Non-Pt Catalysts for PEFCs

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Overview

Timeline

- Project start date: October FY'03
- Project end date: Open
- Percentage complete: n/a

Budget

- Total funding: $750 K
- Funding for FY'05: $150 K
- Funding for FY'06: $300 K

Barriers

- Barriers addressed
  - B. Cost
  - C. Electrode performance

Partners

- Los Alamos National Laboratory
- Prof. John Regalbuto, University of Illinois at Chicago
- Collaborations with BES-funded groups on characterization
- Regularly providing updates and soliciting feedback from FreedomCAR Fuel Cell Technical Team

Objective

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets
  - Promotes the direct four-electron transfer with high electrocatalytic activity (comparable to that of Pt) (***0.44 A/mg$_{Pt}$ or 720 μA/cm^2 @0.9V***)
    - *O_2 reduction reaction (ORR) in acidic media (e.g, in PEFC)*
      - *Two-electron transfer*

$$O_2 + 2H^+ + 2e^- = H_2O_2$$

      - *Four-electron transfer*

$$O_2 + 4H^+ + 4e^- = 2\ H_2O$$

      - *Four-electron process is desirable due to its higher efficiency and non-corrosive product*
  - Chemically compatible with the acidic polymer electrolyte (***5000h @80^{o}C, < 40% electrochemical area loss***)
  - Low cost (***$8/KW, 0.3 mg PGM/cm^2***)

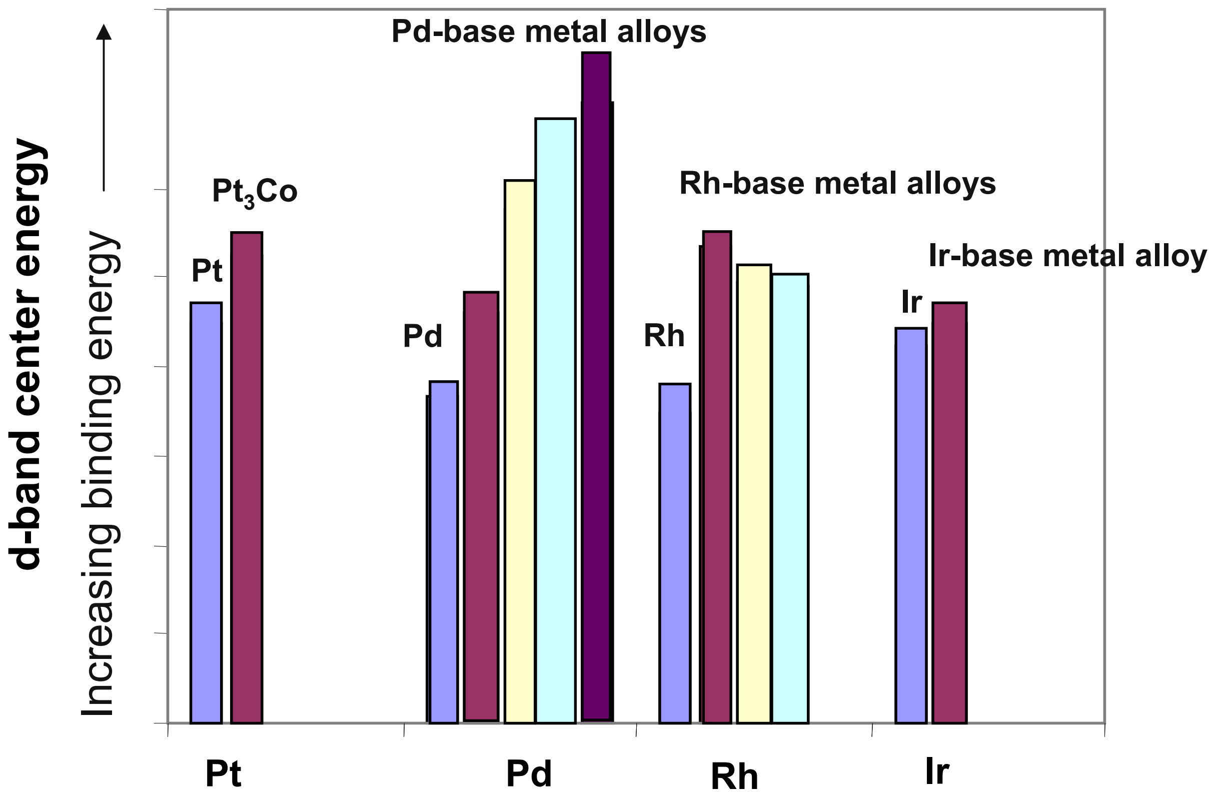
Approach

- **Bi-metallic systems (e.g., base metal, noble metal)**
  - Surface segregation of minor noble metal component to form protective layer
  - Base metal component chosen to modify d-band center of noble metal making it more “Pt-like”
  - Choice of bi-metallic systems is based on the surface segregation energies and d-bend center shift
    (Source: A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990)
  - Examples: Bi-metallics of iridium, rhodium, and palladium
  - Alternative supports to modify electronic properties of small metal particles (e.g., titania)

- **Metal centers attached to electron-conducting polymer backbones**
  - Allows easy control of spacing between metal centers
  - Electron conductor in close proximity to reaction site can promote high catalyst utilization

The d-band centers of candidate noble metals can be shifted to desired value by alloying with base metals

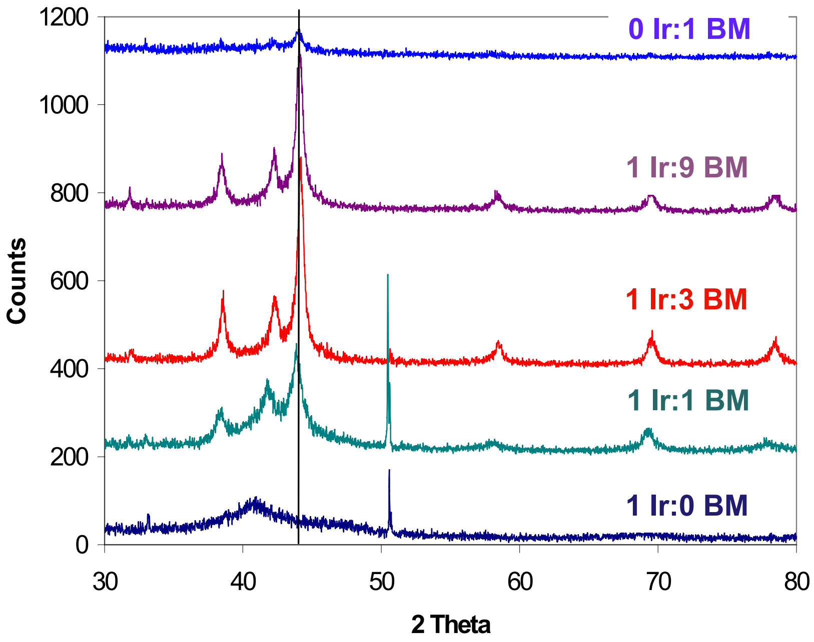
- There is a relationship between the d-band center of the metal and its ORR activity - Nørskov-Hammer theory and results of LBNL group
- Pt_3Co has high ORR activity and, thus, a desirable d-band center (LBNL)



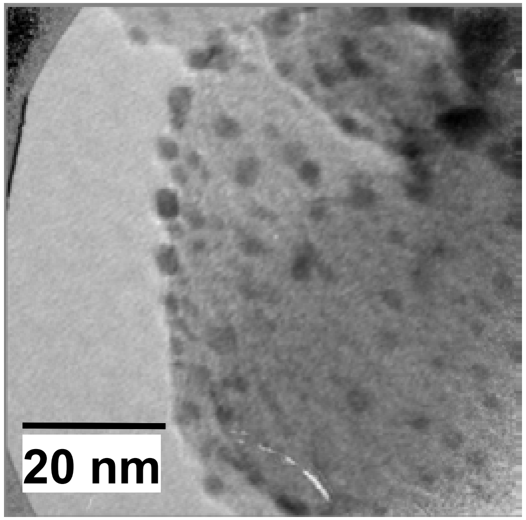
Progress vs. FY '06 Milestones

- Synthesize and determine the ORR activity of two metal center-polymeric, two bimetallic, and one ACNT systems (06/06)
  - Two metal center-polymeric systems
    - *Synthesized and tested two metal center moieties*
    - *Identification of electron conducting polymers as backbone is underway*
  - Two bimetallic systems
    - *Competed one Ir-based bimetallic system for material synthesis (nine compositions) and testing, including materials characterization*
    - *Synthesized one Pd-based bimetallic system (five compositions); testing and characterization is underway*
    - *Finished three more Au-based bimetallic systems*
  - One Aligned Carbon Nanotube system
    - *Tested ORR activity*
- Determine the long-term stability of the electrocatalyst with the highest ORR activity (09/06)

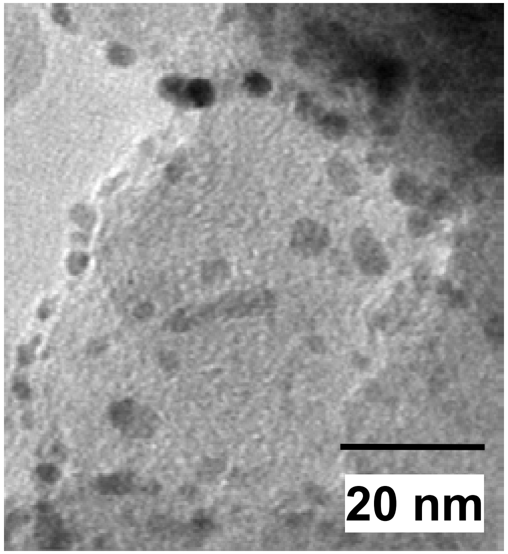
Solid solutions of Ir-BM nanoparticles have been formed on Vulcan carbon



3 Ir:1 BM

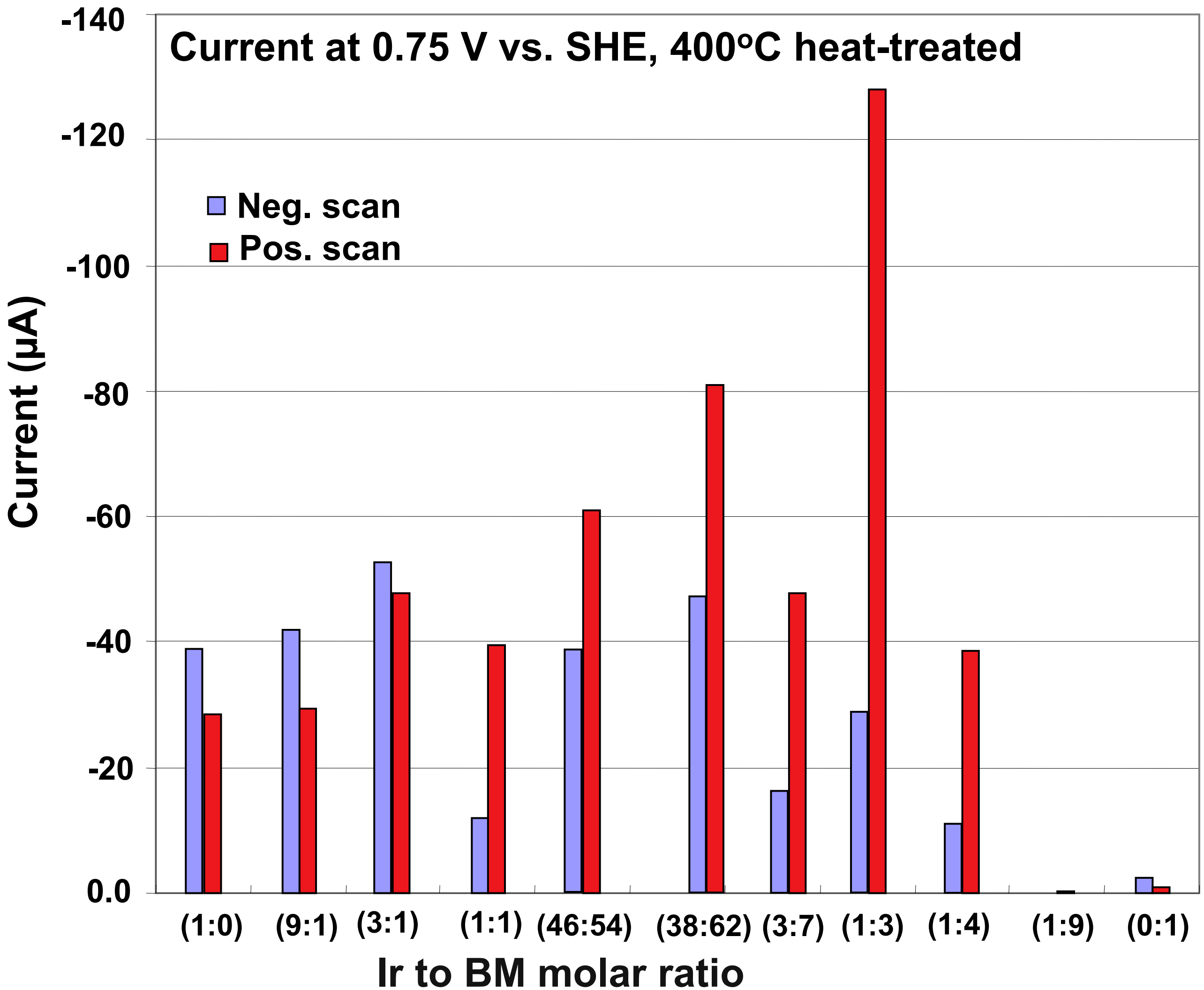


1 Ir:3 BM

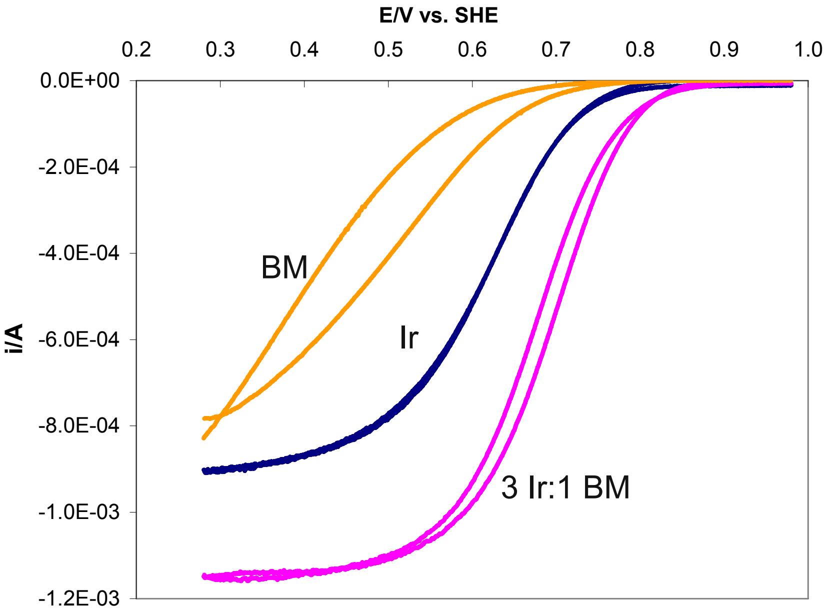


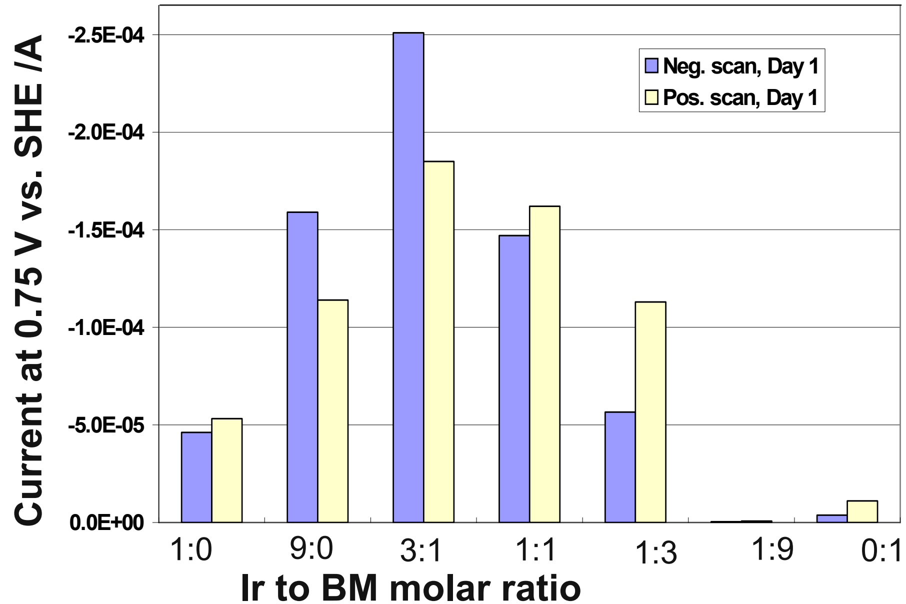
- XRD shows that a solid solution is formed at 400ºC
- TEM shows catalysts to have 2- to 10-nm diameter particles

The Ir to base metal ratio affects the ORR activity

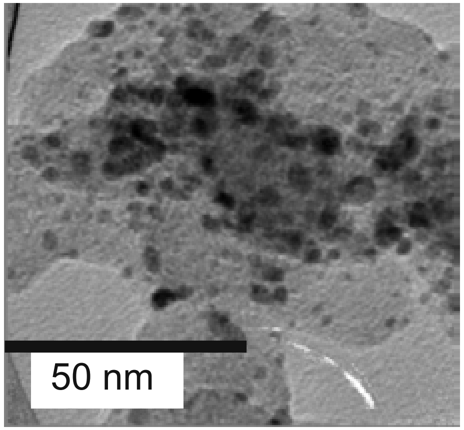


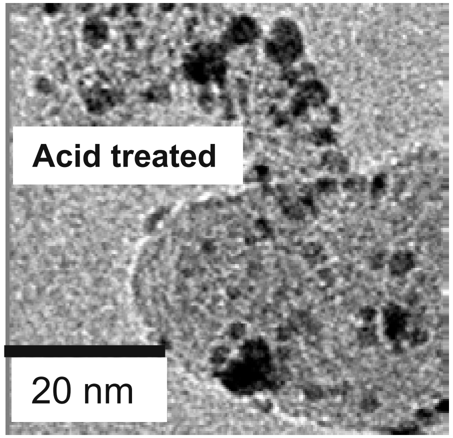
Acid treated Ir:BM catalyst showed improved ORR activity



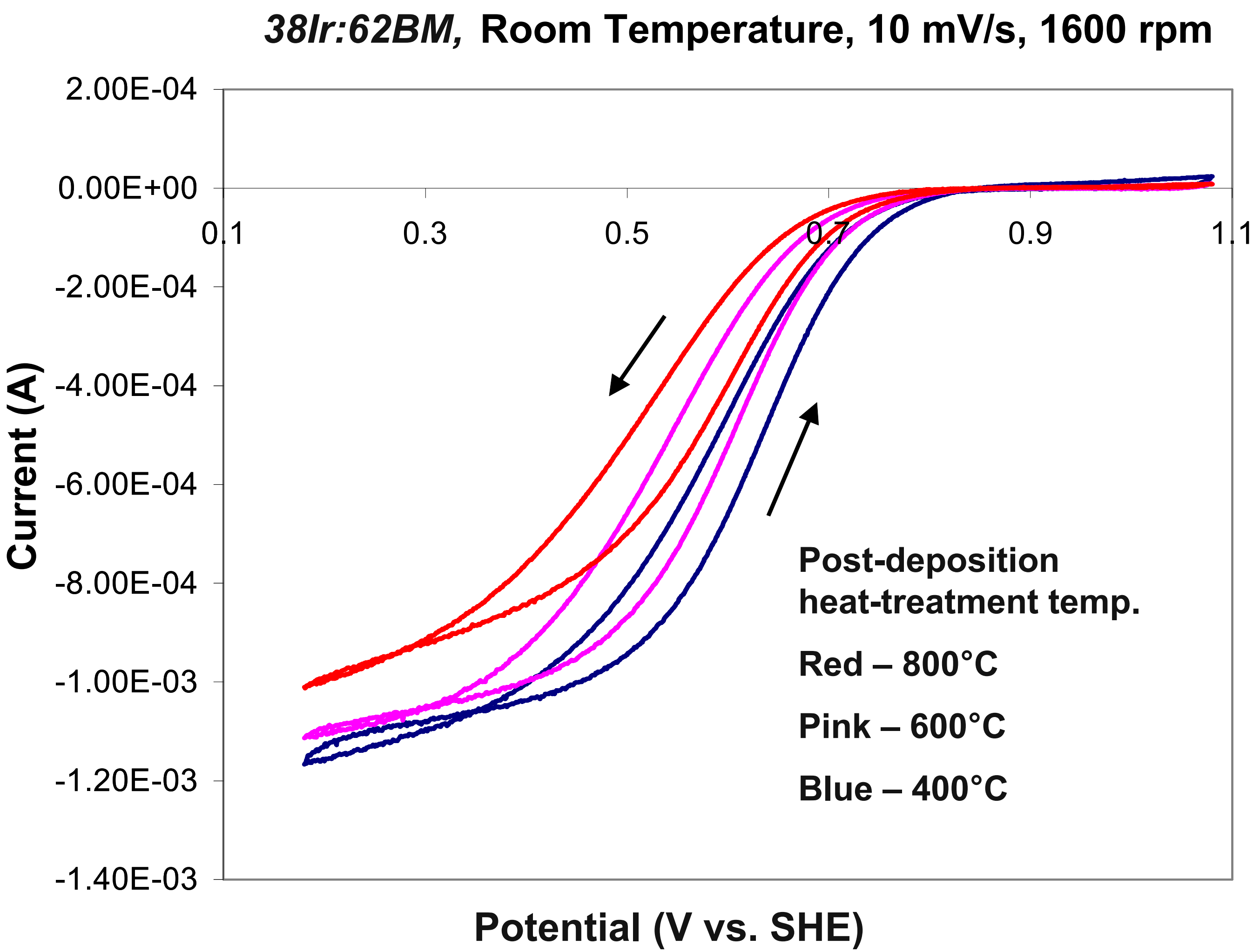


- TEM image indicates that acid treatment did not change particle size
- EDX results shows molar ratio of Ir to BM stayed the same after acid treatment

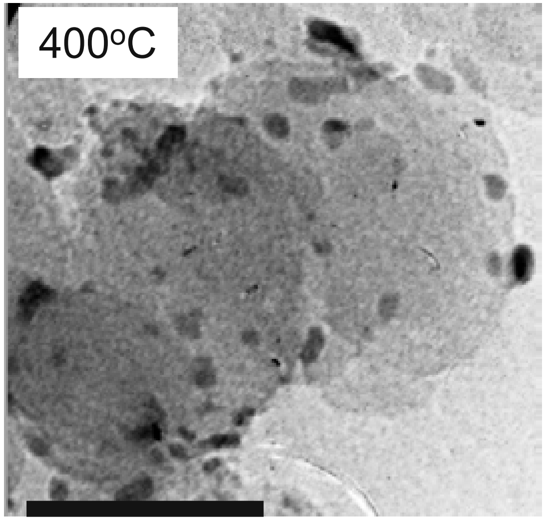




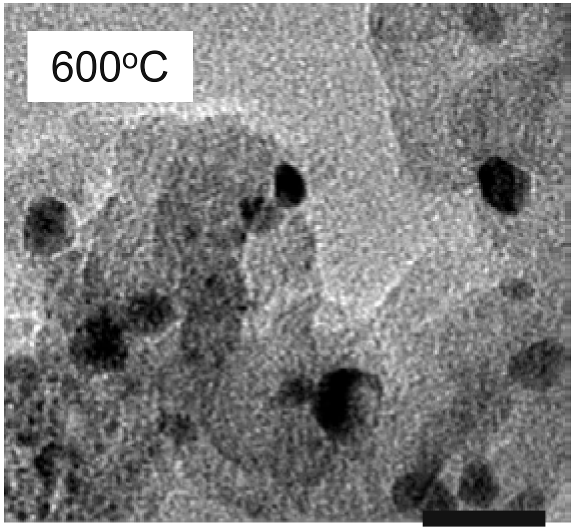
ORR current decreased as the heat treatment temperature increased (Ir:BM)



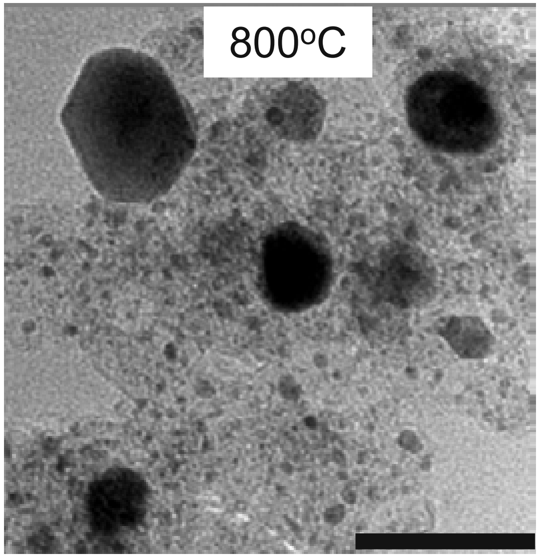
Coarsening of Ir:BM particles occurred at higher heat treatment temperatures



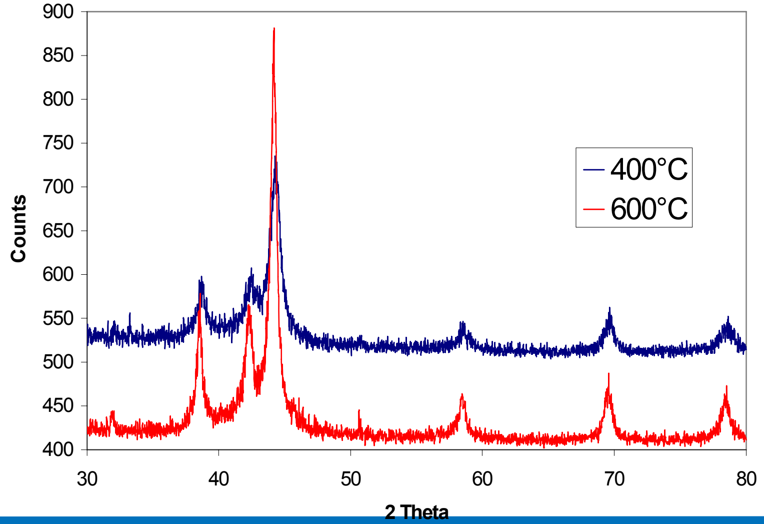
50 nm



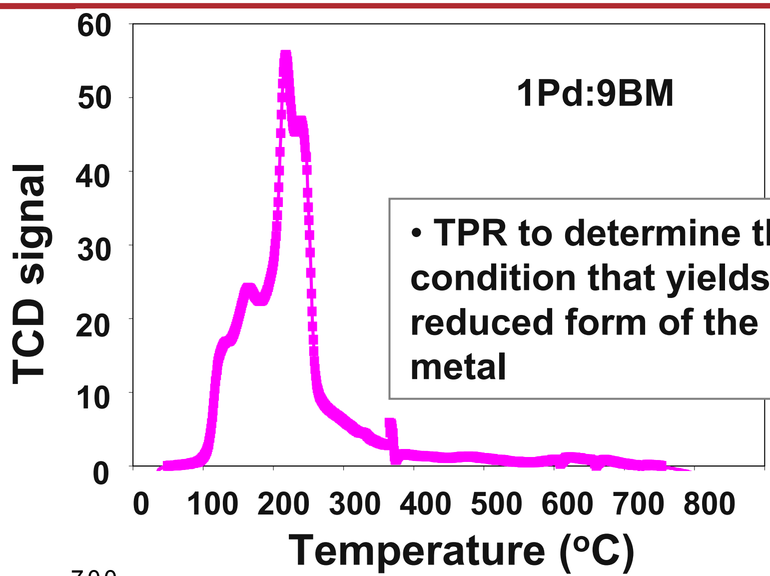
20 nm



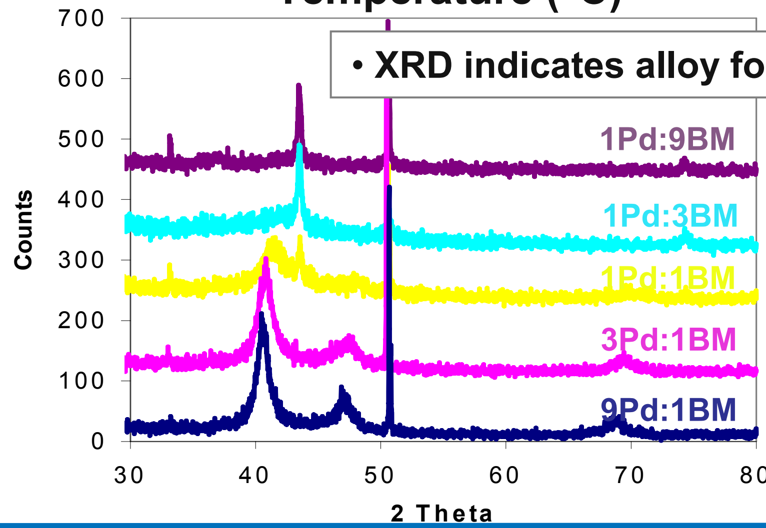
50 nm



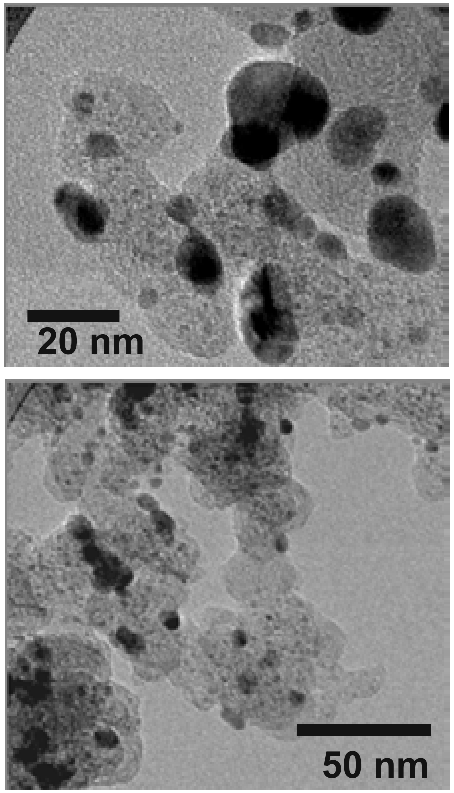
Nanoparticles of Pd-base metal alloy have been formed on Vulcan carbon



• TPR to determine the condition that yields reduced form of the metal

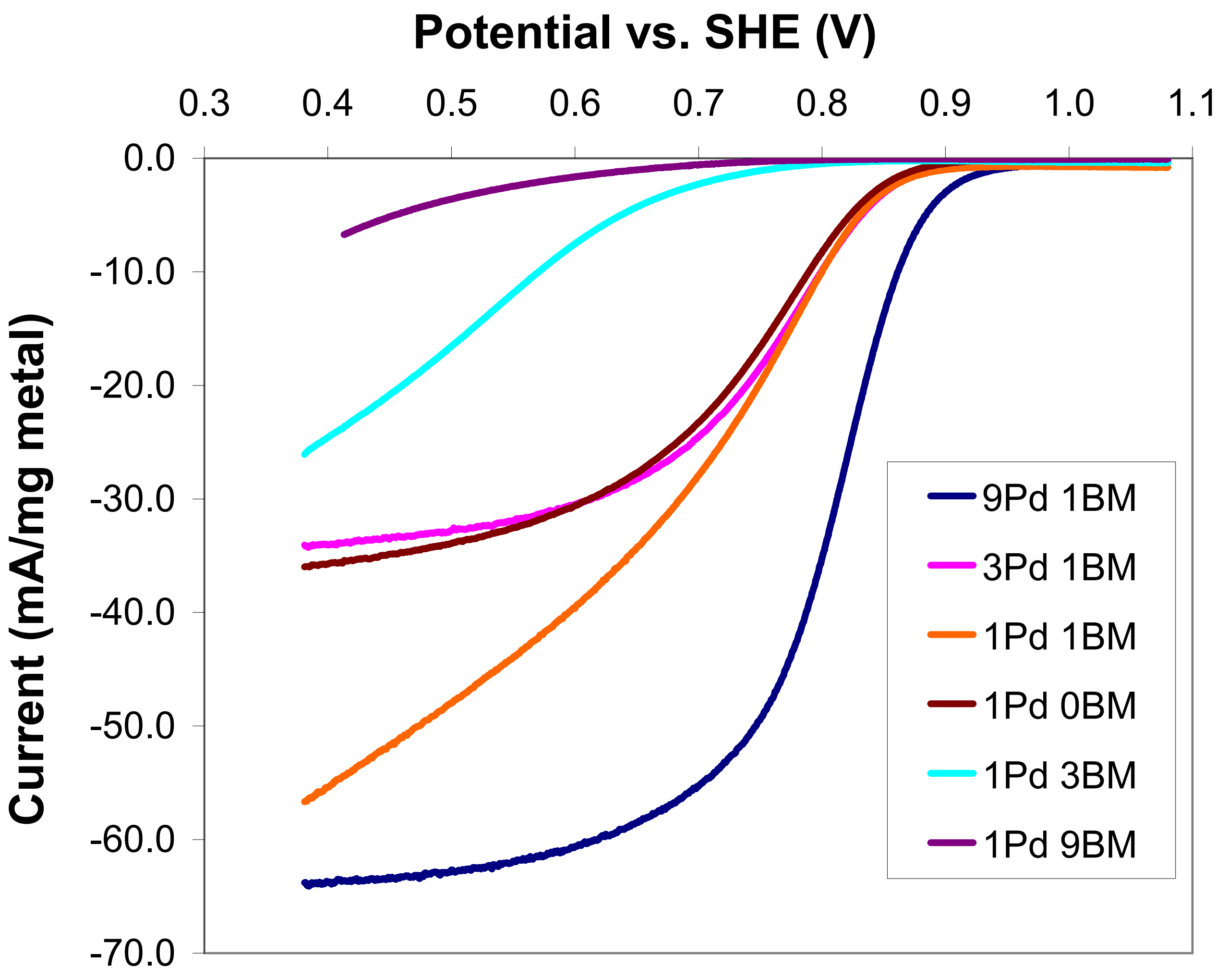


• XRD indicates alloy formation

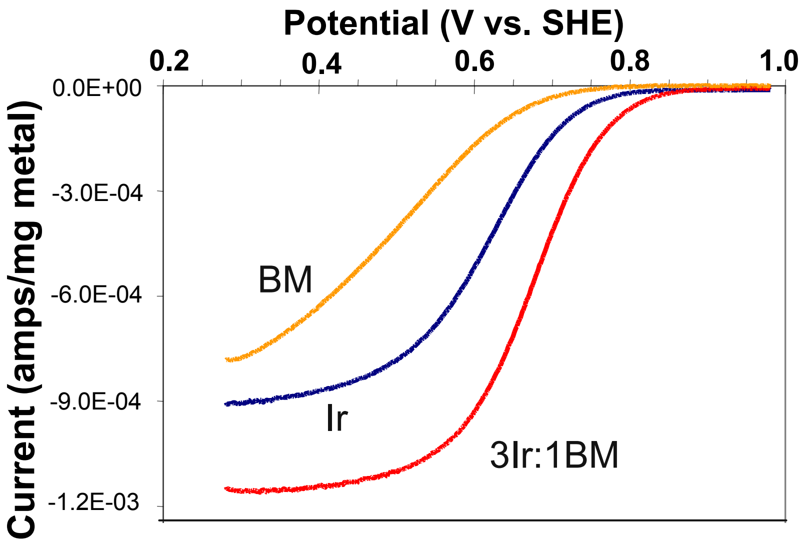


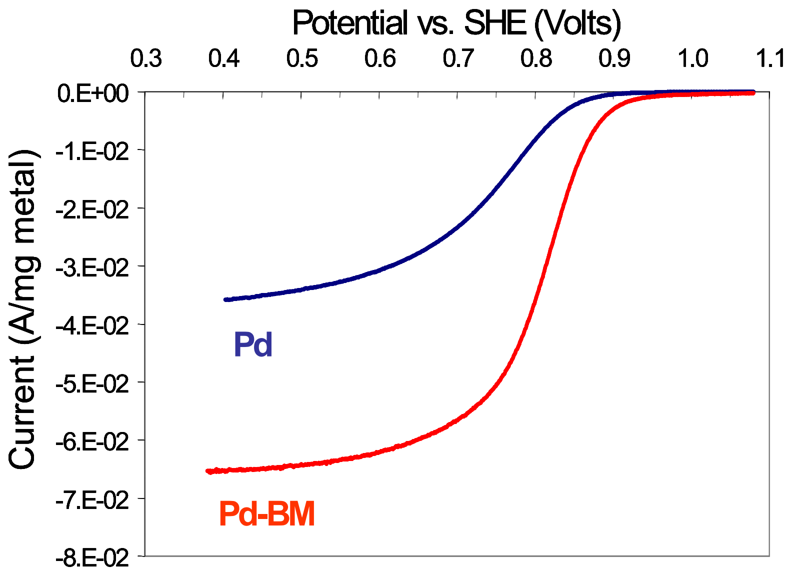
- Bimodal size distribution:
  - 2-5 nm and 10-20 nm
  - 10-20 nm particles more evenly distributed

Base metal increased ORR activity of palladium



Base metals enhance the ORR activity of Ir and Pd, but further improvement is needed





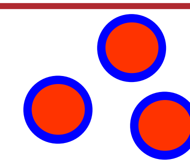
Supported metallic system	Ir-based			Pd-based		DOE 2010 target 0.9 V
	Ir	Ir-BM	BM	Pd	Pd-BM'	
ORR mass activity at 0.8 V per mg metal	20 µA	65 µA	3 µA	8.4 mA	36.6 mA	440 mA (110 mA)

New synthetic approach for desired structure/morphology of bimetallics --- Metal core-organic shell approach

- Nanocrystalline cores encapsulated in a monolayer of organic molecular or surfactant shell have several advantages
  - Size and surface properties of nanoparticles are controllable
  - Organic shell protects nanoparticles from agglomeration
    - *Stable and highly monodisperse nanoparticles*
  - Interparticle interactions of the shell molecules confers spatial controllability in the assembly of the particles on support materials
  - Deliberate tailoring of the surface of the metallic core with suitable shell structures enables the morphology of the bimetallic composition to be very well controlled
  - Large volumes of pre-engineered nanoparticles can be efficiently produced

A procedure has been devised for bimetallic system

Step 1: Seed preparation

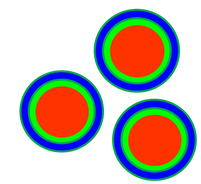


Metal Precursor
(e.g. Base metal$(acac)_3$)
Octyl ether

→ Stirring/N_2, Δ → Organic capping agent, Δ → Reduction, Δ →

Capped base metal seed nanoparticles

Step 2: Seed growth



Second metal precursor
(e.g. $Ir(acac)_3$)
Octyl ether

→ Stirring/N_2, Δ → Organic capping agent, Δ → Seed nanoparticles Reduction, Δ →

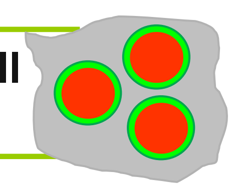
Ir on base metal Core-shell nanoparticles

Step 3: Assemble on support and remove the shell for activation

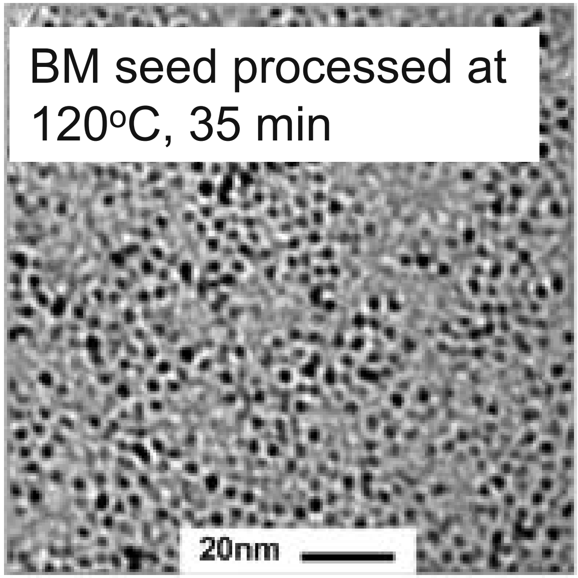
Ir on base metal Core-shell nanoparticles

→ support → O_2/N_2, Δ → H_2/N_2, Δ →

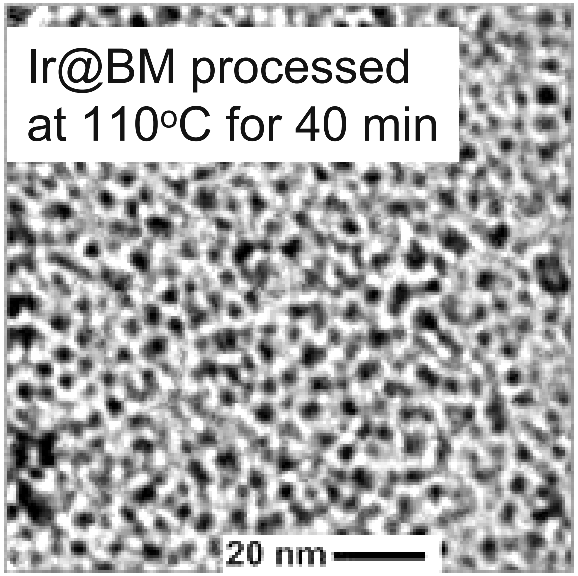
Ir on base metal Core-shell Nanoparticles on support



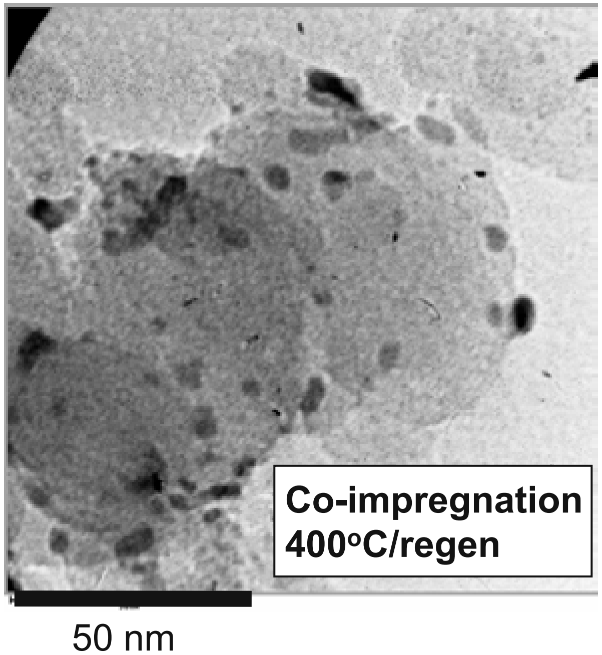
TEM shows nanoparticle size and monodispersity control--- better shaped and more uniform particles than traditional method



Particle size ~ 2 nm

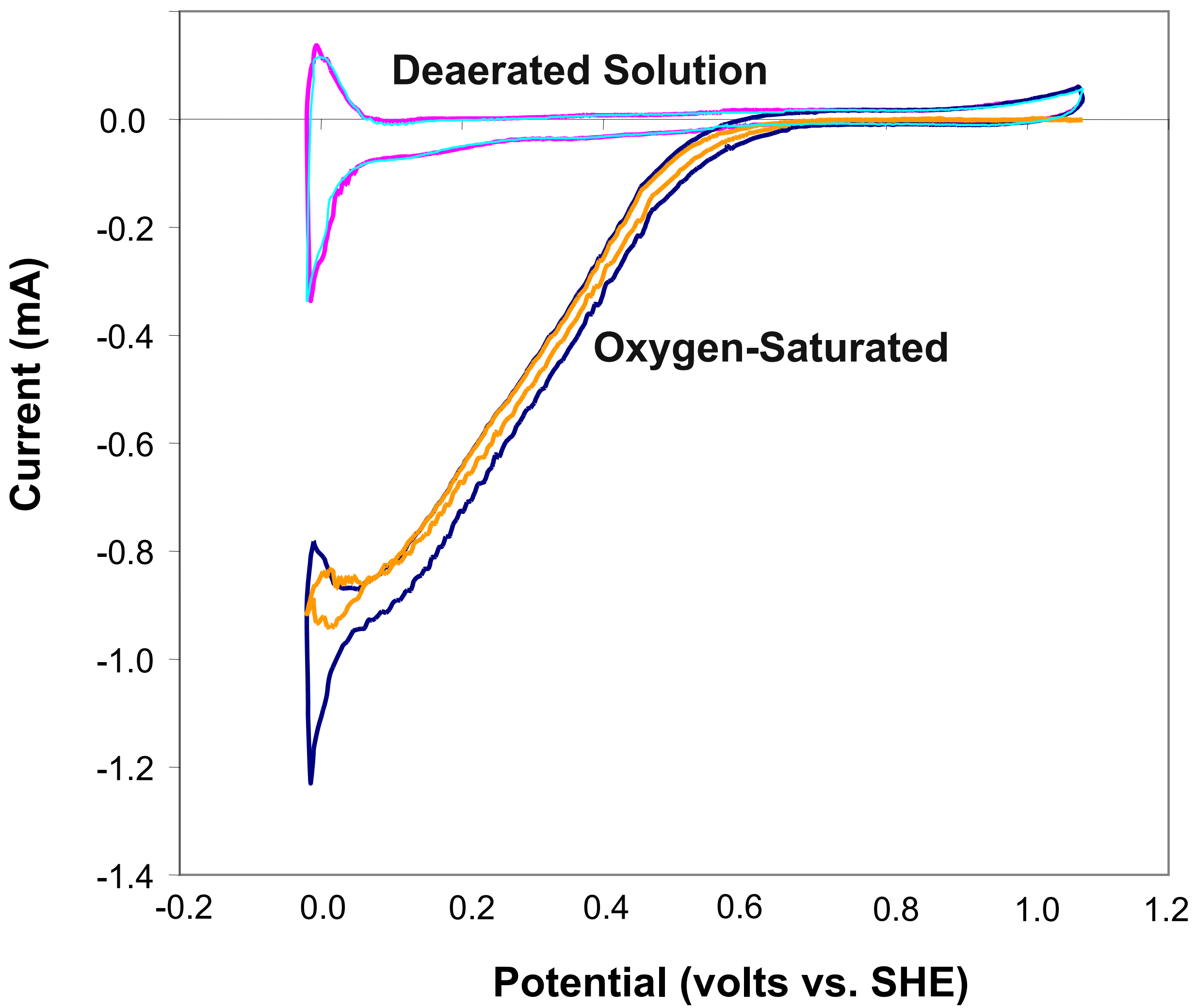


Particle size ~ 3 nm



- TEM of Ir on BM reveals size growth associated with overdeposition of Ir on BM nanoparticles used as seeds
- EDX analysis confirmed bimetallic composition consistent with synthetic feed amounts of metal precursors

ORR activity of cobalt metal centers attached to polymer backbones begins at 0.6 V



Summary

- Both supported Ir- and Pd-based bimetallic systems showed an ORR activity better than supported Ir and Pd alone
  - *ORR started at potential of 0.85 V and 0.93 V, respectively for Ir- and Pd- based system*
- XRD and TEM analysis indicates alloy formation and nanosize particles for both systems
- ORR activity was strongly influenced by type and composition of bimetallic system and catalyst preparation and processing conditions
  (e.g., acid treatment and heat treatment temperature)
- New synthetic approach is being explored to obtain desired structure/morphology

Future work

- Perform elevated temperature RRDE experiment to determine O_2 reduction mechanism (2e^- or 4e^- transfer) for Ir-based system
- For Pd-based system
  - ORR activity testing and TEM work for other compositions prepared
- Prepare and test the ORR activity of additional bimetallic systems identified
- Surface and bulk characterization to verify the desired catalyst composition/structure, particle size, and electronic properties by using various techniques such as XRD, TEM, SEM, FTIR of adsorbed CO, and TPD of CO
- Explore different synthesis methods and temperature treatments
- Perform electrochemical and chemical stability studies
- Fabricate and test a membrane-electrode assembly using newly-developed electrocatalysts

Acknowledgments

- J. Vaughey and T. Cruse for XRD
- J. Mawdsley for TEM
- M. Ferrandon for TPR and TPD
- J. Yang and D.J. Liu for preparing ACNT system

Publications

- "Polymer Electrolyte Fuel Cell Cathode Electrocatalysts", Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, Poster and Abstract, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005

Response to FY ’05 Reviewers’ Comments

- “The work on bimetallic(Au-based), transition metal carbides and nitrides, and metal centers attached to electron-conducting polymer backbone is too broad area for such relatively small project”
  - ***We have focused our effort on bimetallic systems***
- “Need to pull in other characterization techniques to better understand behavior of bimetallic system (microscopy, etc.).”
  - ***We are characterizing catalysts by TEM, XRD, EDX, CO Temperature Programmed Desorption***
- “See no evidence that the claimed LANL collaboration is underway”
  - ***Once material shows adequate activity in screening tests, LANL will fabricate MEAs***
- “The reason for the choice of the new catalysts was not evident”
- “Screening large number of non-Pt catalysts based on Au is no guarantee that one of the proposed catalyst formulations will work”
  - ***We have elaborated on the rationale behind the choice of bimetallic systems in this presentation***