

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

Tian Tian, Zhaohui Wang, Kun Li, Honglei Jin, Yang Tang, Yanzhi Sun, Pingyu Wan and Yonemei Chen *

College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

* Correspondence: chenym@mail.buct.edu.cn; Tel.: +10-64435452

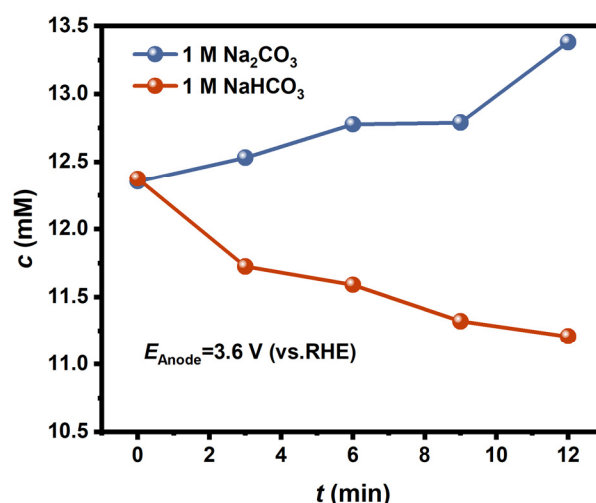


Figure S1. H₂O₂ concentration changed with electrolytic time, adding 12.5 mM H₂O₂ as initial solutions.

Table S1. H₂O₂ concentration by constant-potential (2.8 V) electrolysis with 20 min in 1 M Na₂CO₃ solution and a mixed CO₃²⁻/HCO₃⁻ (mole ratio of CO₃²⁻: HCO₃⁻ = 3:1) solution (the concentration of CO₃²⁻ and HCO₃⁻ is 1 M).

Electrolyte	c _{H₂O₂} (mM)
1 M Na ₂ CO ₃	0.267
1 M Na ₂ CO ₃ /Na ₂ HCO ₃	0.271

Taking the measurement of the oxidative decomposition rate of H₂O₂ at 3.6 V in Na₂CO₃ solution as an example:

Generation of H₂O₂ after electrolysis with certain time is calculated based on the equation (S1):

$$c_{\text{generated}} = (0.1062 \text{ mmol A}^{-1} \text{ min}^{-1} \times t - 0.0238 \text{ mmol A}^{-1}) \times j \times S_{\text{work}} \quad (\text{S1})$$

where 0.1062 mmol A⁻¹ min⁻¹ is generation rate of H₂O₂ at 3.6 V in Na₂CO₃ solution, 0.0238 mmol A⁻¹ is the parameter, due to the fact that the amount of electricity used to form the double layer capacitor at the beginning of the reaction did not generate H₂O₂, *j* is current density, *t* is electrolytic time, and *S_{work}* is working area (1 cm²).

The remaining concentrations after electrolysis with certain time (3 min, 6 min, 9 min, and 12 min) at 3.6 V were determined based on the initial H_2O_2 concentration of 12.351 mM, which resulted from a combination of generation and decomposition, and the H_2O_2 concentrations with only decomposition factors were calculated based on the equation (S2).

$$C'_{\text{only decomposition}} = C_{\text{determined}} - C_{\text{generated}} \quad (\text{S2})$$

And then, fitting the relationship between the decreasing concentration and reaction time to a first-order kinetic model ($\frac{d_c}{dt} = kc$), and we plot and fit a straight line in $\ln(c'/c_0)$ - t . The linear slope would be the decomposition rate constant k_d . Finally, the oxidative decomposition rate constant k' was calculated based on the equation (S3).

$$k' = k_d - k_1, \quad (\text{S3})$$

Table S2. Taking the measurement of the oxidative decomposition rate of H_2O_2 at 3.6 V in Na_2CO_3 solution.

t (min)	C determined	C generated	C' only decomposition	$\ln(c'/c_0')$
0	12.351	0	12.351	0
3	12.530	0.775	11.755	-0.049
6	12.777	1.553	11.224	-0.0957
9	12.789	2.432	10.357	-0.176
12	13.381	3.346	10.035	-0.208

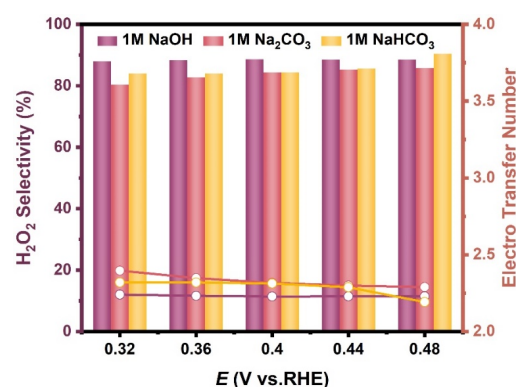


Figure S2. H_2O_2 selectivity and electro transfer number of PEO-CNTs in different electrolytes.

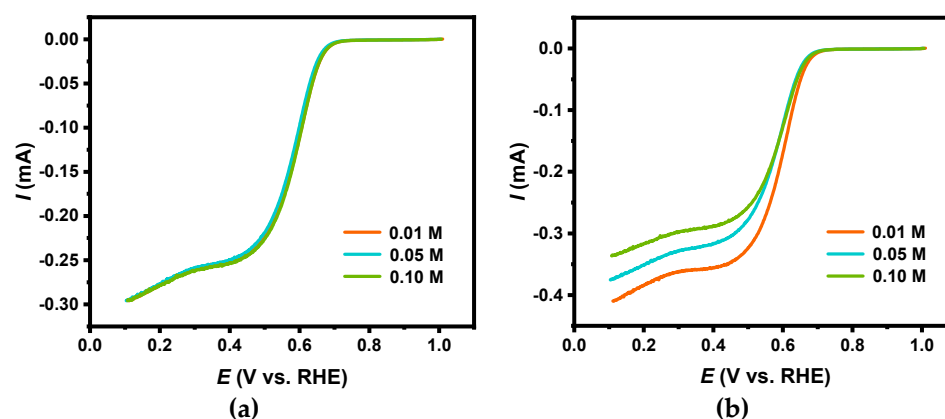


Figure S3. (a) LSV of PEO-CNTs in 1 M KOH adding the different mixed solution of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$; (b) Normalized current of PEO-CNTs in 1 M KOH adding the different mixed solution of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$.

Current normalization

For a rotating disk electrode experiment the observed current is expressed by

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{i_K} + \frac{1}{B\omega^{1/2}} \quad (\text{S4})$$

where i is the observed current, i_K is the kinetic current and i_L is the mass transport limited current. Mass transport limited currents for a rotating disk electrode are described by the Levich equation:

$$i_L = 0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O = B\omega^{1/2} \quad (\text{S5})$$

where n is the overall number of electrons transferred during reaction, F is the Faraday constant, A is the electrode active area, D is the oxygen diffusion coefficient, ω is the rotation rate, ν is the kinematic viscosity and C is the dissolved oxygen concentration. B is expressed by

$$B = 0.62nFAD_O^{2/3}\nu^{-1/6}C_O \quad (\text{S6})$$

Table S3. Taking the measurement of the oxidative decomposition rate of H_2O_2 at 3.6 V in Na_2CO_3 solution.[1].

Electrolyte	pH	ν (cSt)	C_{oxygen}	$D \cdot 10^5 \text{ cm}^2 \text{ s}^{-1}$
A	13.70	0.93	0.86	2.04
B	13.64	0.96	0.81	1.94
C	13.46	1.0	0.76	1.83

Since oxygen concentration and diffusion coefficient decrease and kinematic viscosity increases when more salt is present in solution (Table S3). To provide a balanced comparison between the RRDE disk plots, it is useful to normalize the observed current to the oxygen diffusion coefficient, electrolyte kinematic viscosity and the oxygen saturation concentration, which can be done by

$$i_{\text{normalized}} = \frac{i_{\text{observed}}}{D_O^{2/3}\nu^{-1/6}C_O} = 0.62nFA \quad (\text{S7})$$

Table S4. The cell voltage of diaphragm bath system and diaphragm-free bath system.

E (V vs. RHE)	Q (C)	E_{cell} (V)	
3.05	14.311	3.0	Diaphragm-free
	13.901	2.9	
3.15	21.326	3.3	Diaphragm-free
	20.433	3.2	

References

- Vega, J.A.; Mustain, W.E. Effect of CO_2 , HCO_3^- and CO_3^{2-} on Oxygen Reduction in Anion Exchange Membrane Fuel Cells. *Electrochimica Acta* **2010**, *55*, 1638–1644.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.