

Interfacial Contributions of H₂O₂ Decomposition-Induced Reaction Current on Mesoporous Pt/TiO₂ Systems

*Nathan J. Ray, Vladislav V. Styrov[†], and Eduard G. Karpov**

Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, Illinois, 60607, USA

[†]Institute of Nanotechnology and Physical Engineering, 71100 Berdyansk, Ukraine

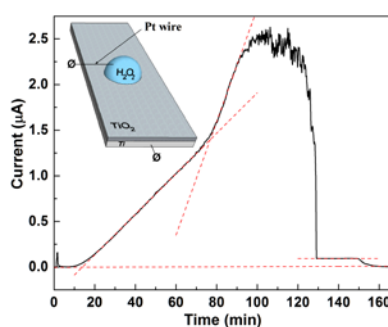
AUTHOR INFORMATION

Corresponding Author

*E-mail: ekarpov@uic.edu

ABSTRACT We report on conversion of energy released due to chemical reactions into current for the decomposition of aqueous hydrogen peroxide solution on single phases Pt and TiO₂, in addition to Pt and TiO₂ simultaneously. We observe that H₂O₂ decomposition-induced current on TiO₂ drastically overshadows the current generated by H₂O₂ decomposition on Pt. Photo-effects avoided, H₂O₂ decomposition was found to yield a conversion efficiency of 10⁻³ electrons generated per H₂O₂ molecule. Further understanding of chemical reaction-induced current shows promise as a metric with which the surface reaction may be monitored and could be greatly extended into the field of analytical chemistry.

TOC GRAPHICS



KEYWORDS Mesoporous titania, plasma electrolytic oxidation, reaction current, hydrogen peroxide decomposition

Energy transfer in the form of excessive surface released energy originating from chemical reactions into an electrical signal has been a steadily growing field, with much emphasis recently placed on gas phase surface reaction-initiated generation of electron-hole pairs in heterojunctions with Schottky barriers.[1–7] Other proposed mechanisms include the interaction of gas phase reaction product H_2O with surface oxygen vacancies[8] and proton spillover at catalytic metal/oxide interfaces.[9] Regardless of the underlying mechanism, gas-phase chemical reactions on the surface have been shown to generate detectable, and in many cases significant, electric current as the heterostructures function as electrical signal transducers. Liquid-phase reactions, however, stand to be much more efficient from a catalysis viewpoint due to the marked increase in medium density.

While the decomposition of hydrogen peroxide in aqueous solution is well understood, $H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$, the reactivity of H_2O_2 solutions with metal and metal oxide systems is far less straightforward. The decomposition of H_2O_2 solutions has ramifications in the fields of catalysis[10–14], hydrogen production and energy storage systems[15–17], geochemistry[18–20], medicinal science[21–23], and many others; for this reason a full comprehension of the decomposition process is decidedly important. More recently work has been reported for the generation and detection of hot electrons through a liquid-phase decomposition of aqueous H_2O_2 solution at the interface of catalytic metals such as Ag, Pt, and Pd.[24,25]

Here we report on the generation of surface chemical reaction-induced electrical signal as an aqueous hydrogen peroxide solution experiences decomposition on (1) Pt-phase catalyst alone, (2) Pt phase catalyst simultaneously with TiO_2 phase, and (3) TiO_2 phase alone. We observe a combination of equilibrium and nonequilibrium processes at the $H_2O_2/Pt/TiO_2$ interface, but in this letter we also report on H_2O_2 decomposition-induced reaction current at the liquid- TiO_2 interface.

Electrical power is produced well over an hour, thus giving a novel analytical approach to detect and monitor H_2O_2 decomposition.

TiO_2 films with mesoporous morphology were grown anodically through a plasma electrolytic oxidation (PEO) process reported in detail elsewhere.[9,26–28] An aqueous electrolyte of 3M H_2SO_4 was used in the galvanostatic oxidation of $36 \times 12 \times 0.5 \text{ mm}^3$ strips of 0.989 pure titanium metal. Fastened parallel to a graphite cathode and suspended in the electrolyte, the titanium strip functioned as the anode of this electrochemical cell as a current density of $93.2 \text{ mA} \cdot \text{cm}^{-2}$ was applied. After the first 3 minutes the potential difference had reached a value of $\sim 95 \text{ V}$; at this time micro-arc discharges became visible along the surface of the Ti anode. These discharges lead to a self-assembled mesoporous morphology with pore penetration depths into the TiO_2 film on the order of several micrometers. The micro discharges are volatile and chaotic in nature, the result of local regions of high intensity electric field. However, the porosity is homogenous when viewed on a larger scale with a fairly uniform pore density.[26,28] The voltage reached a stable value of 150 V after 15 minutes, and approached $155 \pm 2 \text{ V}$ in the following 5 minutes. After 20 minutes the oxidation process was halted abruptly, resulting in a mesoporous TiO_2 film of thickness $10 - 11 \text{ }\mu\text{m}$ with a ratio of rutile TiO_2 to anatase TiO_2 of 11:1.[9] Further characteristics of films grown via this synthesis method have been studied systematically in the past.[9,26]

A metal-semiconductor heterojunction was then fabricated through the deposition of a Pt layer onto the TiO_2 film by method of wide-angle physical vapor deposition (PVD) sputtering at a constant rate of $0.02 \text{ nm} \cdot \text{s}^{-1}$. Due to the porous framework of the underlying substrate, the deposited Pt layer creates a mesh-like nanogranular topography. Figure 1 displays FESEM images of the TiO_2 substrate both before Pt deposition (A and B), as well as after the Pt nanomesh had been

deposited (C and D). Comparison of Figure 1 (A – B) to (C – D) shows that the porous structure remains unchanged following deposition; the result is an electrically continuous Pt nanomesh. Monitored by an Inficon quartz microbalance, the source shutter was closed to halt the deposition process when the thickness of the Pt layer reached 15 nm. The final stage of sample fabrication consists of using SEM grade Ag paste to attach a 0.5 mm diameter Ag wire to the end of the Pt mesh in an Ohmic contact, see Figure 2. The current-voltage characteristics of this Schottky barrier system have been studied systematically in the past, including, but not limited to, the I-V curves under different gas environments.[9]

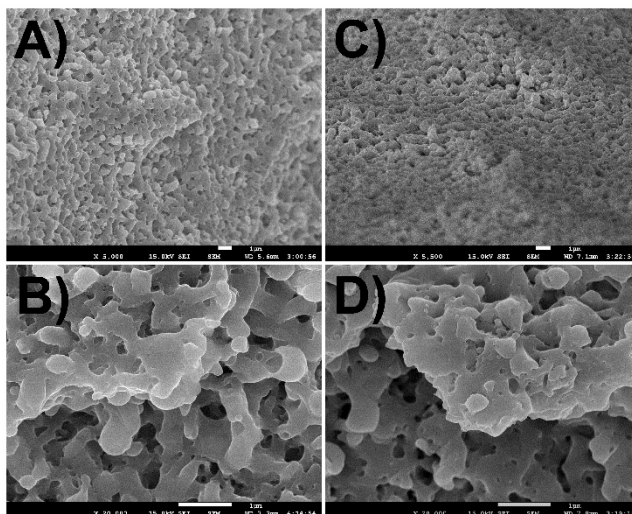


Figure 1. FESEM images of TiO₂ before Pt deposition, (A and B), and after Pt deposition (C and D).

For all reaction current measurements to be discussed, the electrical terminals during data acquisition were the Pt phase and the underlying Ti substrate. The current collected from the surface reaction was directed through a 1 k Ω resistor with a data logging device connected in parallel. After the sample was connected to this external circuit under atmospheric conditions, 60.0 μ L of medical-grade 3% aqueous hydrogen peroxide solution was added to the surface. As

depicted in Figure 2, three conditions were investigated: (1) hydrogen peroxide completely on the Pt nanomesh, (2) hydrogen peroxide in contact with both the Pt phase (52%) and the TiO₂ phase (48%), and (3) hydrogen peroxide completely on the TiO₂ surface. The surface area exposed to the H₂O₂ solution droplet was closely monitored to ensure the wet surface area of the sample was not changing. Analysis of the H₂O₂ solution before and during the experiments revealed that in case (2), the H₂O₂ droplet covered 31.4 mm² of the Pt surface and 28.5 mm² of the TiO₂ surface. For case (3), the TiO₂ area in contact with H₂O₂ solution was 40.6 mm². Due to the fact that only 60 µL solution was being used, in all cases the droplet dimensions remained stable prior to the onset of evaporation.

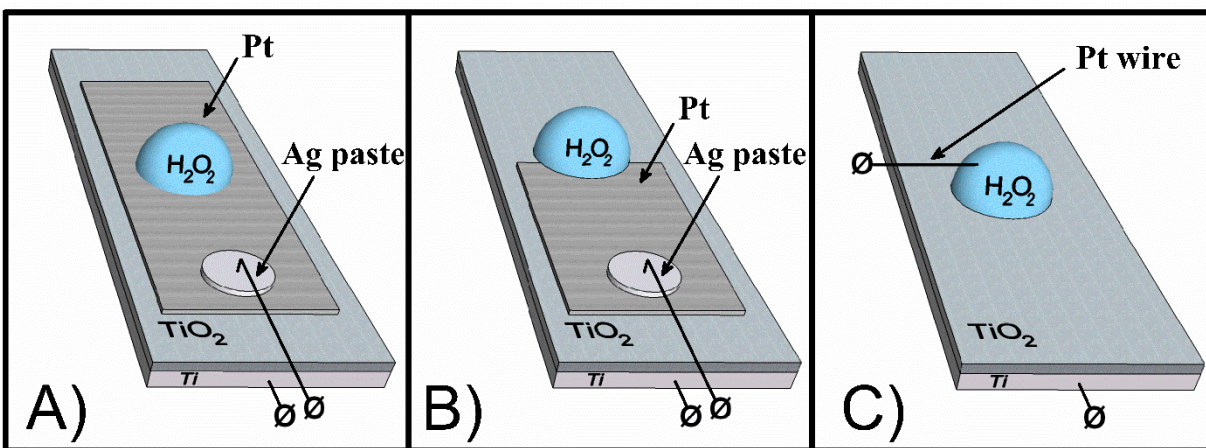


Figure 2. Sample geometry with three conditions: A) H₂O₂ on Pt only, B) H₂O₂ on Pt and TiO₂, and C) H₂O₂ on TiO₂ only. In A) and B) the +V terminal is on the Pt phase, while in C) the +V terminal is the Pt wire suspended above the TiO₂ surface.

In cases 1 and 2, see Figure 2 (A) and (B), the data acquisition device (+) V terminal was connected to the Pt layer. In case 3, see Figure 2 (C), the (+) V terminal was connected to a Pt wire suspended above the TiO₂ surface. In this configuration the Pt wire was positioned within the H₂O₂ droplet at a distance of 1 mm above the TiO₂, with the conductance of the hydrogen peroxide

solution completing the circuit between the wet TiO_2 surface and the Pt wire while the wire is immersed in the solution. In all three cases, a resistive temperature sensor (Omega F2020-100) was positioned in the middle of the H_2O_2 droplet. The sensor was supported by its connection wires only to avoid the use of adhesive, and it was also suspended 1 mm above the surface to avoid detracting from the H_2O_2 /solid phase interface.

In order to avoid photo-contributions, all reaction measurements were conducted in a dark room. As mentioned previously, a constant volume of 60.0 μL H_2O_2 solution was applied during all experiments. The temperature and current data for the three H_2O_2 placement cases are shown in Figure 3, with panels (A), (B), and (C) corresponding to H_2O_2 on Pt nanomesh, H_2O_2 on Pt and TiO_2 , and H_2O_2 on TiO_2 only, respectively. Recalling that the (+) V terminal is on the Pt phase in all three cases, a positively biased current indicates that electrons are traversing the external circuit from the Ti substrate to the Pt phase. Focusing first on the temperature trends, it is seen that in all cases the temperature drops an average of 2.6 $^\circ\text{C}$ upon admission of H_2O_2 solution. Further investigation, however, revealed an identical temperature drop was observed when adding pure deionized water to the surfaces, indicating the decrease in temperature is attributed to the endothermic reaction of evaporation.

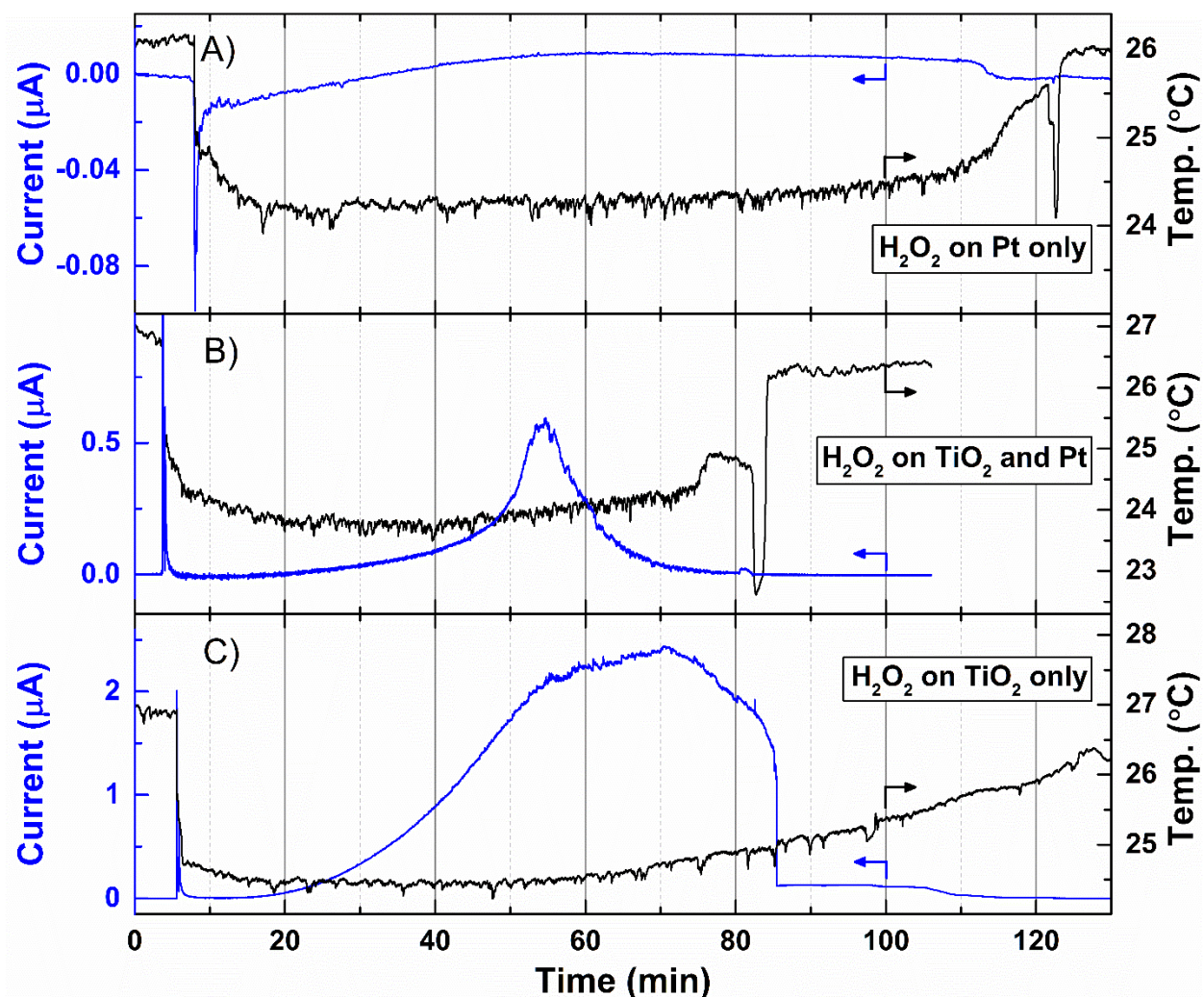


Figure 3. Liquid-phase H_2O_2 reaction current. Panel (A) corresponds to H_2O_2 on Pt phase only, (B) H_2O_2 on Pt and TiO_2 , and (C) H_2O_2 on TiO_2 only. The arrows indicate which axis the data is associated with.

The first scenario to be discussed is the addition of H_2O_2 to the Pt nanomesh only; as seen in Figure 3 (A). The temperature decrease when H_2O_2 is added at time 8 min, as previously noted, is attributed to evaporation of the H_2O_2 solution from the surface. It is seen that from time $t = 20$ min until $t = 80$ min the temperature remains fairly constant, indicating the H_2O_2 catalytic decomposition on the Pt interface is happening at a constant rate. The slight temperature increase is due to the exothermicity of H_2O_2 decomposition. One peculiarity in the temperature plot emerges

at time $t = 122$ min where it is seen that the temperature drops sharply, followed by a rapid increase. Visual inspection at the time leading up to that point revealed that the H_2O_2 solution level was evaporating below the temperature sensor, and as a result H_2O_2 ‘necking’ began as attractive forces continued to draw the liquid phase toward the temperature sensor. The temperature drop at time 122 min was a result of rapid surface evaporation as the solution lost contact with the temperature sensor; likewise, the slight current irregularity at that time was a consequence of the available H_2O_2 solution volume increasing slightly as the necking failed.

The current generated by the addition to H_2O_2 to the Pt, on the other hand, experiences a sharp increase (negative in polarity, $\Delta t \approx 15$ s from H_2O_2 addition to peak minimum) when H_2O_2 is added and a decay quickly ensues. Noting that the underlying TiO_2 is an n -type semiconductor, the initial negative current is thermoelectric current as negative charge carriers migrate from the TiO_2 that is thermally equilibrated at room temperature to the TiO_2/Pt interface that is ~ 2 °C cooler. The current then begins to decrease in magnitude, reverses polarity, and asymptotically approaches +9 nA, consistent with findings reported elsewhere[29]; this transition is indicative of competing mechanisms at the interface. The positively-biased current cannot be thermal current due to its polarity, but rather it is due to a combination of equilibrium and nonequilibrium transport processes. Given the mesoporous morphology, there are two contributions to this positively-biased current: 1) H_2O_2 decomposition at the $\text{H}_2\text{O}_2/\text{TiO}_2$ interface within the porous structure, and 2) H_2O_2 decomposition-initiated ballistic transport of hot electrons through the surface Pt mesh and across the Pt/ TiO_2 Schottky barrier analogous to the mechanism reported elsewhere.[24,25] The component generated at the $\text{TiO}_2/\text{H}_2\text{O}_2$ interface is limited by the available oxide surface area within the pores, and is thus restricted by the saturation limit. In agreement with Nedrygailov et al.[25], we find the current induced by H_2O_2 on Pt is stable and longstanding, continuing 50 min

after obtaining its maximum value. At time 112 min the current decreases quickly, coupled with an increase in the temperature, as the last remaining H_2O_2 solution evaporates away. The formation of gas bubbles on the Pt nanomesh serves to confirm the decomposition of H_2O_2 .

The next condition investigated was the presence of hydrogen peroxide on both Pt and TiO_2 , illustrated schematically in Figure 2 (B) with the data displayed in Figure 3 (B). The temperature plot exhibits similar characteristics to the case of H_2O_2 on Pt, with an identical H_2O_2 necking event at time $t = 83$ min. Of more interest, however, are the reaction current kinetics as hydrogen peroxide was allowed to interact with both Pt and TiO_2 . An initial spike in current is present as H_2O_2 is added, followed by a thermally-induced decay shortly thereafter. Around the 15 min point, however, current begins to increase in a quasi-exponential form, obtaining the maximum value of $0.6 \mu\text{A}$ at time $t = 55$ min. This current cannot be attributed to thermoelectric current for the following reasons: 1) it has opposite polarity for an n -type semiconductor with a cool surface relative to the bulk, and 2) it is of the wrong order of magnitude. It was visually observed that the H_2O_2 solution on the TiO_2 phase began diminishing rapidly after 55 min, leading to the current decay seen in Figure 3 (B). The H_2O_2 solution on the Pt phase disappeared at a slower rate until time 80 min, after which all solution had evaporated and current returned to the zero value.

In the case of H_2O_2 on TiO_2 only, Figure 3 (C), the current increases exponentially, reaching a maximum of $2.4 \mu\text{A}$ at time 70 min; gas bubble formation was observed on the Pt wire throughout the process. Recalling that in this scenario a Pt wire was suspended inside the H_2O_2 bubble as the second electrode, see Figure 2 (C), the plateauing of the current starting around time 50 min was observed simultaneously with the H_2O_2 level evaporating below the Pt wire. As the solution level fell, surface tension around the wire caused the fluid in contact with the wire to move

erratically, resulting in an uneven contact area with the wire and the stochastic nature of the current magnitude. The H_2O_2 fluid level decreased below the Pt wire at the 85-minute mark, evoking the swift drop in current. An autonomous feature arose between times 85 min and 105 min during which the Pt wire was completely *above* the H_2O_2 solution, and yet a nearly stationary current of $0.12\ \mu\text{A}$ persisted. This feature was observed in multiple samples, with the likely underlying source being a gas-phase reaction as H_2O_2 evaporates from the still-wet surface and adsorbs on the Pt wire where it is free to recombine with electrons to generate an electromotive force. This unusual finding warrants further investigation for confirmation of the underlying mechanism. The remaining current decayed to the zero value during time $t = 105 - 123$ min, with the last of the solution evaporating 123 min into the data collection.

The reaction current may be limited by hot electron generation during the decomposition of H_2O_2 on the Pt phase alone, as has been reported with other catalytic metal systems[24,25], but the situation in which H_2O_2 interacts with both Pt and TiO_2 concurrently reveals that the generation of hot electrons on the Pt phase is dwarfed by the $\text{TiO}_2/\text{H}_2\text{O}_2$ interaction. It has been shown that Ti ions have a tendency to adsorb hydroxide ions formed upon the heterolytic cleavage of water[30]; hence the production of the hydroxide ion by means of cleavage of water molecules or the O–O bond breakage in adsorbed H_2O_2 results in the further hydroxylation of the adsorbate layer at the TiO_2 /liquid interface. This hydroxylation of the surface likely leads to the sharp (and positively biased) transient peak observed for H_2O_2 on TiO_2 , see Figure 3 (B) and (C), which contrasts with the case of H_2O_2 on the Pt mesh solely. The current magnitude begins to decay shortly thereafter as the surface becomes saturated with hydroxyl groups. Verification of this mechanism requires further investigation.

It has been reported that the severance of the O–O bond during H₂O₂ decomposition is the major reaction route for metal oxides in which the metal is in its highest oxidation state, with adsorption of OH• being a more energetically favorable event than adsorption of H₂O (molecular or dissociative) or molecular adsorption of H₂O₂. [30,31] Although free radicals generally have a short half-life, the OH• radicals produced by O–O bond breakage are stable as adsorbed species on TiO₂ with half-lives on the order of hours or even days. [30–33] These newly created radicals are free to interact further with H₂O₂, see Suh et al. [34], according to



The electrons generated through titanium reduction may diffuse through the oxide layer to the Ti substrate, where they traverse the external circuit to recombine with hydrogen ions at the Pt electrode. We emphasize that the above mechanism is proposed as a possible component of the generated steady-state current and needs to be examined further. The overall steady-state current shown in Figure 3 (C) likely stems from Equations 1 – 2, in addition to a component from the redox processes at Pt and TiO₂ given by



A detailed investigation into the contribution of the mechanisms outlined in Equations 1 – 2 and Equations 3 – 4 is currently underway.

The data presented in Figure 3 can be used to compute the conversion efficiency of electrons produced per H₂O₂ molecule, providing a valuable metric for the reaction current generation. Such a calculation was carried out for the case of H₂O₂/TiO₂ interaction, see Figure 3 (C). The total number of electrons traveling through the external circuit is proportional to the

integration of the current vs. time curve, and is given by $N_{e^-} = (\text{area under curve})(0.625 \times 10^{19} \text{ e}^- \cdot \text{A}^{-1} \cdot \text{s}^{-1})$. Evaluation of this expression after integrating the data yields $N_{e^-} \approx 3.7 \times 10^{16}$ electrons. In the 60 μL of 3% aqueous H_2O_2 solution used there are $\sim 3.2 \times 10^{19}$ H_2O_2 molecules, therefore the conversion efficiency η is found to be on the order of 10^{-3} e^- per H_2O_2 molecule. It is good to make the distinction that this efficiency was calculated per available H_2O_2 molecule and not necessarily per decomposed H_2O_2 molecule, and as such this represents a *lower* limit for the conversion efficiency. In a closed system with constrained evaporation, it can be expected that the efficiency η will exceed 10^{-3} as the available H_2O_2 will be more likely to adsorb and decompose.

In conclusion, we have shown the interfacial influence on H_2O_2 decomposition-induced reaction current through the investigation of H_2O_2 solution when applied to Pt phase alone, TiO_2 phase alone, and Pt and TiO_2 phases simultaneously. It was observed that the catalytic decomposition of H_2O_2 by the Pt nanomesh generates a stationary current that cannot be attributed to thermal current due to its polarity. In the case of H_2O_2 on Pt and TiO_2 , the decomposition-induced current generated by TiO_2 dominates the Pt phase-generated current, with current magnitude dependent upon H_2O_2 availability. For reaction current induced by TiO_2 , the produced current is governed by elementary decomposition reactions with an observed conversion efficiency of 10^{-3} electrons produced per available H_2O_2 molecule. This result demonstrates the possibility of altering the oxidation state of titanium to generate electrons which diffuse through the metal oxide; the generation of this current is governed by the chemical reaction occurring at the solid-liquid interface. Additionally, a stationary reaction current, which endured for ~ 20 min, was observed *after* the H_2O_2 solution lost contact with one of the electrodes. Further refinement of the oxidation parameters and a better understanding of the rate-controlling H_2O_2 decomposition should enable

the optimization of this novel analytical approach to easily detect and monitor the rate of H₂O₂ decomposition; this methodology could be greatly extended into the field of analytical chemistry.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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