

## V.F.13 PGM Free Catalysts for PEMFC

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Applications) in section 3.4.4 (Technical Challenges) of the Fuel Cell Technologies Office MYRDD Plan. The technical targets of the project are as follows.

- Volumetric catalyst activity in a membrane electrode assembly (MEA) at 0.80 V<sub>iR-free</sub>, 80°C:  $\geq 300 \text{ A cm}^{-3}$  (2020 target)
- Demonstrate performance of non-PGM catalysts prepared using CVD system with the potential to meet 6 A cm<sup>-3</sup> under rotating ring disk electrode (RRDE) at 0.8 V in acid solutions (near-term)
- Use a single step, highly scalable process to decrease the cost of producing non-PGM catalysts (near-term)
- Demonstrate a favorable 4e<sup>-</sup> reaction pathway (near term)

### FY 2015 Accomplishments

### Overall and Fiscal Year (FY) 2015 Objectives

- Synthesize nitrogen activated metal complexes on a novel nanocarbon support in a single step process that is easily scalable and market relevant with highly active, low cost non-platinum group metal (non-PGM) catalysts
- Use chemical vapor deposition (CVD) to produce nitrogen doped carbon nanotube (NCNT) catalysts with surface morphology specifically tailored to maximize oxygen reduction reaction (ORR) catalyst site density
- Use traditional non-PGM preparation techniques to identify and down-select nitrogen and carbon precursors for CVD synthesis
- Increase surface area and enhance catalyst activity by exfoliating the NCNT surface during CVD synthesis using oxidative or catalytic hydrogenation

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells (3.4.5) section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

- (A) Durability (catalyst)
- (B) Cost (catalyst)
- (C) Performance (catalyst)

### Technical Targets

Non-PGM fuel cell catalyst research in this project focuses on the DOE technical targets outlined in Table 3.4.13 (Technical Targets: Electrocatalysts for Transportation

- In situ nitrogen doping of carbon nanotubes was performed using CVD with simultaneously injected liquid and gas nitrogen containing precursors. Using pyridine as the liquid precursor, the ensuing catalyst's ORR onset potential was found to occur at 0.95 V (vs. reversible hydrogen electrode [RHE] in 0.1 M HClO<sub>4</sub>) as compared to previously reported values of 0.35 V [1]. In addition, high pyridinic nitrogen content (~50%) was measured in the catalyst using X-ray photoelectron spectroscopy (XPS).
- A significant increase in electrochemical surface area (ESA) and ORR activity was observed with increasing CVD growth temperature (750°C to 850°C). A kinetic current density maximum of 1.0 A cm<sup>-3</sup> at 0.8 V was measured for NCNTs grown at 850°C. The number of electrons transferred for the ORR was measured to be >3.8 showing a high selectivity for the 4e<sup>-</sup> reaction.
- Oxidative partial unzipping of the 750°C grown NCNTs resulted in a 2.5x increase in ORR kinetic current at 0.8 V and a 10x increase in ESA while maintaining the three dimensional architecture of the pristine carbon nanotubes (CNTs).
- Traditional synthesis techniques were used to optimize CVD precursor formulations. Diazines were identified as a promising nitrogen/carbon precursor for synthesizing electrocatalysts. XPS analysis of Fe-diazine catalysts shows uncommonly high pyridinic nitrogen content (~50%). The catalyst shows high selectivity for the 4e<sup>-</sup> ORR pathway with the number of electrons measured at >3.6.
- An amination pyrolysis for metal-free graphene-oxide electrocatalysts was demonstrated, resulting in an ESA increase of 50x and an ORR current increase of 2.5x at 0.8 V vs. RHE.



## INTRODUCTION

Reducing the high cost of the proton exchange membrane fuel cell (PEMFC) stack, which accounts for more than 50% of the total system cost, is currently a major focus of fuel cell research. The high stack cost is in large part due to the high cost of platinum catalysts which accounts for approximately half of the stack cost. This platinum-based cost component cannot be reduced through economies of scale, would likely be driven up through increased demand, and introduces geopolitical challenges. Reducing the PEMFC stack cost is typically achieved through decreasing platinum cathode loading, where slow ORR kinetics must be addressed, or by replacing platinum catalysts with non-PGM catalysts.

Eliminating platinum entirely from the cathode is the ideal solution to this problem, as it could result in the most significant reduction in stack cost; however, to date non-PGM catalysts show inferior performance compared to platinum catalysts, particularly in acidic media. The best performing non-PGM catalysts are typically composed of carbon, nitrogen, and transition metals (e.g., iron or cobalt), and usually employ a high temperature thermal treatment. The precise identity of the M-N-C catalysts' ORR site is under debate, but there are indications that the sites are composed of pyridinic or pyrrolic heterocycles coordinated through nitrogen to a transition metal, with pyridinic heterocycles showing the highest activity.

## APPROACH

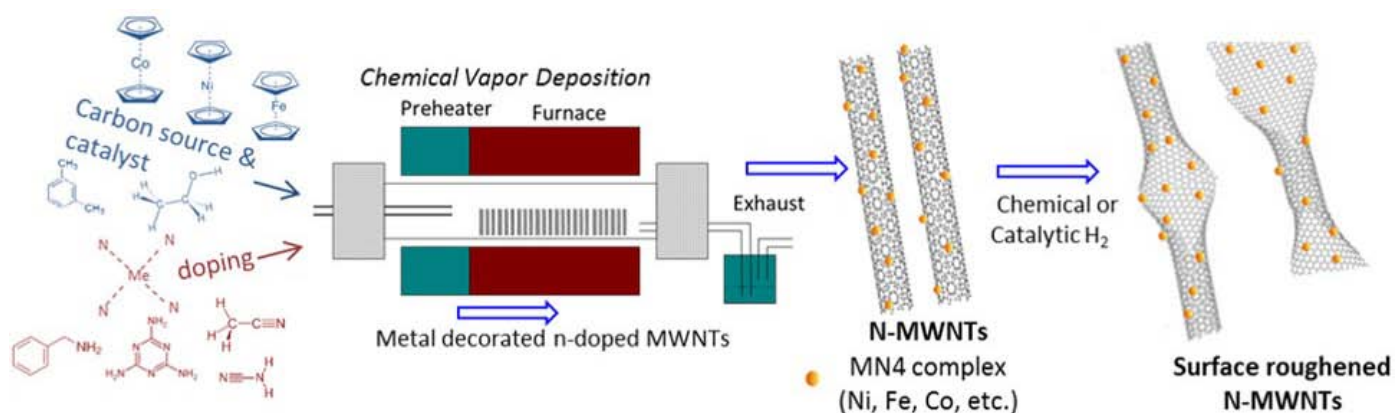
To facilitate an easily scalable and market relevant non-PGM catalyst with high ORR activity, our approach centers on the use of CVD to tailor nitrogen doped carbon nanotubes specifically designed to possess a high density of ORR catalyst sites via in situ doping and in situ surface enhancement treatments. This work differs from traditional

methods by synthesizing both catalyst and support with well controlled surface morphology in a highly scalable single step growth process instead of first creating and modifying a support through multiple process-intensive steps, which ultimately leads to poor scalability and high cost. A major benefit of our approach is maintaining economic viability without compromising performance. Current, state-of-the-art, commercial CVD production of multi-walled carbon nanotubes costs approximately \$20 per gram, with economy of scale projections estimated as final production costs as low as \$0.33 to \$1.00 per gram.

Figure 1 shows a simplified schematic that details the catalyst production process. During the production process, metal and nitrogen precursors are injected via spray pyrolysis in to the reaction zone where the carbon based catalysts deposit. It is during the growth that graphene edges are further exposed by oxidation and/or catalytic  $H_2$  opening of the NCNT structure via surface roughening.

## RESULTS

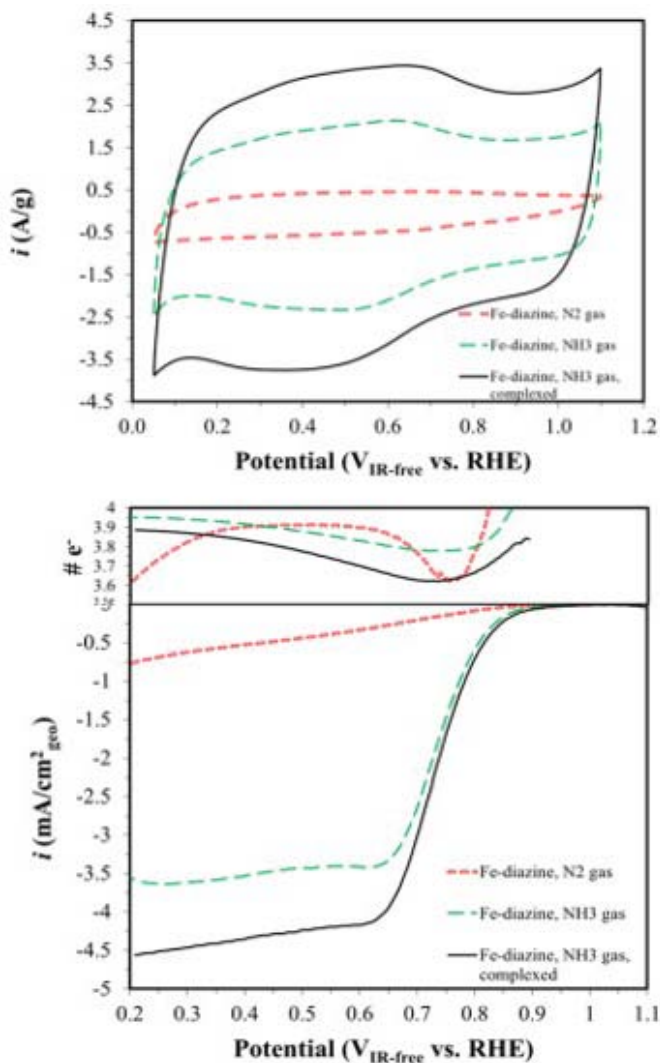
During FY 2015, our work focused on preparing and characterizing non-PGM catalysts using traditional synthesis techniques, identifying and down selecting nitrogen and carbon precursors for use in CVD synthesis, assembling and fine tuning a specialized CVD system, and preparing catalysts using CVD. Optimization and development using traditional synthesis techniques provides chemical and structural information on potential precursors that can be utilized in CVD synthesis to make highly active ORR catalysts of the Fe-N-C type. Carbon supports were combined with iron (II) acetate and nitrogen precursors which included amines (primary, secondary), nitrogen heterocycles (pyridine, bipyridine, phenanthroline, diazines, polyazines), urea, selenourea, metal organic framework synthesis templates (polyaniline, polyethylene amine), and macrocycles (functionalized phthalocyanines). Of the screened catalysts, the Fe-diazine catalysts exhibited the highest kinetic current



**FIGURE 1.** Simplified schematic of the one step process for the production of ORR active catalysts

densities (Figure 2), with higher current densities measured following a post synthesis amination pyrolysis. XPS analysis shows the highly active Fe-diazine electrocatalyst has a high atomic percent of pyridinic nitrogen (47.4–51.9%).

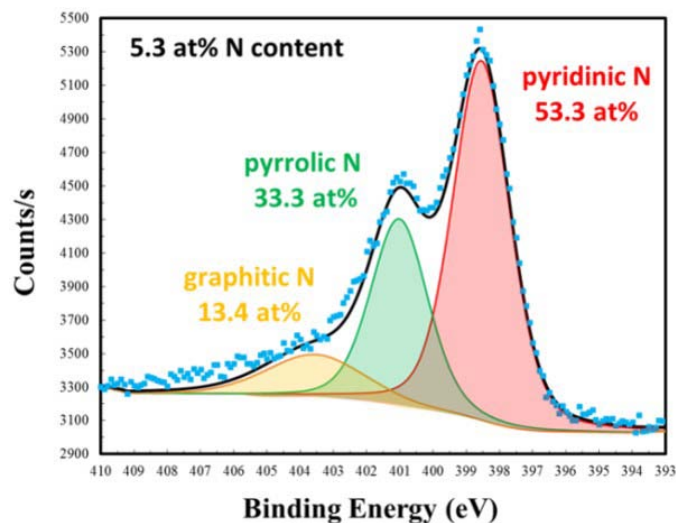
In parallel with the traditional synthesis work, the CVD system was assembled and fine-tuned to produce carbon nanotubes using nitrogen and carbon precursors identified through traditional synthesis. Analysis of nanotubes prepared by CVD show excellent performance for the ORR, with initial trends indicating higher performance is achievable once optimization is completed. A major accomplishment during 2015 includes synthesizing catalysts with a one-step CVD growth method that incorporates a high surface concentration of nitrogen (Figure 3), about 5 at%, of which more than 50% is pyridinic. It is noteworthy that there are only a handful of non-PGM catalysts possessing such a high



**FIGURE 2.** Fe-diazine catalyst before and after amination pyrolysis. (top) CV shows ESA and (bottom) RRDE disc current shows ORR activity and number of electron transferred.

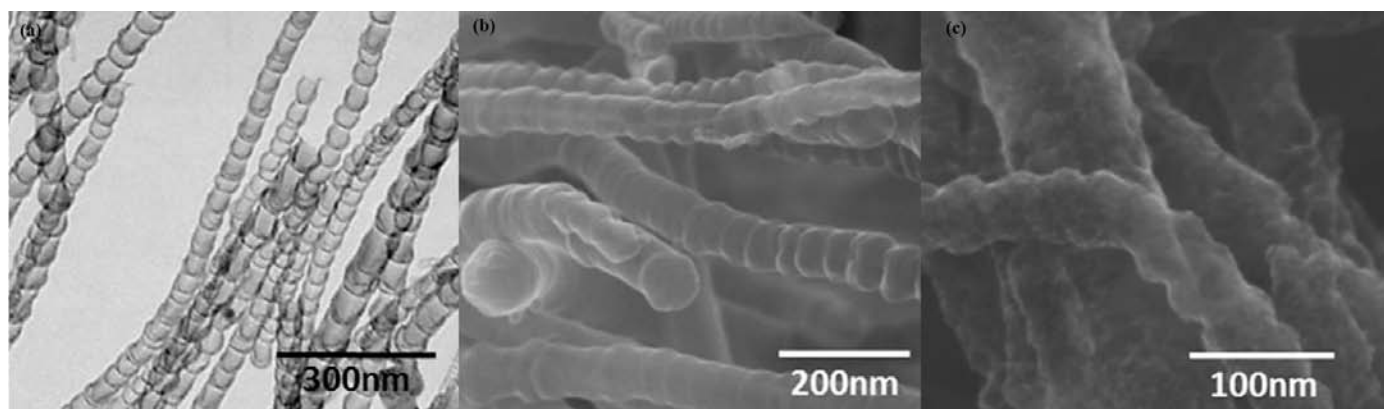
atomic percent of pyridinic nitrogen, and none produced in a single step synthesis.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 4a and 4b) show the typical compartmentalized “bamboo”-like morphology of the nitrogen-doped CNTs. The NCNT catalyst grown at 750°C was treated with a mild oxidizer resulting in surface roughening and partial opening of the CNTs, observable by SEM as shown in Figure 4c. Electrochemical analysis of the catalysts prepared via CVD shows high performance in the ORR. As shown in Figure 5 (left), the onset potential for the ORR is around 0.95 V vs. RHE. Catalyst activity increases as a function of pyrolysis temperature. This trend suggests that catalysts with higher activity can be reasonably expected with further optimization of the method. Initial cyclic voltammetry (CV) experiments (cycling 0.05 V to 1.1 V) show unusually high peak current/ESA ratios for the redox couple at 856 mV (Figure 5, left-inset), believed to be of the  $\text{Fe}^{\text{II/III}}\text{N}_x$  ( $x = 2$  or 4) type, which is stable even under acidic conditions (0.1 M  $\text{HClO}_4$ ). The stability of this moiety is attributed to the formation of stable coordination complexes where pyridinic nitrogen coordinates to  $\text{Fe}^{\text{II}}$  and the pyridine  $\pi$  orbital provides additional stabilization through the  $\text{sp}^2$  hybridized carbon support. The surface roughening treatment results in a substantial increase in ESA which can be observed in the CV (Figure 5, right-inset) and increases the number of available active sites resulting in an ORR activity enhancement, shown in Figure 5 (right). Currently, surface roughening treatments for optimizing the higher activity 850°C N-doped CNT samples are underway. The increased onset potential for the ORR at higher growth temperatures as seen in linear sweep voltammetry (LSV) measurements in conjunction with the increased ESA achieved through surface

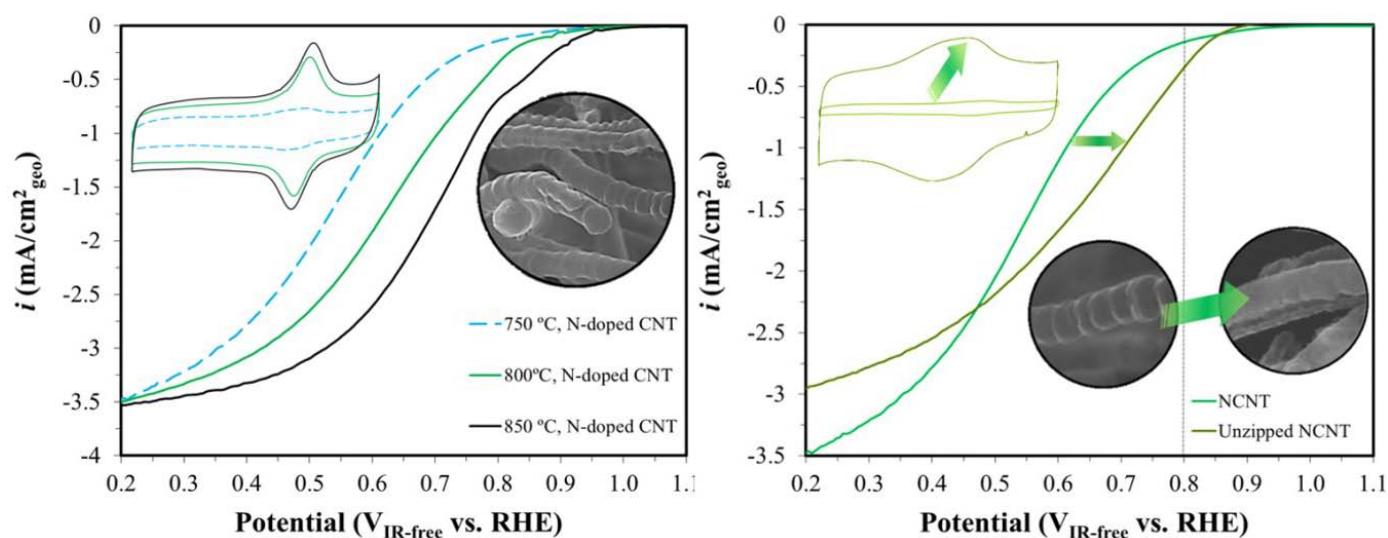


**FIGURE 3.** XPS N1s spectra of non-PGM catalyst grown in the CVD setup, image shows high pyridinic surface nitrogen





**FIGURE 4.** (a) TEM and (b) SEM of as grown bamboo-like NCNTs, (c) partially unzipped NCNTs exhibiting surfacing exfoliation with graphene edges



**FIGURE 5.** (left-inset) CV demonstrates high current/ESA redox couple at ~850 mV. (left) LSV measured ORR activity for the CVD-grown catalysts. (right-inset) CV demonstrates electrochemical active surface area enhancement achieved through chemical roughening methods. (right) ORR activity comparison for the CVD prepared catalyst and after surface roughened catalyst. SEM images show the typical morphology of the tested catalysts.

roughening/unzipping treatments both indicate that further optimization holds potential for producing higher activity catalysts and trends that will approach the DOE performance target.

## CONCLUSIONS AND FUTURE DIRECTIONS

- We established a novel non-PGM catalyst production process based on CVD that is highly scalable, economically viable, and produces an active catalyst for the ORR with a high density of catalyst sites and high selectivity for the  $4e^-$  reaction ( $\# e^-$  transferred  $>3.8$ ).
- Analysis of nanotubes prepared by CVD show excellent performance for the ORR, with initial trends indicating higher performance is achievable once optimization is completed.
- We will continue development of novel CVD growth mechanisms that can accomplish the following.
  - Increase surface area and alter active site morphology through mild surface roughening or opening of nanotubes through in situ gaseous or ex situ mild chemical treatments
  - Characterize the effect of higher temperatures and different nitrogen precursors on active site morphologies, oxidation states, and electrochemically active surface area
  - Incorporate novel non-PGM bimetallic catalysts using in situ and ex situ synthesis techniques

- We will study the high potential redox couple at 850 mV and determine if there is a correlation with the ORR onset potential or the kinetic current using the high peak current/ESA ratio as a handle.

## REFERENCES

1. H. Drew, M. Doralice, and C. Zhongwei, *J. Phys. Chem. C*, 114 (2010) 21982–21988.