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PGM Free Catalysts for PEMFC

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Project ID

FC119

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Overview

Timeline

- Project Start Date: July 2014
- Project End Date: 9/30/2015
- Percent Complete: 60%

Barriers

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

Budget

- Total Project Budget: \$250k
 - DOE Share: \$250k
 - Contractor Share: \$0
- Total DOE Funds Spent*: \$194k

* As of 3/31/15

Partners/Collaborators

- Ballard Power Systems
- NanoTechLabs
- Greenway Energy

Relevance

Project Objectives

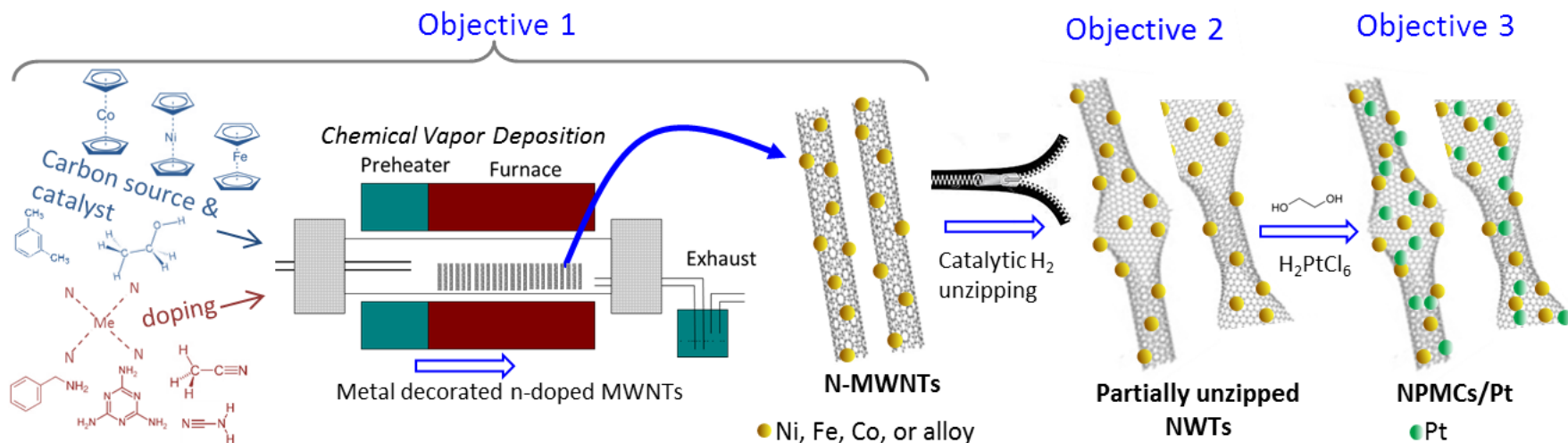
- To co-synthesize highly active, low-cost non-precious metal catalysts for the oxygen reduction reaction by doping nitrogen-activated metal complexes into a novel nano-carbon support in a single-step process that is easily scalable and market relevant.

<u>Characteristic</u>	<u>Units</u>	<u>Target</u>
Non-Pt Catalyst Activity per volume of supported catalyst	A / cm ³ @ 800 mV _{iR-free}	≥ 300

Technical Targets

- **Performance**-Demonstrate performance of non-PGM catalyst prepared using CVD system to meet 6 A/cm³ in RRDE at 0.8 V in acid solutions
- **Cost**-Use single step, highly scalable process to decrease cost production of non-PGM catalysts
- **Durability**-Demonstrate favorable 4e⁻ reaction pathway

Approach



Traditional Synthesis

- Solution synthesis
- Heat Treatment

Chemical Vapor Deposition (CVD)

- One step synthesis
- In-situ surface modification
- Heat Treatment

Characterization

- RRDE, XPS, FTIR, BET



Approach: Project Milestones

<u>Date</u>	<u>Milestone</u>	<u>Status</u>
10/1/2014	Down select on non-PGM catalyst materials and precursors needed for the synthesis	Complete
1/6/15	Establish performance baseline of non-PGM catalyst through traditional synthesis processes through RRDE testing at RT	Complete, ongoing
5/31/15	Compare performance of selected surface modified non-PGM catalysts with un-modified non-PGM catalysts	On schedule
9/15/15	Demonstrate performance of non-PGM catalyst prepared using CVD system using the selected different precursors with the potential to meet 6 A/cm ³ in RRDE at 0.8 V vs RHE in acidic conditions	On schedule



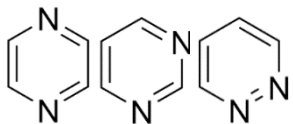
Accomplishments: Traditional Synthesis

Carboxyl-functionalized carbon source

Oxidized carbon black

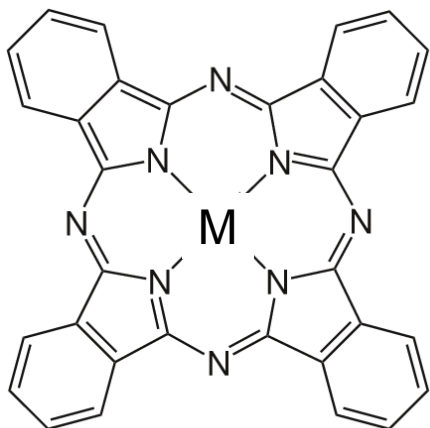


Nitrogen containing heterocyclic building blocks



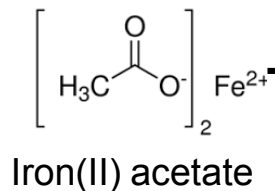
diazines,
poly-azines

amines



Macrocycles

Iron(II) source

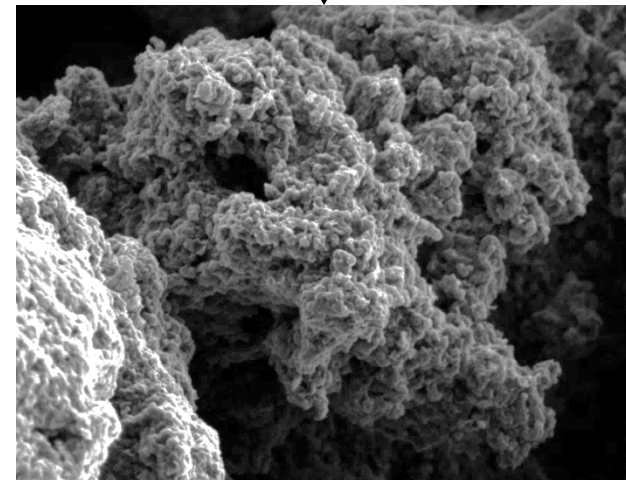


Solution Synthesis
 Δ , 70 - 100 °C

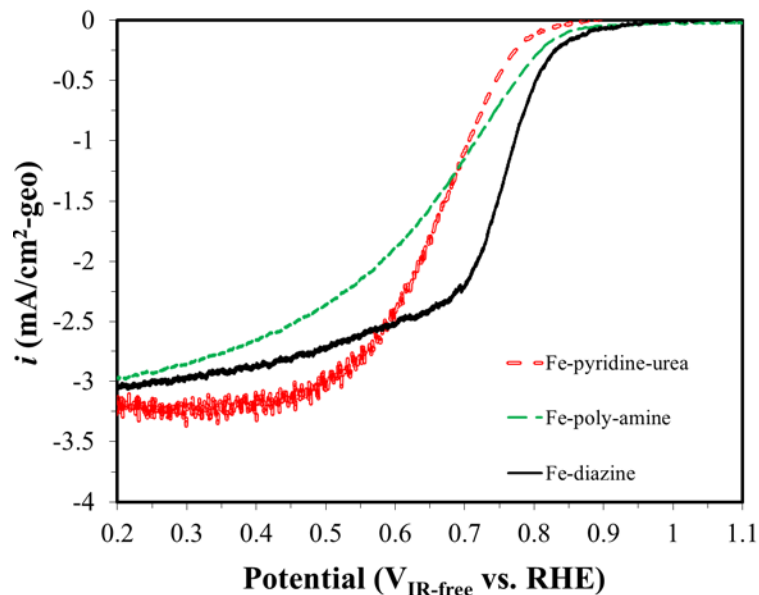
Fe-N-carbon precursor

Pyrolysis
 Δ , 800 - 900 °C

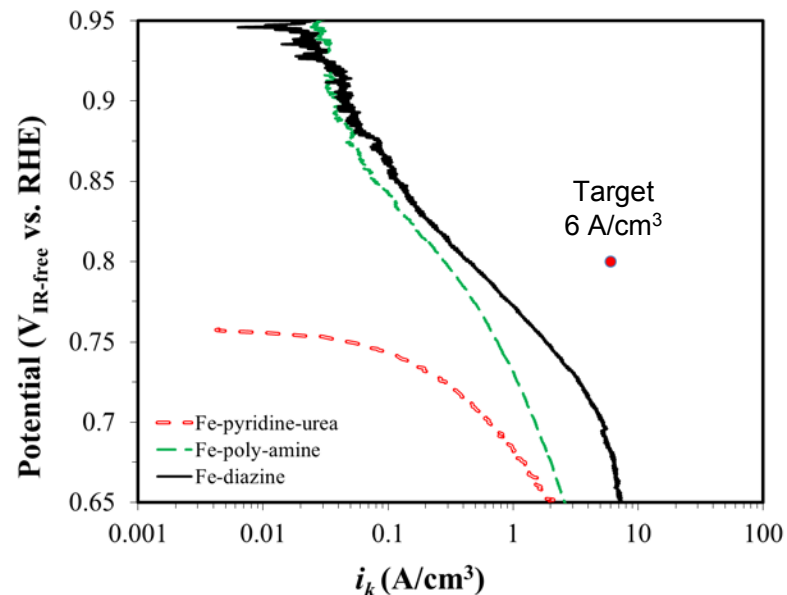
Fe-N-carbon black catalyst



Accomplishments: Traditional Synthesis (initial screening)



- RDE evaluation of different precursors on carbon black



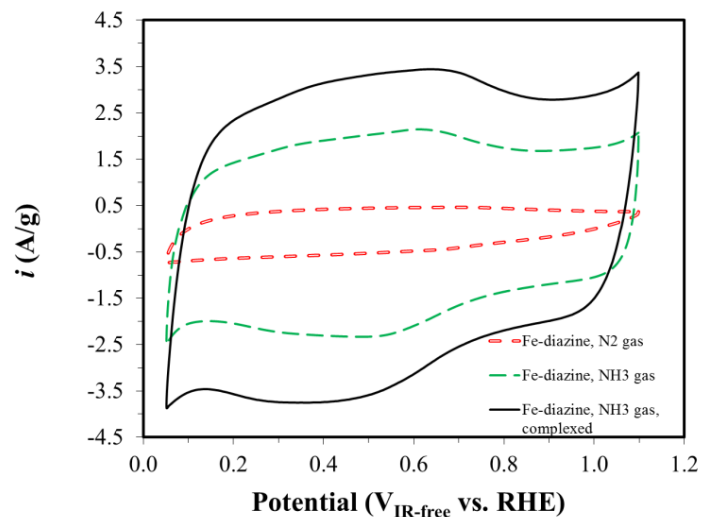
- The highest kinetic current densities of the screened procedures was obtained for Fe-diazine complex

Fe-diazine complex was selected for the optimization of the synthesis reaction and thermal treatments

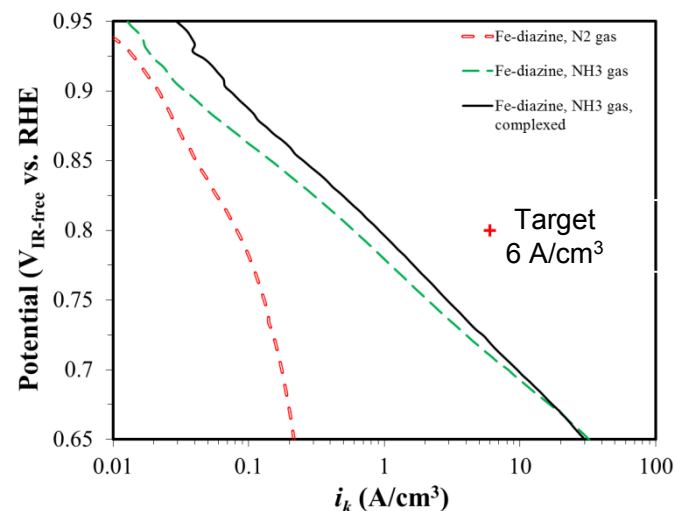
CV/RRDE: 0.1 M HClO₄; 900 rpm; 25°C;
RHE reference electrode; graphite counter
electrode; 20mV/s, 600 μg/cm²



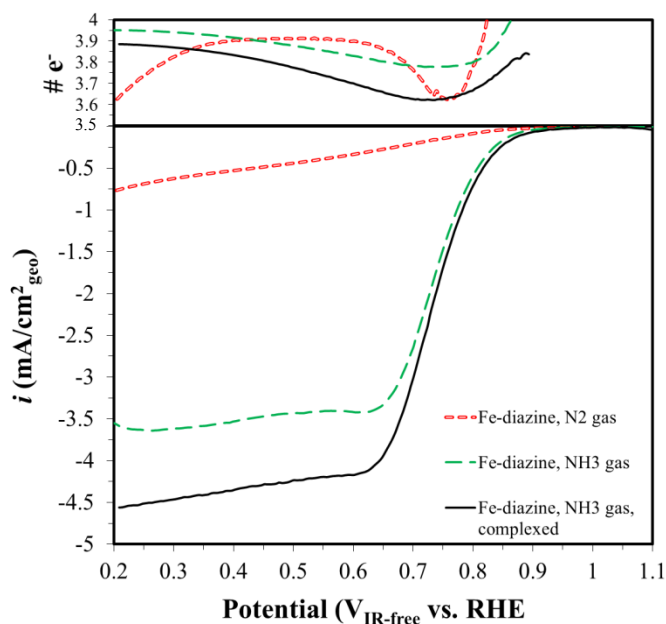
Accomplishments: Traditional Synthesis (optimized synthesis)



- CV shows the effect of heat treatment conditions on the electrochemically accessible surface area
- After pyrolysis of complexed catalyst, higher surface electrochemical surface area is obtained



- Kinetic current densities 0.93 A/cm^2 have been obtained at the optimized synthesis conditions



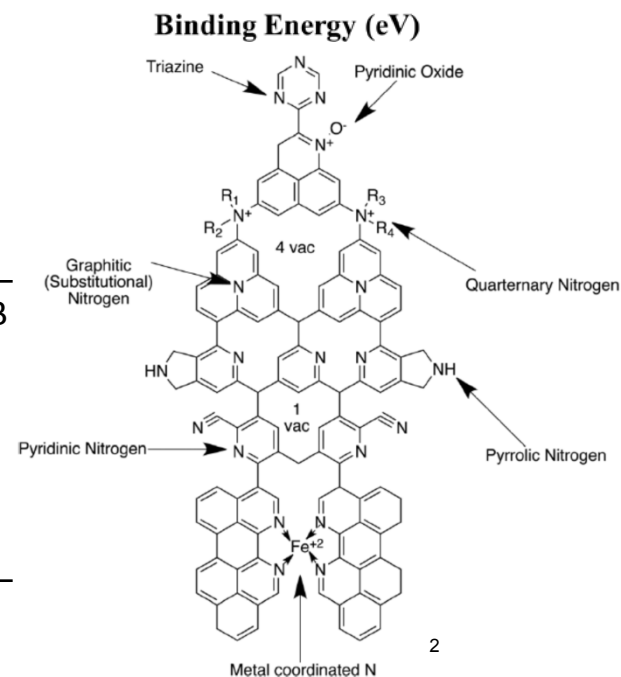
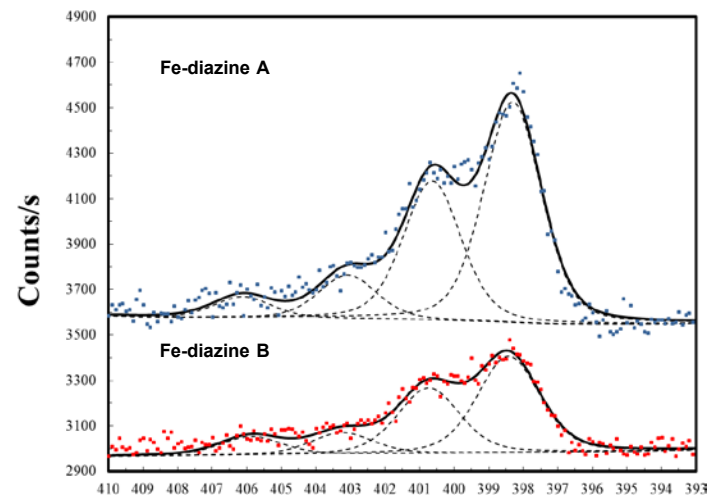
- Exposure of functional groups by the larger surface area and activation by the heat treatment results in higher ORR activity
- Ring currents shows high selectivity toward the $4 e^-$ reaction.

With optimized synthesis condition, Fe-diazine complex results in high activity/high surface area catalysts with low peroxide formation.
(2x initial screening current density)

CV/RRDE: 0.1 M HClO_4 ; 900 rpm; 25°C ;
 RHE reference electrode; graphite counter electrode; 20mV/s, $600 \mu\text{g/cm}^2$

Accomplishments: Traditional Synthesis

- X-ray photoelectron spectroscopy (XPS) used to determine surface composition.
- Atomic and weight percent of surface species were determined for C, O, N, and Fe.
- Nitrogen functionality determined
- To obtain a functional iron-based ORR catalyst, nitrogen atoms on the carbon support have to be of the pyridinic type¹ and must be coordinated to iron.
- Traditional synthesis methods results in the preferential formation of N-pyridinic (51.9, 47.7 %).
- Iron loading reduction (2→1 wt%) studied performed without loss of performance



Element	Fe-diazine A		Fe-diazine B		N-functionality	Fe-diazine A	Fe-diazine B
	At%	Wt%	At%	Wt%		At%	At%
C	91.5	88.2	93.3	90.8	Pyridinic	51.9	47.7
O	4.7	6.1	4.6	6.0	Pyrrolic	32.9	32.5
N	3.3	3.7	1.9	2.1	Graphitic	10.3	10.7
Fe	0.5	2.1	0.2	1.1	Pyridinic N ⁺ O ⁻	5.0	9.1

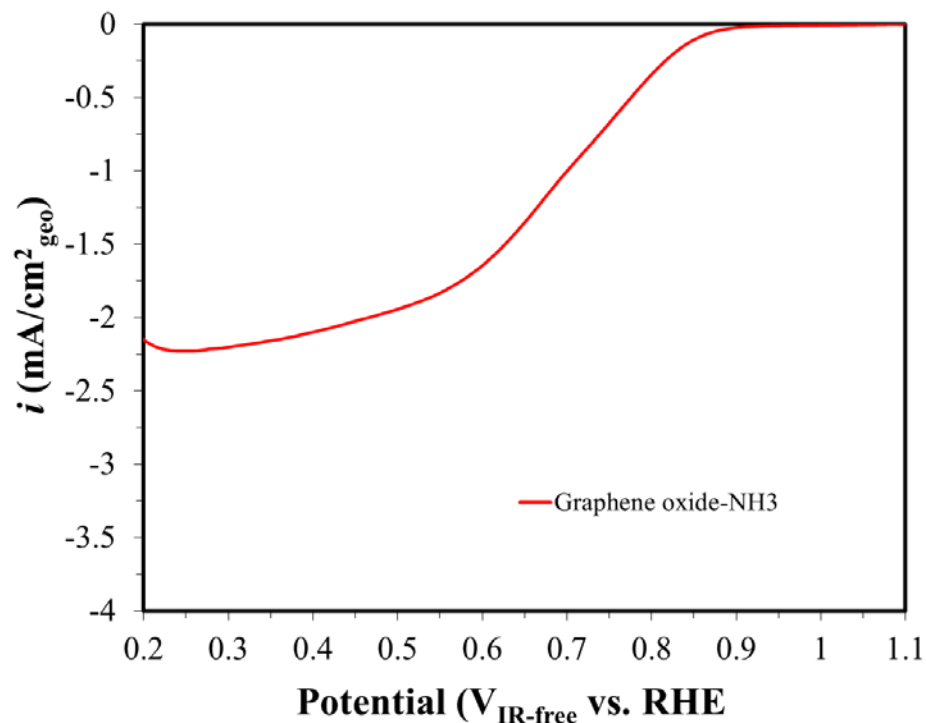
¹Faubert, G.; et al., Electrochim. Acta, 44 (1999) 2589

²Wood, KN, et al., Energy Environ. Sci., 7 (2014) 1212

Accomplishments: Metal-free Catalysts

The use of metal free carbon was evaluated, by heat treating oxidized graphene (GO)

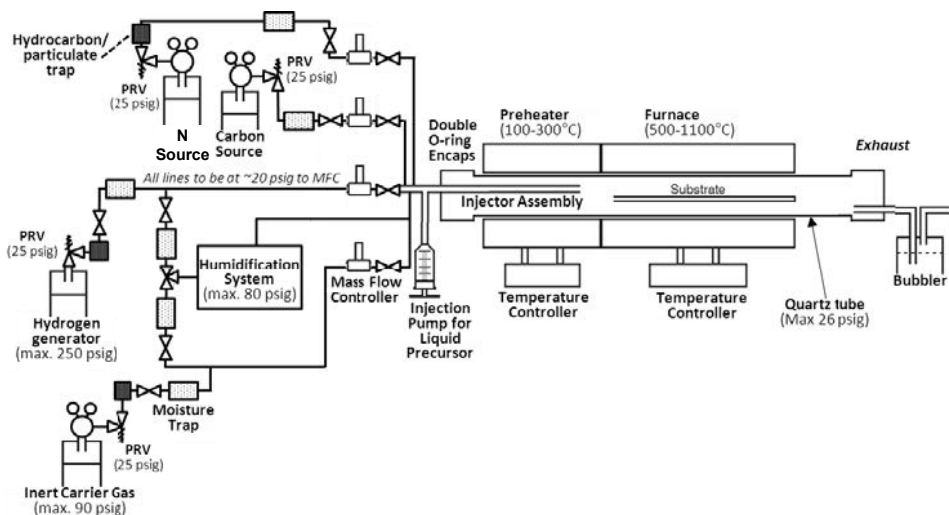
- RDE evaluation of heat-treatment on graphene oxide
- GO was selected in order to provide sites where the NH_3 can attack and dope the carbon
- The effects of the ammonia treatment results in significant currents at 0.8 V even in the absence of metal
- Kinetic current densities 0.6 A/cm^3 have been obtained at the conditions



CV/RRDE: 0.1 M HClO_4 ; 900 rpm; 25°C;
RHE reference electrode; graphite counter
electrode; 20mV/s, 600 $\mu\text{g/cm}^2$

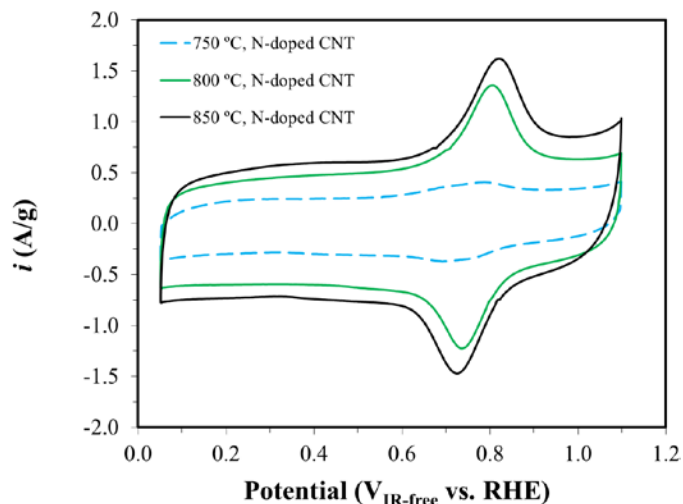
Accomplishments: CVD Synthesis

Schematic and picture of CVD system built at SRNL to handle multi-gas mixtures.

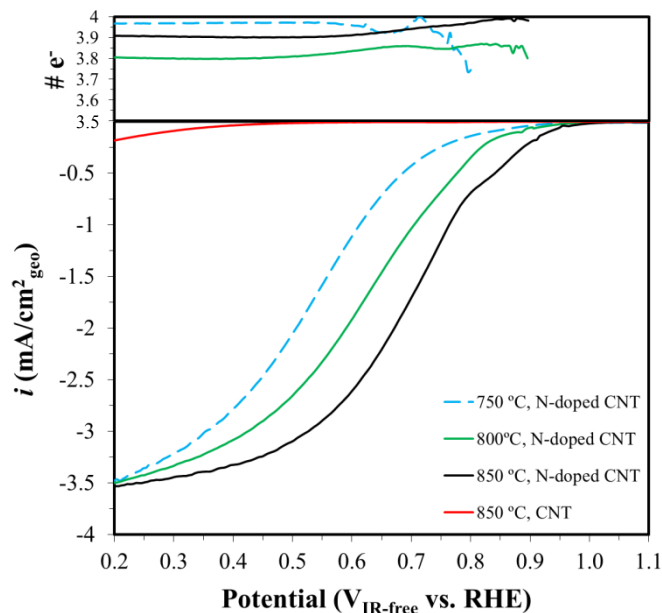


- Carbon source and catalyst is injected and vaporized in pre-heater and carried into the reactor furnace. The nanomaterials grow *in-situ* inside the furnace during spray pyrolysis of the precursor.
- The CVD system is outfitted with an ultraclean gaseous atmosphere and capabilities for water-assisted growth
 - Allows complete catalyst synthesis in 5-120 minutes depending on conditions
- We began growth using n-doping precursors in different gas atmospheres.

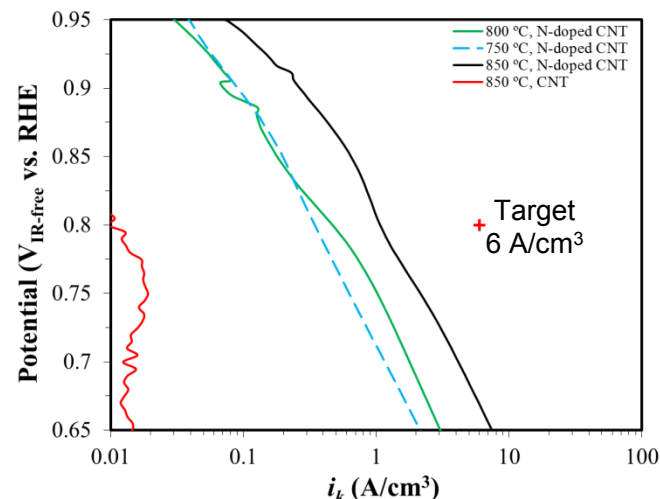
Accomplishments: CVD Synthesis



- CV shows the effect of growth on the electrochemical available surface area as well as the functional groups
- Sample shows high $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple
- Lower electrochemical surface area is observed than in the traditional synthesis



- Higher available surface area and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple results in higher ORR activity
- Lower ring currents are observed than in the traditional synthesis



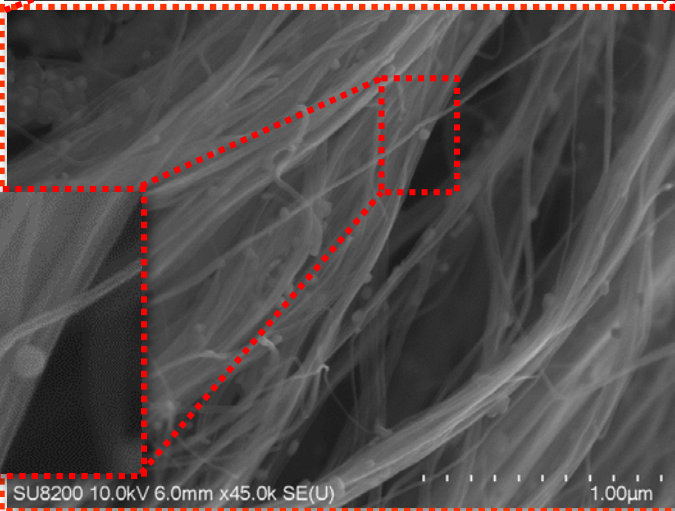
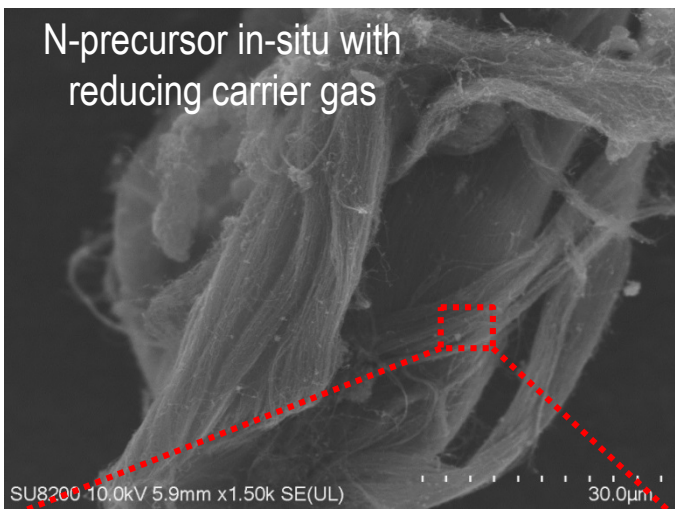
- Kinetic current densities 1.0 A/cm^2 have been obtained

High performance have been obtained, though low surface area was observed

CV/RRDE: 0.1 M HClO_4 ; 900 rpm; 25°C ; RHE reference electrode; graphite counter electrode; 20mV/s , $600 \mu\text{g/cm}^2$

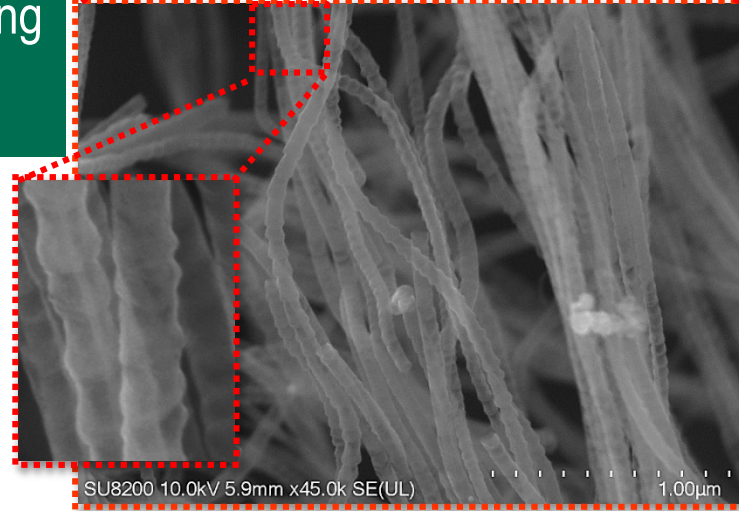
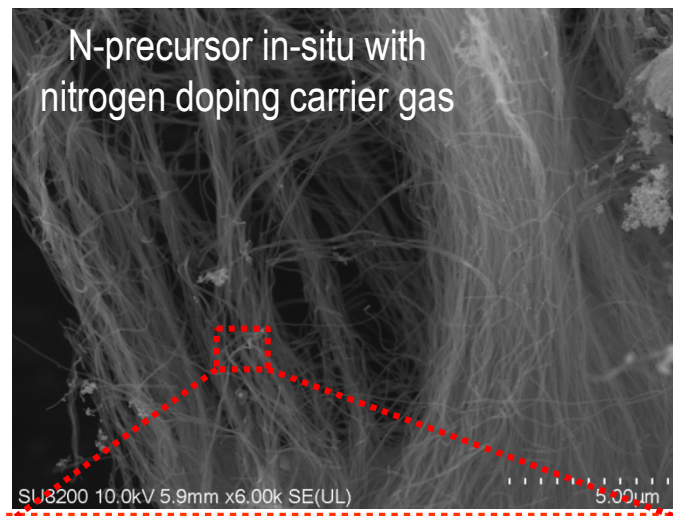
Accomplishments: CVD Synthesis

N-precursor in-situ with
reducing carrier gas



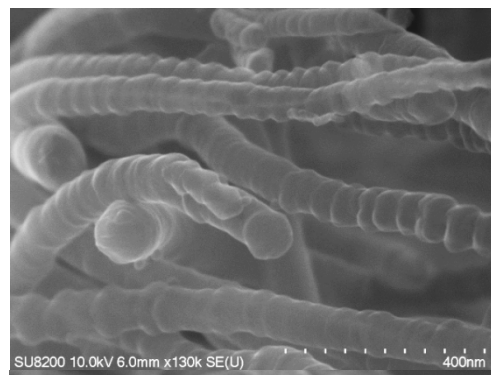
Nitrogen doping gas
needed to form
defects and N-doping
on the nanotube

N-precursor in-situ with
nitrogen doping carrier gas

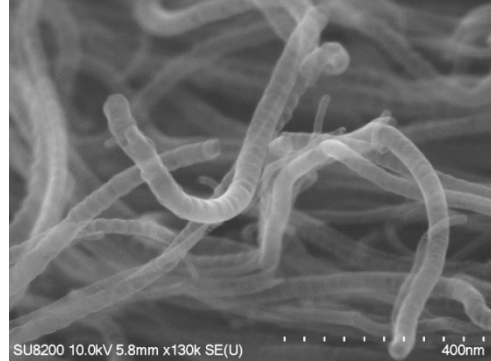


Accomplishments: CVD Synthesis

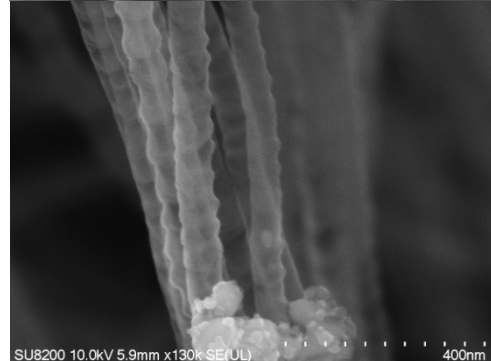
750 °C



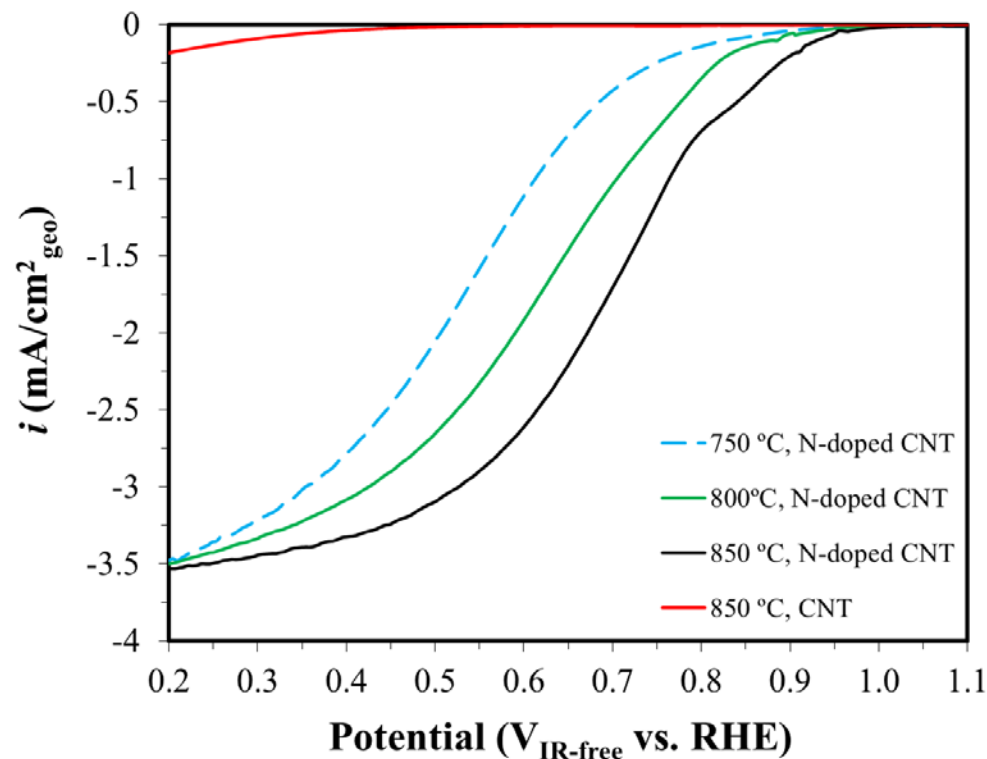
800 °C



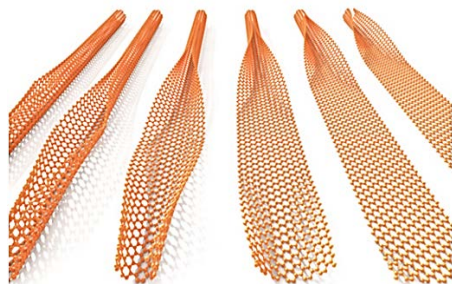
850 °C



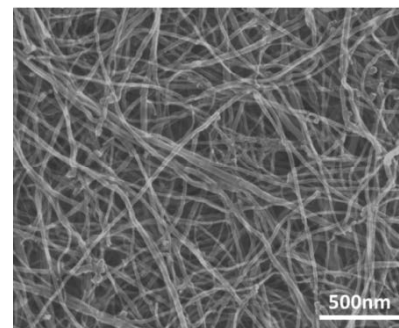
- Morphologically, the different samples look similar
- The electrochemical performance is higher at the higher synthesis temperatures
- XPS will be performed to determine surface composition



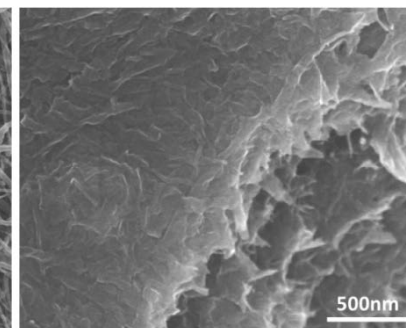
Accomplishments: CVD Synthesis



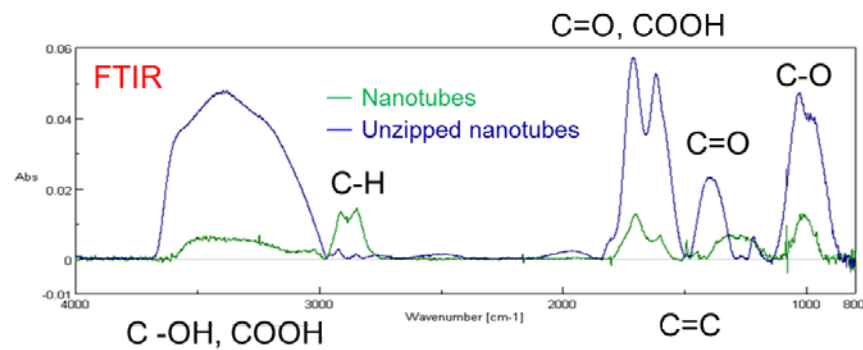
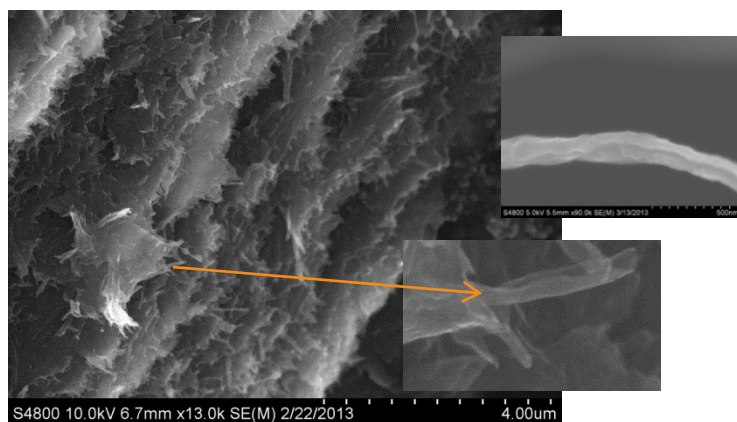
C-grade MWNTs



Unzipped C-grade MWNTs



Buckynanor surface

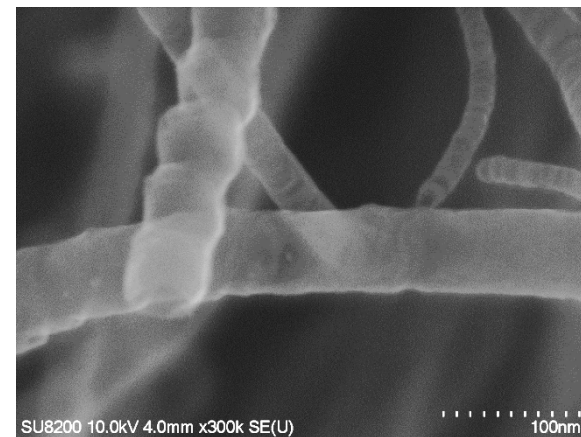
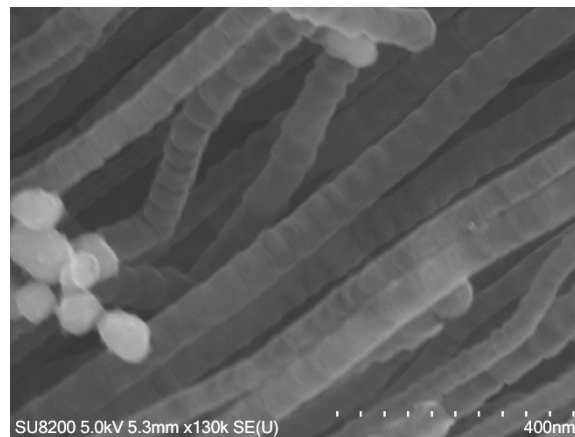


- Different surface modification methods are being explored as means to unlock active sites and improve activity
- Chemical oxidation has been used in the past to open or “unzip” the CNTs
 - This results in graphene sheets that stack easily and therefore are mass transfer limited
- Mild oxidation is being performed as well as in-situ “unzipping” during growth

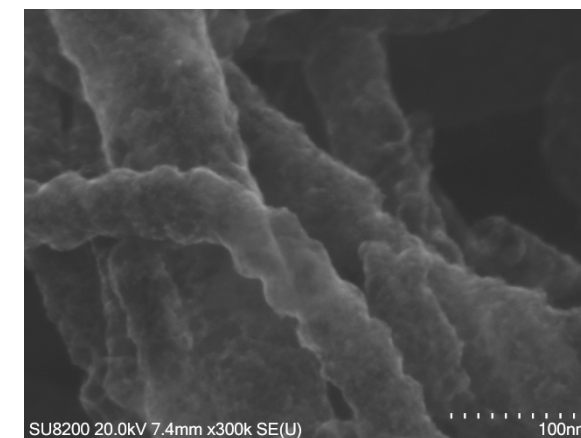
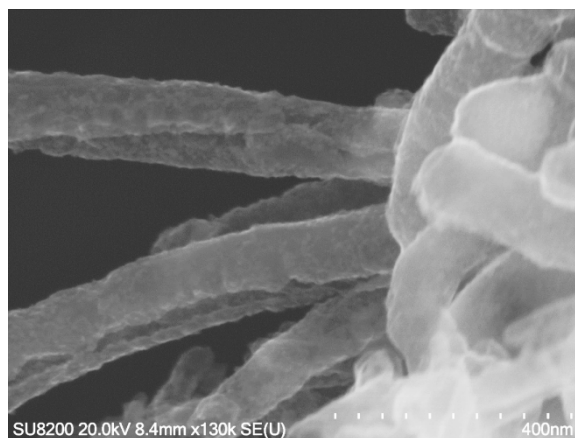


Accomplishments: CVD Synthesis

As prepared



After mild
oxidation



- Using a mild chemical unzipping method we are able to partially open the surface of the CNT as well as exfoliate and roughen the surface of the tube
- This maintains the surface morphology, that allows the tube to form 3D structures when incorporated in the electrode
- The oxidized tube can then be further processed in order to decrease the oxygen content by replacing it with active groups and improve its stability

Reviewer Comments

- This project was not reviewed last year.



Collaborations

- SRNL is working with OEMs as well as small business partners specializing in nanomaterials synthesis and characterization that can help to rapidly move technologies developed under this project to market:
- Ballard Power Systems
 - Provide guidance on the commercial viability of catalyst production processes and fuel cell products based on the nanotube NPMC catalysts
 - Test promising catalyst samples
- NanoTechLabs
 - Carbon nanomaterial provider
 - Provide guidance on commercial scalability of n-doped nanotube production
 - Test the feasibility of the developed recipes in commercial production furnaces
- Greenway Energy
 - Characterization of traditional and CVD electrocatalysts
 - Synthesis of traditional catalysts

Remaining Challenges and Barriers

Activity

- Increase electrocatalyst activity by varying precursors, processing conditions, post-treatments, and dopants
- The effect of varying relative amount of pyridinic and pyrrolic nitrogen will be explored more in depth along with the impact on doping with metal catalysts

Durability

- Increase the durability of catalysts to degradation due to elevated electrochemical potentials and aggressive fuel cell operating conditions
- Ensure that electrocatalysts cannot cause degradation to membranes or other cell components during operation due to leaching of metals and formation of peroxides

Cost

- Cost reductions will be demonstrated through the use of CVD synthesis methods
- The ability to reduce the cost of electrocatalyst synthesis through CVD growth of electrocatalysts will be demonstrated through techno-economic modeling

Proposed Future Work

- Continue development of novel CVD growth mechanisms that can:
 - Increase surface area and alter active site morphology through mild 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
- Utilize novel carbon nanomaterials as supports for catalysts synthesized using traditional synthesis techniques
- Explore the use of novel non-PGM bi-metallic catalysts incorporated using in-situ and ex-situ synthesis techniques
- Provide materials to project partners for evaluation and comparison with state-of-the-art materials

Summary

- Established performance baselines for non-PGM electrocatalysts through traditional synthesis processes using RRDE testing
- Screened nitrogen precursors and identified diazines as forming nitrogen groups that have over 50% pyridinic nitrogen
- Optimized the synthesis of electrocatalysts using diazines to increase the number of electrons to >3.6
- Demonstrated metal-free graphene-oxide electrocatalysts with significant currents at 0.8 V
- Chemical opening methods for nanomaterials has been developed to increase available surface area while maintaining the overall nanotube structure
- Initiated synthesis and testing of in-situ nitrogen doped carbon nanotubes using nitrogen containing liquid precursors and demonstrated >3.8 electron transfer in ORR and high current densities at 0.8 V