

# Pyrolyzed Cobalt Corrole as Potential Non-precious Catalyst for Fuel Cells

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## Abstract

Non-precious metal catalysts of the oxygen reduction reaction are highly favored for use in polymer electrolyte fuel cells (PEFC) because of their relatively low cost. This work demonstrates a new carbon black-supported pyrolyzed Co-corrole (py-Co-corrole/C) catalyst of the oxygen reduction reaction (ORR) in a PEFC cathode, with high catalytic performance. The py-Co-corrole/C at 700 °C exhibits the optimized ORR activity, and participates in a direct four-electron reduction pathway for the reduction of O<sub>2</sub> to H<sub>2</sub>O. The H<sub>2</sub>-O<sub>2</sub> PEFC test of py-Co-corrole/C in the cathode reveals a maximum power density of 275 mW cm<sup>-2</sup>, which yields a higher performance and a lower Co loading than previous studies of Co-based catalysts for PEFCs. The enhancement of the ORR activity of py-Co-corrole/C is attributable to the four-coordinated Co-corrole structure and the oxidation state of the central cobalt.<sup>[1, 2]</sup>

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

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## 1 Introduction

A polymer electrolyte fuel cell (PEFC) is an electrochemical device that transforms chemical energy to electrical energy by the redox reaction of hydrogen and air (oxygen), which are fed into the anode and the cathode, respectively. The core unit of the PEFC, a

membrane-electrode-assembly (MEA), comprises a polymer electrolyte membrane that is sandwiched between an anode and a cathode, both of which contain precious catalysts i.e. platinum. The oxygen reduction reaction (ORR) in the cathode is much slower than the hydrogen oxidation reaction in the anode,<sup>[3]</sup> and therefore, to accelerate the ORR, a high loading of platinum (Pt) catalyst is used in the cathode, making the PEFC expensive. The high price associated with use of an extremely rare earth Pt catalyst in fuel cells is the factor that mostly limits their commercialization. Unconventional non-platinum catalysts, which are efficient, durable and inexpensive, must be developed to replace Pt catalysts in the ORR.

Since Jasinski investigated cobalt phthalocyanine as a catalyst of the reaction at the cathode in a fuel cell in 1964,<sup>[4]</sup> various studies have demonstrated that macrocyclic complexes with transition metal, including porphyrin,<sup>[5-9]</sup> phthalocyanine<sup>[10, 11]</sup> and tetraazannulene<sup>[12]</sup> are candidate catalysts of ORR. Among those, iron and cobalt-based macrocyclic compounds have been claimed to have the highest catalytic activity in the ORR.<sup>[13-15]</sup> In 2006, Bashyam *et al.* were the first to demonstrate the use of non-precious metal composite (cobalt-polypyrrole) catalysts in the cathode of a H<sub>2</sub>-O<sub>2</sub> PEFC at 80 °C, with a maximum power density of approximately 150 mW cm<sup>-2</sup>, and no significant degradation over at least 100 hours.<sup>[16]</sup> Lefevre *et al.* showed that the current density of microporous carbon-supported iron-based catalysts in the ORR equals that of precious metals at a cell voltage of  $\geq 0.9$  V.<sup>[17]</sup> Recently, Wu *et al.* utilized polyaniline as a precursor to a carbon-nitrogen template in the high-temperature

synthesis of catalysts that incorporate iron and cobalt that exhibited high activity and remarkable performance stability.<sup>[18]</sup> Proietti *et al.* used an iron-acetate/phenanthroline/zeolitic-imidazolate-framework k-derived electrocatalyst with increased volumetric activity and enhanced mass-transport properties. The PEFCs test in H<sub>2</sub>-O<sub>2</sub>, has a power density of 0.75 W cm<sup>-2</sup> at 0.6 V, which is the best performance of non-precious metal ORR catalyst to date.<sup>[19]</sup> Some review articles have been studied non-precious metal ORR catalyst, which transition metal nitrogen-containing complexes are considered the most promising ORR catalysts.<sup>[15, 20-23]</sup>

This work elucidates a simple synthesis of pyrolyzed Co-corrole supported by carbon black (py-Co-corrole/C) use in the ORR. The py-Co-corrole/C catalyst accelerates the ORR in a fuel cell beyond the rate achieved using other cobalt-containing macrocyclic compounds, such as porphyrin, phthalocyanine, and tetraazannulene. This work is the first to report on pyrolyzed Co-corrole as a non-precious metal catalyst for use in fuel cells.

## 2 Experimental and Instructions

### 2.1 Preparations of catalyst

Co-corrole,(triphenylphosphine)(5,10,15-triphenylcorolato)cobalt(III), was synthesized following modified version of a procedure in the literature<sup>[24]</sup>. And the final catalyst was prepared according to the following procedure. A Co-corrole and carbon black (Vulcan XC-72R) was dissolved in 10 mL of tetrahydrofuran with stirring for 30 minutes at room temperature. 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 Co-corrole supported by carbon black was prepared at various temperatures of 300, 500, 700 and 900°C.

### 2.2 Instrumentation

The X-ray absorption near-edge structure (XANES) at the Co K-edge was recorded at beam line 17C1, which is based on a multi-pole wiggler source with a critical energy of 2.7 keV. The electron storage ring was operated at energy of 1.5 GeV with a beam current of 120–200 mA.

The beam line employs a double Si(1 1 1)-crystal monochromator for energy selection with a resolution ( $\Delta E/E$ ) of better than  $2 \times 10^{-4}$  in the energy range 5 - 15 keV. The standard material, cobalt foil was measured simultaneously in the third ionization chamber to enable energy calibration scan by scan. The XANES data were processed, involving background subtraction, normalization with respect to the edge jump, Fourier transformation, and curve fitting, using computer programs that were implemented in the IFEFFIT software package.

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 HClO<sub>4</sub> solution.

A membrane-electrode-assembly (MEA) with an area of 5 cm<sup>2</sup> was made by hot-pressing two electrodes on both sides of a Nafion® 212 (H<sup>+</sup>, DuPont) at 135 °C and 130 kg cm<sup>-2</sup> for 2 min. The cathode catalyst was hand-painted onto the carbon cloth, giving py-Co-corrole/C loading of about 2.0 mg cm<sup>-2</sup>. The anode of MEA was a commercial electrode (E-TEK) - Pt/C with a metal loading of 0.25 mg cm<sup>-2</sup>. A polarization experiment was carried out on the PEFC at 70°C. The PEFC performance was measured using a fuel-cell test station (Asia Pacific Fuel Cell Technologies, Ltd.) by recording the cell voltage and current after when they had reached steady values.

## 3 Results and Discussion

**Figure 1a** presents the ORR activities of py-Co-corrole/C-300, py-Co-corrole/C-500, py-Co-corrole/C-700 and py-Co-corrole/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 700 °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 (%H<sub>2</sub>O<sub>2</sub>) 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 %H<sub>2</sub>O<sub>2</sub>, respectively. The observations demonstrate that the pyrolysis at 700 °C yields the highest *n* and the lowest % H<sub>2</sub>O<sub>2</sub>.

**Figure 2** presents the recorded polarization plots of the PEFCs using py-Co-corrole/C-700 in the cathode, which generates a maximum power density of 275 mW cm<sup>-2</sup>. Since Co-based catalysts have commonly shown less ORR activities than Fe-based catalysts from recent reviews,<sup>[11, 18]</sup> the performance of py-Co-corrole/C-700 is less than the recent reports using Fe-based catalysts.<sup>[15, 16]</sup> The 100-hour durability test of py-Co-corrole/C-700 as the cathode catalyst in the fuel cell by flowing H<sub>2</sub> and air fed into the anode and the cathode, respectively, is demonstrated in **Fig. 3**. At 0.4 V, the cell current density remains nearly constant of 0.221 A cm<sup>-2</sup> for the 100-hour operation.

Additionally XANES results, plotted in **Fig. 4a**, reveal that the Co cations oxidation states of pristine Co-corrole, py-Co-corrole-700, pristine CoTMPP, py-CoTMPP-700 and CoO powder are 3+, 2+, 2+, 2+ and 2+, respectively, revealing that pyrolysis changes the oxidation state after the pyrolysis. In a study of the mechanism of the ORR with an organic cobalt complex, Okada *et al.* identified four-, five- and six-coordinated Co(II)- or Co(III)-based compounds, of which the four-coordinated Co(II)-based compounds with a coplanar chelate structure exhibited the best catalytic performance.<sup>[1]</sup> Pristine Co-corrole is a five-coordinated species with Co(III), but after the pyrolysis, py-Co-corrole-700 is a four-coordinated Co(II) species. The magnified XANES results between 7700 and 7720 eV in **Fig. 4b** indicate that the characteristic peak at about 7710 eV from CoO powder and pristine Co-corrole is strong; CoO and pristine Co-corrole are six-coordinated and five-coordinated species, respectively. However, the peak associated with

py-Co-corrole-700 is shifted to a higher energy of 7713 eV has very low intensity. The six- and five-coordinated cobalamin (with M-N<sub>4</sub> structure of Co-corrin) reportedly yields the characteristic peaks at 7710 eV, but the four-coordinated cobalamin yields a characteristic peak at 7714 eV such as pristine CoTMPP,<sup>[25]</sup> revealing that the characteristic peak is at a higher energy when the M-N<sub>4</sub> species has a lower coordination number. These results support the claim that py-Co-corrole-700 is a four-coordinated species rather than a five-coordinated species.

## 4 Conclusion

Py-Co-corrole/C-700 demonstrates high potential activity in the ORR and favorable PEFC performance. The RRDE technique shows that py-Co-corrole/C-700 exhibits a preference for a direct four-electron reduction pathway. The H<sub>2</sub>-O<sub>2</sub> PEFC uses py-Co-corrole/C-700 in the cathode, which shows higher performance but lower Co loading than previous studies in Co-based catalysts. The pyrolysis changes the coordination structure and oxidation state of Co-corrole, leading to the increase of ORR activity. The modifications of corrole structure with central metals and surrounding ligands have to be investigated furthermore.

## 5 Acknowledgments

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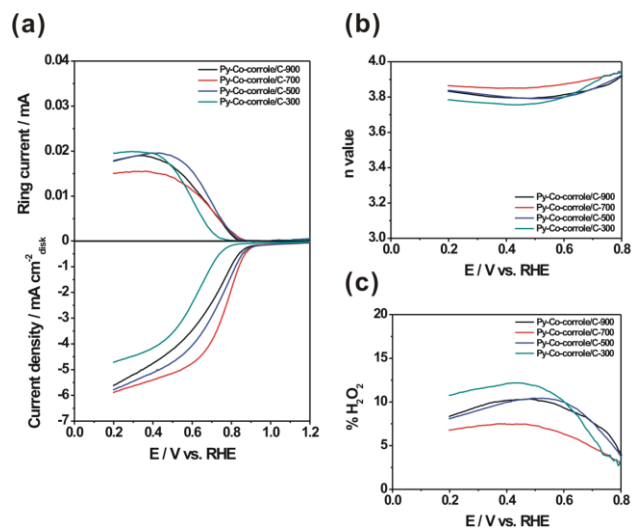
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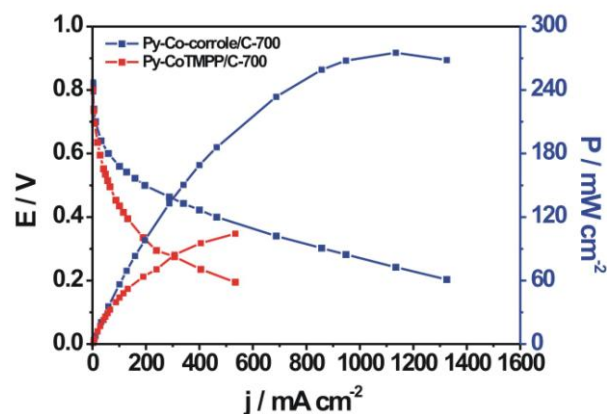
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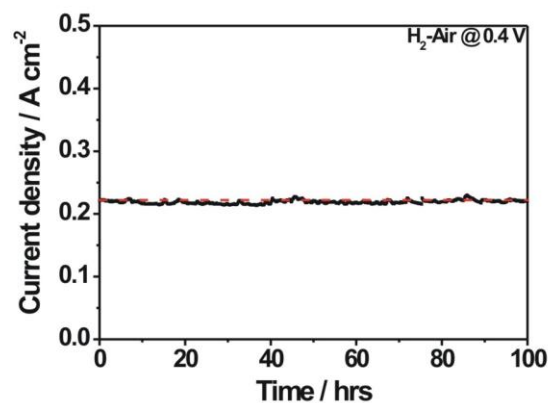
## 7 Figures and tables



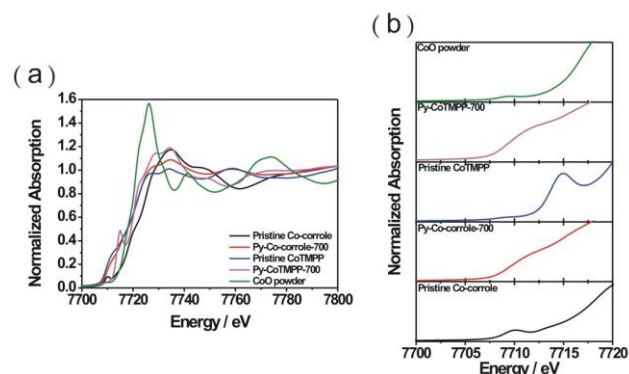
**Figure 1.** (a) ORR curves for py-Co-corrole/C at different temperatures; (b) the  $n$  values and (c) %H<sub>2</sub>O<sub>2</sub> of the catalysts dependence on disk potentials. Rotating speed: 1600 rpm; scan rate: 10 mV s<sup>-1</sup>; ring potential: 1.2 V.



**Figure 2.** Polarization curve of the H<sub>2</sub>-O<sub>2</sub> PEFC using py-Co-corrole/C-700 as the cathode. Operation temperature: 70 °C; back pressure of H<sub>2</sub> and O<sub>2</sub>: 1 atm



**Figure 3.** The 100-hour durability test of H<sub>2</sub>-O<sub>2</sub> PEFC using py-Co-corrole/C-700. Operation conditions: H<sub>2</sub>-Air, 70°C and 1atm of back pressure. Operation temperature: 70 °C; back pressure of H<sub>2</sub> and O<sub>2</sub>: 1 atm



**Figure 4.** (a) XANES spectra of pristine Co-corrole, py-Co-corrole-700, pristine CoTMPP, py-CoTMPP-700 and CoO powder; (b) the enlarged XANES spectra between 7700 to 7720 eV.