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VIEWPOINT

Fate and Reactivity of Peroxides Formed over $BiVO_4$ Anodes in Bicarbonate Electrolytes

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Hydrogen peroxide is one of the most important chemical compounds, employed for many different processes,[1] including chemical synthesis,[2] bleaching,[3] disinfection,[4] and water treatment.[5] The high content of active oxygen and the fact that it forms only water as a byproduct make it a very environmentally friendly oxidant, giving it a rise in prominence as green chemistry grows in significance. However, hydrogen peroxide is currently produced almost exclusively using the anthraquinone process,[6] which is very energy-intensive, leading to high CO_2 emissions from the steam reforming used to produce the required hydrogen gas. The process is also only efficient in centralized large plants, requiring complex logistics to bring it to the usually delocalized consumers. Due to the instability of hydrogen peroxide, stabilizers must be added for transport and storage.[7]

In order to solve these problems, new synthesis routes for the production of hydrogen peroxide directly at the place of use are highly sought-after. Electrochemical[8] and photocatalytic[9] processes are particularly suitable for this purpose. The electrochemical method offers a safe, environmentally friendly, and technically feasible variant of H_2O_2 production. Hydrogen peroxide can be produced via two different electrochemical reactions. One possibility is the well-known reduction of molecular oxygen at the cathode in a two-electron process (eq 1). On the other hand, the oxidation of water may also yield hydrogen peroxide at the anode (eq 2). The challenge in this reaction is to prevent the subsequent overoxidation of the peroxide to oxygen (eq 3). Also, the direct four-electron oxidation to oxygen (eq 4) needs to be prevented.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.68\ V \tag{1}$$

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad E^0 = 1.76\ V \tag{2}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad E^0 = 0.68\ V \tag{3}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23\ V \tag{4}$$

Two strategies have so far been employed to improve the selectivity toward hydrogen peroxide: electrode and electrolyte optimization. In the first aspect, it has been found that semiconducting electrodes such as TiO_2, SnO_2, WO_3, and $BiVO_4$ perform particularly well due to their inherently large electrochemical window and high overpotential for the four-electron water oxidation.[10,11]

In terms of electrolyte, the first promising results were obtained by Izgorodin et al. in an ionic liquid using MnO_x anodes.[12] Pioneering work by Fuku et al. later established a 2 M potassium bicarbonate ($KHCO_3$) electrolyte as the best choice for anodic hydrogen peroxide production using $BiVO_4$ anodes,[13−15] and this has since been the established standard.[16,17] Recent reports on other anode materials such as ZnO, $CaSnO_3$, or $LaAlO_3$ also employ this electrolyte.[18−21]

The mechanism of hydrogen peroxide formation in bicarbonate buffer is proposed to start with the oxidation of bicarbonate to peroxomonocarbonate ($HOOCO_2^-$, PMC) (eq 5).[13] In all reports discussing the mechanism of hydrogen peroxide formation from water oxidation over $BiVO_4$ anodes, it is assumed that PMC is unstable and subsequently hydrolyzed immediately to hydrogen peroxide and bicarbonate (eq 6).[13,22] The electrolyte itself thus acts as a redox catalyst so that a higher efficiency of the peroxide synthesis is achieved. The fate and reactivity of PMC are then not further considered or discussed.

$$HCO_3^- + H_2O \rightarrow HCO_4^- + 2e^- + 2H^+ \tag{5}$$

$$HCO_4^- + H_2O \rightarrow HCO_3^- + H_2O_2 \tag{6}$$

The electrochemical production of percarbonates by oxidation of bicarbonate or carbonate electrolytes has previously also been reported with other electrodes such as boron-doped diamond (BDD), albeit at typically higher voltage and current.[23] However, those reports claim that significant amounts of stable percarbonates are produced in addition to hydrogen peroxide.[23]

When performing our own experiments with $BiVO_4$ anodes, we were at first not able to reproduce the high faradaic efficiencies (FEs) of up to 80% reported in the literature for 2 M $KHCO_3$ electrolytes but instead only achieved around 10−20%. We quantified the hydrogen peroxide using a very sensitive and specific enzymatic assay based on horseradish peroxidase (HRP).[24] To validate this method, we then also employed peroxide test strips (QUANTOFIX), which are

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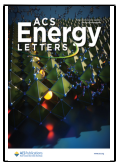

commonly used in the literature.[11,16−19] Surprisingly, these test strips yielded dramatically higher values for the peroxide, which would translate into FEs of >60%, sometimes even exceeding 100% (see Figure 1, blue triangles).

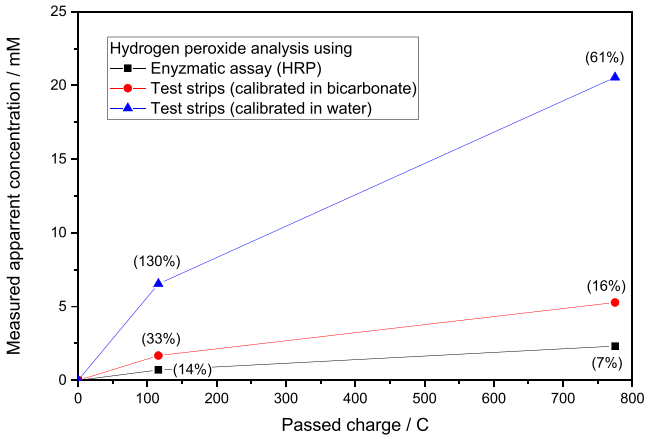

Figure 1. Time-course (expressed as passed charge) of the measured peroxide concentrations during a potentiostatic electrochemical experiment with the enzymatic HRP assay (black squares) and the QUANTOFIX test strips, calibrated in either water (blue triangles) or 2 M $KHCO_3$ (red circles). The numbers in parentheses over the data points indicate the respective faradic efficiency. Conditions: 4.5 cm^2 $BiVO_4$ working electrode (anode), 4.9 cm^2 gas diffusion electrode (cathode), divided cell (cation exchange membrane), 120 mL of 2 M $KHCO_3$ in each chamber, 2.8 V vs Ag/AgCl; for current measurements during the experiment, refer to Figure S4.

However, we calibrated these test strips using aqueous dilutions of hydrogen peroxide stock solutions, as is commonly done. When instead the same electrolyte from the electrochemical experiments (2 M $KHCO_3$) enriched with known hydrogen peroxide concentrations was used, this technique yielded very different results (Figure 2). The test strips appear to be much more sensitive in this electrolyte, by a factor of about 4.

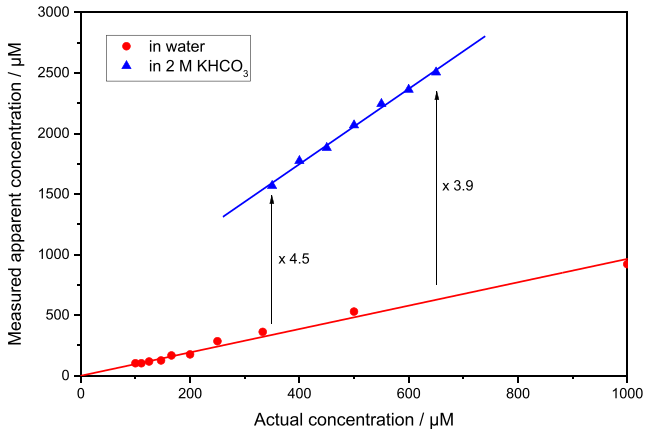

Figure 2. Comparison of the response of the peroxide test strips (*y*-axis) to defined concentrations of hydrogen peroxide (*x*-axis) in water (red circles) and 2 M $KHCO_3$ solution (blue triangles). In the latter case, the solution was allowed to equilibrate for 30 min before measuring.

We were still able to identify a linear response regime between approximately 350 and 650 μM (Figure 2); values above or below that range were out of bounds of the method, yielding no usable response. So, with the updated calibration, the test should still be applicable even in bicarbonate electrolytes within this concentration range (or appropriately diluted).

Yet, even factoring in this updated calibration, the values obtained with the test strips still yielded consistently higher values than the enzymatic assay, approximately twice as high (see also Figure 1). A similar behavior was also observed at other applied potentials (Figure S5), indicating that this is a fundamental issue and not just limited to specific reaction conditions. To clear up this disparity, we conducted a third test for peroxide based on colorimetric iodometry. This confirmed the results of the properly calibrated test strips and also showed higher values than the enzymatic assay. We hypothesized that this may be due to several peroxide species being present, since the enzymatic assay is very specific for hydrogen peroxide but the test strips are just based on the oxidation of a dye, which may be induced by any suitable oxidant. Similarly, iodometry is just based on unspecific oxidation, which may be triggered by other oxidants. The obvious candidate for this additional oxidant is peroxomonocarbonate (PMC), which has been suggested as the intermediate in the reaction anyway. If this intermediate is not short-lived but instead forms stable concentrations in the electrolyte, it may explain our observations.

In the absence of any precise data, the assumption of PMC's fast hydrolysis is usually based on estimates of its half-life time in water, which is on the order of few minutes.[25] However, at lower temperatures and more alkaline solutions, the hydrolysis rate may be significantly slower.[26] For instance, at pH 8.6, the half-life time is increased to almost 3 h.[27] Since the pH of concentrated bicarbonate solutions is near that value, e.g., pH 8.3 for 2 M $KHCO_3$, spontaneous complete hydrolysis cannot be assumed.

The next thing to consider is the chemical equilibrium. Not only can PMC be hydrolyzed to hydrogen peroxide, but it can also be formed from a reaction of hydrogen peroxide with bicarbonate (reverse of eq 6). The equilibrium of this reaction is characterized by an equilibrium constant, as shown in eq 7, that is dependent on not only the concentration of hydrogen peroxide and PMC but also that of bicarbonate.

$$K = \frac{[H_2O_2][HCO_3^-]}{[HCO_4^-]} \quad (7)$$

Based on ^{13}C NMR experiments, the equilibrium constant K is approximately 1.7−3.1 mol/L at room temperature and neutral pH.[26,27] To confirm this for the reaction conditions typical for anodic peroxide synthesis (2 M $KHCO_3$, pH 8.3), we also performed our own experiments. Adding 1 M H_2O_2 to 2 M bicarbonate solution yielded an approximate equilibrium concentration of 214 mM PMC by ^{13}C NMR analysis (Figure S1), which equates to a slightly higher equilibrium constant of 6.6 mol/L.

This means that dissolving PMC in pure water will lead to the assumed almost quantitative hydrolysis. However, in bicarbonate electrolyte, the bicarbonate present pushes the equilibrium toward the PMC side. According to the beforementioned equilibrium constants, 21−54% of the total peroxide should be in the form of PMC in 2 M bicarbonate,

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correlating well with our results suggesting that roughly half the peroxide is bound as PMC. These data are subject to numerous uncertainties, but it is clear that spontaneous and quantitative hydrolysis of PMC cannot be assumed in bicarbonate electrolytes. On the contrary, there will always be a significant fraction of it present alongside hydrogen peroxide in the experiments.

This has important implications not only for the potential industrial application but also for the employed measurement techniques. Percarbonate has an only slightly higher oxidation potential than hydrogen peroxide (+1.8 V_{SHE} vs +1.77 V_{SHE} at pH 0),[25] which further indicates that their equilibrium will yield similar concentrations of each. However, despite this minute difference, PMC is reported to have much better kinetics in typical oxidation reactions, e.g., 300-fold faster reaction rates versus sulfides.[25] Therefore, this bicarbonate-activated peroxide system (BAS) is considered as a promising emerging technology for remediation applications.[28,29] This explains why the employed test strips are more sensitive toward PMC than H_2O_2. They are based on the oxidation of precursors to form a dye—presumably this can be achieved by any oxidant with sufficient oxidation potential. A more potent oxidant such as PMC may even invoke a disproportionally higher response. Based on the observed 4-fold response of the solution containing percarbonate (21% of total peroxide), the reaction of PMC is about 14 times as strong as that of H_2O_2 in the test employed here.

Almost all reports on anodic hydrogen peroxide generation employ detection and quantification methods for the peroxide which are based on either its reductive or oxidative properties. This may be problematic in the presence of bicarbonate and consequently PMC due to its higher reactivity. Many of the recent publications reporting high FE (>50%) in potassium bicarbonate electrolytes use commercial peroxide test strips.[11,16−19] This means that some of these results may be affected by this phenomenon as well. Researchers should therefore critically evaluate this issue and calibrate their procedures using stock solutions of H_2O_2 in bicarbonate (and allowing for time to reach the equilibrium) rather than water.

While on the one hand this means that there may not be as much peroxide formed from $BiVO_4$ anodes in bicarbonate electrolyte as previously believed, it also means that the (smaller) amount formed is more potent in terms of oxidative power. So, at the end of the day, if the peroxide is produced for the purpose of use as an oxidant, the net result may be significantly higher than the measured peroxide concentration suggests. To illustrate this, we performed exemplary experiments with methylene blue as a model compound for bleaching applications. We measured the discoloration of 40 μM of this compound photometrically after addition of an equal volume of oxidation solution. As can be seen in Figure 3, it takes only 780 μM of H_2O_2 in 2 M $KHCO_3$ electrolyte to effect about the same discoloration rate as 200 mM H_2O_2 in water. Presumably, this is the result of the much higher reactivity of the PMC formed *in situ*. This means that, for this application, the bicarbonate/peroxide is more than 250 times as potent as pure hydrogen peroxide. A sample of the electrolyte that had been oxidized using a $BiVO_4$ anode (2.385 V vs Ag/AgCl, 175 C), thus containing 780 μM total peroxide (both hydrogen peroxide and PMC), achieves almost exactly the same discoloration rate as the synthetic percarbonate mixture of the same concentration (see also Table S1 for the

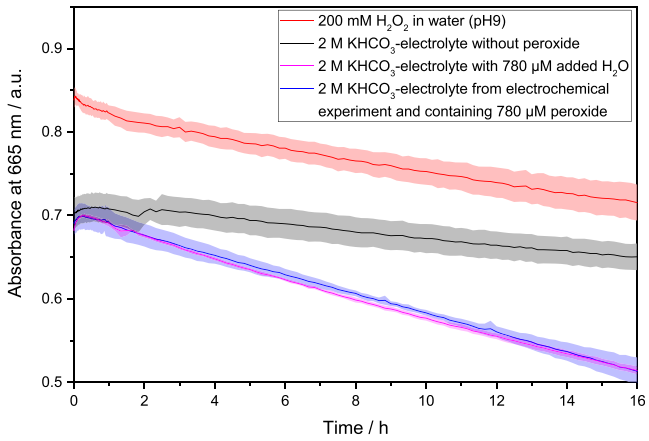

Figure 3. Time-course of the absorbance at 665 nm of a 40 μM methylene blue solution in water after addition of an equal volume of either a 200 mM H_2O_2 solution in water at pH 9 (red) or the 2 M $KHCO_3$ electrolyte, either as is (black), with added 780 μM H_2O_2 (magenta), or polarized by a $BiVO_4$ anode and containing 780 μM total peroxide (blue). The shaded areas depict the standard deviation (at least duplicates).

kinetic constants). Further measurements performed at different voltages confirm that, in every case, the anodized electrolyte effects approximately the same discoloration rate as a synthetic percarbonate mixture of the same total peroxide concentration (Figures S9−S12 and Table S1). This is a strong indication that the anodized electrolyte contains the same peroxide composition as the synthetic mixture, corresponding to the equilibrium concentrations described by eq 7.

We were able to show that the electrochemical oxidation of bicarbonate electrolytes by $BiVO_4$ anodes produces stable concentrations of peroxomonocarbonate (PMC) in addition to hydrogen peroxide. This has important implications not just for the application of the technology but also for the analytics of the so-formed peroxides.

As PMC is a much more potent oxidant than hydrogen peroxide, analytical methods relying on its oxidation properties may be more sensitive to PMC. If this is not accounted for, it may in turn lead to overestimation of the peroxide concentration. In particular, the often-employed commercial test strips appear to be susceptible to this phenomenon. Researchers employing such methods should critically re-evaluate their results to make sure that no inflated efficiencies for peroxide production are reported.

On the other hand, the presence of PMC is likely very beneficial for many applications. PMC in itself is a very promising oxidant due to its ease of handling and favorable kinetics compared to hydrogen peroxide, demonstrated herein by the more than 250-fold reactivity versus methylene blue. So overall, even though less peroxide is formed, its effective oxidation power may be even higher than previously thought.

Experimental Details. *NMR Experiments for Peroxomonocarbonate Quantification.* Aqueous hydrogen peroxide (30%, VWR Chemicals) was added to a solution of 1.9 M $KHCO_3$ (Thermo Scientific) and 0.1 M $NaH^{13}CO_3$ (98 atom % ^{13}C, Sigma-Aldrich) to yield a concentration of 1 M. This solution was then analyzed using ^{13}C NMR (Magritek Spinsolve 60 MHz Carbon ULTRA). The corresponding NMR measurements lasted several hours, so equilibrium between hydrogen peroxide and percarbonate could be readily established. The spectra were recorded with 16 384 scans, a 2 s

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repetition time, and a 30° flip angle. The resulting spectra delivered a new signal (δ 158.36) in addition to the bicarbonate resonance (δ 161.70), which has previously been assigned to peroxomonocarbonate.[26] Quantification was performed by taking the integrals and assuming their sum to equal to the 2 M carbon that was added to the solution in the form of the bicarbonate.

Peroxide Quantification Methods. For the quantification of hydrogen peroxide, a previously established enzymatic assay based on horseradish peroxidase (HRP) was employed.[30,31] This technique is based on the HRP-catalyzed stoichiometric dimerization of *p*-hydroxyphenylacetic acid (POHPAA), which yields a fluorescent product.[30] In defined temporal intervals, samples were taken from the electrolyte. 1 mg of lyophilized powder of HRP (163 U mg^{-1} type II, Sigma-Aldrich) and 4 mg of freshly recrystallized POHPAA (Alfa Aesar) were each dissolved in 12.5 mL of TRIS buffer (1.0 M, pH 8.8, Carl Roth). 100 μL of the electrolyte sample was then mixed with 12.5 μL of each solution for 30 min, and the fluorescence signal (λ_{ex} = 315 nm, λ_{em} = 406 nm, 25 °C) was measured in a microplate reader (SynergyMx, BioTek). The concentrations were calculated according to calibration with an authentic H_2O_2 standard diluted in 2 M $KHCO_3$. Based on the specific interaction of the enzyme with the oxidant inside the active site, this technique is assumed to be specific for H_2O_2.

Hydrogen peroxide was also quantified using the QUANTOFIX (Macherey-Nagel) test strips that have already been used in many studies for this purpose.[11,17] Samples were taken from the electrolyte and diluted with 2 M $KHCO_3$ to achieve a final peroxide concentration appropriate for the dynamic range of the test. The test strips were then held into the diluted sample for 1 s, dried in the air for 10 s, and placed in a reflectometer (QUANTOFIX Relax, Macherey-Nagel). For reproducible results, it is important to keep the timespans between the individual steps constant and match them with those of the calibration procedure.

As a third test, we also used a colorimetric iodometry method.[32] For this purpose, 100 μL of electrolyte sample was mixed with 135 μL of pH 4.1 potassium phosphate (Carl Roth) buffer, 10 μL of 1.2 M potassium iodide (Alfa Aesar) solution, and 5 μL of a 35 mM Mo^{VI} solution (ammonium molybdate(VI) tetrahydrate, Acros Organics) in a 96-well plate. The absorption of the resulting triiodide could then be measured at 350 nm and compared to that of a calibration using an H_2O_2 standard.

Preparation of $BiVO_4$ Anodes. The $BiVO_4$ anodes (doped with 12% gadolinium and 0.1% molybdenum) were produced by dip-coating onto a FTO (7 Ω/sq, Sigma-Aldrich) substrate. First, the FTO was cleaned with acetone and water. A precursor solution was prepared by dissolving 0.616 M bismuth 2-ethylhexanoate (Alfa Aesar) and 0.7 M vanadium(V) oxytriethoxide (Acros) in chloroform (Carl Roth). For the doping, 84 mM gadolinium(III) isopropoxide (abcr) and 0.7 mM molybdenum(VI) oxide bis(2,4-pentanedionate) (Alfa Aesar) were added. The anodes were subsequently prepared by dip-coating the cleaned FTO slides from this precursor solution at a drawing speed of 100 mm min^{-1}. The coated electrodes were then first heated to 100 °C for 10 h on a heating plate. Then the temperature was increased to 450 °C in 10 h and then held for 2 h.

Electrochemical Experiments. The electrochemical experiments were carried out in an H-cell in which the anode and cathode chambers each contained 120 mL of 2 M $KHCO_3$ (pH 8.3). The two chambers were separated by a Fumatech cation-exchange membrane. The $BiVO_4$-coated FTO slides (4.5 cm^2, unless stated otherwise) served as the anode, while a gas diffusion electrode (gaskatel, 4.9 cm^2) was used as the cathode. The experiments were run with a Zahner Zennium-E4 potentiostat at a constant potential against a Ag/AgCl reference electrode (chronoamperometry). The electrochemical experiments were all performed at room temperature and with stirring.

Methylene Blue Bleaching. The methylene blue decolorization experiments were performed in a 96-well plate. For this purpose, 100 μL of a 40 μM methylene blue solution was placed in each well. 100 μL of the respective peroxide solution was then added, with the final concentration in the well then being half the initial concentration of the peroxide solution and 20 μM methylene blue. The peroxide solution was either the result from diluting a stock solution in water to 200 mM (titrated to pH 9 by NaOH) or a sample of the electrochemically oxidized $KHCO_3$ electrolyte which contained 780 μM of total peroxide. After the addition of the peroxide solution, the kinetic measurement was started immediately. Here, the absorption was monitored over time at 665 nm. For the first 10 min, measurements were made every 30 s, then for another 10 min measurements were every minute, followed by 40 min with measurements every 2 min. Finally, measurements were taken every 10 min for 15 h more. Before each measurement, the plate was shaken for 1 s.

Tobias Schanz
Bastien O. Burek
Jonathan Z. Bloh

■ ASSOCIATED CONTENT

Supporting Information

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^{13}C NMR spectra, calibration curves of the different H_2O_2 analysis techniques, chronoamperometric data for the electrochemical experiments, additional data of the results of the different H_2O_2 analysis techniques at different applied voltages, methylene blue discoloration experiments using electrolytes anodized at different voltages and kinetic analysis of methylene blue discoloration (PDF)

■ AUTHOR INFORMATION

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.
The authors declare no competing financial interest.

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