



# A family of platinum group metal-free catalysts for oxygen reduction in alkaline media

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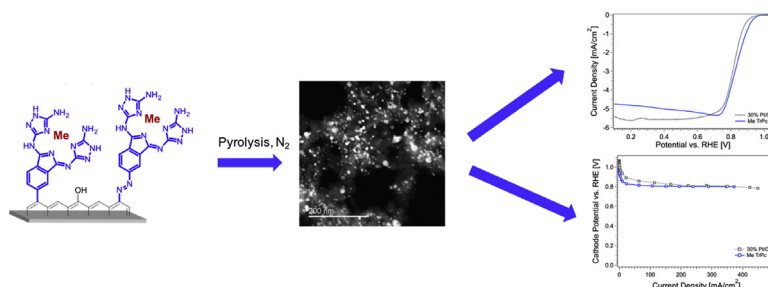
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## HIGHLIGHTS

- PGM-free catalysts for oxygen reduction reaction in alkaline media.
- Catalyst layer parameter's optimization.
- Reference electrode separates anode and cathode polarization contributions.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

In this work a series of platinum group metal-free catalysts based on iron, cobalt, copper, nickel, silver and their bimetallic combinations are synthesized and their behavior for oxygen reduction in alkaline media is tested. A phthalocyanine-like ligand supported on carbon black serves as the nitrogen source and carbon support, respectively, for the catalysts. The as-prepared materials are thermally activated by pyrolysis at temperatures ranging from 600 °C to 1000 °C. Oxygen reduction reaction (ORR) activity and stability in 0.1 M KOH are tested by rotating ring disk electrode (RRDE) experiments. Several of the catalysts show ORR activities in the RRDE experiment that are superior to Pt, with Co, Co/Fe and Ag/Co being the best. All catalysts show remarkable stability, even when they are tested under air for 5000 RRDE cycles. RRDE experiments are also used to study the effect of catalyst loading and to determine reaction order. A thorough study of the catalyst performance in a single cell fuel cell test is conducted; exploring different methods to prepare the electrodes and the effects of catalyst loading, the catalyst-to-binder ratio and the removal of excess metal on the cell performance. Different methods of preparation of membrane electrode assemblies are also studied.

## 1. Introduction

Despite decades of ongoing research, the cost of low temperature hydrogen fuel cell systems remains a barrier to their widespread adoption for transport and portable power applications. One factor that

contributes to the high cost is the use of expensive platinum group metal (PGM) catalysts to facilitate the electrode reactions. Research into alternative catalysts is motivated by the goal of reducing system costs [1]. One approach focuses on decreasing the amount of Pt [2,3] or using Pt alloys [4–7] on the cathode, at which the sluggish oxygen

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reduction reaction (ORR) occurs. A more direct approach, completely replacing PGM-based materials with PGM-free catalysts for the ORR, could significantly lower the overall cost of fuel cell though performance cannot be sacrificed. Great progress has been made in recent years on the design and development of PGM-free catalysts for fuel cells that work in acidic environment. Among these efforts, work on polyaniline-derived catalysts using cobalt and iron as the metal center demonstrated high performance in both RRDE experiments and single cell testing [8,9]. Materials based on pyrolyzed metal organic framework (MOF) compounds also showed enhanced performance of these catalysts, demonstrating the versatility of MOF-based materials [10–13].

Despite the extensive body of work described in the literature, there is still work to do to improve the catalyst performance and stability in acidic environments for proton exchange membranes fuel cells (PEMFC) applications. However, it is well known that PGM-free catalysts that do not perform well or have high stability in acidic environment can still perform well in alkaline media due to the less corrosive environment and higher catalytic kinetics for the ORR in anion exchange membrane fuel cells (AEMFCs) compared to that of PEMFCs [14]. In recent years there has been renewed interest in alkaline fuel cells due to the broad innovation in the synthesis of PGM-free catalysts [14–25].

In alkaline media, PGM-free materials have shown similar or even superior performances to Pt/C [21,26,27]. Recently, Gokhale et al. synthesized a Fe-N-C catalyst derived from a benzimidazole carboxylic acid [21]. Linear sweep voltammetry for this material showed a ~50 mV half-wave potential improvement relative to a commercial Pt/C catalyst. The membrane electrode assembly (MEA) polarization test produced a ~25 mA cm<sup>-2</sup> current density value at 0.6 V with 4 mg cm<sup>-2</sup> Fe-N-C as cathode electrocatalyst, 0.3 mg cm<sup>-2</sup> Pt as anode electrocatalyst and the Tokuyama's A201 membrane as electrolyte at 60 °C. Kruusenberg et al. studied the effect of the operation temperature on the fuel cell performance employing a FAA3 membrane [28]. In this study, they reported an increase from ~100 mA cm<sup>-2</sup> (35 °C) to 150 mA cm<sup>-2</sup> (50 °C) at 0.6 V using a Co-N-C cathode electrocatalyst. Tests performed with commercial Pt/C, A201 anion exchange membrane and AS4 ionomer have produced 280–340 mA cm<sup>-2</sup> current density at 0.6 V under 100% humidified H<sub>2</sub>/O<sub>2</sub> conditions [24].

While the ORR benefits from more favorable kinetics in an alkaline environment, the hydrogen oxidation reaction (HOR) has been reported to be at least two orders of magnitude slower in alkaline media than in acid media [29,30]. Such limitations can produce significant overpotential losses in the AEMFC anode, requiring higher Pt loadings when compared to PEMFCs. The increased cost associated with higher anode catalyst loadings may diminish the benefit of AEMFCs over PEMFCs. Work conducted by St. John et al. on platinum-ruthenium catalysts with novel structures has demonstrated significantly higher activity over traditional Pt catalysts [31]. Given the relatively low cost of ruthenium compared to platinum, the expected impact of slow HOR kinetics increased cost of AEMFC anodes can be, at least partially, mitigated.

In this work, we describe the synthesis of a family of PGM-free catalysts for the ORR in AEMFCs, using iron (Fe), cobalt (Co), copper (Cu), nickel (Ni), silver (Ag) and their bimetallic combinations. Materials were thermally activated under inert atmosphere at temperatures ranging from 600 °C to 1000 °C to make them catalytically active towards the ORR. The pyrolyzed catalysts were characterized by Brunauer–Emmett–Teller (BET) gas adsorption, X-ray powder diffraction (XRD), transmission electron microscope/scanning transmission electron microscope (TEM/STEM) and energy dispersive X-ray spectroscopy (EDS). Their catalytic activity and stability were tested using the RRDE experiment.

Most studies on PGM-free catalysts for alkaline fuel cells only report the catalytic activity observed in the RRDE experiment. However, catalyst behavior can be different in the RRDE than in the single cell due to radically different conditions. Currently, a major limitation to AEMFCs is the membrane stability and ionic conductivity. Since the focus of our

work here is an exhaustive study of catalysts, cell testing was conducted with a commercial AEM (A201) and binder (AS4) provided by Tokuyama Corp and only focused on beginning of life performance. The paucity of data related to single cell AEMFC testing using PGM-free catalysts for ORR is reflected in few reports of electrode and MEA preparation methods, catalyst loadings and ionomer to catalyst ratios effects on the cell performance [32]. To gain a better understanding of the contribution of each electrode (Pt/C anode and PGM-free cathode) on the overall performance of the cell, a reference electrode was used to separate the anode and cathode polarization curves. We found a major contribution to the overpotential comes from the anode electrode at cell voltages beyond the ORR kinetic region, which we attribute to flooding of the catalyst layer.

## 2. Experimental

### 2.1. Catalyst synthesis and thermal activation

Our catalyst synthesis procedure was previously reported [33,34]. In summary, catalysts were prepared using a two-step process. In the first step, 1,2-benzenedinitrile was covalently anchored to the carbon support Black Pearls 2000 (BP2000) from Cabot Corp using diazonium-coupling chemistry. In the second step, the dried modified carbon was suspended in water and aqueous solutions of 3,5-diaminotriazole and metal acetates were added, resulting in the Metal (Me) -TriazoloPthalocyanine (TrPc) materials. The metals used in this work were Ag, Co, Cu, Fe, Ni and their bi-metallic combinations, and are outlined in supporting Table S1. A catalyst containing no metal, referred to simply as modified carbon was also synthesized as a reference.

The as-synthesized samples were heat treated at temperatures ranging from 600 °C to 1000 °C under inert atmosphere to yield the Me-TrPc catalysts [34]. For the purpose of this study, we report only characterization of the catalysts at the pyrolysis temperature for which they showed the highest ORR catalytic activity.

### 2.2. Rotating ring disk electrode experiments

Rotating ring disk electrode (RRDE) experiments were carried out using a multi-channel VMP3 potentiostat from Bio-Logic, a Pine instruments MSR rotator and RRDE electrode with a 0.2472 cm<sup>2</sup> glassy carbon disk and Pt ring (320 μm ring-disk gap, 6.25 mm and 7.92 mm ring inner and outer diameter, respectively). The RRDE collection efficiency *N* was measured experimentally and determined to be 38%. A gold counter electrode mounted in a glass tube with a frit at one end was used. A Radiometer Analytical XR400 Hg/HgO reference electrode with 1 M KOH fill solution was used.

The potential of the reference electrode versus the reversible hydrogen electrode (RHE) was determined by saturating 0.1 M KOH with hydrogen and measuring the OCV with a polycrystalline Pt working electrode. Ultra-high purity (UHP) gases from Airgas Co. were used for each experiment.

Inks were prepared using a 30 wt% Nafion<sup>®</sup> to 70 wt% catalyst ratio and methanol as solvent. Aliquots of the inks were solution-cast onto the GC disk electrode to reach loadings of 200, 400, or 600 μg<sub>PGM-free</sub> cm<sup>-2</sup> for PGM-free catalysts or 25 μg<sub>Pt</sub> cm<sup>-2</sup> for Pt/C. Catalysts were tested in aqueous 0.1 M KOH electrolyte. For each experiment, the electrolyte was deaerated for at least 30 min with nitrogen; voltammograms were collected between 1.1 and 0.1 V vs. RHE with a 10 mV s<sup>-1</sup> scan rate with the electrode static and rotating at 1600 rpm for background correction. This procedure was repeated in O<sub>2</sub>-saturated electrolyte, using 625, 900, 1225, 1600 and 2500 rpm rotation speeds. RRDE onset potentials were defined as the potential (vs. RHE) at which the ORR current density reaches a value of 50 μA cm<sup>-2</sup>. The ring electrode was held at 1.3V vs. RHE to collect any peroxide generated at the disk electrode.

Oxygen reduction reaction activity in different partial pressures of

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