scenario, experiments with full recycle of the cathode product solution were performed for 72 h. For the continuous recycle operation experiments, the AQ–C (half CCM) cathode with the Ti mesh-based anode configurations (Type II, Fig. 1) was employed to mitigate the carbon corrosion on the anode side. (Fig. 6). Results show that the AQ–C catalyst produced 3000 ppm (0.3 wt %) of H$_2$O$_2$ by the end of the 72-hour experiment (Fig. 6b). The H$_2$O$_2$ production rate peaked after approximately 20 h (Fig. 6a). Beyond 20 h the production rate decreased and the net accumulated H$_2$O$_2$ concentration virtually levelled off (Fig. 6b). This is due to the competition between H$_2$O$_2$ generation and losses through pathways such as secondary electro-

reduction, and thermocatalytic decomposition (see next section).

Effect of catalyst and temperature on H$_2$O$_2$ degradation.—The H$_2$O$_2$ stability was investigated at three different temperatures (40, 60, 80 °C) using a fully assembled electrolysis cell consisting of AQ–C cathode catalyst and a half-CCM Pt anode with a Ti mesh current collector. The goal was to determine the H$_2$O$_2$ loss under open circuit conditions due to thermocatalytic (i.e., non-electroche-

mical) degradation. Figures 7a and 7b show clear evidence for thermal decomposition of H$_2$O$_2$ with higher temperatures leading to increased decomposed of H$_2$O$_2$. Figures 7c and 7d display the data on a semi logarithmic plot, where dashed lines show the linear regression. Clearly, full recycle operation of the electrolyzer at 80 °C for over two hours is not beneficial. Furthermore, the presence of O$_2$ gas enhanced the H$_2$O$_2$ decomposition in a positive synergistic interaction effect with temperature (i.e., the higher the temperature the higher was the interaction effect between gas presence and temperature regarding H$_2$O$_2$ decomposition, compare Figs. 7c and 7d, 80 °C data). Similar behavior was reported before as well.\(^{18}\)

In addition, the membrane degradation was also evaluated by analyzing the fluoride released. The median fluoride release rate was \(~0.03\) ng hr$^{-1}$ cm$^{-2}$ for the sixteen samples analyzed. Drinking water guidelines from the Government of B.C. in Canada suggests a fluoride limit of 1.0–1.5 mg l$^{-1}$.\(^{21}\) The long-term recycle experiments showed the cumulative fluoride concentration over the three day runs was well below the limit set out by the guidelines, at about 2.2 μg l$^{-1}$.

Conclusions

The electroreduction of O$_2$ to H$_2$O$_2$ was investigated in a PEM electrolyzer under near-neutral pH operation using deionized water. Two novel cathode catalysts, a cobalt–carbon composite (Co–C) and an organic redox catalyst, anthraquinone-riboflaviny1 supported on carbon (AQ–C), were investigated. Using a superficial current density of 245 mA cm$^{-2}$ and an operating temperature of 40 °C, H$_2$O$_2$ molar fluxes of 360 μmol hr$^{-1}$ cm$^{-2}$ and 580 μmol hr$^{-1}$ cm$^{-2}$ were obtained in single pass mode with the Co–C and RF-AQ catalysts, respectively. To the best of our knowledge, this is the first time that H$_2$O$_2$ production in a PEM electrolyzer with an organic redox catalyst has been reported.

Longer term (72 h) experiments conducted at a constant superficial current density of 61 mA cm$^{-2}$ with complete recycle of the cathode carrier water solution showed a maximum steady-state

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**Figure 6.** Continuous recycle operation (for up to 72 h) of the PEM electrolyzer for H$_2$O$_2$ production. AQ–C cathode catalyst with Pt on Ti-mesh anode. (a) H$_2$O$_2$ production rate, (b) total accumulated H$_2$O$_2$ concentration and (c) cell voltage. Current density 61 mA cm$^{-2}$, temperature 40 °C and rest of the conditions identical to Fig. 5.
H$_2$O$_2$ concentration of 3000 ppm for the AQ-C catalyst. The electrolytic production of H$_2$O$_2$ using the AQ–C composite catalyst in a PEM electrolyzer can provide an adequate supply of H$_2$O$_2$ for advanced oxidation drinking water treatment applications on-site and on-demand.

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References

1. https://transparencymarketresearch.com/pressrelease/hydrogen-peroxide-market.htm (accessed February 2, 2020).
2. J. M. Campos-Martín, G. Blanco-Brieva, and J. L. G. Fierro, “Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process.” *Angew. Chemie—Int. Ed.*, 45, 6962 (2006).
3. C. W. Oloman, in *Electrochemical Processing for the Pulp & Paper Industry* (The Electrochemical Consultancy, New York) (1996).
4. I. Yamamaka, S. Tazawa, T. Murayama, T. Iwasaki, and S. Takenaka, “Catalytic synthesis of neutral hydrogen peroxide at a CoN$_2$C$_x$ cathode of a polymer electrolyte membrane fuel cell (PEMFC).” *Chem. Sus. Chem.*, 3, 59 (2010).
5. W. Zhang, A. U. Shaikh, E. Y. Tsui, and T. M. Swager, “Cobalt porphyrin functionalized carbon nanotubes for oxygen reduction.” *Chem. Mater.*, 21, 3234 (2009).
6. H. J. Zhang, X. Yuan, W. Wen, D. Y. Zhang, L. Sun, Q. Z. Jiang, and Z. F. Ma, “Electrochemical performance of a novel CoTETA/C catalyst for the oxygen reduction reaction.” *Electrochem. Commun.*, 11, 206 (2009).
7. K. Zhao, Y. Su, X. Quan, Y. Liu, S. Chen, and H. Yu, “Enhanced H$_2$O$_2$ production by selective electrochemical reduction of O$_2$ on fluorine-doped hierarchically porous carbon.” *J. Catal.*, 357, 118 (2018).
8. J. Park, Y. Naba, T. Hayakawa, and M. A. Kakimoto, “Highly selective two-electron oxygen reduction catalyzed by mesoporous nitrogen-doped carbon.” *ACS Catal.*, 4, 3789 (2014).
9. T. P. Fellinger, F. Hasch, P. Strasser, and M. Antonietti, “Mesoporous nitrogen-doped carbon for the electrocatalytic synthesis of hydrogen peroxide.” *J. Am. Chem. Soc.*, 134, 4072 (2012).
10. Y. Liu, X. Quan, X. Fan, H. Wang, and S. Chen, “High-yield electrolysis synthesis of hydrogen peroxide from oxygen reduction by hierarchically porous carbon.” *Angew. Chemie—Int. Ed.*, 54, 6837 (2015).
11. P. Drogui, S. Elmaleh, M. Rumeau, C. Bernard, and A. Rambaud, “Hydrogen peroxide production by water electrolysis: application to disinfection.” *J. Appl. Electrochem.*, 31, 877 (2001).
12. C. Ridruejo, F. Alcalà, G. Álvarez, E. Brillas, and I. Sirés, “On-site H$_2$O$_2$ electrogeneration at a Co$_2$S$_2$-based air-diffusion cathode for the electrochemical degradation of organic pollutants.” *J. Electroanal. Chem.*, 808, 364 (2018).
13. A. Verdaguer-Casadevall, D. Deiana, M. Karamad, S. Siahrostami, P. Malacrida, T. W. Hansen, J. Rossmeisl, I. Chorkendorff, and I. E. L. Stephens, “Trends in the electrochemical synthesis of H$_2$O$_2$: enhancing activity and selectivity by electrocatalytic site engineering.” *Nano Lett.*, 14, 1603 (2014).
14. S. Siahrostami et al., “Enabling direct H$_2$O$_2$ production through rational electrocatalyst design.” *Nat. Mater.*, 12, 1137 (2013).
15. V. Viswanathan, H. A. Hansen, and J. K. Nørskov, “Selective electrochemical generation of hydrogen peroxide from water oxidation.” *J. Phys. Chem. Lett.*, 6, 4224 (2015).
16. A. Bonakdarpour, D. Esan, H. Cheng, A. Gylene, and D. P. Wilkinson, “Preparation and electrochemical studies of metal-carbon composite catalysts for small-scale electrolysiss of H$_2$O$_2$.” *Electrochim. Acta.*, 56, 9074 (2011).
17. A. Wang, A. Bonakdarpour, D. P. Wilkinson, and E. Gylene, “Novel organic redox catalyst for the electroreduction of oxygen to hydrogen peroxide.” *Electrochim. Acta.*, 66, 222 (2012).
18. W. Li, A. Bonakdarpour, E. Gylene, and D. P. Wilkinson, “Drinking water purification by electrolysiss of hydrogen peroxide in a power-producing PEM fuel cell.” *Chem. Sus. Chem.*, 6, 2137 (2013).
19. W. Li, A. Bonakdarpour, E. Gylene, and D. P. Wilkinson, “Design of bifunctional electrodes for co-generation of electrical power and hydrogen peroxide.” *J. Appl. Electrochem.*, 48, 985 (2018).
20. N. V. Kladsen, D. Marchington, and H. C. E. McGowan, “H$_2$O$_2$ Determination by the I$_3^−$—method and by KMnO$_4$ titration.” *Anal. Chem.*, 66, 2921 (1994).
21. BC Ministry of Environment and Climate Change Strategy, “B.C. Source Drinking Water Quality Guidelines: Guideline Summary.” *Water Quality Guideline Series WQG-01* (2017).

Figure 7. H$_2$O$_2$ stability in the electrolysis cell at open circuit as a function of temperature and oxygen gas flow. (a), (c) no oxygen gas; (b), (d) with oxygen gas flow. Cathode catalyst: AQ-C 3.6 mg AQ-C cm$^{-2}$ on TGP-H060 (10 wt% PTFE). Continuous recycle of the cathode water carrier flow at 15 ml min$^{-1}$. O$_2$ flow rate 1,000 ml min$^{-1}$, pressure 150 kPa(g). Anode conditions: water flow 15 ml min$^{-1}$, Ti-Pt anode.