

The Role of Bicarbonate-Based Electrolytes in H_2O_2 Production through Two-Electron Water Oxidation

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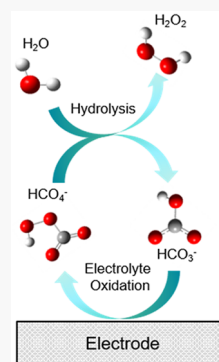


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ABSTRACT: Two-electron water oxidation (2e^- WOR) is a promising route toward efficient production of a valuable product in H_2O_2 . Recent attention has focused on developing new electrocatalysts for 2e^- WOR, but the role of the electrolyte species in determining water oxidation selectivity and promoting 2e^- WOR has not been established. Here, we use electroanalytical experiments to confirm the role of HCO_3^- as a selective 2e^- WOR redox catalyst. We find minimal differences in H_2O_2 consumption pathways among common electrolytes, indicating that the role of HCO_3^- is to promote H_2O_2 production. Mechanistically, our rotating ring disk experiments show that H_2O_2 is not generated directly at the disk electrode in KHCO_3 but formed after a time delay, suggesting electrolyte oxidation and subsequent hydrolysis as the promotional mechanism. Further electrochemical and spectroscopic experiments confirm this hypothesis, demonstrating anodic oxidation of carbonaceous electrolyte species occurs at Faradaic potentials relevant for water oxidation and that these species (likely HCO_4^- or $\text{C}_2\text{O}_6^{2-}$) subsequently oxidize water to H_2O_2 ($t_{1/2} \approx 5$ min). The H_2O_2 production rate at 2.5 V vs RHE scales linearly with the concentration of HCO_3^- , confirming the catalytic role of HCO_3^- in 2e^- WOR and suggesting the electrolyte can be leveraged to enhance electrochemical H_2O_2 production.



Hydrogen peroxide (H_2O_2) exhibits strong oxidizing properties with benign byproducts, making it useful in wastewater treatment,¹ bleaching,² and chemical synthesis.³ H_2O_2 can also serve as both a fuel and oxidizer in single-compartment fuel cells, making it an emergent energy storage chemical.^{4–6} Though H_2O_2 is currently produced by the anthraquinone process, its electrochemical production via two-electron water oxidation (2e^- WOR) has recently garnered research attention as a potential means to store renewable electricity.^{7–10} Because 2e^- WOR is thermodynamically less favorable than the oxygen evolution reaction (OER), substantial efforts have aimed to establish active and selective electrocatalysts for 2e^- WOR. Little work has systematically studied the role of electrolytes in modulating the selectivity of WOR, despite the electrolyte species being known to greatly affect water oxidation selectivity. Sayama et al. first reported that KHCO_3 yields the greatest amount of H_2O_2 among LiSO_4 , NaClO_4 , H_3BO_3 , phosphate buffer, and K_2CO_3 electrolytes over fluorine-doped tin oxide (FTO) surfaces.¹¹ The importance of HCO_3^- in promoting H_2O_2 formation was recognized, and HCO_3^- -based electrolytes have since been used broadly for H_2O_2 production through 2e^- WOR.^{7–9,12–14} It was postulated that aqueous bicarbonate (HCO_3^-) itself may be oxidized at the anode to peroxydicarbonate (HCO_4^-) and/or peroxydicarbonate ($\text{C}_2\text{O}_6^{2-}$), which then

oxidize water to produce HCO_3^- and H_2O_2 . Moreover, several other mechanisms have been suggested to explain the promotional role of HCO_3^- in H_2O_2 production, including enhanced homogeneous stability of H_2O_2 in bicarbonate solutions, the buffering effect of HCO_3^- ,¹⁵ and HCO_3^- preventing further oxidation of H_2O_2 at the electrode surface.¹⁶ Recent reviews have concluded that experimental evidence for the role of HCO_3^- is incomplete at best.¹⁷

Here, we use a combination of electrochemical and spectroscopic methods to investigate the role of bicarbonate-based electrolyte species (HCO_3^- and CO_3^{2-}) for 2e^- WOR. We use BiVO_4 as an anode throughout, as it is among the most selective electrocatalysts for 2e^- WOR.^{12,18} First, we determine the electrochemical production rate of H_2O_2 by accounting for both the accumulated H_2O_2 and H_2O_2 lost through homogeneous decomposition and anodic oxidation. We find H_2O_2 production increases in the order of $\text{Na}_2\text{SO}_4 < \text{KPi} < \text{K}_2\text{CO}_3 < \text{KHCO}_3$, confirming the promotional effect of

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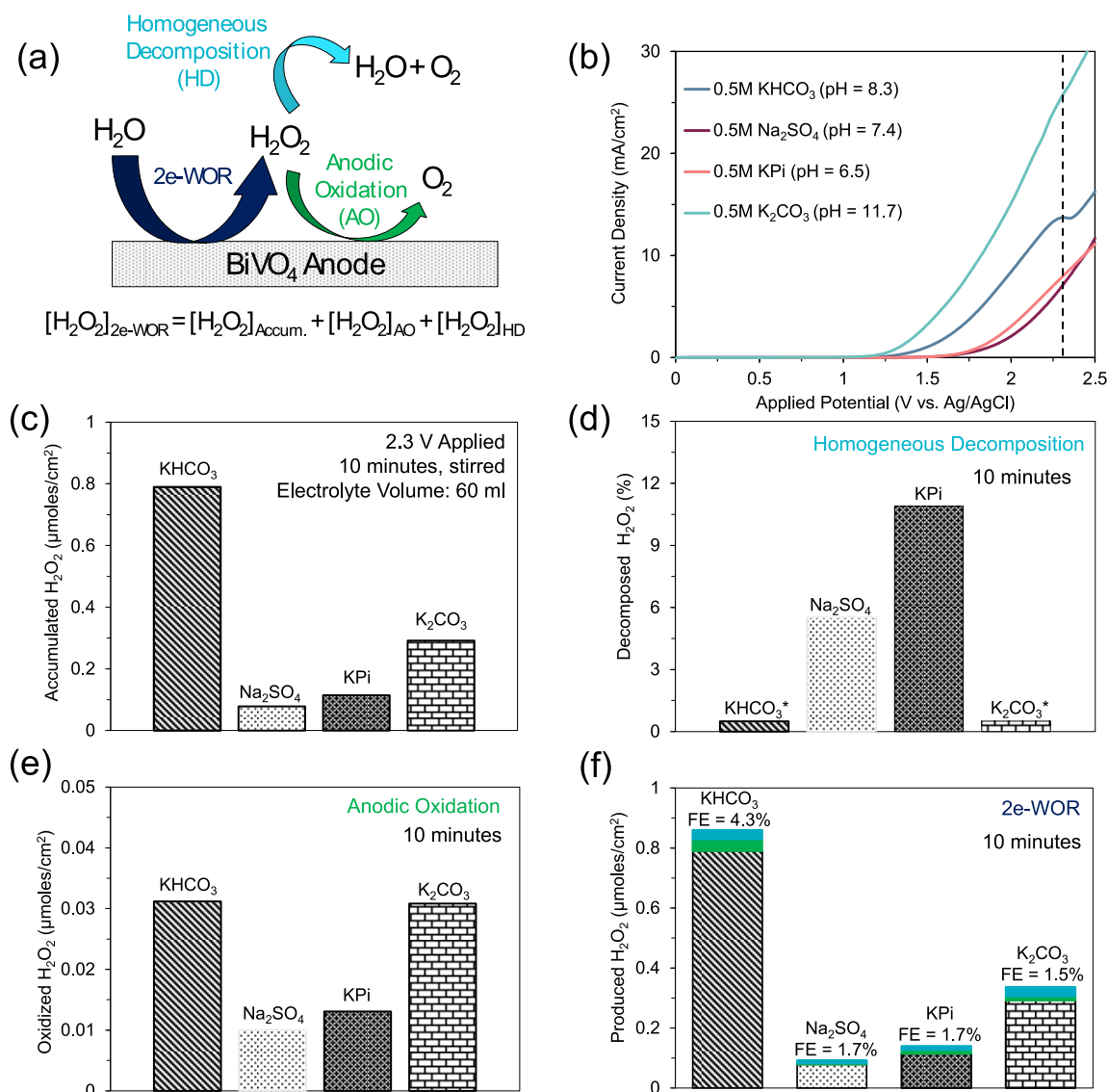


Figure 1. Accounting for production and consumption pathways of H_2O_2 in various 0.5 M aqueous electrolytes. A constant potential of 2.3 V was applied between BiVO_4 samples and a Ag/AgCl reference electrode for 10 min in a 60 mL H-cell under vigorous stirring. All H_2O_2 amounts were determined by UV-vis spectroscopy. (a) Schematic representation of pathways relevant to H_2O_2 during two-electron water oxidation (2e-WOR). (b) Linear sweep voltammograms obtained in each of the four electrolytes at a scan rate of 25 mV/s. The dashed black line indicates the applied potential in subsequent tests. (c) Total H_2O_2 accumulated in the anodic chamber of the H-cell. (d) Decomposition of H_2O_2 due to homogeneous instability. (e) Amount of H_2O_2 oxidized at the anode as determined by the peroxide addition method. (f) Total amount of H_2O_2 produced by 2e-WOR after correcting for losses due to anodic oxidation (green) and homogeneous decomposition (blue) and corresponding Faradaic efficiency (FE) toward H_2O_2 . * H_2O_2 decomposition in KHCO_3 and K_2CO_3 were found to be negligible over time scales of the experiment. See the Supporting Information (Figure S1b) for details.

carbonate-based electrolytes, and that KHCO_3 exhibits selectivity approximately 3-fold higher than that of the other electrolytes. Second, we find that less than 19% of produced H_2O_2 is consumed by homogeneous decomposition and anodic oxidation combined under our experimental conditions (<1 h) in all electrolytes studied. Together, these results suggest that the dominant role of HCO_3^- in 2e-WOR is neither homogeneous nor anodic stabilization of H_2O_2 but rather generation of H_2O_2 . Combining rotating ring disk, voltammetric, and spectroscopic experiments, we demonstrate that oxidation of carbonaceous electrolyte species occurs at Faradaic potentials for 2e-WOR, which we speculate subsequently oxidize water to H_2O_2 . Finally, we show that the partial current density toward H_2O_2 increases linearly with

the concentration of HCO_3^- at 2.5 V vs RHE but that this relationship changes at higher potential. Together, these findings establish that HCO_3^- serves as a redox catalyst in H_2O_2 production at relatively modest potentials but that the roles of HCO_3^- and other carbonate-based species are likely potential-dependent.

To understand the role of electrolytes in H_2O_2 production, the multitude of reactions in which H_2O_2 can be involved under 2e-WOR conditions must be considered. H_2O_2 may be produced by 2e-WOR but can be consumed by two subsequent pathways (Figure 1a). First, the thermodynamic potential for H_2O_2 generation by 2e-WOR (1.76 V vs RHE) is sufficiently positive to oxidize H_2O_2 to O_2 (0.68 V vs RHE)¹⁹ by anodic oxidation (AO). Second, H_2O_2 can homogeneously

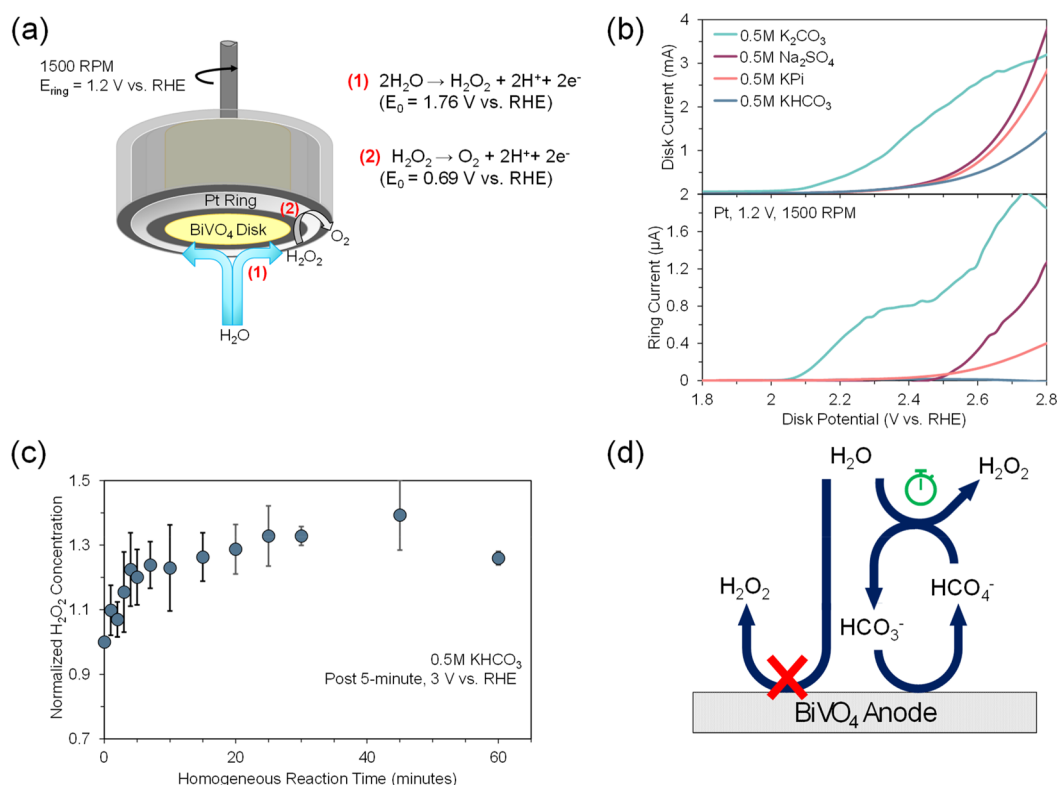


Figure 2. Hydrodynamic and equilibration experiments demonstrating the unique electrochemical oxidation behavior in KHCO_3 . (a) Schematic representation of rotating ring disk electrode experiment and reactions. (b) Disk and ring current during a linear sweep of the disk potential at a scan rate of 10 mV/s. (c) Normalized concentration of H_2O_2 present in a single-compartment electrochemical cell after conclusion of a constant potential test. The measured H_2O_2 concentration is normalized by the concentration of H_2O_2 measured immediately after the conclusion of the constant potential test by colorimetric strips. Error bars indicate sample standard deviation. (d) Schematic representation of the reaction mechanism in which HCO_3^- is electrochemically oxidized, followed by hydrolysis to produce H_2O_2 .

decompose (HD) to H_2O and O_2 in aqueous solutions, especially in the presence of ions that catalyze H_2O_2 decomposition.²⁰ In previous studies, the accumulated amount of H_2O_2 has been used almost universally to characterize the Faradaic efficiency (FE) of $2e^-$ WOR.^{14,17} However, this method accounts only for the net difference between the production of H_2O_2 and its consumption through AO and HD. It is necessary to evaluate the effect of the electrolyte species on each of these pathways to understand the role of bicarbonate in maximizing $2e^-$ WOR efficiency.

We investigate the impact of the electrolyte in $2e^-$ WOR by quantifying the production and consumption of H_2O_2 (reaction fluxes) in four common electrolyte species: sodium sulfate (Na_2SO_4), potassium phosphate buffer (KPi), potassium carbonate (K_2CO_3), and potassium bicarbonate (KHCO_3) all at 0.5 M concentration (for details, see Figure S1 and supplementary note 1 in the Supporting Information). For all tests, we use sol-gel derived bismuth vanadate thin films (BiVO_4 ; thickness, ~ 100 nm; area range, $3\text{--}4$ cm^2) coated on FTO substrates as the anode.¹² Figure 1b shows that the four electrolytes exhibit distinct current densities at the same applied potential. We compare the H_2O_2 reaction fluxes at 2.3 V vs Ag/AgCl at which the current density (>5 mA/cm^2) is large enough for appreciable H_2O_2 accumulation on short time scales in all electrolytes studied. Panels c, d, e and f in Figure 1 show the experimentally determined H_2O_2 fluxes for accumulation, HD, AO, and calculated H_2O_2 production by $2e^-$ WOR after 10 min of reaction, respectively. Figure 1c shows that KHCO_3 yields the highest accumulated H_2O_2

amount of 0.8 $\mu\text{mol}/\text{cm}^2$, while K_2CO_3 is second with 0.3 $\mu\text{mol}/\text{cm}^2$, more than 2.5 times that of KPi and Na_2SO_4 . Though the superiority of K_2CO_3 over other electrolytes is small, Li and co-workers recently reported similar results on H_2O_2 production rates among KHCO_3 , K_2CO_3 , and $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ at 1 M concentrations evaluated at 2.8 V vs RHE, confirming the promotional effect of carbonaceous species.²¹ Though the promotional effect of HCO_3^- was shown, no explicit investigation was made as to the role it plays in H_2O_2 production, consumption, and stabilization. Figure 1d shows that H_2O_2 loss through HD over 10 min is negligible for KHCO_3 and K_2CO_3 but significant for both KPi ($\sim 11\%$) and Na_2SO_4 ($\sim 6\%$). The amount of H_2O_2 consumed by anodic oxidation (Figure 1e) is most substantial in the K_2CO_3 and KHCO_3 electrolytes (~ 0.03 $\mu\text{mol}/\text{cm}^2$), corresponding to the destruction of $\sim 11\%$ and $\sim 4\%$ of the accumulated H_2O_2 , respectively. Note that the magnitude of AO is expected to depend strongly on the electrocatalyst surface. For example, the normalized AO current on our BiVO_4 electrode is estimated to be ~ 11 $\mu\text{A}/\text{cm}^2\cdot\text{mM}$ H_2O_2 , more than an order of magnitude smaller than the AO current on Pt in phosphate buffer at comparable mixing speed (~ 600 $\mu\text{A}/\text{cm}^2\cdot\text{mM}$ H_2O_2).²² The total amount of H_2O_2 produced by $2e^-$ WOR calculated using eq 1 (Figure 1f) decreases in the order of $\text{KHCO}_3 > \text{K}_2\text{CO}_3 > \text{KPi} > \text{Na}_2\text{SO}_4$, which matches the trend using accumulated H_2O_2 (Figure 1c).

$$[\text{H}_2\text{O}_2]_{2e^- \text{ WOR}} = [\text{H}_2\text{O}_2]_{\text{Accum.}} + [\text{H}_2\text{O}_2]_{\text{AO}} + [\text{H}_2\text{O}_2]_{\text{HD}} \quad (1)$$

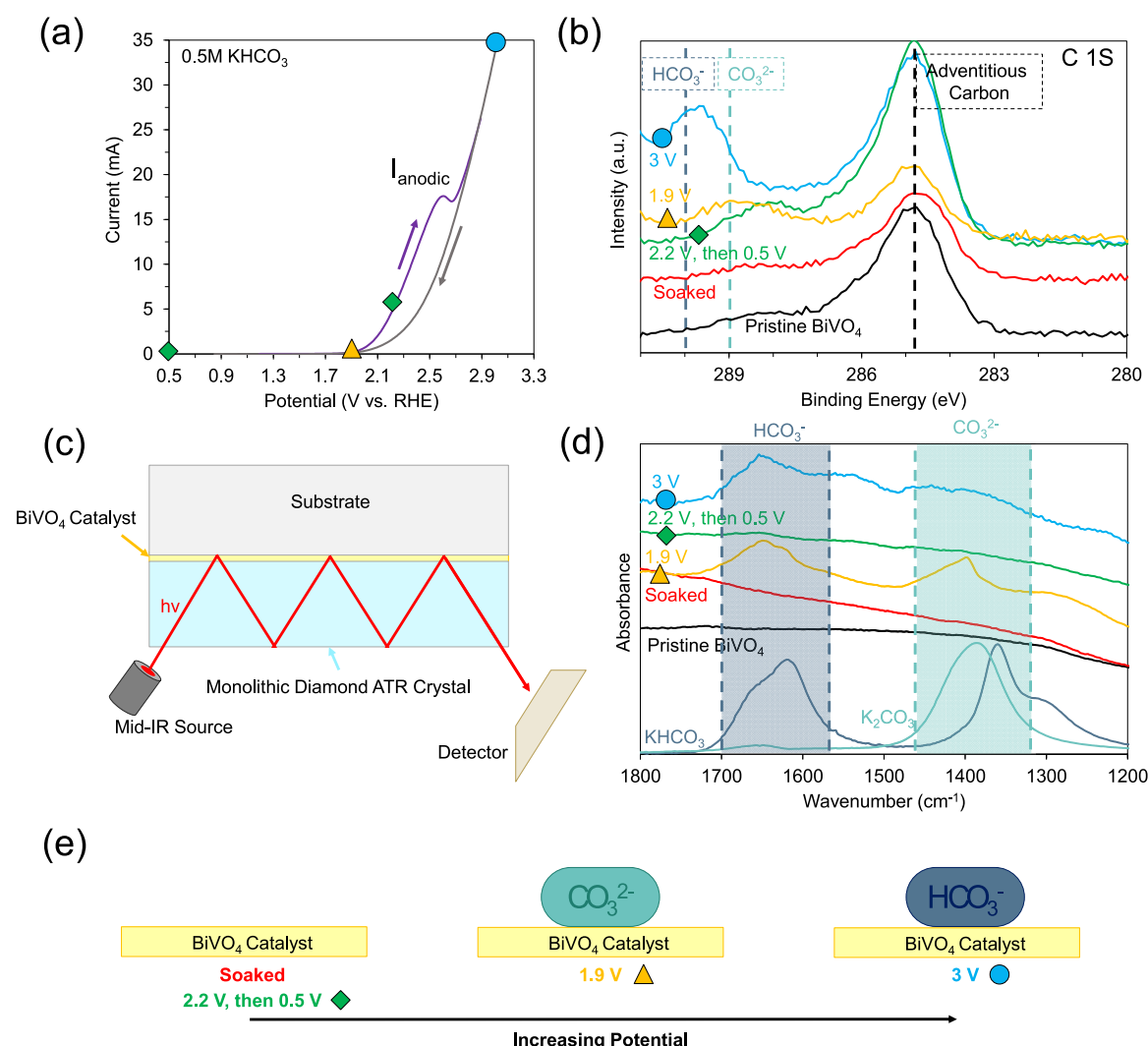


Figure 3. Spectroscopic and electrochemical evidence for oxidation of the electrolyte and its subsequent interaction with the electrode surface. (a) Characteristic cyclic voltammogram obtained at 250 mV/s in 0.5 M KHCO_3 showing a prominent peak feature in the anodic sweep. Arrows indicate sweep direction, and marker shapes and colors correspond to spectroscopic traces in panels b and d indicating potentials applied therein. (b) X-ray photoelectron spectra taken after subjecting the samples to the indicated bias for 10 min in 0.5 M KHCO_3 , followed by cleaning in water. (c) Schematic of ATR-FTIR experimental setup. (d) Fourier transform infrared spectra for the same samples depicted in panel b along with solution-phase spectra of 0.5 M KHCO_3 and K_2CO_3 for reference. (e) Schematic representation of surface-adsorbed species as a function of applied potential.

Accordingly, the use of accumulated H_2O_2 is a reasonable approximation to estimate FE under our experimental conditions, but this approximation underestimates FE significantly (18% (relative) in KPi for 10 min). The FE in KHCO_3 (~4.3%) is nearly 3 times higher than the other three electrolytes (~1.6%), confirming the previously observed superior performance of KHCO_3 (more generally HCO_3^-) and to a lesser extent CO_3^{2-} ,¹⁰ for electrochemical production of H_2O_2 .¹¹ These results demonstrate the importance of considering all relevant reaction fluxes in future $2e^-$ WOR studies. We emphasize that the metrics for H_2O_2 production and consumption found here likely depend on the electrochemical cell setup and test duration (see supplementary note 2 in the [Supporting Information](#) for further discussion).

The above reaction flux analysis reveals the complexity in understanding $2e^-$ WOR performance by measuring accumulated H_2O_2 due to its instability in electrochemical environments. In comparison, H_2O_2 produced by $2e^-$ WOR can be directly quantified by rotating ring disk electrode (RRDE)

measurements. In these experiments, H_2O_2 is produced on the BiVO_4 disk electrode and subsequently oxidized to O_2 on the platinum (Pt) ring electrode held at 1.2 V vs RHE (Figure 2a). Because the RRDE assembly is rotated at 1500 rpm, little time transpires between production and measurement, minimizing the consumption of H_2O_2 by anodic oxidation and homogeneous decomposition. Moreover, at 1.2 V vs RHE, the only substantial reaction at the ring is the oxidation of H_2O_2 to O_2 (Figure S2). Figure 2b shows the disk and ring currents versus disk potential for the four electrolytes, their resulting ratio being proportional to the FE toward H_2O_2 under mass transport limited conditions.^{23,24} Unfortunately, the evolution of O_2 gas at the ring and disk electrodes at higher electric potentials (>2.8 V vs RHE) yields very noisy data, preventing exact FE quantification and direct comparison with accumulation-based data in Figure 1f. Still, the ring current in each electrolyte excluding KHCO_3 has an onset potential similar to that of the disk current, indicating that some of the oxidative current at the disk is attributable to direct $2e^-$ WOR.

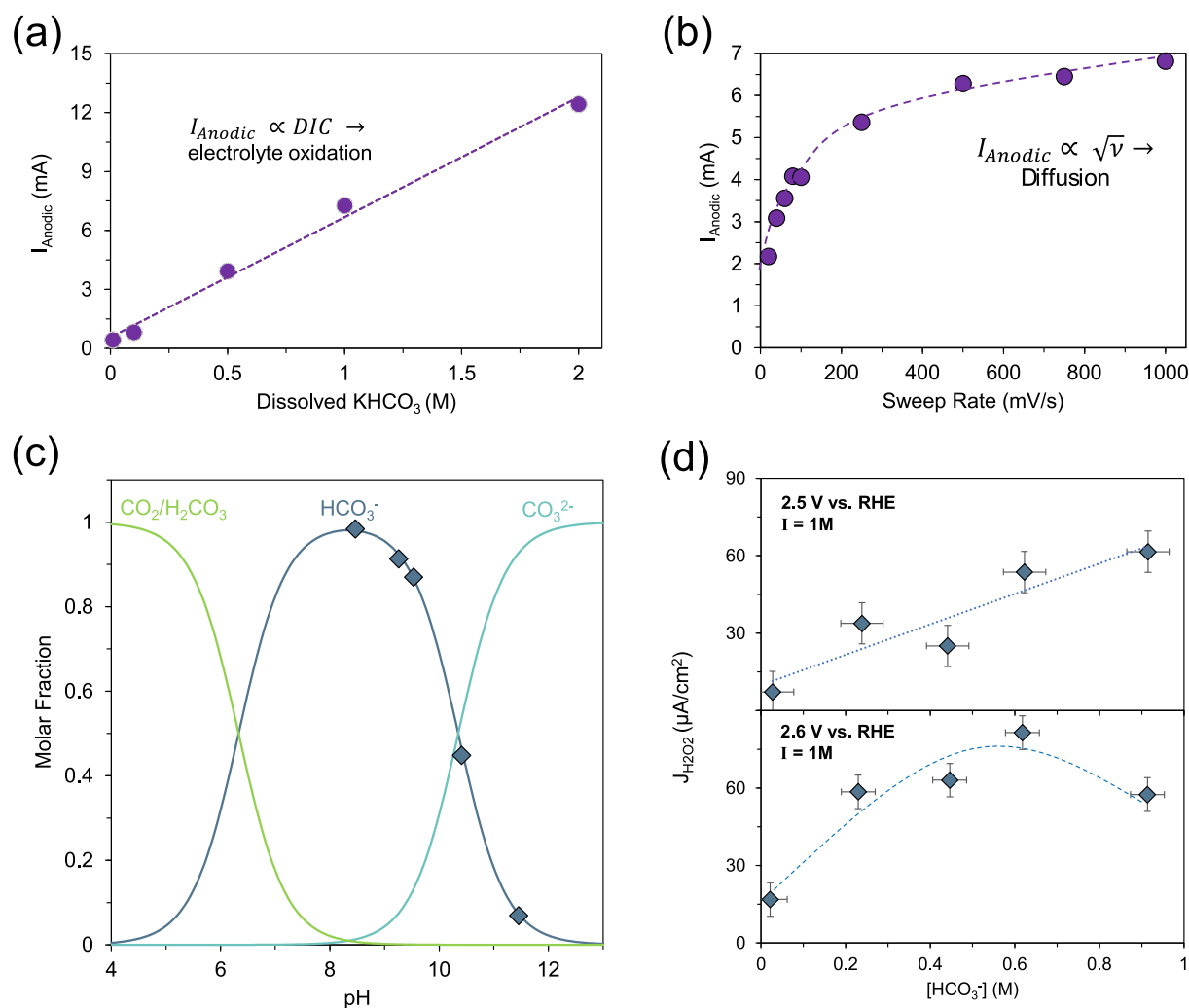


Figure 4. Relation between bulk concentrations of electrolyte species, overall current, and H_2O_2 partial current density. (a) Linear relationship between dissolved KHCO_3 concentration (alternatively, dissolved inorganic carbon, “DIC”) and the anodic peak current, I_{Anodic} , obtained under constant ionic strength conditions ($I = 2 \text{ M}$) with KClO_4 as a supporting electrolyte. (b) Square root dependence of I_{Anodic} on the scan rate indicating a diffusion-limited current. I_{Anodic} was determined by subtracting the cathodic from the anodic current at the peak potential. Dashed lines are guides-to-the-eye, not fits to the data. (c) Equilibrium mole fractions of dissolved inorganic carbon species as a function of pH, known as a Bjerrum plot, calculated using the first and second acid dissociation constants of carbonic acid (3.6 and 10.3, respectively). Diamonds indicate pH/molar fractions tested in panel d. (d) Partial current density toward H_2O_2 as a function of HCO_3^- concentration. The ionic strength was held constant ($I = 1 \text{ M}$), and the indicated bias was applied for 10 min in an H-cell under vigorous stirring. Vertical error bars indicate measurement uncertainty. Horizontal error bars indicate concentration error due to variation in the bulk solution pH. Dashed lines are guides-to-the-eye, not fits to the data.

However, there is no measurable ring current for KHCO_3 even as its disk current rises appreciably. This suggests that a negligible amount of H_2O_2 is directly produced on the BiVO_4 disk in 0.5 M KHCO_3 , seemingly contradicting the enhanced production of H_2O_2 in KHCO_3 shown in Figure 1f. One possible explanation for the discrepancy is that H_2O_2 is not primarily produced by direct $2e^-$ WOR on the BiVO_4 anode in KHCO_3 , but by other reactions which may include oxidation of the electrolyte.^{11,25} In contrast to these results, Zhang and co-workers recently observed a measurable H_2O_2 ring current in 1 M NaHCO_3 stemming from a BiVO_4 disk electrode.²⁶ Given the differing ring electrode material (BiVO_4), electrolyte cation (Na^+), disk potential ($<2.25 \text{ V vs RHE}$), and electrolyte concentration (1 M), substantial differences between their RRDE results and ours are expected. Despite these differences, Zhang’s work and ours yield similar qualitative conclusions about the direct water oxidation pathway: given the ratio of

ring ($\sim 5 \mu\text{A}$) to disk ($\sim 500 \mu\text{A}$) currents observed in their study, direct water oxidation to H_2O_2 on BiVO_4 is a relatively minor pathway in HCO_3^- electrolytes. Further discussion is offered in the Supporting Information (supplementary note 3).

For KHCO_3 electrolytes, we test the possibility of H_2O_2 produced homogeneously via oxidation of the electrolyte by measuring the H_2O_2 concentration as a function of time after applying a potential to the anode. We applied 3 V vs RHE to BiVO_4 for 5 min in a single-compartment electrochemical cell to accumulate a measurable amount of H_2O_2 and then stopped the bias. If H_2O_2 is produced by a homogeneous reaction between the oxidized electrolyte and water, the concentration of H_2O_2 should increase over time, which is indeed revealed by the data (Figure 2c). This anomalous increase in H_2O_2 was also observed during the homogeneous decomposition experiments (Figure S1b). The concentration of H_2O_2 takes $\sim 15\text{--}20 \text{ min}$ to equilibrate, a time scale similar to the previously

reported kinetics for the reaction between HCO_4^- and H_2O to form H_2O_2 ($t_{1/2} \approx 5$ min).²⁷ Because of this minutes-long time scale, the observed near-zero ring current for KHCO_3 in the RRDE experiments is presumably due to insufficient time for the homogeneous following reaction to produce H_2O_2 during the transit from the disk to the ring (Figure 2b). These results support the hypothesis suggested by Sayama¹¹ that HCO_3^- is electrochemically oxidized, followed by hydrolysis to yield H_2O_2 (Figure 2d). We will refer to the oxidized electrolyte species as HCO_4^- , though several attempts to identify the exact species were unsuccessful. Patra et al.²⁸ and Zhang and Oloman²⁵ have provided a more detailed mechanistic description of carbonate and bicarbonate oxidation, which has been adapted and summarized in supplementary note 4 in the Supporting Information.

If HCO_3^- is electrochemically oxidized at the anode, spectroscopic signatures of the species may be visible when studying the anode surface. We used electroanalytical and spectroscopic experiments to investigate surface-bound carbonaceous species resulting from the KHCO_3 electrolyte. Figure 3a shows a typical cyclic voltammogram (CV) of the BiVO_4 anode in 0.5 M KHCO_3 . One observable feature, an anodic peak (the current at which is denoted I_{anodic}), motivated us to use X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared spectroscopy (FTIR) to determine the surface-bound species on BiVO_4 at different applied potentials relative to the feature. We characterized five BiVO_4 samples: pristine, submerged in KHCO_3 without applying potential (soaked), subjected to 1.9 V, subjected to 3.0 V, and one sample first subjected to an oxidizing potential (2.2 V) and then a more cathodic potential (0.5 V). All indicated potentials are voltages versus a reversible hydrogen electrode (RHE) and were held for 10 min. The four BiVO_4 samples that contacted the electrolyte were thoroughly rinsed and sonicated in deionized water for 1 min followed by drying with air to remove residual electrolyte. The carbon 1s region was probed using XPS to study surface-bound carbonaceous species because of its surface sensitivity. Here, the peak at ~ 290 eV indicates HCO_3^- and ~ 289 eV indicates CO_3^{2-} ; 284.8 eV indicates the adventitious carbon used for calibrating the data (Figure 3b). For FTIR measurements samples were placed on a diamond ATR crystal with the BiVO_4 catalyst facing the crystal to achieve greater surface sensitivity through multiple internal reflections (Figure 3c). KHCO_3 and K_2CO_3 solutions were measured as references to identify the wavelength range for HCO_3^- ($1550\text{--}1700\text{ cm}^{-1}$) and CO_3^{2-} ($1320\text{--}1450\text{ cm}^{-1}$) derived species.³⁰

The XPS and FTIR spectra (Figure 3b,d) reveal similar information. First, neither pristine nor soaked BiVO_4 samples exhibit any signatures of HCO_3^- and CO_3^{2-} . Second, the BiVO_4 samples that have been exposed to high (1.9 and 3.0 V) potential show the presence of CO_3^{2-} and HCO_3^- , respectively. The 1.9 V sample more prominently shows surface-bound CO_3^{2-} , while 3.0 V shows surface-bound HCO_3^- based on the XPS spectra. Moreover, the 3.0 V sample shows an FTIR absorption peak near 1650 cm^{-1} , which matches relatively well with the suggested absorption of HCO_4^- at wavenumbers of 1630 or 1685 cm^{-1} .³¹ Interestingly, the “2.2 V then 0.5 V” BiVO_4 sample shows no signs of surface-bound HCO_3^- or CO_3^{2-} . Collectively, these results indicate that CO_3^{2-} and/or HCO_3^- are present on the BiVO_4 anode surface at potentials necessary to generate H_2O_2 but may not be present at lower bias or under potential cycling. Moreover,

HCO_3^- seems to predominate at higher anodic potential, whereas modest Faradaic bias favors CO_3^{2-} (Figure 3e). The presence of CO_3^{2-} on the surface despite the near-neutral pH in the bulk electrolyte (~ 8) may be explained by the dramatically different surface and bulk equilibria observed in bicarbonate systems, especially at elevated potentials.³² In conjunction with the greater production of H_2O_2 observed in the bicarbonate-based electrolytes, it is apparent that these surface-bound species are involved in the production of H_2O_2 , though further spectroscopic studies are needed to fully understand their mechanistic role. In particular, Raman spectroscopy has recently shown potential as a technique for observing HCO_3^- and its derivatives on electrochemical surfaces.³³

Given their presence on the electrode surface during $2e^-$ WOR and their hypothesized oxidation, the concentration of HCO_3^- and CO_3^{2-} should impact the anodic current. To study this, we varied the concentration of dissolved KHCO_3 in the electrolyte while keeping the ionic strength constant at 2 M using KClO_4 as a coelectrolyte. The previously mentioned I_{anodic} feature shows a linear dependence on dissolved KHCO_3 (Figure 4a). The observed linear dependence of I_{anodic} holds while varying the ionic strength (10 mM to 2 M) as well (Figure S3a). Moreover, when the KHCO_3 concentration was held constant at 0.5 M, I_{anodic} scales with the square root of scan rate (ν) at modest scan rates, indicating a diffusion-limited process per the Randles–Sevcik equation (Figure 4b).³⁴ Stirring the electrolyte increased the current near the I_{anodic} feature, further confirming transport-limited electrolyte oxidation (Figure S3b). These results suggest that anodic oxidation of HCO_3^- to HCO_4^- (1.8 V vs RHE) occurs on BiVO_4 .^{27,35} Nonetheless, we cannot rule out the possibility of anodic oxidation of CO_3^{2-} to carbonate radical and/or $\text{C}_2\text{O}_6^{2-}$ (1.57 V vs RHE)²⁵ as HCO_3^- and CO_3^{2-} always coexist in solution because of equilibrium.²⁸ Notably, a similar I_{anodic} feature has been observed previously on Fe-derived surfaces in acidified 0.5 M Na_2CO_3 (pH 9.1),³⁶ and carbonate oxidation in aqueous Na_2CO_3 on Pt has previously been demonstrated.²⁵ Though the oxidized species is uncertain, electrochemical oxidation of bicarbonate-based electrolytes clearly occurs on many surfaces and likely contributes mechanistically to $2e^-$ WOR. Previous reports in molecular catalysis have hypothesized a similar system for H_2O_2 production from H_2O and HCO_3^- .³⁷ Briefly, HCO_4^- is formed as a bound intermediate on an aluminum porphyrin molecular catalyst (AlTMPyP) and is subsequently liberated by reaction with H_2O to form HCO_3^- and H_2O_2 . Interestingly, the authors find that CO_3^{2-} can undergo a similar mechanism.

As both oxidized bicarbonate (i.e., HCO_4^-) and carbonate (i.e., $\text{C}_2\text{O}_6^{2-}$) can reportedly react with H_2O to produce H_2O_2 ,^{16,25} we measured the current density toward H_2O_2 ($J_{\text{H}_2\text{O}_2}$, a metric of the electrochemical production rate) as a function of HCO_3^- and CO_3^{2-} concentrations as determined by the Bjerrum plot in Figure 4c. We fixed the ionic strength at 1 M and varied the concentration of HCO_3^- by adding different ratios of K_2CO_3 and KHCO_3 powder to the solution. The electrochemically active surface area was determined by cyclic voltammetry and used for the normalization of the current (Figure S4a). At 2.5 V vs RHE (~ 740 mV overpotential for $2e^-$ WOR), $J_{\text{H}_2\text{O}_2}$ increases linearly with $[\text{HCO}_3^-]$ within error, indicating that HCO_3^- is the reactant primarily responsible for H_2O_2 production (Figure 4d). At 2.6

V vs RHE, which roughly corresponds with I_{anodic} in these experiments, $J_{\text{H}_2\text{O}_2}$ first increases and then decreases or plateaus with $[\text{HCO}_3^-]$. Recent work by Mavrikis et al. demonstrated that a 1:1 mixture of KHCO_3 and K_2CO_3 outperforms pure KHCO_3 for H_2O_2 production at potentials above 2.6 V vs RHE, confirming that the presence of CO_3^{2-} can be beneficial for H_2O_2 production.³⁸ This suggests that, as the electrolyte oxidation reaction becomes diffusion limited at higher bias, other competing reactions become appreciable at the anode as well.³⁶ To clarify these results, it is important to evaluate the role of the pH. As we vary the concentration of HCO_3^- , the pH value varies from ~ 8.4 to ~ 11.5 . To isolate the impact of pH, we also measured $J_{\text{H}_2\text{O}_2}$ at constant $[\text{HCO}_3^-]$ but differing pH values, demonstrating that $J_{\text{H}_2\text{O}_2}$ is agnostic to pH within error (Figure S4b). Finally, we evaluated the stability of H_2O_2 in 0.5 M KHCO_3 at various pH ($8.0 \leq \text{pH} \leq 12$), demonstrating that pH has a negligible impact over the time scale of our experiments (Figure S4c). Still, experimental results in Figures 2c, S1b, and S4c suggest that H_2O_2 is mildly unstable in KHCO_3 solutions over longer time scales (>1 h), which may be addressed in future work via the use of stabilizers or sequestration. Together, these results show that the pH value has a negligible effect on H_2O_2 production within our experimental range and further confirm the dominant role that HCO_3^- plays in 2e^- WOR at modest bias.

Our experimental results demonstrate that HCO_3^- acts as a catalyst in H_2O_2 production through 2e^- WOR processes. By independently evaluating the role that electrolytes play in H_2O_2 generation and consumption pathways, we attribute the enhanced H_2O_2 production observed in KHCO_3 to its role in the production mechanism. Principally, our electrochemical and spectroscopic experiments demonstrate that oxidation of carbonaceous electrolyte species occurs at Faradaic potentials relevant for 2e^- WOR, and these species subsequently oxidize water to H_2O_2 . In summary, $\text{HCO}_3^-/\text{HCO}_4^-$ serves as a redox catalyst for H_2O_2 production in KHCO_3 electrolytes, which leads to a much higher production rate of H_2O_2 than other tested electrolytes (i.e., Na_2SO_4 , KPi, and K_2CO_3). Given the potential dependence of the relationship between $J_{\text{H}_2\text{O}_2}$ and HCO_3^- and the spectroscopic results, the role of CO_3^{2-} in H_2O_2 production remains uncertain.²⁸ Our results suggest complex relationships between the bulk equilibrium and surface-mediating roles HCO_3^- and CO_3^{2-} play in 2e^- WOR which have been observed in other studies.^{28,32} Furthermore, this work demonstrates the importance of evaluating reaction fluxes in 2e^- WOR studies and the potential to utilize electrolyte oxidation at the anode to improve H_2O_2 production rates. *Operando* spectroscopic studies of single-crystalline electrode surfaces, computational chemistry calculations, and detailed electrokinetic analyses are urgently desired to further specify the roles of carbonaceous anions, especially CO_3^{2-} , in water oxidation.

EXPERIMENTAL METHODS

All reagents used in this study were obtained from Sigma-Aldrich and used as received, unless otherwise noted.

Electrochemical H_2O_2 Production Accounting. Production of H_2O_2 was measured under chronoamperometric conditions in a glass H-cell (Pine Research). The anodic and cathodic chambers were separated by a porous frit to prevent cathodic effects from impacting H_2O_2 production and

consumption. All glassware was cleaned in dilute piranha solution before use. Carbon paper was used as a counter electrode, and Ag/AgCl as a reference. All electrochemical experiments were carried out using a Gamry Interface 1000 or 1010 potentiostat. For the accumulation-based H_2O_2 experiments detailed in Figure 1, studies were conducted at 2.3 V applied electric potential sustained for 10 min under constant vigorous stirring of the anodic chamber of an H-cell to prevent concentration polarization.

Electrode Preparation. For accumulation experiments, monoclinic scheelite bismuth vanadate (BiVO_4) was synthesized on fluorine-doped tin oxide (FTO) substrates as previously described.¹² Briefly, bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $>98\%$) and vanadyl acetylacetonate ($\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$, $>98\%$) were dissolved in a solvent mixture of 2-methoxyethanol, glacial acetic acid, and acetylacetone. The resulting precursor solution was then spin-coated on the FTO substrate, followed by annealing in air at 500°C .

H_2O_2 Measurement Procedure. For all H_2O_2 quantifications excluding those in Figure 2c (which used Quantofix colorimetric strips for H_2O_2 detection), the previously established cobalt/carbonate UV-vis procedure was utilized.⁴³ Briefly, an aliquot of the electrochemically produced H_2O_2 (0.5–2.0 mL) was added to a 2 M solution of KHCO_3 and CoSO_4 . The solution was allowed to react for 30 min, after which the absorbance at 260 nm was measured. Calibrations were obtained independently in each electrolyte and were recreated each day. All spectra were collected using an Agilent Cary 6000i spectrophotometer at 1 nm resolution and a scan rate of 2 nm/s and baseline corrected using the background matrix containing no H_2O_2 .

Rotating Ring Disk Electrode Experiments. Rotating ring disk electrode (RRDE) experiments were carried out using a Pine Research setup with the rotation rate controlled by a Gamry RDE710 modulator. All experiments were carried out in a glass heart cell using an E6R1PK tip assembly with a platinum ring electrode and a glassy carbon disk insert.

For the preparation of the BiVO_4 disk electrode in the RRDE experiments, a novel precipitation procedure was used. The same precursor as was used for the spin-coating method was first prepared. The precursor solution was then placed in an oil bath at 100°C and was magnetically stirred, resulting in a color change of the precursor solution to transparent brown, followed by an opaque reddish color after about 10 min. A 250 μL portion of commercial hydrogen peroxide solution was then added (H_2O_2 , 30 wt %, Fisher Chemical), followed by 50 mL of deionized water. The solution was allowed to settle, and the supernatant liquid was decanted. The successive additions of H_2O_2 and water were repeated, ultimately resulting in a bright yellow precipitate indicative of BiVO_4 powder. The supernatant was again decanted, after which the powder was collected by filtration, followed by drying on a hot plate at 100°C for 3 h to remove any residual solvent. Finally, the dry powder was annealed in a box furnace at 500°C to allow for crystallization, and the resulting monoclinic scheelite phase was confirmed by X-ray diffraction.

The BiVO_4 powder was then prepared in a catalyst ink by adding 2 mg of the powder to 2 mL of isopropyl alcohol, 600 μL of deionized water, and 320 μL of Nafion (Fuel Cell Earth). The catalyst ink was sonicated for 30 min to ensure homogeneous dispersion and was subsequently drop cast on the glassy carbon insert, followed by drying in a box furnace at 160°C for 10 min.

Spectroscopic Experiments. X-ray photoelectron spectra were collected using a PHI VersaProbe 3. Radiation was supplied with an Al ($K\alpha$) source (1486 eV) at a vacuum pressure of $\sim 1.2 \times 10^{-7}$ Pa and a spot size of $1400 \mu\text{m} \times 100 \mu\text{m}$ under the “high power setting” to improve the signal-to-noise ratio.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was conducted using a Nicolet iS-50 FTIR spectrometer and a monolithic diamond ATR element. Results, as shown, are the average of 64 scans which are background subtracted using air as a standard.

HCO₃[−] Impact on $J_{\text{H}_2\text{O}_2}$. Experiments relating the concentration of HCO₃[−] to the current density toward H₂O₂ were conducted chronoamperometrically at the indicated electric potential in an electrochemical H-cell with a porous glass frit separating the anodic and cathodic chambers. Notably, we elected to perform these experiments under the constant overpotential condition on an RHE scale. The electrolyte was vigorously stirred using a magnetic stir bar. The pH was measured using a Mettler Toledo FiveEasy plus probe. Because of the observed increase of the H₂O₂ concentration over time, H₂O₂ was measured using the aforementioned UV–vis procedure after allowing for 15 min of equilibration, post chronoamperometry. The electrochemically active surface area used for current density normalization was found using cyclic voltammetry in a non-Faradaic region of the voltammogram and varying the sweep rate from 250 to 1000 mV/s.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenergylett.1c01264>.

Detailed experimental schematics, procedures for quantifying anodic oxidation of H₂O₂, rotating ring disk control experiments, supplementary voltametric evidence for electrolyte oxidation, electrochemically active surface area quantification, impact of pH on H₂O₂ stability, detailed mechanistic description of electrolyte oxidation leading to H₂O₂ production, and supplementary notes which provide further context for experimental findings (PDF)

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Author Contributions

T.M.G. and X.L.Z. conceived of the overall study and the design of experiments. T.M.G. conducted all experiments excluding XPS spectra, which were obtained by L.V. T.M.G. and X.L.Z. wrote the manuscript.

Notes

The authors declare no competing financial interest.

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