Supporting Information For:

An innovative dual-compartment flow reactor coupled with a gas diffusion electrode for in-situ generating H₂O₂

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Analytic methods

Electrochemical Impedance Spectroscopy was conducted on the electrochemical workstation (Instruments Reference 3000, America). The sinusoidal excitation voltage applied to the cells was 1 mV, whose frequency ranged from 10 to 10⁶ Hz. The conductivity of the membrane is an important parameter to characterize the membrane performance and calculated using the following formula:¹

$$\sigma = \frac{d}{R \times S} \tag{1}$$

Where σ is conductivity (S/cm), *d* is the thickness of the membrane (cm), *R* is membrane resistance (Ω), and *S* is the membrane surface area exposed to the electric field (cm²). These measurements gave the resistance and ionic conductivity of the membrane in a 0.05 M H₃PO₄ solution.

Electrochemical tests were carried out at room temperature based on the rotating

ring-disk electrode (RRDE) measurements using a standard three-electrode (GC working electrode, platinum wire counter electrode, as well as Ag/AgCl reference electrode) electrochemical cell with a SP-300 bipotentiostat. The ORR was performed in 0.05 M Na₂SO₄ with oxygen saturation at room temperature. Prior to the electrochemical measurements, the bubbles were eliminated on the surface of the electrode through the conducting cycle voltammetry (CV) at least 5 times to ensure accuracy. Linear sweeping voltammetry (LSV) curves were performed at varying rotation rates (400 - 2500 rpm) over the potential from -0.8 V to 0.2V vs. Ag/AgCl at a sweep rate of 5 mV s⁻¹.

The electron transfer numbers (n) in ORR process was calculated according to the Koutecky - Levich (K-L) equations as follows:²

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{-\frac{1}{2}}} + \frac{1}{J_K}$$

$$B = 0.62nFC_0 D_0^{\frac{2}{3}} V^{-\frac{1}{6}}$$
(2)
(3)

where *J* is the detected current density, J_K and J_L are the kinetic and limiting current densities (mA cm⁻²), ω is the angular velocity of electrode rotation, *n* is the electron transfer numbers, *F* is the Faraday constant (C mol⁻¹), *v* is the kinematic viscosity of the electrolyte (cm² s⁻¹), *C*₀ is the bulk concentration of O₂ (mol cm⁻³), and *D*₀ is the diffusion coefficient of O₂ in the electrolyte solution (cm² s⁻¹).

Result and dissuasion

The conductivity of the membrane.

The conductivity is an important index to measure the transport of ions. It reflects the mobility of all ions in the system and the embodiment of membrane conductivity. Using the impedance measurements by the way of a Nyquist plot, the bulk resistance of the membrane samples, R, were obtained and specific ionic conductivities were calculated using equation (1). Table S1 displays the conductivity of different membranes in 0.05 M H₃PO₄ electrolyte solutions. The α -Al₂O₃ ceramic membrane (1 mm, 1.8 mm, 2.5 mm) were marked as A-1 A-1.8 A-2.5 respectively. It can be seen that the α -Al₂O₃ ceramic membranes display higher conductivity than

Nafion117 membrane. A-1 exhibited higher electrical conductivity. Since the mechanical strength of the membrane increases with the thickness, we choose A-1.8 in consideration of the mechanical strength for subsequent experiment.

Table S1. The resistance and conductivity of different membranes in 0.05 M H₃PO₄ electrolyte solutions.

Membrane	Resistance (Ω)	σ (S/cm)
Nafion117	1.105	5.188×10 ⁻³
A-1	5.056	6.299×10 ⁻³
A-1.8	10.250	5.593×10 ⁻³
A-2.5	14.837	5.366×10 ⁻³

Electrochemical test.

LSV curves at different rotation rates were recorded, as shown in Figure S1. The corresponding K-L plots for the GDE show good linearity with the slopes almost constant at the potential range of -0.5- -0.4 V (vs. Ag/AgCl). The n is calculated to be 2.1-2.3, 2.0-2.3, 1.9-2.2 for the catalytic layers with 20% PTFE,35%PTFE and 50%PTFE, at the selected potential range, respectively.



Figure S1. LSV curves of different PTFE contents in catalyst layer (Conditions: scanning rate 20 mV/s, 0.05 M Na₂SO₄, oxygen saturation). Inset: The corresponding K-L plots at different potentials

Figure S2 shows the production of H_2O_2 and the corresponding current efficiency with various cathodes. The H_2O_2 yield of CL cathode and GDL cathode is 274.2 mg/L and 126.8 mg/L, separately, which is obviously smaller than that of GDE(CL+GDL, 1230.0 mg/L). The possible reason was that the H_2O_2 yield CL cathode was limited by the solubilization and the diffusion of oxygen in the absence of the GDL, while the yield of GDL cathode was restricted by the catalytic activity.



Figure S2. Performance comparison of three different cathodes, (a) the yields of H_2O_2 and (b) current efficiency. Conditions: C_{Na2SO4} = 0.05 M, I = 110 mA, F_{O2} = 10 mL/min and $F_{solution}$ = 1000 μ L/min.

References:

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