

High Activity Folic Acid-treated Non-Precious Metal Catalyst for Oxygen Reduction Reaction

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Abstract

Proton exchange membrane fuel cell (PEMFC) is a power source to convert the chemical energy in fuel and oxidant to electricity. To reduce the cost of the PEMFC, non-precious metal catalysts for the oxygen reduction reaction (ORR) are extremely important, and have attracted substantial attention in recent years. This work demonstrates a carbon black-supported pyrolyzed folic acid-treated catalyst of the ORR, with high catalytic performance. The ORR measurements reveal that the optimized condition of catalyst shows an excellent ORR activity, via the direct four-electron reduction pathway for the reduction of O₂ to H₂O.

Keywords: Non-precious metal catalysts, Oxygen reduction reaction, Fuel cells.

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1 Introduction

The proton exchange membrane fuel cell (PEMFC), which efficiently transforms chemical energy into electrical energy *via* electrochemical reactions, is considered an ideal future power source. However, cost and available resources are important development issues since most PEMFCs use

expensive platinum catalysis. Accordingly, catalysis using non-precious metals must replace platinum catalysis.

The various factors that affect oxygen reduction reaction (ORR) activity include transition metal nitrogen-containing complexes, the species of the transition metal, the structure of the catalyst, the surface properties of the carbon support, the nitrogen content and others. The ligand–metal interaction has an important effect on ORR activity. Lalande *et al.* noted that the surface nitrogen content of the catalyst is the main factor in ORR activity.^[1] Studies also show that increasing the surface nitrogen content directly improves ORR activity.^[2-7] Nitrogen precursors used for non-precious metal catalyst include macrocyclic complexes, organic compounds, organic polymers, inorganic salts and gaseous precursors.^[8-11]

Here, we use folic acid as a new nitrogen precursor mixed with iron and carbon black as a catalyst. The carbon black-supported pyrolyzed folic acid-treated catalyst can provide stronger catalytic activity in the ORR *via* the direct four-electron reduction pathway. Therefore, the proposed catalysis method improves fuel cell performance.

2 Experimental

2.1 Preparations of catalyst

A folic acid, iron chloride hexahydrate and carbon black (Vulcan XC-72R) was dissolved in 10 mL of ethanol with stirring for 30 minutes at room temperature. The folic acid and iron precursor added to the mixture in different ratios. The mixture was heated using steam to 80 °C to eliminate the solvent. The suspension was filtered through filter paper to obtain the slurry, which was dried at room temperature under vacuum for 12 hours. Pyrolyzed folic acid-treated catalyst supported by carbon black was prepared at various temperatures.

2.2 Instrumentation

Electrochemical measurements were made in a three-compartment cell using a potentiostat/galvanostat instrument (Biologic Bi-stat). The working electrode was a rotating-ring disk electrode (RRDE, PINE AFE7R9GCPT) with a glassy carbon (GC) disk and a ring made of platinum. The counter electrode and reference electrode were Pt foil and a saturated calomel electrode (0.242 V vs. NHE), respectively. All potentials in this work are with reference to the reversible hydrogen electrode (RHE). The electrolyte in the ORR test was oxygen-saturated 0.1 M HClO₄ solution.

3 Results and Discussion

Figure 1a presents the ORR activities of py-Fe-FA/C-500, py-Fe-FA/C-700, py-Fe-FA/C-800 and py-Fe-FA/C-900. The lower part of Fig. 1a plots disk current (I_d) against applied potential and the upper part plots the ring current (I_r) as a function of applied potential. At a pyrolyzed temperature of 800 °C, the highest absolute value of I_d and the lowest absolute of I_r were. The total electron-transfer number (n) and the hydrogen peroxide yield (%H₂O₂) in the catalyzed ORR were utilized,

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}} \quad \%H_2O_2 = \frac{\frac{2I_r}{N}}{I_d + \frac{I_r}{N}} \times 100\% \quad (1)$$

where N is the RRDE collection efficiency, which was determined to be 0.37 herein. **Figures 1b and 1c** display the n values and %H₂O₂, respectively. For the

py-Fe-FA/C-800, the n values and %H₂O₂ remain at approximately 3.98 and 1.0%, respectively, over a wide range of overpotentials up to 0.7 V, indicating that the ORR of py-Fe-FA/C-800 proceeds preferentially along the four-electron direct ORR pathway. The observations demonstrate that the pyrolysis at 800 °C yields the highest n and the lowest % H₂O₂.

Figure 2 shows the ORR activities of different iron contents in folic acid-treated catalysts from 5~20 wt%. The lower part of Fig. 2a plots disk current (I_d) against applied potential and the upper part plots the ring current (I_r) as a function of applied potential. The optimal Fe loading with the highest absolute value of I_d and the lowest absolute of I_r is 15 wt%.

Figure 3 presents the ORR activities of various nitrogen/carbon ratios in folic acid-treated catalysts (5:1, 1:1, 1:5). The lower part of Fig. 3a plots disk current (I_d) against applied potential and the upper part plots the ring current (I_r) as a function of applied potential. The optimal ratio of nitrogen to carbon (FA/C) with the highest absolute value of I_d and the lowest absolute of I_r is 5:1.

4 Conclusion

Pyrolyzed folic acid-treated catalyst supported by carbon black has high potential activity in the ORR and PEMFC application. Folic acid was selected as one N-containing precursor to prepare a new ORR catalyst. The compounds were then heat-treated at temperatures ranging from 500 °C to 900 °C to synthesize py-Fe-FA/C catalysts. Additionally, the metal and nitrogen contents were also optimized. The RRDE measurements reveal that py-Fe-FA/C favors a direct four-electron reduction pathway from O₂ to H₂O. Although identifying this catalyst is an important advance in the use of non-precious metal metals for catalysis in PEMFC, the mechanisms of nitrogen precursors with central metal and surrounding ligands in ORR require further study.

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7 Figures

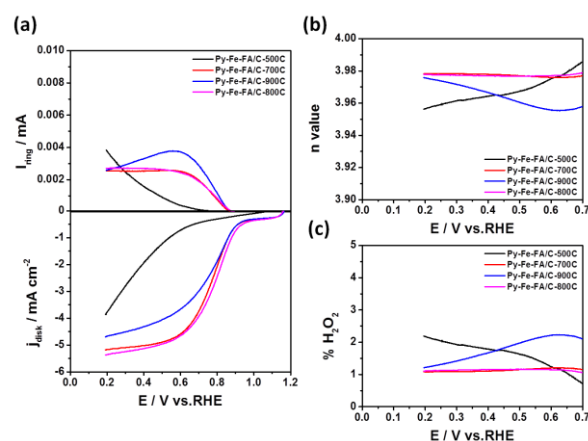


Figure 1. (a) ORR curves for py-Fe-FA/C at different temperatures; (b) the n values and (c) %H₂O₂ of the catalysts dependence on disk potentials. Rotating speed: 1600 rpm; scan rate: 10 mV s⁻¹; ring potential: 1.2 V.

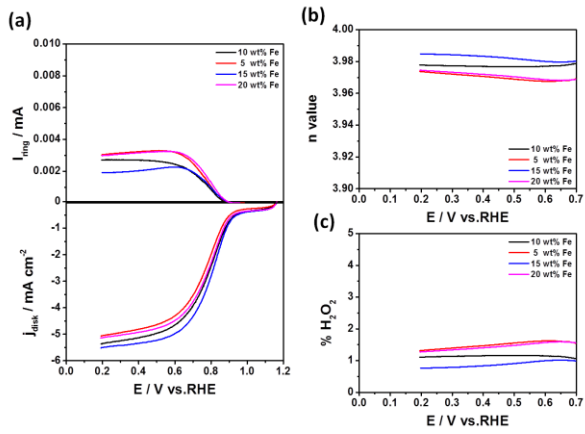


Figure 2. (a) ORR curves for py-Fe-FA/C at different iron loading; (b) the n values and (c) %H₂O₂ of the catalysts dependence on disk potentials. Rotating speed: 1600 rpm; scan rate: 10 mV s⁻¹; ring potential: 1.2 V.

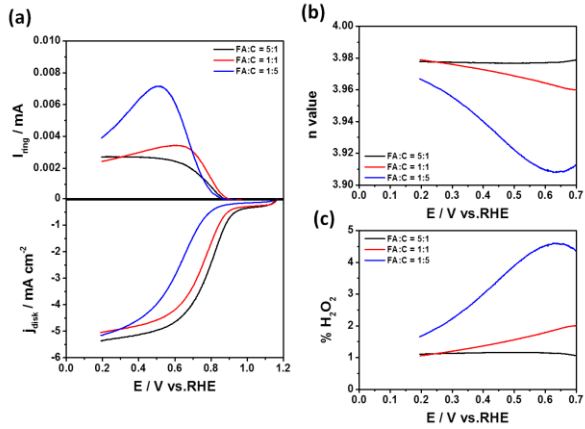


Figure 3. (a) ORR curves for py-Fe-FA/C at different ratio of nitrogen precursor to carbon black; (b) the n values and (c) %H₂O₂ of the catalysts dependence on disk potentials. Rotating speed: 1600 rpm; scan rate: 10 mV s⁻¹; ring potential: 1.2 V.