



Article Study on Influence Factors of H₂O₂ Generation Efficiency on Both Cathode and Anode in a Diaphragm-Free Bath

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Abstract: Electrosynthesis of H_2O_2 via both pathways of anodic two-electron water oxidation reaction (2e-WOR) and cathodic two-electron oxygen reduction reaction (2e-ORR) in a diaphragm-free bath can not only improve the generation rate and Faraday efficiency (FE), but also simplify the structure of the electrolysis bath and reduce the energy consumption. The factors that may affect the efficiency of H_2O_2 generation in coupled electrolytic systems have been systematically investigated. A piece of fluorine-doped tin oxide (FTO) electrode was used as the anode, and in this study, its catalytic performance for 2e-WOR in $Na_2CO_3/NaHCO_3$ and NaOH solutions was compared. Based on kinetic views, the generated H_2O_2 via 2e-WOR, the self-decomposition, and the oxidative decomposition rate of the generated H_2O_2 during electrolysis in carbonate electrolytes were investigated. Furthermore, by choosing polyethylene oxide-modified carbon nanotubes (PEO-CNTs) as the catalyst for 2e-ORR and using its loaded electrode as the cathode, the coupled electrolytic systems for H_2O_2 generation were set up in a diaphragm bath and in a diaphragm-free bath. It was found that the generated H_2O_2 in the electrolyte diffuses and causes oxidative decomposition on the anode, which is the main influent factor on the accumulated concentration in H_2O_2 in a diaphragm-free bath.

Keywords: hydrogen peroxide; carbonate-bicarbonate solution; 2e-ORR pathway; 2e-WOR pathway; coupled electrolytic system

1. Introduction

Hydrogen peroxide possesses a moderate oxidizing capacity with no secondary pollution [1,2], and it is used in various industrial and domestic applications, such as textile and pulp bleaching, waste water treatment, chemical synthesis, circuit board cleaning, clinical disinfection, etc. [3–6]. The state-of-the-art anthraquinone process for H₂O₂ production requires massive infrastructure investment and refined production management, by which an aqueous solution of H₂O₂ up to 75 wt% can be obtained while a H₂O₂ solution of 30 wt% is marketed and used because of transportation and storage safety [7,8]. However, a low concentration (~3 wt%) is enough in many cases, such as in hospitals and the cosmetics industry, for disinfection and sterilization [9]. For these application situations, preparing H₂O₂ solution on-site with a small electrochemical device becomes the most environmentally friendly and economical pathway [10–13].

There are two electrode reactions of electrosynthesis H_2O_2 : (1) the two-electron oxygen reduction reaction (2e-ORR) on the cathode with $E^{\theta} = 0.78$ V vs. NHE [14,15], and (2) the two-electron water oxidation reaction (2e-WOR) on the anode with $E^{\theta} = 1.76$ V vs. NHE [16]. Many 2e-ORR catalytic electrolysis systems with good selectivity, high activity, and good durability have been proposed [17–19], but the 2e-WOR catalytic electrolysis system for H_2O_2 generation is still unsatisfied in terms of generation rate and Faraday efficiency (FE) [20]. Many efforts have been made to design excellent



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). catalysts to improve the 2e-WOR selectivity [21], to find a suitable electrode substrate, to fasten the catalyst onto the surface of the substrate, and so on [22].

Usually, the counter-electrode reaction for 2e-WOR is the hydrogen evolution reaction (HER), and it is the oxygen evolution reaction (OER) for 2e-ORR [23,24]. Theoretically, if the anodic 2e-WOR and the cathodic 2e-ORR are coupled in one electrolysis bath, the overall FE of H_2O_2 generation would be 200%. However, there are several challenges to setting up these coupled electrolytic systems. The primary problem is the distinct electrolyte requirements of the anodic and cathodic catalysts, stemming from the inherently different nature of the two electrode processes. For instance, most metal-based and carbonbased electrocatalysts for 2e-ORR adapt to caustic alkaline electrolytes (i.e., NaOH or KOH solutions) [25,26], but only a few carbon-based electrocatalysts are suitable for weakly alkaline or neutral electrolytes (i.e., Na₂SO₄ or PBS solutions) [27–29]. In contrast, most of the reported 2e-WOR electrocatalysts with excellent performance require a carbonate electrolyte (Na₂CO₃ or NaHCO₃ solutions) [30–32]. Therefore, some studies have setup diaphragm electrolytic systems in which the 2e-ORR and 2e-WOR electrode processes are separated, and the preferential conditions of electrode substrates, catalysts, and supporting electrolytes for each process could be met in this way to achieve optimal productivity of the entire system [33,34].

In contrast to a diaphragm electrolytic system, a diaphragm-free electrolytic system is beneficial for its simple structure, easy operation, omitting electrolyte purification, and eliminating additional diaphragm resistance. However, till now, there have been a few research reports on the H_2O_2 generation in diaphragm-free-coupled electrolytic systems [35,36]. The challenges mainly arise from two aspects: (1) using a uniform electrolyte in a bath, which implies that the productivity on either the cathode or the anode would be sacrificed, and (2) the loss of the generated H_2O_2 in the electrolyte due to the more concentrated H_2O_2 in the cathodic chamber diffusing and going through oxidative decomposition on the anode.

Here we report the study on influent factors of H_2O_2 generation efficiency in coupled electrolytic systems. A piece of FTO electrode was used as the anode in this study. And its catalytic performance for 2e-WOR in different electrolytes (i.e., NaOH, Na₂CO₃, and mixed Na₂CO₃/NaHCO₃ solutions) was compared. Furthermore, the FTO electrode was coupled with the PEO-CNT cathode. Then, the influent factors on the accumulated concentration of H_2O_2 in the electrolyte by a coupled electrolytic system in a diaphragm bath or in a diaphragm-free bath were comparably investigated.

2. Materials and Methods

2.1. Preparation of Materials and Electrodes

Fluorine-doped tin oxide (FTO) electrode: A piece of FTO-coated glass measuring 20 cm \times 20 cm was purchased from MSE Supplies and cut into small pieces measuring 2 cm \times 1 cm. It is cleaned by sonication with acetone, ethanol, and water for 15 min each to remove surface impurities. After drying, it is partially covered with 704 silicone rubber to control the working area to 1 cm \times 1 cm. Before each electrochemical measurement or electrolysis, the FTO electrode is pre-stabilized at 3.0 V for 20 min in an H-type cell to clean and activate the surface.

Polyethylene oxide-modified carbon nanotubes (PEO-CNTs) loaded electrode: PEO-CNTs were prepared according to the previous report [27] and are briefly described below. The mixture of carbon nanotubes and polyethylene oxide was calcined at 600 °C in an Ar atmosphere for 3 h to get PEO-CNTs. PEO-CNTs was suspended in a mixture of isopropanol and H₂O (7:3, volumetric ratio), and with the help of some glues (5% Nafion), it was sprayed evenly onto the surface of carbon paper (TORAY, TGP-H-060) with a loading density of 0.5 mg cm⁻². After drying, it was used as a cathode in the 2e-ORR system.

A piece of hydrophobic carbon fiber paper (CFP) was prepared according to a previous report [36], and it was used as the anode in a flow electrolysis system.

2.2. Electrochemical Measurements and Electrolysis Systems

The electrochemical measurements and electrolysis experiments (except for the flow electrolysis system in which a two-electrode system was used) were performed on an electrochemical workstation (CHI 760E, CH Instruments, Chen Hua, Shanghai, China) in a three-electrode system, in which a saturated calomel electrode (SCE) connected by a salt bridge was used as the reference electrode. All potentials described in the text have been converted to the RHE scale using the following Equation (1).

$$E_{\rm RHE} = E_{\rm SCE} + 0.2438 + 0.0592 \times \rm pH \tag{1}$$

1. Evaluation of catalytic performance for 2e-ORR

PEO-CNTs suspended in a mixture of isopropanol and H₂O (7:3 in volume) and adding glues (5% Nafion) were mixed via sonication to get a homogeneous ink. Then the ink was dropped onto the disk electrode (0.2475 cm²) of the rotating ring-disk electrode (RRDE) with a loading density of 0.06 mg cm⁻². The LSV curves were collected in O₂-saturated solution with a scan rate of 5 mV s⁻¹ at 1600 rpm with a platinum sheet as the counter electrode. The applied potential on the Pt ring (0.1866 cm²) during the LSV test was fixed at 1.2 V to record the ring current (I_{ring}). The selectivity for H₂O₂ generation (H₂O₂ selectivity) in the cathodic ORR process was calculated based on Equation (2).

$$H_2O_2 \text{ Selectivity } (\%) = 200 \times \frac{I_{\text{ring}}/N_c}{I_{\text{disk}} + I_{\text{ring}}/N_c}$$
(2)

where I_{ring} is the ring current, I_{disk} is the disk current, and N_c represents the collection efficiency. The theoretical value of N_c is 0.37, which is determined by the external dimensions of the ring-disk electrode. In practical application, the value of N_c was obtained in K₃[Fe(CN)₆] after each polishing of the ring-disk electrode.

2. Evaluation of catalytic performance for 2e-WOR

The catalytic performance of FTO electrode in different electrolytes was measured in a H-type glass cell separated by Nafion 117 diaphragm with 8 mL electrolyte in each chamber. The electrolysis was executed in a three-electrode system (WE: FTO 1 cm \times 1 cm; CE: platinum sheet, 1 cm \times 1 cm \times 0.1 cm; RE: SCE) under constant-potential model. The concentration of H₂O₂ in electrolyte after electrolysis was determined by KMnO₄ titration method or Ce⁴⁺ ultraviolet-visible (UV-vis) spectrophotometric method (see Section 2.3 in detail), and FE for H₂O₂ generation is calculated based on Equation (3).

$$FE(\%) = \frac{2 \times c \times V \times F}{Q} \times 100\%$$
(3)

where *c* is the determined H_2O_2 concentration, *V* is the total volume of the electrolyte, *F* is the Faraday constant and takes the value of 96,485 C mol⁻¹, and *Q* is the total amount of passed charge during electrolysis, obtained by integrating the current against time in constant-potential electrolysis.

3. Evaluation of the performance of H_2O_2 generation in coupled electrolytic systems

The coupled electrolytic system in a diaphragm bath was setup in the same diaphragm bath for evaluating the performance of 2e-WOR, except that the counter electrode was replaced with a PEO-CNTs loaded electrode (1 cm \times 1 cm). After a certain amount of electrolysis, the electrolytes in the cathodic and anodic chambers were respectively sampled to determine the FE of H₂O₂ generation on cathode or anode.

The coupled electrolytic system in a diaphragm-free bath was setup in the same H-type glass cell, but no diaphragm was installed, to which 16.00 mL of electrolyte was added. After a certain time of electrolysis under constant potential, the electrolyte was sampled to determine the FE for H_2O_2 generation.

The coupled electrolytic system in a diaphragm-free flow electrolytic system was setup in a home-made electrolysis cell with electrolyte flow in and out, with a CFP electrode (the working area is 1 cm \times 1 cm) as the anode and PEO-CNTs electrode (the working area is 1 cm \times 1 cm) as the cathode. Constant current electrolysis was operated in this two-electrode system with a current density of 80 mA cm⁻².

2.3. Determination of H_2O_2 in Electrolytes

The KMnO₄ titration method or the Ce⁴⁺ UV-vis spectrophotometric method is selected to determine the H₂O₂ concentration, depending on the concentration range. The KMnO₄ titration method is chosen when the H₂O₂ concentration is higher than 50 mM. At this point, this method will use a large volume of KMnO₄ (>10 mL), which reduces the error due to the estimated reading volume. And if the H₂O₂ concentration is in the range of 0.2 mM to 50 mM, the Ce⁴⁺ UV-vis spectrophotometric method is preferred to provide more accuracy. At this point, the absorbance after the reaction can be between 0.1 and 0.9, and UV spectrophotometric method is as follows: the absorbance. The principle of Ce⁴⁺ UV-vis spectrophotometric method is as follows: the absorption of Ce⁴⁺ in a Ce(SO₄)₂ standard solution at 320 nm might weaken in the presence of H₂O₂ due to the reduction of Ce⁴⁺ to Ce³⁺, and the change in absorption intensity is in direct proportion to the concentration of H₂O₂ [37].

2.4. The Analysed Steps of Oxidative Decomposition Rate Constant of H_2O_2 on Anodic Surface

As shown in Figure 1, the expected concentration at a certain moment during the electrolysis would be the sum of the generated H_2O_2 via electrode reaction and the added H_2O_2 in advance, while the deviation between the actually determined concentration and the expected one is deemed to be the loss of the self-decomposition and the oxidative decomposition. Finally, fitting the relationship between the decreasing concentration and reaction time to a first-order kinetic model, the linear slope (deducted from self-decomposition rate constant k_1) would be the oxidative decomposition rate constant k'. Taking the measurement of the oxidative decomposition rate of H_2O_2 at 3.6 V in Na₂CO₃ solution as an example, the detailed procedure has been described in Supplementary Materials.

$$c_{0} \xrightarrow{\text{electrolysis}} c_{t} \xrightarrow{\text{deduced H}_{2}O_{2} \text{ generation}} c'(\text{Decomposition effects only})$$

$$c_{\text{generated}} = r \times j \times t$$

$$fitting$$

$$based on$$

$$first-order kinetics$$

$$k'$$

$$c'(\text{Decomposition rate constant})$$

$$k' = k_{1}: \text{Self-decomposition rate constant}}$$

rate constant

 c_0 : Initial concentration of H_2O_2

c_t: Determined concentration of H₂O₂ after electrolysis

 $c_{\text{generated}}$: H₂O₂ concentration generated by 2e-WOR

 $r: H_2O_2$ generation rate the corresponding potential

- j: Current density at the corresponding potential for electrolysis
- t: Electrolytic time

Figure 1. The analysis steps of oxidative decomposition rate constant of H₂O₂ at andic surface.

3. Results and Discussion

3.1. FE for H_2O_2 Generation via 2e-WOR on FTO in Different Electrolytes

With other electrolysis conditions the same, the variations of FE for H_2O_2 generation on FTO in 1 M NaOH, 1 M NaHCO₃, and 1 M Na₂CO₃ solutions when electrolyzed at different potentials are shown in Figure 2. It is obvious that the performance in Na₂CO₃ solution and NaHCO₃ solution is significantly better than that in NaOH solution at all potentials. FEs in NaOH were less than 5% at all potentials, but a FE of 21.0% was obtained at 3.0 V in NaHCO₃, and a FE of 22.7% was obtained at 3.6 V in Na₂CO₃.



Figure 2. FE and corresponding current densities for H_2O_2 generation via 2e-WOR on FTO electrodes in 1 M NaOH (pH = 13.50), 1 M NaHCO₃ (pH = 8.10), and 1 M Na₂CO₃ (pH = 11.53) solutions (vs. PBS solution, pH = 8.10).

A PBS solution (pH = 8.10) whose pH is comparable to that of 1 M NaHCO₃ solution was purposely prepared and used as the electrolyte for the same test, and the FE was only about 5%. It is also noteworthy that the current densities at each potential in these electrolysis tests were in the magnitude of mA cm⁻². For example, the current density in NaOH solution at 3.0 V reached 16.0 mA cm⁻², which was much larger than that in Na₂CO₃ solution (7.7 mA cm⁻²) and NaHCO₃ solution (6.0 mA cm⁻²). However, the determined concentrations of H₂O₂ in the electrolyte after electrolysis for 20 min were 0.24 mM, 1.02 mM, and 0.95 mM, respectively. It implies that carbonate and bicarbonate solutions are more favorable for H₂O₂ generation than alkaline solutions.

In a further study, we prepared a series of CO_3^{2-}/HCO_3^{-} solutions with different ratios but held the total concentration of CO_3^{2-} and HCO_3^{-} to be 1.0 M. As shown in Figure 3, the Fes for H_2O_2 generation on the FTO anode in these solutions are similarly around 20% at relatively low anodic potential (3.0 V). Moreover, in the electrolyte with the molar fraction of HCO_3^{-} at 0.25, the FE increased as the potential positively shifted, and the FE reached 25.4% at the anodic potential of 3.6 V. While in the electrolyte with a higher proportion of HCO_3^{-} , the FE decreased significantly at a more positive potential; for example, the FE in the NaHCO₃ solution was only 6% at a potential of 3.6 V.



Figure 3. FEs for H_2O_2 generation via 2e-WOR on FTO electrodes in CO_3^{2-}/HCO_3^{-} mixture solutions (pH = 11.53, 10.00, 9.53, 9.16, 8.10) with various ratios at different anodic potentials.

In the above discussion, the FEs for H_2O_2 generation via 2e-WOR were calculated based on the accumulated concentration of H_2O_2 in the electrolyte. As shown in Figure 2, the difference among the FEs in different CO_3^{2-}/HCO_3^{-} solutions became more significant as the potential shifted positively, indicating that the oxidative decomposition of the generated H_2O_2 on the anode is a non-negligible factor for the apparent FEs.

The following experiment might provide evidence for this proposal. An amount of 12.5 mM of H_2O_2 was respectively added into Na_2CO_3 and $NaHCO_3$ solutions in advance, and then electrolysis was conducted for 12 min at 3.6 V. As shown in Figure S1 (Supplementary Materials), the H_2O_2 concentration in Na_2CO_3 increased to 13.4 mM, while that in $NaHCO_3$ decreased to 11.0 mM.

3.2. Factors Affecting the Accumulated Concentration of H₂O₂ in Carbonate Electrolytes

The accumulated concentration of H_2O_2 in the electrolyte after electrolysis for a certain time is closely related to the generation of H_2O_2 via 2e-WOR on the anode and the decomposition of the generated H_2O_2 in the electrolyte. Therefore, in the following text, the factors on FE for H_2O_2 generation via 2e-WOR are systematically discussed in kinetic terms.

3.2.1. Self-Decomposition Rate of H₂O₂ in Different Solutions

Many groups have reported the various kinetic models of H_2O_2 decomposition in different solutions [38–42]. At least one point of consensus can be obtained: the self-decomposition reaction of H_2O_2 in aqueous solution follows first-order kinetics, but the rate constant k_1 is related to the species and concentration of coexisting chemicals in the solution because some chemicals act as catalysts or inhibitors for H_2O_2 decomposition.

To avoid the interference of the stabilizers in the commercially available H_2O_2 reagents on the test results in this study, we used the electrolytes after electrolysis in the carbonate electrolytes as the initial solutions and determined the change in H_2O_2 concentration with time at room temperature (20 °C). The curve of $\ln(c/c_0)$ -*t* is plotted as shown in Figure 4a, which showed that the rate constants k_1 of H_2O_2 self-decomposition in Na₂CO₃ and NaHCO₃ solutions were 0.0023 min⁻¹ and 0.0020 min⁻¹, respectively. Based on the above discussion, the effect of self-decomposition on the accumulated concentration of H_2O_2 during electrolysis could be ignored because both the rate constant k_1 and the H_2O_2 concentration in the electrolyte are relatively low, especially at the beginning of the electrolysis.



Figure 4. (a) The rate constants of H_2O_2 self-decomposition in 1 M Na₂CO₃ and 1 M NaHCO₃ solutions at room temperature (20 °C); (b) The rate constants of H_2O_2 generation via 2e-WOR on FTO electrode at potentials of 3.2 V and 3.6 V in 1 M Na₂CO₃ solution; (c) The rate constants of H_2O_2 oxidative decomposition on FTO at 3.2 V and 3.6 V potentials in 1 M Na₂CO₃ and 1 M NaHCO₃ solutions.

3.2.2. Generation Rate of H₂O₂ via 2e-WOR on Anode

Supposing no decomposition of H_2O_2 occurs during the electrolysis, the partial current density for H_2O_2 generation (j_{H2O_2}) would be the same at any moment during a constantpotential electrolysis using a given anode in a certain electrolyte. So, the generation rate (r) of H_2O_2 via 2e-WOR on the anode might be described as Equation (4), which is the differential equation of Equation (3).

$$r = \frac{dc}{dt} = \frac{j_{\rm H_2O_2}}{V \cdot 2 \cdot F} \tag{4}$$

This means that the accumulated concentration (*c*) in the electrolyte would increase linearly with the electrolysis time (*t*), in which the coefficient of *c*-*t* (with the dimension of mmol $A^{-1} \text{ min}^{-1}$) might be a kinetic indicator for the electrode reaction whose value is dependent on the catalyst, the electrolyte, the electrolytic potential, and so on.

We tried to estimate the generation rate of H_2O_2 via 2e-WOR by the following method: The accumulated concentrations of H_2O_2 in Na₂CO₃ solution after electrolysis at different potentials for a short time (about 3 to 8 min) were determined. In this case, it is reasonable that the decomposition of H_2O_2 in the electrolyte can be ignored since the total concentration is low at the beginning of electrolysis. Based on this supposition, the coefficients of *c*-*t* of H_2O_2 generation via 2e-WOR on the FTO electrode in Na₂CO₃ were estimated to be 0.0905 mmol A⁻¹ min⁻¹ at 3.2 V and 0.1062 mmol A⁻¹ min⁻¹ at 3.6 V (Figure 4b), respectively. The results conform to the basic principle of electrochemistry: that the anodic process is faster and has more positive potential.

We also determined the generation rate in various $\text{HCO}_3^-/\text{CO}_3^{2-}$ solutions and found that the coefficients of *c*-*t* were basically unchanged at the same anodic potential (see the details in Table S1, Supplementary Materials), which can be explained by the fact that the H_2O_2 generation rate in the carbonate electrolyte is dependent on the formation rate of the percarbonate ions (HCO_4^-) [43], which would be unchanged in carbonate solutions with the same total concentration of CO_3^{2-} and HCO_3^- because of the quick interconversion equilibrium between CO_3^{2-} and HCO_3^- .

3.2.3. Oxidative Decomposition Rate of H₂O₂ on the Anodic Surface

According to basic electrochemistry, it is unavoidable that the generated H_2O_2 in the electrolyte diffuses to the anode and goes through oxidative decomposition on it during the electrolysis because the anodic potential is more positive than 3.0 V and the oxidation potential of H_2O_2 is about 1.76 V. In this study, the oxidative decomposition rate of H_2O_2 at a certain potential is estimated by a deduction method, in which a certain amount of

 H_2O_2 is added to the electrolyte before the electrolysis to magnify the effect of oxidative decomposition. The method is briefly described in Section 2.4.

Based on this method, the rate constants of oxidative decomposition of H_2O_2 on the FTO electrode are determined as 0.0146 min^{-1} at 3.2 V and 0.0167 min^{-1} at 3.6 V in Na₂CO₃ solution, 0.0169 min^{-1} at 3.2 V, and 0.0252 min^{-1} at 3.6 V in NaHCO₃ solution, respectively (shown in Figure 4c). It is easy to understand that the oxidative decomposition rate of H_2O_2 increases on anodes with more positive potential. What is noticeable is that the oxidative decomposition rate of H_2O_2 in NaHCO₃ is higher than that in Na₂CO₃, and this trend became more significant at more positive anodic potentials. This phenomenon is in conformity with the previous studies by Wang et al. [43] and by Zheng et al. [44]. The possible reason is that the acidification near the anode due to OER, especially at a more positive potential, promotes the hydrolysis of HCO_4^- to H_2O_2 , and the latter is more likely to go through oxidative decomposition than HCO_4^- species [45].

Based on the above discussions, the apparent Fes of H_2O_2 generation on the FTO electrode in the carbonate electrolyte shown in Figure 2 can be rationalized. Since the self-decomposition rate of H_2O_2 in electrolyte can be ignored, and the generation rate is only related to the anodic potential, the main factor affecting the accumulated concentration of H_2O_2 in electrolyte during electrolysis is oxidative decomposition. In carbonate electrolytes with a higher ratio of HCO_3^- and a more positive potential, the oxidative decomposition rate of H_2O_2 is higher, which results in a decrease in the apparent Fes.

3.3. Efficiency of H₂O₂ Generation via 2e-ORR in Carbonate Solutions

PEO-CNTs have been proven to be an effective catalyst for 2e-ORR in a caustic electrolyte by our previous studies, which demonstrated a selectivity better than 85% in a 1 M NaOH solution at a cathodic potential of 0.4 V [27]. In this study, we investigated the changes in the catalytic performance of 2e-ORR in different electrolytes by using PEO-CNTs as cathodic catalysts.

The catalytic performance for 2e-ORR of PEO-CNTs in different solutions (i.e., 1 M NaOH, 1 M Na₂CO₃, and 1 M NaHCO₃) was investigated by the RRDE method. As shown in Figure 5a, the H₂O₂ selectivity in all three electrolytes is around $85 \pm 5\%$ (the electron transfer number is calculated as 2.3) at potentials in the range of 0.3 V to 0.5 V (Figure S2, Supplementary Materials). However, the onset potentials of the ring current in Na₂CO₃ and NaHCO₃ solutions were significantly negatively shifted (0.55 V) compared with that in NaOH solution, which indicates that the catalytic activity of PEO-CNTs in carbonate electrolyte is weaker than that in caustic electrolyte.



Figure 5. (a) RRDE polarization curves of PEO-CNTs loaded electrodes in 1 M NaOH, 1 M Na₂CO₃, and 1 M NaHCO₃ solutions, where the dashed line is the ring current and the solid line is the disk current; (b) Tafel curves of PEO-CNTs loaded electrodes in $Na_2CO_3/NaHCO_3$ mixed solutions and the corresponding slope.

Tafel and other electrochemical methods were conducted to explore the reasons for the decrease in the catalytic activity of 2e-ORR in different electrolytes. The LSV became almost the same after being normalized when different concentrations of equal amounts of Na₂CO₃/NaHCO₃ were added to a 1 M KOH solution [46] (see Figure S3, Supplementary Materials). And it proves that the decrease in 2e-ORR catalytic activity in carbonate electrolytes is partly due to the decreased solubility of oxygen gas in the electrolytes. The measured Tafel slopes in carbonate solutions with different ratios of CO_3^{2-}/HCO_3^{-} (i.e., with the same concentration of Na₂CO₃ and NaHCO₃ mixed solutions and at different pH) are shown in Figure 5b. The Tafel slope increased from 70.8 mV dec⁻¹ to 92.3 mV dec⁻¹ with decreasing pH, indicating that the reaction resistance on the electrode surface increased as the pH in the electrolyte decreased. It might be explained that less concentrated OH⁻ ions in the electrolyte hindered the rate of 2e-ORR, of which the protonation process in the first electron transfer step is the rate-controlling step.

3.4. The Efficiency of H_2O_2 Generation in a Coupled Electrolytic System

A coupled electrolytic system for H_2O_2 generation in a diaphragm bath was set up by using an FTO electrode as anode, a PEO-CNTs-loaded electrode as cathode, and a 2 M CO_3^{2-}/HCO_3^{-} solution (mole ratio of $CO_3^{2-}:HCO_3^{-} = 3:1$) as the supporting electrolyte. The electrolysis was carried out under the constant potential model. It was found that the actual current density in the bath was only about 10 mA cm⁻² when the potential was kept constant at 3.0 V (Figure 6a). This current density is comparable to the value when HER occurs on the corresponding cathode at the same anodic potential in a diaphragm bath, while the current density on the PEO-CNTs-loaded cathode could be up to 40 mA cm⁻² when OER occurs on the corresponding anode. It appeared that the actual current density in a coupled electrolytic system for H_2O_2 generation was limited by the sluggish 2e-WOR on the anode, and the catalytic activity for 2e-ORR on the cathode was severely inhibited.

However, it is fortunate that the selectivity for H_2O_2 generation both on the cathode and the anode remained in the coupled electrolytic system. The FEs were calculated based on the accumulated H_2O_2 concentration in the separated cathode and anode chambers after electrolysis for a short time of 20 min, as shown in Figure 6b. It showed that the FEs were above 85% on the cathode and above 20% on the anode in the diaphragm-coupled electrolytic system, which are comparable to the values in the uncoupled systems. In other words, the total FE of H_2O_2 generation on both the cathode and anode in a diaphragm bath could exceed 100%.

The accumulated concentrations of H_2O_2 in the cathode and anode chambers were tracked, respectively. The H_2O_2 concentration in the cathode chamber increased linearly with electrolytic time and reached 155 mM after electrolysis for 5 h. Whereas, the H_2O_2 concentration in the anode chamber increased slower than that in the cathode chamber, and it started to decrease when the concentration reached 26 mM after 3 h of electrolysis (Figure 6c). This phenomenon is related to the low efficiency of H_2O_2 generation via 2e-WOR on the anode, and the oxidative decomposition rate accelerated as the concentration increased.

The coupled electrolytic system for H_2O_2 generation in a diaphragm-free bath was also setup, in which all the electrolysis conditions were the same as those in the diaphragm bath except for the diaphragm being removed. The FEs determined by the H_2O_2 concentration in the electrolyte after a short time of electrolysis are shown in Figure 6b. The total FE in the diaphragm-free bath was slightly lower than that in the diaphragm bath because the H_2O_2 concentration was decreased by the anodic oxidative decomposition since there was no diaphragm to avoid the generated H_2O_2 via 2e-ORR diffusing to the anode. But it still exceeded 100%, and the cell voltage in the diaphragmfree electrolytic system was lowered compared with the diaphragm-coupled system (see



the data in Table S4, Supplementary Materials), which might be the result of removing the diaphragm resistance.

Figure 6. (a) The comparison of current densities during electrolysis in 2e-WOR, 2e-ORR, and diaphragm-coupled electrolytic systems under constant potential models; (b) The comparison of determined FEs for H_2O_2 generation in CO_3^{2-}/HCO_3^{-} mixed solution in a diaphragm bath and diaphragm-free bath; (c) The accumulated concentration of H_2O_2 in cathodic and anodic chambers with electrolysis time in the diaphragm-coupled system; (d) The accumulated concentration of H_2O_2 in the diaphragm-free-coupled system at different potentials.

It is worth noting that the anodic oxidative decomposition significantly affected the accumulated concentration in the diaphragm-free electrolytic system for a longer electrolysis time. As shown in Figure 6d, the H_2O_2 concentration in the electrolyte decreased as the electrolysis time extended. The inflection point appeared earlier when electrolysis was conducted at an anodic potential of 4.0 V than at 3.2 V, and the maximum concentration was about 75 mM in both cases. This phenomenon can be explained by the fact that the increased generation rate at higher anodic potentials simultaneously accelerates the oxidative decomposition rate as the concentration increases.

The above results show that the oxidative decomposition of the generated H_2O_2 in the electrolyte during the electrolysis is the main factor troubling the efficiency of H_2O_2 generation by the coupled electrolytic system in a diaphragm-free bath. The following strategies might be taken to solve this problem: One strategy is to find an excellent catalyst for 2e-WOR, i.e., at a lower anode potential and/or with a larger current density, by which to increase the H_2O_2 generation rate on the anode and simultaneously decrease the oxidative decomposition rate. The other strategy is to adopt a flow bath, in which the electrolyte could flow out of the bath in time when the accumulated concentration reaches a certain value to avoid anodic oxidative decomposition. A CFP electrode has been reported to possess good catalytic performance for 2e-WOR, but its durability is not satisfied. As shown in Figure 7a, using a CFP electrode as anode in a diaphragm-free bath coupled with a PEO-CNTs-loaded electrode, the electrolysis could be operated at an anodic potential of 2.4 V with a large current density of 80 mA cm⁻², but the performance degraded after electrolysis for only 1.5 h. It is noticeable that the inflection points of the accumulated concentration in electrolyte also appeared; the maximum concentration improved to 146 mM due to the lower anodic potential.



Figure 7. (a) The accumulation concentration of H_2O_2 in a CFP-PTFE/FTO diaphragm-free system by a long electrolysis time; (b) H_2O_2 concentration, accumulated volume, and cell potential in the flow bath with a flow rate of 0.33 mL min⁻¹ at a constant current of 80 mA cm⁻².

Furthermore, we established a diaphragm-free flow bath with an electrode effective area of 1 cm², and electrolysis was carried out under the constant current model at a current density of 80 mA cm⁻² and a flow rate of 0.33 mL min⁻¹. As shown in Figure 7b, the H_2O_2 concentration in the effluent was basically maintained at about 85 mM during electrolysis for 4 h.

4. Conclusions

The generation of H_2O_2 in a diaphragm-free bath by coupling the 2e-ORR pathway on the cathode and the 2e-WOR pathway on the anode has the advantages of simple device structure and energy savings, while the challenges are the choice of the electrolyte and how to avoid the oxidative decomposition of the generated H_2O_2 on the anode. The following results have been obtained in this study:

- (1) The effect of the electrolyte on the H_2O_2 generation efficiency via 2e-WOR was investigated by using the FTO electrode as an anode in different electrolytes. The highest FE was observed in a mixed $Na_2CO_3/NaHCO_3$ solution, and the reason is attributed to the oxidative decomposition of generated H_2O_2 on the anode being slow in this electrolyte.
- (2) The comparison of the coupled electrolytic system in a diaphragm bath and a diaphragm-free bath was performed. The results showed that the oxidative decomposition of generated H₂O₂ on the anode was the main reason for the decrease in accumulated concentration in the diaphragm-free electrolytic system.
- (3) A diaphragm-free coupled flow electrolysis system was developed to reduce anodic potential and prevent excessive accumulated concentration. This system successfully achieved the continuous generation of an 85 mM H₂O₂ concentration at a constant flow rate.

The results of this study might lighten the application of diaphragm-free coupled systems for H_2O_2 generation in the future, in which an excellent catalyst for the 2e-WOR pathway and a well-designed diaphragm-free electrolytic system are prerequisites.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/ma17081748/s1, Figure S1: H_2O_2 concentration changed with electrolytic time, adding 12.5 mM H_2O_2 as initial solutions; Table S1: H_2O_2 concentration by constantpotential (2.8 V) electrolysis with 20 min in 1 M Na₂CO₃ solution and a mixed CO_3^{2-} /HCO₃⁻ (mole ratio of CO_3^{2-} :HCO₃⁻ = 3:1) solution (the concentration of CO_3^{2-} and HCO₃⁻ is 1 M); Table S2: Taking the measurement of the oxidative decomposition rate of H_2O_2 at 3.6 V in Na₂CO₃ solution; Figure S2: H_2O_2 selectivity and electro transfer number of PEO-CNTs in different electrolytes; Figure S3: (a) LSV of PEO-CNTs in 1 M KOH, adding the different mixed solution of Na₂CO₃/NaHCO₃; (b) normalized current of PEO-CNTs in 1 M KOH, adding the different mixed solution of Na₂CO₃/NaHCO₃; Table S3: Physical properties of (A) 1 M KOH, 0.01 M Na₂CO₃, 0.01 M NaHCO₃; (B) 1 M KOH, 0.05 M Na₂CO₃, 0.05 M NaHCO₃; (C) 1 M KOH, 0.1 M Na₂CO₃, 0.1 M NaHCO₃; Table S4: The cell voltage of diaphragm bath systems and diaphragm-free bath systems.

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