

# Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts



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# Objectives

Develop cost-effective, reliable, durable fuel cells for portable power applications (e.g., cell phones, computers, etc.) that meet all DOE targets.

<b>Table 3.4.7 Technical Targets: Consumer Electronics (sub-Watt to 50-Watt)</b>				
<b>Characteristic</b>	<b>Units</b>	<b>2005 Status<sup>a, b</sup></b>	<b>2006</b>	<b>2010</b>
Specific power	W / kg	20	30	100
Power density	W / L	20	30	100
Energy density	Wh / L	300	500	1,000
Cost	\$ / W	40 <sup>c</sup>	5	3
Lifetime	hours	>500	1,000	5,000

Note that the energy density (Wh/L), volumetric (W/L), and specific power (W/kg) all depend on knowing the weight and volume of the entire DMFC system as well as the volume and concentration of fuel, which are system specific (power application and manufacturer dependent). In our model study the surface power density levels on HOPG will allow for indirect evaluation of our system to DOE's energy density and power density targets.

# Technical Barriers

**Performance:** Methanol oxidation reaction (MOR) on the anode, rather than the ORR on cathode, that limits the performance of DMFCs. (Improving the catalytic activity of the anode for MOR will help achieve a high specific density (30- 60mW/cm<sup>2</sup>) for HOPG and will allow us to indirectly meet DOE's energy density and power density targets)

**Durability:** Current state of the art (SOA) is  $\approx$ 1500 hrs, must improve to 5000 hrs. (We expect the unique stabilization of Pt nanocatalyst observed in the Pt/N-doped HOPG system will translate to the PtRu system and improve DMFC's durability)

**Cost:** Current cost  $\approx$  \$38/W, must achieve \$3/W. To reduce cost, catalyst activity must be increased by  $>13x$  of current SOA system with lower catalyst loading. (In our preliminary work, we demonstrated a 52X increase in mass activity for MOR on the Pt/N doped-HOPG our work centers on translating that improvement to PtRu)

# Premise:

Improve the catalytic activity and durability of the anode for the MOR via optimized catalyst-support interactions that substantially improve the activity, selectivity, and durability of PtRu-carbon based substrates

## NOVEL APPROACH:

Utilize ion implantation to change the surface chemistry of carbon substrates without altering bulk properties.

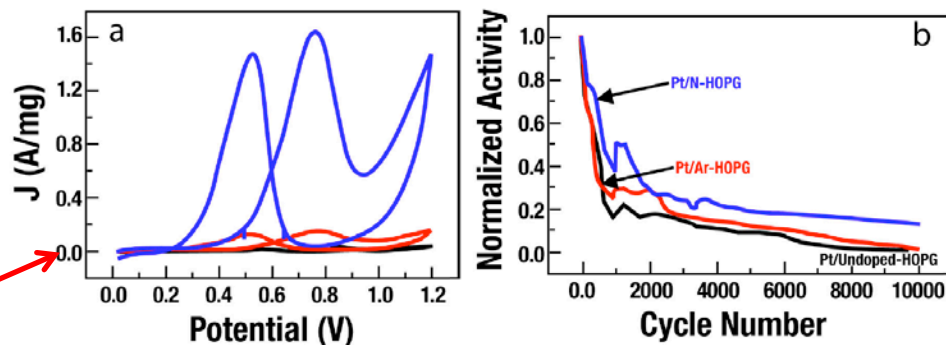
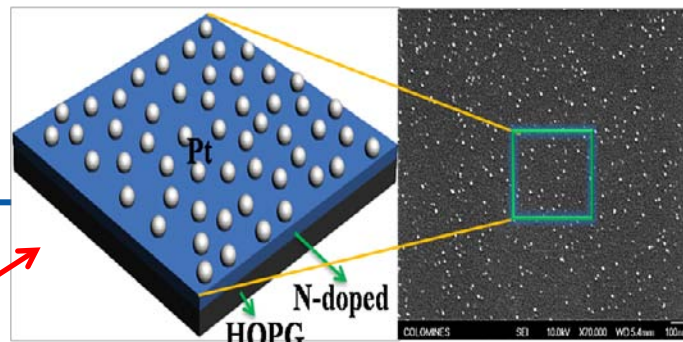
Model System-HOPG. Previous results for Pt

- N-doped HOPG showed 52X higher in mass activity for MOR compared to undoped HOPG

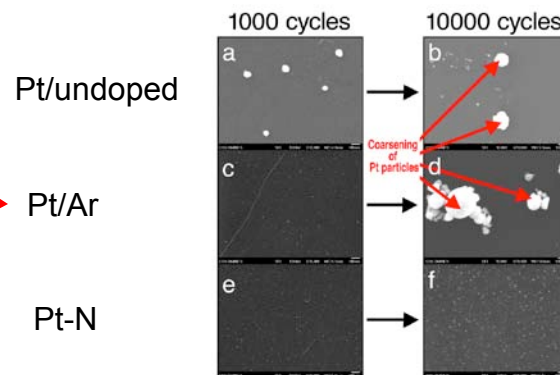
- N doping promoted Pt nanoparticle dispersion, yielding significantly smaller average Pt particle size (ca. 2 nm) and a narrower Pt particle size distribution (2-7 nm) compared to the undoped sample (3 – 35 nm).

- N doping improved durability of system with minimal aggregation/coarsening of particles.

Yingke Zhou, Robert Pasquarelli, Timothy Holme, Joe Berry, David Ginley and Ryan O'Hayre, *J Mater. Chem.* Published on-line July 2009.

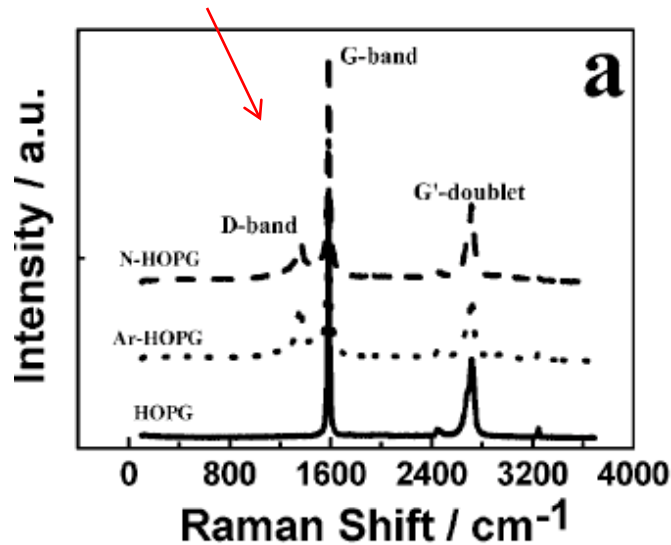


(a) Mass activity (A/mg) of methanol oxidation (MOR) on Pt/undoped, Pt/Ar-, and Pt/N-HOPG, at room temperature (scan rate = 50 mV/s; Reference electrode = Ag/AgCl); (b) MOR peak current density (activity) normalized against first cycle activity as a function of cycle number. These data show that N-doped Pt has enhanced catalytic activity and durability for MOR.

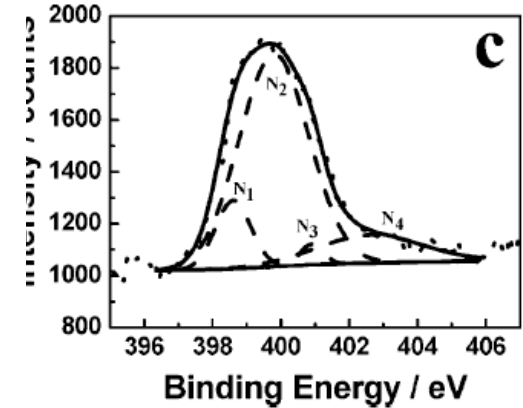
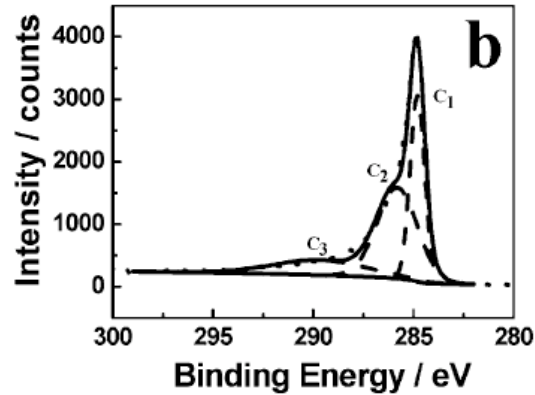


# Approach (surface)

N-doped samples, ion implanted using a non-mass-separated nitrogen-ion beam ( $N_2$  and  $N$  ions) at room temperature at an estimated ion dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup>. Implanted at an angle to minimize channeling.



Raman D-band increase illustrates more disorder on HOPG surface



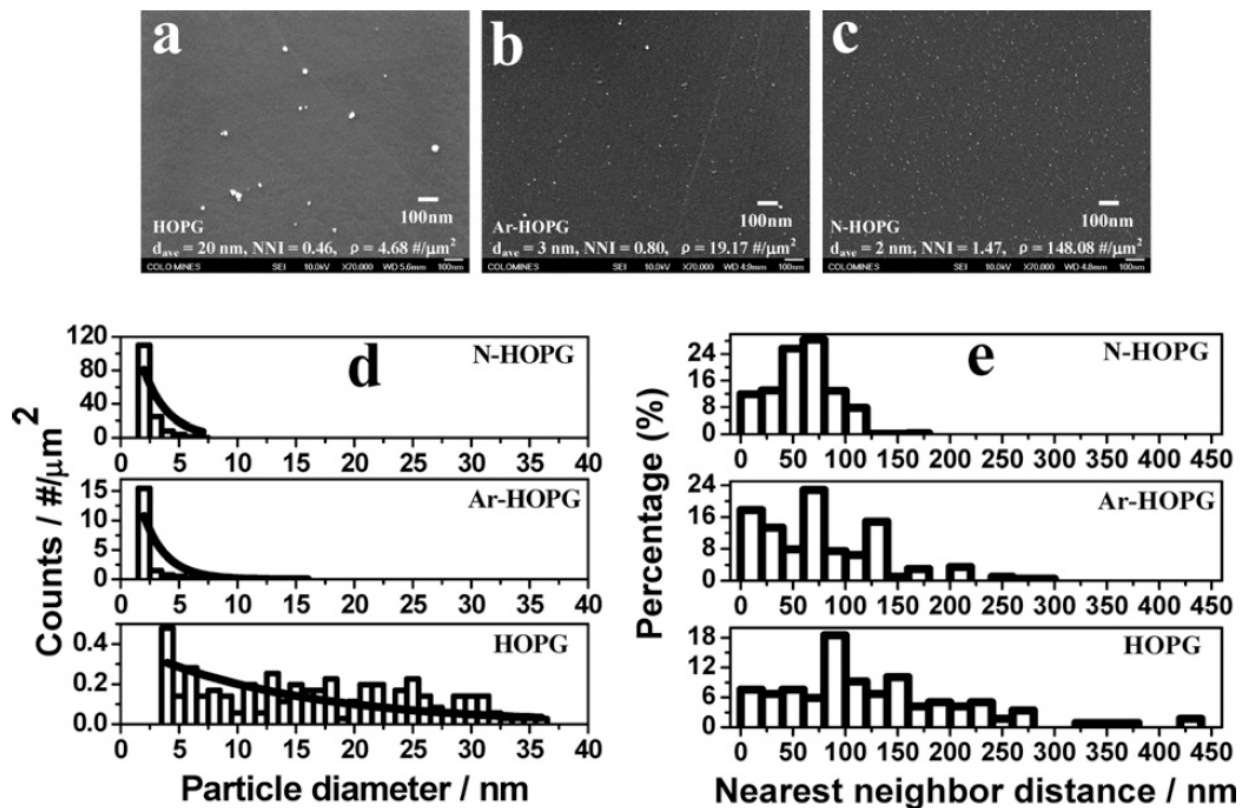
XPS data indicate formation of C-N interactions upon nitrogen implantation.

Table 1 Comparison and component assignments of the XPS results

	Index	Binding energy/eV	%	Assignment
N-HOPG	N <sub>1</sub>	398.6	13.4	Pyridinic
	N <sub>2</sub>	399.8	38.7	Pyrrolic
	N <sub>3</sub>	400.9	35.8	Quaternary coordination
	N <sub>4</sub>	402.6	12.1	Pyridine-N-oxide
HOPG	C <sub>1</sub>	284.8	26.9	Graphitic
	C <sub>2</sub>	285.8	32.7	Sub-nitrides mixture
	C <sub>3</sub>	289.7	40.4	Carbon nitrides (C <sub>3</sub> N <sub>4</sub> )
Ar-HOPG	C <sub>1</sub>	284.8	47.3	Graphitic
	C <sub>2</sub>	285.8	16.1	Defects or disordering
	C <sub>3</sub>	289.7	36.6	Defects or disordering
Ar-HOPG	C <sub>1</sub>	284.8	35.8	Graphitic
	C <sub>2</sub>	285.8	25.4	Defects or disordering
	C <sub>3</sub>	289.7	38.8	Defects or disordering



# Approach (Pt-N-doped HOPG)



SEM images of Pt nanoparticles on:

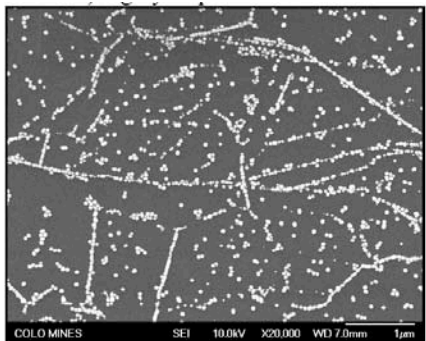
(a) undoped, (b) Ar-doped and (c) N-doped HOPG;

(d) particle diameter distribution of Pt nanoparticles on undoped, Ar- and N- HOPG;

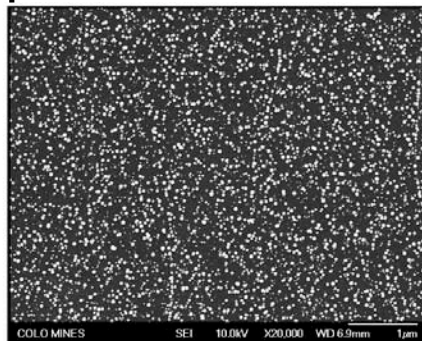
(e) nearest neighbor distance distribution of Pt nanoparticles on undoped, Ar- and N-HOPG.

# Approach (catalyst)

## Electrochemical Deposition



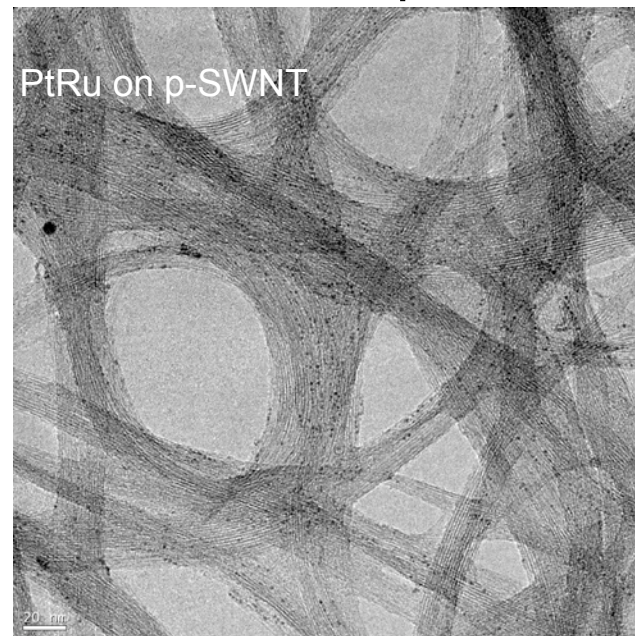
(a) PtRu on undoped-HOPG



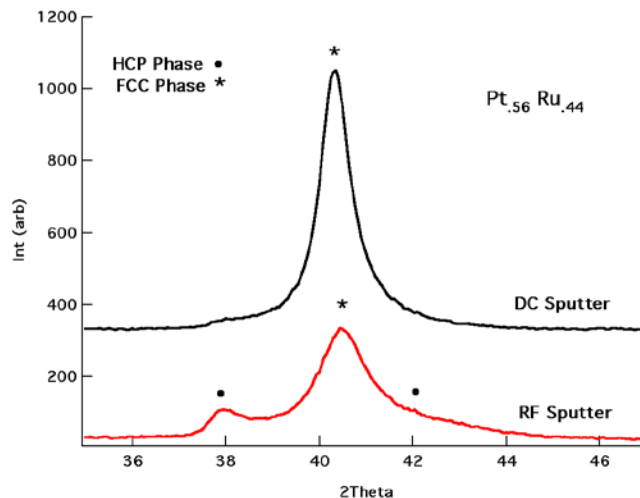
(b) PtRu on N-doped HO

SEM images comparing PtRu particles electrodeposited onto (a) undoped and (b) N-doped HOPG substrate, show that doping can affect the particle size and dispersion of PtRu catalyst nanoparticles.

## Microwave Deposition



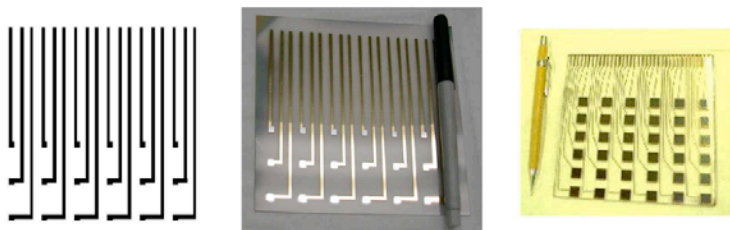
## Magnetron Sputter



Plan to leverage HOPG implantation results for application to high surface area carbon materials

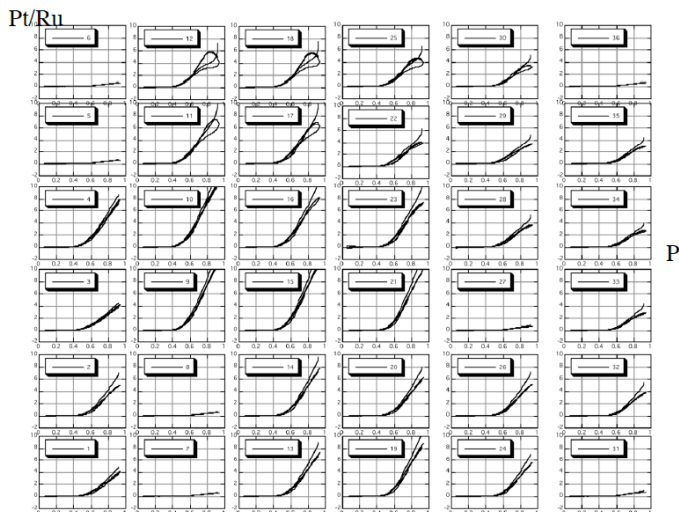
# Approach (Combinatorial Electrochemical Analysis)

## Preparation of Multi-Electrode Array



- 18 electrodes on a single sheet
- Gold substrate supported on 100  $\mu\text{m}$  thick PVDF/glass
- <10 nm thick, 0.5 x 0.5 cm active areas
- Room temperature deposition in <2 minutes

## Results of Parallel Polarization Scans



### Combinatorial data analysis to guide composition selection for combinatorial screening:

Combinatorial data obtained from the high-throughput screening technique will be analyzed to understand the effect of dopant composition on catalyst performance and predict the useful composition for the design of new libraries of dopants. Utilize Quantitative Structure-Activity Relationships (QSAR) which is a Multivariate, mathematical technique aimed at developing correlations between a set of physicochemical properties (descriptors) and an activity (mass activity).



# Short Term Tasks

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## NREL & CSM:

- Prepare a combinatorial library of different N-doping levels ion implanted on HOPGs
- Evaluate PtRu deposition approaches on HOPG substrates (Vapor Deposition, Electrochemical, Microwave)
- Initiate investigation of other atomic species for implantation

## JPL:

- High throughput electrochemical screening of the combinatorial library (HOPGs doped with different nitrogen levels)
- Electrochemically deposit PtRu nanoparticles (2-5 nm) onto N-doped HOPGs
- High throughput electrochemical screening of PtRu/N-doped HOPG combinatorial library

# Budget Overview

## Timeline

Start: July 2009

End: September 2011

% complete: 2%

## Partners

Colorado School of Mines (CSM)

Jet Propulsion Laboratory (JPL)

BASF Fuel Cells (BASF)

MTI MicroFuel Cells (MTI)

## Budget

DOE Cost Share	Recipient Cost Share	TOTAL
\$2.4M	\$69,714	\$2.47M*
97%	3%	100%

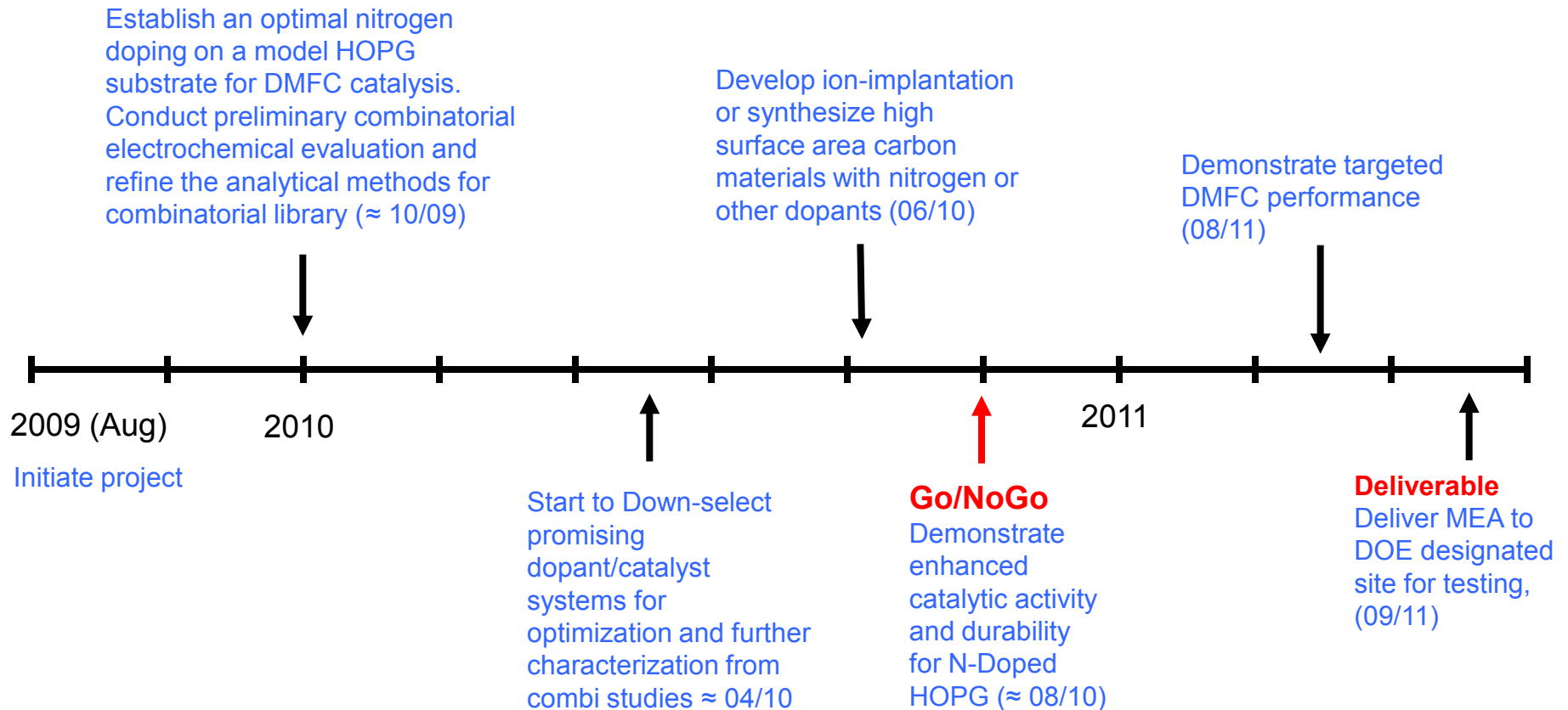
DOE Budget  
(\$K)

FY 2009	760
FY 2010	490
FY 2011	1235

**\*Final award amounts are subject to appropriations and award negotiations.**

# Timeline 2009 - 2011

“*In this project, the team, led by the National Renewable Energy Laboratory (NREL), will develop and demonstrate direct methanol fuel cell (DMFC) anode catalyst systems that meet or exceed DOE’s 2010 targets for high power density (50W/L), lower cost (\$3/W), and more durable fuel cells (2000 hours) for consumer electronics applications.*” This is a two year project.



# Project Participants

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Novel Catalyst-Doped Supports (NREL, CSM)

Combinatorial Electrode Studies (JPL, NREL)

Generate doped carbon supported catalysts for DMFC MEA based on results. (NREL, CSM, BASF\*)

MEA Evaluation (NREL, CSM, MTI#)

\*Provide SOA catalyst for benchmarking

#Independent MEA performance evaluation