Engineered Nano-scale Ceramic Supports for PEM Fuel Cells

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Fuel Cell Technologies Program Kick-off Meeting

September 30 – October 1, 2009

Washington DC

Objectives

- Develop a ceramic alternative to carbon material supports for a polymer electrolyte fuel cell cathode that exhibits an enhanced resistance to corrosion and Pt coalescence while preserving positive attributes of carbon such as cost, surface area, conductivity, and a compatibility with present MEA architecture/preparation.

- Goals…
  - high Pt utilization
  - enhanced Pt – support interaction
  - high surface area
  - adequate electronic conductivity
  - resistance to corrosion
  - synthesis method designed for scale-up

Technical Targets and Barriers

DOE Technical Targets[1,*]

- Precious metal loading: ~0.25 mg/cm^2 (with ~ 0.05 mg/cm^2 anode)
- Cost: < 5$/kW
- Activity (precious-metal based catalyst): 0.44 A/mg_{Pt} @ 0.90 $V_{iR\text{-}free}$; 720 $\mu A/cm^2$ @ 0.90 $V_{iR\text{-}free}$
- Electrocatalysis support loss: <30 mV after 100 hrs @1.2V
- Electrochemical surface area (ESA) loss: <40%

Technical Barriers Addressed[2,*]

A. Durability (Pt sintering, dissolution, corrosion loss, effects from load-cycling & high potential)

B. Cost (Better Pt utilization balanced by cost difference of new support)

C. Electrode Performance (Pt sintering, corrosion loss, and loss of ESA)

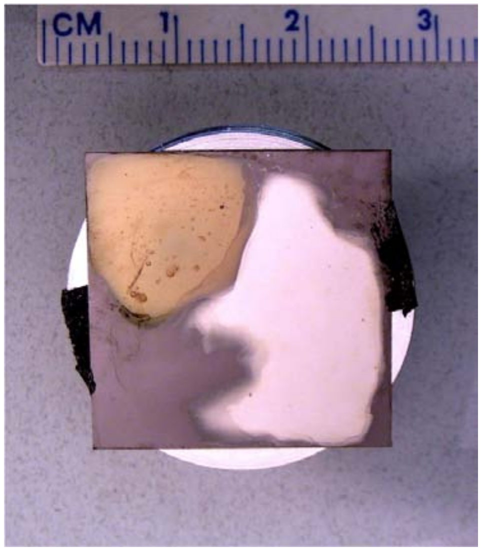
1. (Multi-Year Research, Development and Demonstration Plan, Table 3.4.12)
2. (Multi-Year Research, Development and Demonstration Plan, Section 3.4.4 “Technical Challenges”)

*From http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Approach

- This Project: *a focus on 3 ceramic materials as possible supports*
- Rare-earth Hexaborides
  - Low work function material
  - Refractory – withstand high temperatures
  - Insoluble in acid media
  - Present use: abrasives and thermionic emitters
- Sub-stoichiometric titania (TiO_{2-x}) : Ti_4O_7 (Magnéli phase)
  - Bulk e^- conductivity exceeds graphitized carbon
  - Reports of strong metal-support interactions with noble metals
  - High resistances to dissolution in acid media
  - Resistance to oxidation
  - Demonstrated electro-catalytic activity for both hydrogen and oxygen / Pt
- Conductive metal oxides : NbO_2 and RuO_2 (UNM)
  - Demonstrated corrosion stability (UNM)
  - Highly dispersed Pt on conductive mesoporous spheres can be synthesized in a single step process (UNM)

Approach/Relevant Prior Work

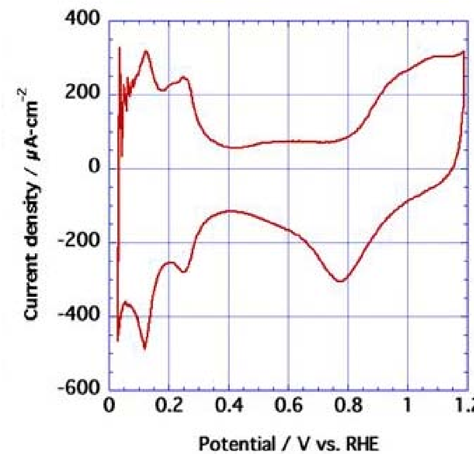


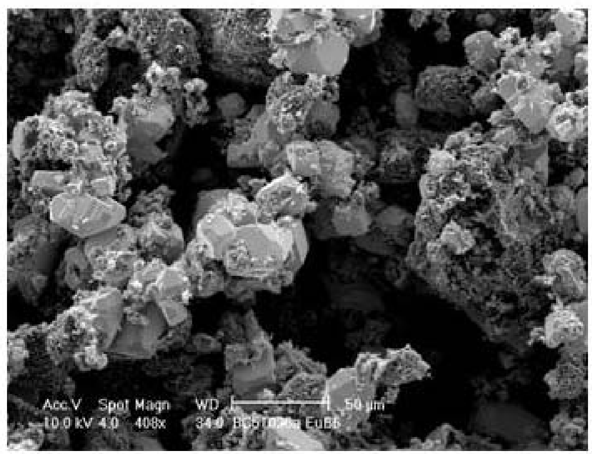
Metal hexaborides spontaneously deposit noble metals from solution.

Pt, Au, Pd, Os, Ag, Ru, Rh, Ir onto Ca, Ce, Eu, Gd, La, and YB_6

Glassy carbon disk electrodes: bare, coated with YB_6, and after spontaneous deposition of Au.

CV performed on 4 wt% Pt/EuB_6 powder-coated electrode with 6μg Pt/cm^2 loading immersed in 0.5M H_2SO_4, sparged with Ar.



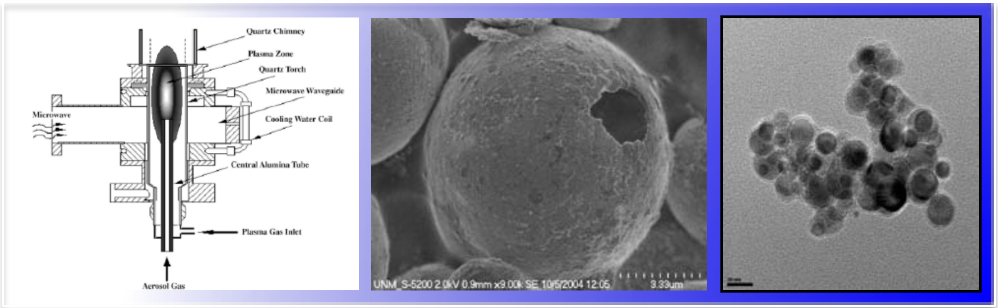


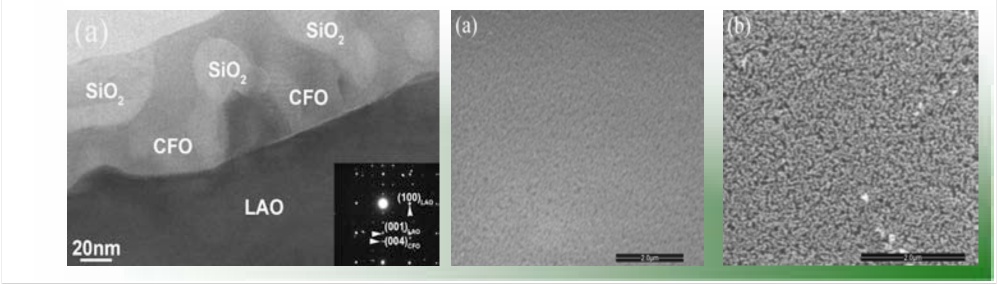
LANL prepared 1 m^2/gr EuB_6 using BC and Eu-acetate, 6hr @ 1500°C/H_2 .

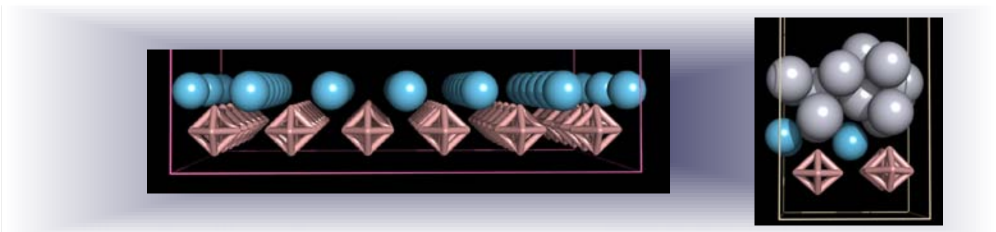
F.A. Uribe, F.H. Garzon, E.L. Brosha, C.M. Johnston, S.D. Conradson, and M.S. Wilson, J. Electrochem. Soc. ***154*** *(11) (2007) D623.*

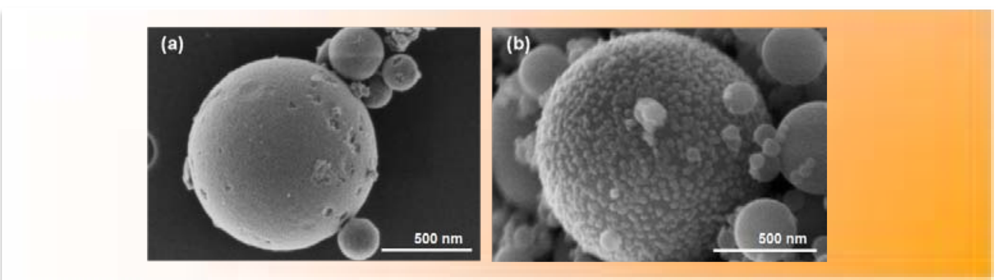
Approach

- Microwave aerosol-through-plasma (ATP) torch synthesis of (RE)B_6 and TiO_{2-x}
  - Utilize flow of plasma gas through plasma to create high temperature/short contact times
  - T > 3500K, t < 0.1 sec
  - Plasma gas mixtures: Air, Ar, O_2, N_2 and H_2
- Polymer assisted deposition (PAD) for (RE)B_6
  - PAD precursor routes to produce catalysts supports.
  - Films (CVs), powders (bulk catalysts, MEA prep)
  - Methods developed to generate surface area have been demonstrated.
- Theory/Modeling support to aid experimental effort to provide data on stability in absence of Pt particles
  - Surface/cluster models useful to predict effects of particle size reduction, conductivity.
  - Study nature of Pt binding sites, interaction energy, etc.
- Conductive NbO_2 and RuO_2 supports (UNM)
  - Spray pyrolysis methods to prepared conductive metal oxide supports.









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Participating Organizations/Task Leads

Los Alamos National Laboratory

- Rare earth hexa-boride supports; Eric Brosha (PI) & Jonathan Phillips
- Sub-stoichiometric TiO_{2-x} supports; Jonathan Phillips
- PAD synthesis, hexa-boride films, powder supports; Anthony Burrell
- Electrochemistry/MEA prep/FC testing; Tommy Rockward
- Support Modeling; Neil Hensen

The University of New Mexico

- Conductive RuO_2 and NbO_2 Supports; Timothy Ward (lead)

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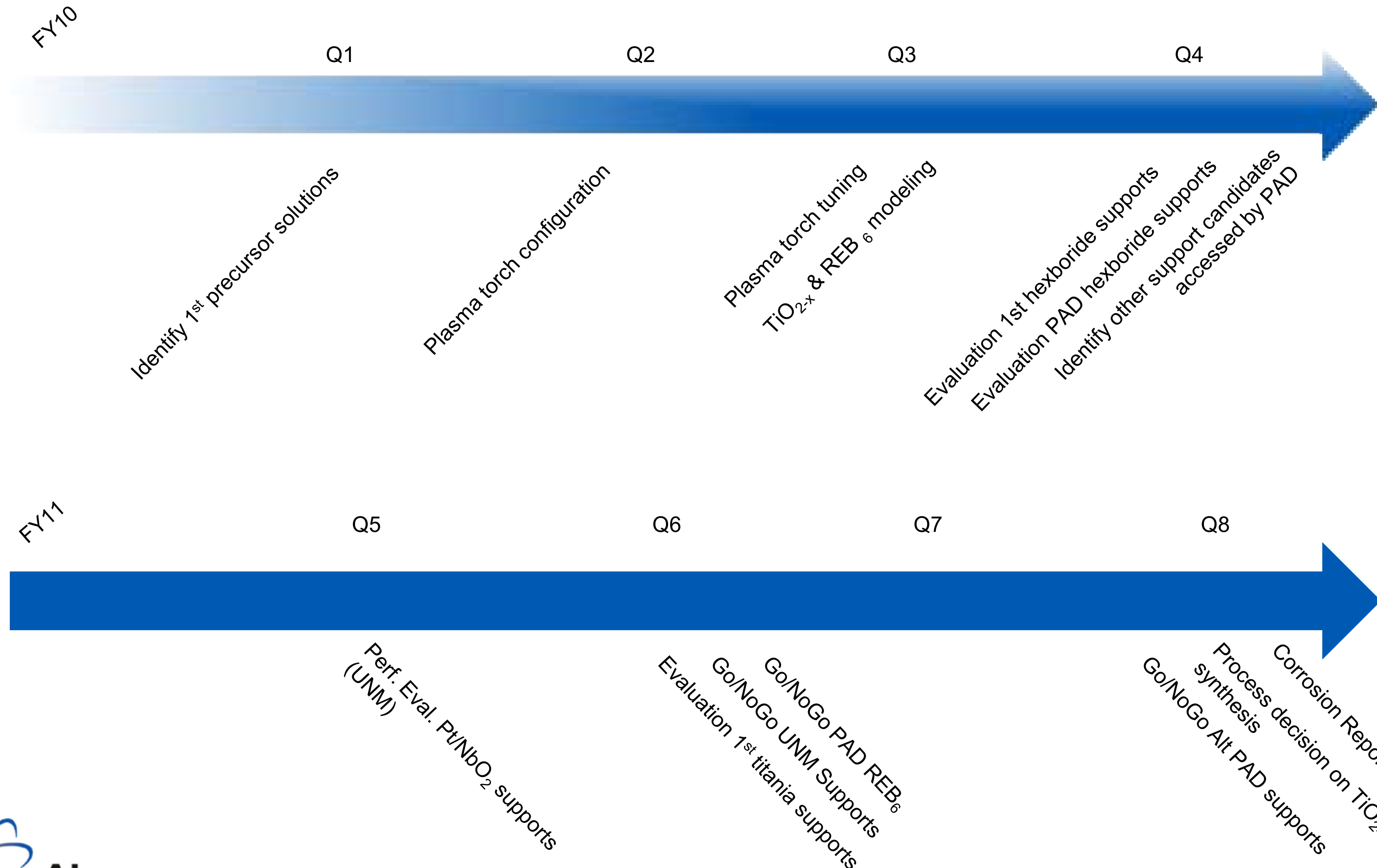
- Characterization; Karren More (PI – special materials)

Project Timeline



Milestones & Go / No-Go Decisions / Criteria

FY10 FY11 FY12 FY13

LANL/Hexaboride Supports A-T-P

LANL/Hexaboride Supports PAD

LANL/Conductive Titania

UNM/Conductive Ru-NbO_2

Characterization & testing

Corrosion measurements

MEA Preps/single cell

Start up/shutdown effects

Task Schedule, by Quarters (Q) with Milestones (M) and Decision Points (G)

Q / Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1a			M	M		M					G			G		
1b				M G		G		M G				M G				
1c			M	M		M		M			G			G		
1d					M	G		G								
2a	< - - -	- - -	- - -	- - -	- - -	- - -	- o n	- g o	i n g	- - -	- - -	- - -	- - -	- - -	- - -	- - >
2b								M								
2c															M	
2d														M		M M
2e																D D

Deliver single cell for testing/formal cost estimate

- Criteria used to judge G/NG decision points
  - Particle size, surface area, conductivity
  - Pt - support interaction, activity
  - Corrosion studies
  - Modeling input
  - MEA fabrication

Extensive Support Materials Characterization

- X-ray diffraction (XRD – *structure, phase identification/analysis, particle size*)
- X-ray fluorescence (XRF – *composition, stoichiometry*)
- X-ray general (EDS – *composition, mapping*)
- Thermogravimetic Analysis (TGA – *solution properties, thermal stability*)
- Microscopy (SEM, ESEM, TEM – *structure, morphology*)
- Surface Area (BET)
- Cyclic voltammetry, micro-electrode (*activity, corrosion testing*)
- Spectroscopy (ICP-MS – *corrosion studies*)

Project Funding

	FY10	FY11	FY12	FY13
LANL	$500K	$500K	$500K	$500K
UNM (subawardee)	$75K	$75K	$75K	$75K

Project total: $2M