

## Cobalt and Iron Porphyrins–Polyoxometalates as Non-Noble Metal Catalyst for Oxygen Reduction Reaction in a Fuel Cell

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### Highlights

- More effective combination of the cobalt (iron) porphyrin cation with Keggin-type POM.
- Co porphyrin and FePWA exhibited a high ORR as a nonplatinum catalyst.
- The active species are Co<sup>2+</sup> (or Fe<sup>2+</sup>) and PWA after heat-treatment.
- The strong acid of the POM is more effective for the ORR.

### 1. Introduction

Recently, alternative platinum electrolytes in polymer electrolyte fuel cells have focused on the catalysts containing iron and cobalt metals supported on carbon and nitrated carbon. The Co porphyrin and polyoxometalate (POM) assembly was more active than the previously reported non-platinum catalysts compared to other non-platinum catalysts [1]. These assembled catalysts were effectively adsorbed, interacted with the carbon to conduct electrons and generated a greater reduction of oxygen. Recent non-platinum cathode catalysts have become much more active, but they are not very compatible as a commercial platinum catalyst. In this study, the assemblies of the Co (or Fe) porphyrin and various metal-exchanged polyoxotungstates (MePWA) as precursors supported on graphite were prepared by heat-treatment from 523 to 973 K. The ORR activity was related to the surface properties of the catalysts based on the XPS and NH<sub>3</sub>-TPD. The mechanism of the assembly for the ORR was also discussed.

### 2. Methods

The water-soluble 5,10,15,20-tetrakis(1-methyl-4-pyridinio) porphyrinato (Co porphyrin) was synthesized using a methanol aqueous solution of CoCl<sub>2</sub> and tetrakis(1-methyl-4-pyridinio)porphyrin. Also, tetraphenylporphyrin iron was prepared. VulcanXC-72R carbon or Ketjen black was added to the solution, followed by the addition of various MePWA compounds. The heat-treatment was carried out by temperature programmed treatment to 573–1073 K, maintained at the final temperature for 2 h and then cooled to room temperature in helium gas. The catalyst was characterized based on XRD, XPS, Raman and TEM.

A 147 μg portion of the suspension was deposited on the glassy carbon of a ring disk electrode. A commercial Pt/C was used for comparison. The electroactivity was measured at room temperature in a three-compartment cell containing a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution attached to the disk used as the working electrode, a carbon rod as the counter electrode and Ag/AgCl as the reference electrode which was labeled RHE (+0.199 V vs. RHE). For the linear sweep voltammetry (LSV) measurement, the electrode rotating rate was 2000 rpm, the scan rate was 5 mV in flowing oxygen gas and under argon saturation. The activity for the LSV was obtained by measuring the ORR onset potential at 5 μA/cm<sup>2</sup>. The amount of produced H<sub>2</sub>O<sub>2</sub> was measured on the half-cell rotating ring disk electrode.

### 3. Results and discussion

#### 3.1. ORR activity of Co porphyrin and several polyoxotungstates on carbon

The polarization of the 823 K-treated Co porphyrin, PWA and both containing Co porphyrin-PWA supported on carbon is studied. The Co porphyrin alone was more active (0.8 V) than the PWA alone (0.58 V). The addition of PWA to the Co porphyrin significantly increased the ORR activity by 80 mV which was a 35-times higher current density at 0.8 V. The Co porphyrin-PWA assembly showed a high ORR activity. The Co porphyrin played a role of adsorbing an oxygen molecule and dissociation in the cathode.

The polarization of the 823 K-treated Co porphyrin and several MePWA assemblies is studied. These catalysts had the same Keggin-type structure. The catalysts containing the following exchanged cation of the

MePWA decreased:  $\text{Fe} > (\text{PWA}) > \text{Co} > \text{Al} > \text{Cs} > \text{Ag}$ . The Co porphyrin-FePWA/carbon had the highest ORR activity (0.90 V) of the other catalysts. The current density at 0.9 V was  $0.3 \text{ A/cm}^2\text{g}$  which was a 2% activity compared to that of  $6.6 \text{ A/cm}^2\text{g}$  for the commercial 46.5 wt% Pt/C. Thus, the Co porphyrin-FePWA/carbon had a high ORR activity among the recent non-Pt catalysts. Furthermore, the added polyoxotungstate plays the additional role of decomposing and removing the produced hydrogen peroxide (3.98 reaction electrons). The ORR on these Co porphyrin-MePWA assemblies occurred almost with a four-electron reaction. The exchange current density of the Co porphyrin-FePWA and PWA/carbon was 5.49 and  $2.7 \times 10^{-6} \text{ mA/cm}^2$ , respectively, which was 2% lower than that of  $7.35 \times 10^{-6} \text{ mA/cm}^2$  for the commercial Pt/C. The 823 K-treated Co porphyrin-PWA/carbon in a stream of helium exhibited the highest activity of 30 mV more than the other temperature treated catalyst. From the XRD analysis, the PWA was not decomposed up to 823 K, but at 923 K, the PWA was decomposed to form  $\text{WO}_{2.92}$  and  $\text{WO}_{2.90}$ . The ratio of Co porphyrin to FePWA in unity had the best ORR activity (0.90 V) compared to the ratios of 0.66 and 2. As a result, the Co porphyrin and PWA assembly was composed of one to one molecule that became one assembly with a face to face structure.

### 3.2. The structure of Co porphyrin-PWA on graphite by the XPS N 1s and Co 2p

The heat-treatment of the Co porphyrin-PWA assembly on carbon up to 873 K almost decreased the N-CH<sub>3</sub> type nitrogen, but increased the pyridine-type and pyrrole-type nitrogens. The nitrogen of the porphyrin changed from the porphyrin nitrogen to the pyridinic and pyrrolic nitrogens at 823 K. The XPS Co 2p spectra showed that the amount of the  $\text{Co}^{2+}$  ion present is good when related to the ORR. The  $\text{W}^{6+}$  ion decreased at 823 K but was still distributed at 74 %. The distribution of  $\text{W}^{4+}$  and  $\text{W}^{5+}$  ions of the 823 K-treated catalysts increased 1.5-2 times more than those of the non-treated catalyst to create defect sites.

### 3.3 Acidity of POM

The activity of the catalyst using POM was compared to the catalyst using SiWA of which the silicon atom was replaced by the phosphorus atom of PWA. The catalyst using PWA had a higher ORR of 50 mV than the using SiWA catalyst. A low deprotonation indicates a strong acid (PWA at 1087 and SiWA at 1105 kJ/mol). The catalyst using a strongly acidic PWA exhibited a high ORR activity. Consequently, the ORR of the catalysts is responsible for the strong proton acidity of the PWA. The acidity and acid strength of the PWA without the pairs of Co porphyrin and carbon are determined using an  $\text{NH}_3$ -TPD. The ORR onset potential related to the acid strength of the  $\text{NH}_3$ -TPD of several metal-exchanged PWA anions. The acid strength of the individual PWAs was linearly related to the ORR onset potential of the various 823 K-treated Co porphyrin-metal exchanged PWAs on carbon. The Co porphyrin-FePWA/carbon treated at 823 K had the highest ORR and the strongest acid of all the catalysts. The PWA acted as a strong proton acid to release a proton to the oxygen adsorbed on the Co atom of the Co porphyrin. The strong acid of the PWA is more effective for the ORR as a counter cation.

Furthermore, mixtures of tetraphenylporphyrin iron instead of the Co porphyrin and polyoxotungstates,  $\text{H}_{8-n}\text{X}^{n+}\text{W}_{12}\text{O}_{40}$  ( $\text{X} = \text{P}, \text{Si}$ ) or  $\text{Metal}^{n/3}\text{PW}_{12}\text{O}_{40}$  ( $\text{Metal} = \text{Fe}, \text{Co}, \text{Ag}, \text{Ru}, \text{Al}$ ), supported on carbon were prepared by heat-treatment at 723-1023 K in helium. The most active catalyst was that prepared using tetraphenylporphyrin iron and FePWA and heated at 923 K, as evidenced by the ORR onset potential of 0.94 V vs. RHE and  $\% \text{H}_2\text{O}_2 < 2\%$ . The characterization studies showed that  $\text{Fe}^{2+}$  contributes to the activity as an effective active site and that the catalyst structure and leads to the enhancement of catalytic activity.

## 4. Conclusions

The catalysts of Co porphyrin and FePWA exhibited a high ORR onset potential comparable to the commercial Pt catalyst. After heat-treatment, the  $\text{Co}^{2+}$  (or  $\text{Fe}^{2+}$ ) and pyrrole group increased. The active species are  $\text{Co}^{2+}$  (or  $\text{Fe}^{2+}$ ) and PWA which offered intermediate media of protons from the anode and reduction of the produced hydrogen peroxide. The ORR activity was promoted. Thus, the catalyst of the cobalt (Iron) porphyrin cation Keggin-type POM as a precursor was more effective as a nonplatinum cathode catalyst than the other catalysts. The strong acid of the POM is more effective for the ORR as a counter cation.

## References

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## Keywords

"Fuel Cell", "Oxygen reduction reaction", "Cobalt Porphyrin", "Polyoxometalate".