Non-Platinum Bimetallic Cathode Electrocatalysts

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Objective and Technical Targets

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets that:
  - Promotes the direct four-electron oxygen reduction reaction with high electrocatalytic activity
    (***0.44 A/mg$_{PGM}$; 720 μA/cm^2 @0.9 V$_{iR\text{-}free}$***)
    - *O_2 reduction reaction (ORR) in acidic media*
      - *Two-electron transfer*

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

      - *Four-electron transfer*

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

  - Is chemically compatible with the acidic electrolyte and resistant to dissolution (***<40% electrochemical area loss over 5000 h@≤80ºC and 2000 h@>80°C***)
  - Is low cost (***$5/KW, 0.3 mg PGM/cm^2***)

Approach and Technical Barriers Addressed

- Bimetallic systems (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 bimetallic systems is based on surface segregation energies and d-band center shift
  - Examples: Bimetallics of palladium, iridium, and rhodium

- Technical barriers and how we are addressing them
  - A. Durability: altering oxophilicity of catalyst to prevent oxidation-related degradation
  - B. Cost: lowering PGM loading by replacing PGM in electrocatalyst particle core with base metal
  - C. Electrode performance: modifying surface electronic properties to enhance ORR activity

Noble metals were chosen based on stability and tendency to form surface "skins"

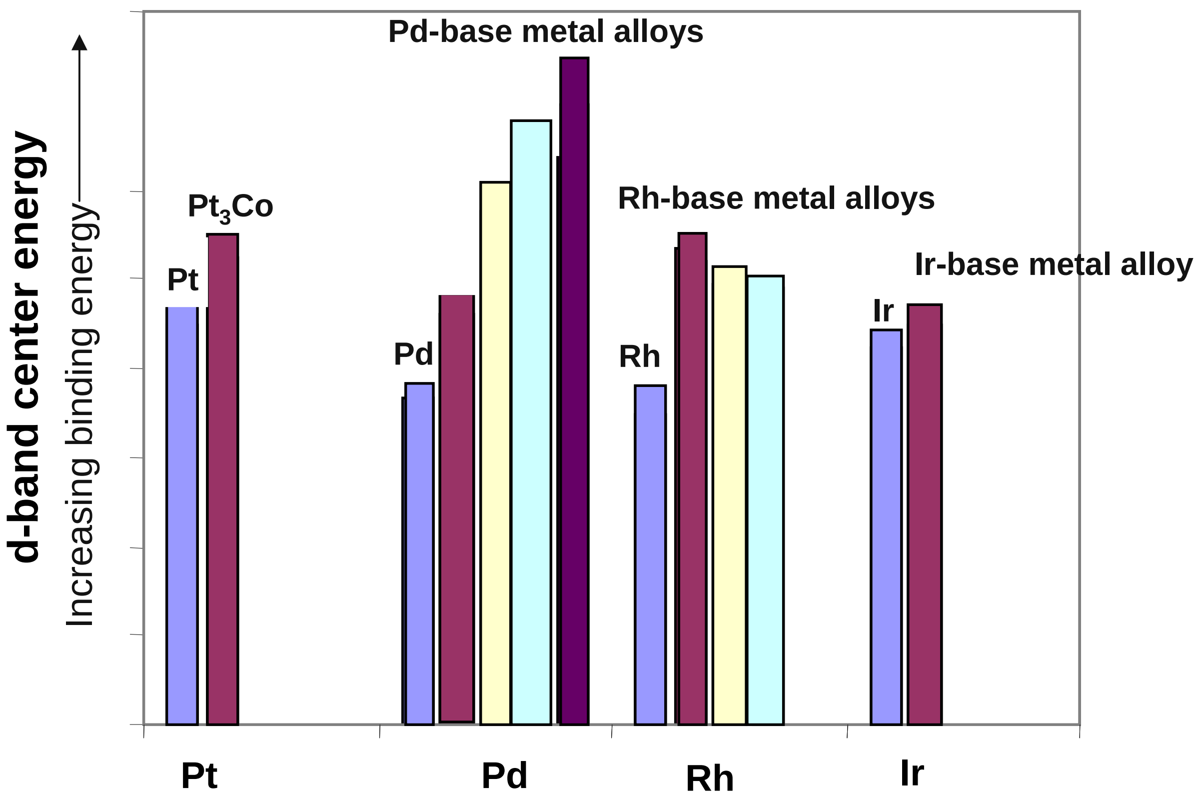
- Noble metals are the most stable in acidic environment
  - Pd $E^{o'}$ for dissolution = 0.987 V
  - Rh $E^{o'}$ for dissolution = 0.76 V
  - Ir $E^{o'}$ for dissolution = 1.156 V
  - Pt $E^{o'}$ for dissolution = 1.188 V

- Base metals were chosen, in part, by the tendency of noble metal to form a protective skin

- Tendencies of noble metals to segregate to the surface of base metal hosts have been calculated by J. Nørskov and co-workers
  [A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990.]

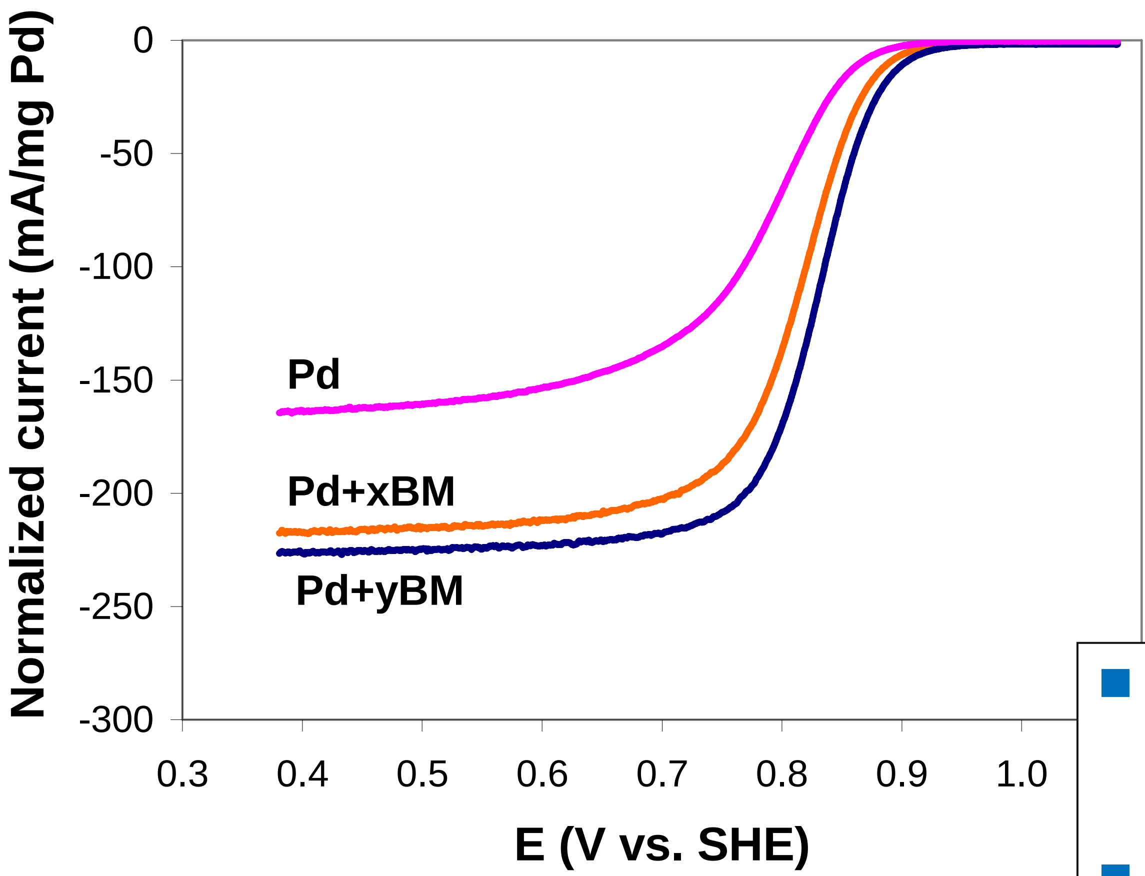
The d-band centers of candidate noble metals can be shifted towards desired values by alloying with base metals

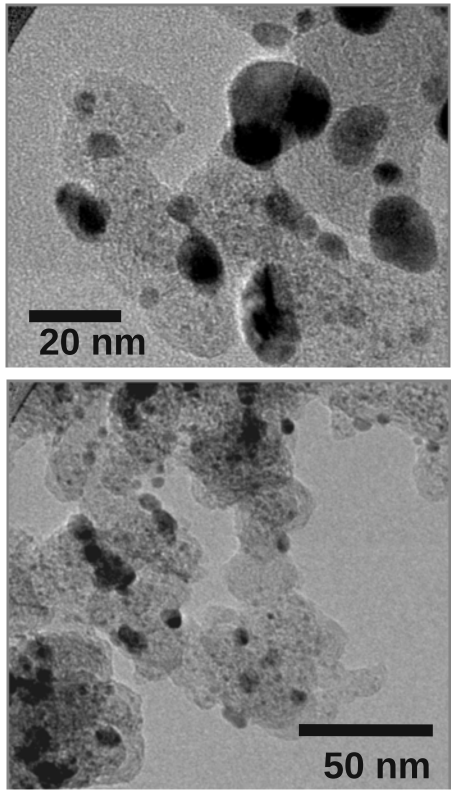
- There is a relationship between the d-band center of the metal and its ORR activity - Nørskov-Hammer theory and results of LBNL group
- Pt_3Co has high ORR activity and, thus, a desirable d-band center (LBNL)



Base metal increased ORR activity of palladium

- Nano-particles formed by co-impregnation, reduction in hydrogen





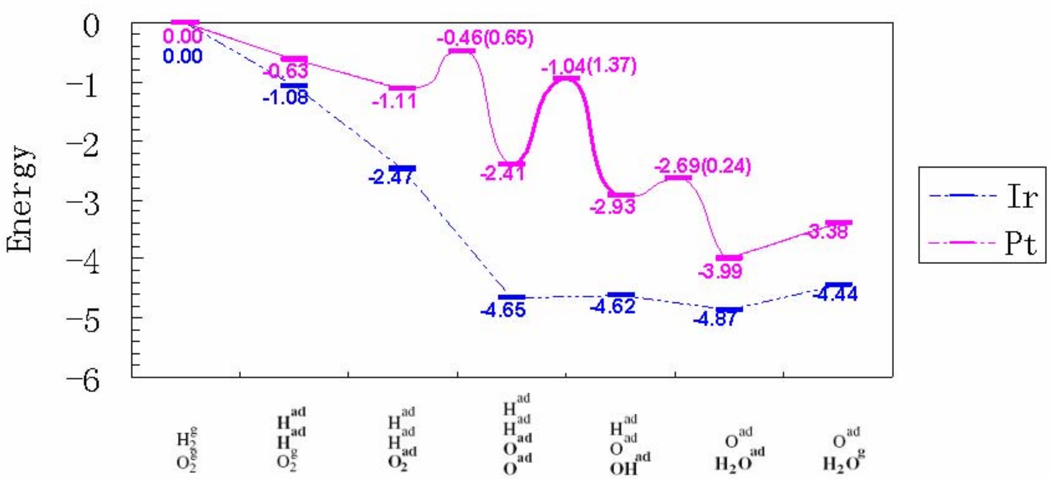
- Standard synthetic route leads to large particle size
  - **2-5 nm and 10-20 nm**
- Alternative synthetic procedures are needed to reduce size and improve mono-dispersity

Project tasks

- Perform computational studies to guide choice of systems and compositions (Caltech)
- Fabricate and characterize model systems-bulk electrodes to guide choice of systems and compositions (UNLV, Argonne)
- Synthesize nano-particles on high-surface-area carbon support (Argonne, UIC)
- Characterize nano-particle ORR activity, composition, electronic structure, and morphology (Argonne, ORNL, UNLV, UIC)
- Determine stability via dissolution measurements, mechanisms of degradation, and predict lifetime via modeling (Argonne)
- Fabricate, test, and characterize membrane-electrode assemblies with newly-developed electrocatalyst (LANL, ORNL)
  - determine performance and durability using accelerated test protocol

Computational analyses will be used to guide the choice of bimetallic systems and compositions

- Quantum mechanical calculations
  - Detailed reaction mechanisms and rate-limiting processes
  - Binding energies and structures for possible intermediates (i.e., O, H, O_2, H_2, OH, OOH, H_2O)
  - How alloying and nano-structure affect the ORR rates
- Large-scale molecular dynamics simulations using ReaxFF
  - Trends in chemisorption energies of oxygen-containing species
  - Effect of nano-particle size, alloying elements, surface defects and segregations, step edges, and kinks on the barriers and rates of the ORR



Caltech computational analysis results:

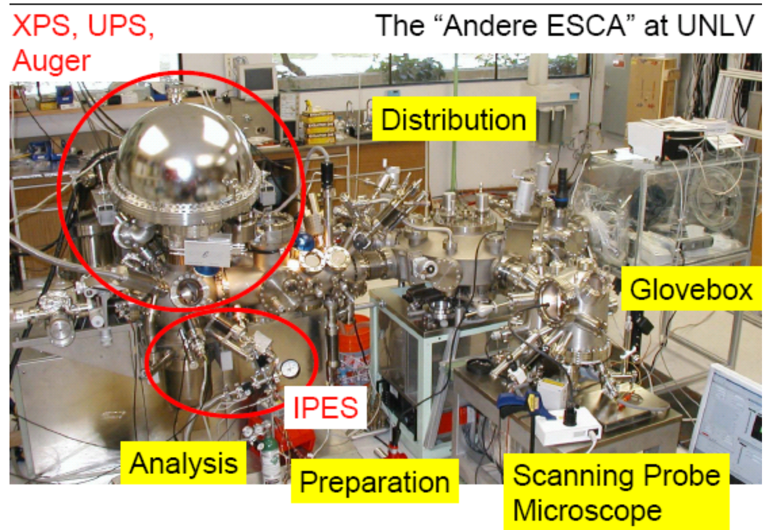
Rate determining step-

OH formation, Ir worse then Pt

Model systems (bulk electrodes) will be used to guide the choice of bimetallic systems

- Used to establish relationship between physicochemical properties and ORR activity
- Model systems
  - Fabrication by arc melting and sputter-cleaning, e-beam evaporation
  - Surface composition verification by XPES

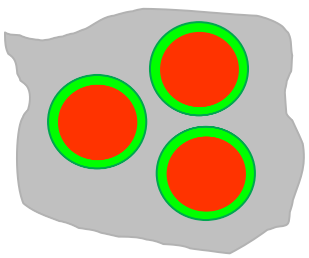
The "Andere ESCA" at UNLV

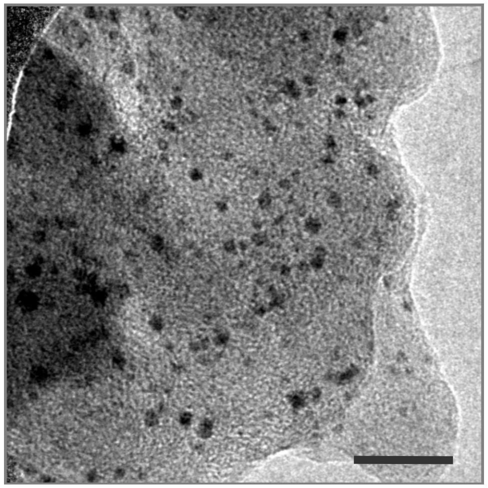


- Electronic characterization (UPS, STS, KPFM)
  - Energy of d-band
  - Density of occupied and unoccupied electronic states
- Oxygen reduction activity, reaction mechanism, and stability
  - Electrochemical measurements via hanging meniscus technique
  - Post-test spectroscopic and microscopic characterization to determine changes in composition, morphology, and electronic properties

Synthesis of nano-particle bimetallic carbon-supported electrocatalysts

- Goals
  - Achieve noble metal-base metal bimetallic core with noble metal skin
  - Minimize particle size, maximize surface area/gram PGM
  - Achieve uniform and controllable particle size and composition
- Techniques
  - Colloidal synthesis
  - Strong electrostatic adsorption

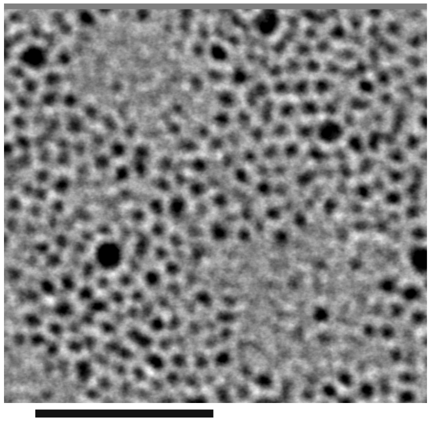




20 nm

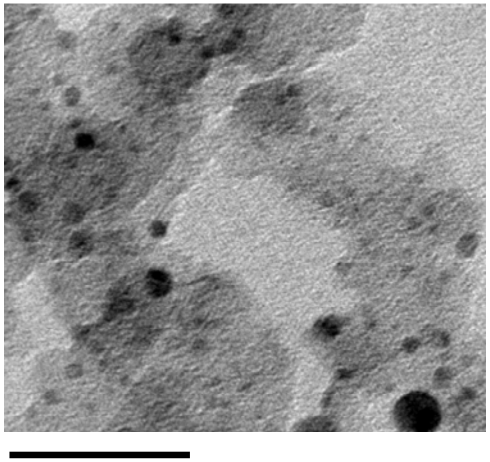
Single-phase colloidal technique for bimetallic nano-particle formation and deposition

- Chemical reduction of metal precursors in the presence of organic capping molecules (e.g., oleylamine and oleic acid)
  - ✓ capping molecules stabilize small particles, limit particle growth
- Pre-formed particles loaded on carbon support
  - ✓ capping molecules maintain particle dispersion
- Removal of capping molecules through thermal or electrochemical decomposition
  - ✓ capping molecules can be removed at moderate temperatures



50 nm

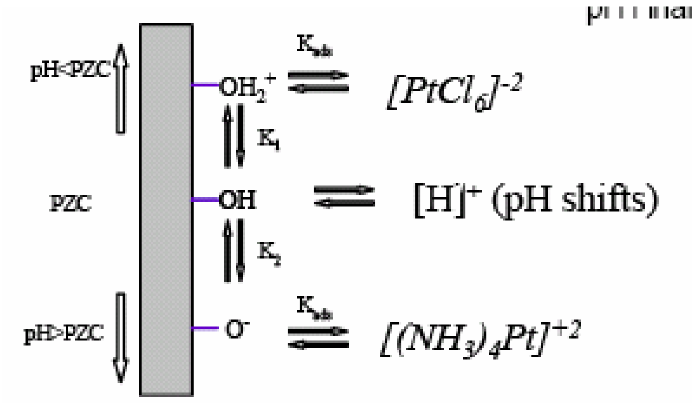
Unsupported Pd-Base Metal



50 nm

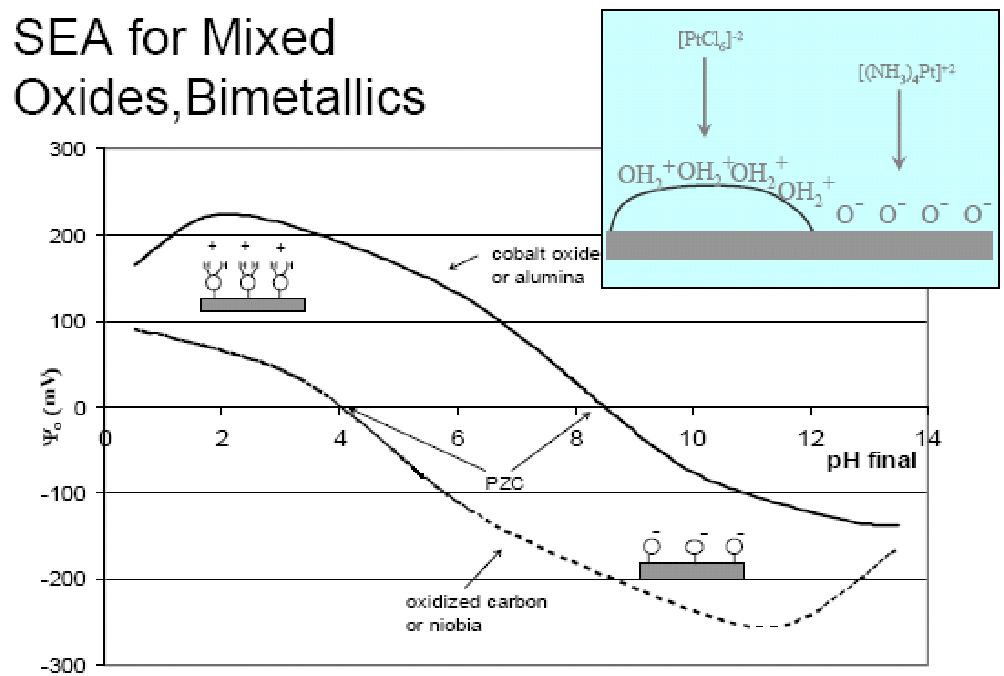
Pd-Base Metal/C

Strong electrostatic adsorption technique for synthesis of core-shell bimetallic nano-particles



- SEA technique has been demonstrated by UIC for Pt-Co bimetallics

- Impregnate at pH between PZCs for selective adsorption and formation of bimetallics

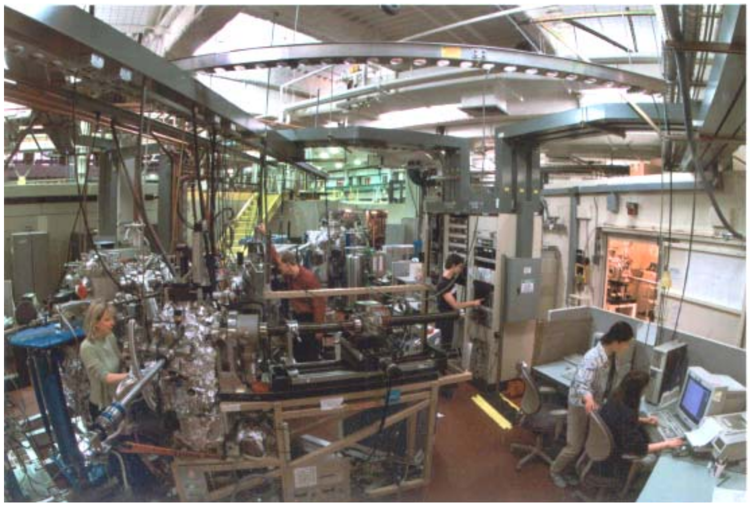


Catalyst activity and structural characterization of carbon-supported nano-particle catalysts

- Determine oxygen reduction activity and reaction mechanism (4 e- or 2 e-)
  - Thin-film rotating ring-disk technique

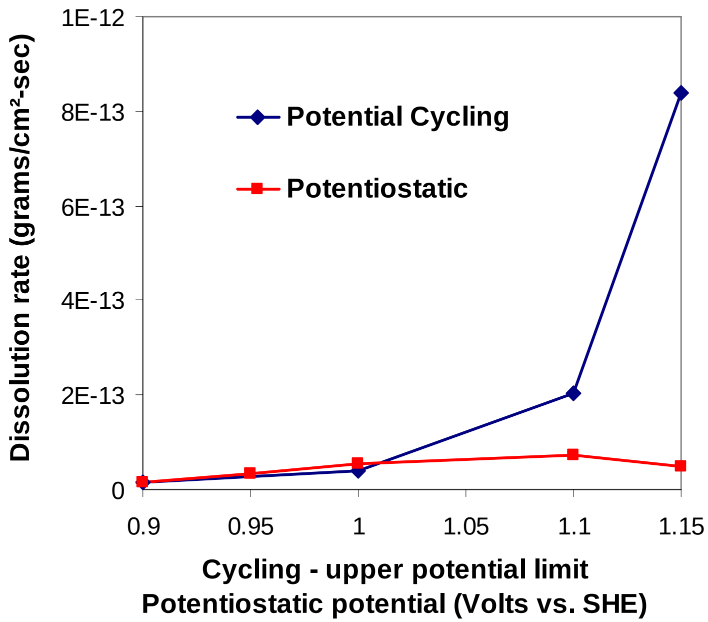
- Verify that desired structures, compositions, and particles sizes are obtained
  - TEM, EDAX, XRD, XAS, XPS, IR of adsorbed CO

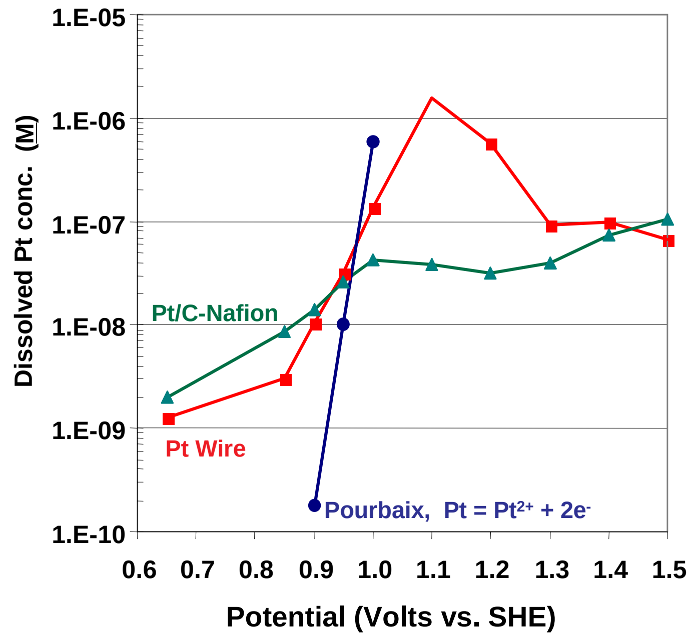
- Characterize nano-particle electronic structure
  - Soft X-ray and UV spectroscopies



Accelerated durability testing of carbon-supported nano-particle catalyst

- Potentiostatic and potential cycling dissolution rates
- Equilibrium concentration of dissolved metallic components of electrocatalysts
- Mechanism of dissolution reaction via rotating ring-disk experiments
- Modeling of performance degradation (beginning with Pt/C commercial electrocatalyst)





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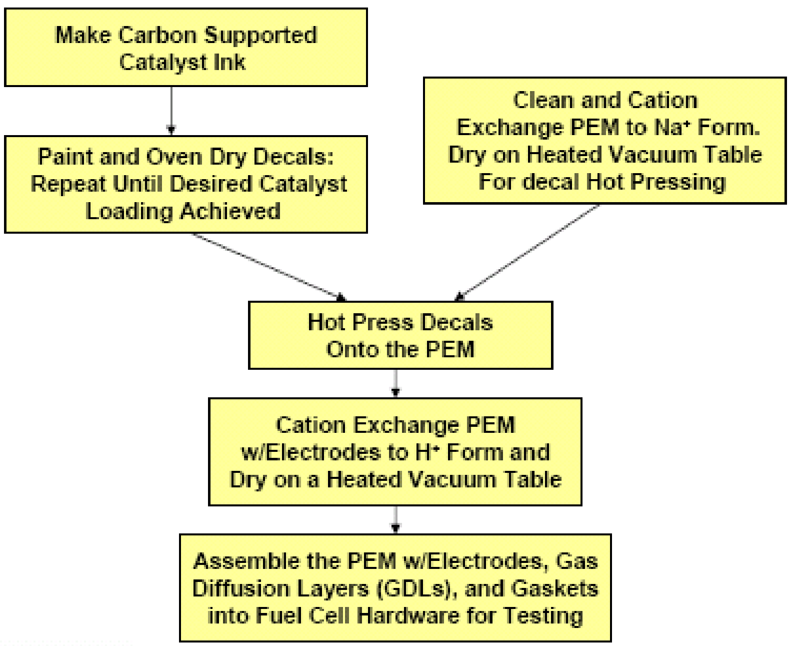
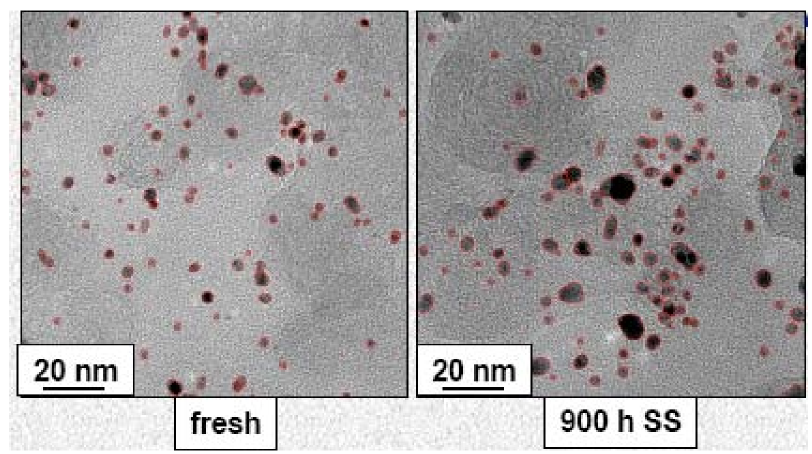
Electrocatalysts that pass activity and durability screening tests will tested in MEAs

- Membrane-electrode assembly fabrication, testing, and characterization
  - MEA fabrication
  - MEA performance and durability testing
    - *Pre- and post-test analyses using TEM, XRD, and SAXS*

LANL H_2-Air MEA Fabrication Procedure



ORNL TEM analyses of LANL MEA



Project schedule

1. Computational analyses
2. Model systems
3. Synthesis of nano-particles
4. Characterization of nano-particles
5. Accelerated durability testing and modeling
6. MEA fabrication and testing

Project Schedule/Milestones

	Year 1				Year 2				Year 3				Year 4			
Task	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1. Computational analyses																
Task 1.1 QM calculations on prototypes																
Task 1.2 New cathode catalyst materials																
Task 1.3 Development of the ReaxFF to reproduce QM results																
Task 1.4 Large-scale ReaxFF MD simulations on binary alloys																
Task 2. Model systems																
Task 2.1 Model system fabrication																
Task 2.2 Model system electronic characterization																
Task 2.3 Model system ORR and stability																
Task 3. Synthesis of carbon-supported nanoparticles																
Task 3.1 Colloidal technique																
Task 3.2 Strong electrostatic adsorption																
Task 4. Characterization of nanoparticle catalysts																
Task 4.1 Structural and compositional analyses																
Task 4.2 Characterization of electronic structure																
Task 4.3 Oxygen reduction activity and reaction mechanism											1					
Task 5. Accelerated durability testing and modeling																
Task 5.1 Potentiostatic dissolution measurements																
Task 5.2 Potential step dissolution rate measurements																
Task 5.3 Mechanism of the dissolution reaction																
Task 5.4 Modeling of performance degradation																
Task 6. MEA fabrication and testing																
Task 6.1 Membrane-electrode assembly fabrication																
Task 6.2 MEA performance, durability testing														2		

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Go/No-Go decision points

- #1: Year 3, end of quarter 2 (June, 2009) decision criteria:
  - ORR activity of the carbon-supported nanoparticle catalysts

    720 μA/cm², 0.44 A/mg$_{PGM}$ (@900 mV$_{iR\text{-}free}$)
  - Stability of ORR activity with time

    Projected durability >5,000 h (at ≤80°C)
  - Cost: *Projected PGM loading ≤0.3 mg/cm²*
  - Catalysts passing these go/no-go criteria will be incorporated into and tested in 5-cm² and 50-cm² membrane-electrode assemblies

- #2: Year 4, end of quarter 1 (March, 2010) decision criteria:
  - Performance of ≥50-cm² MEAs with the newly-developed cathode catalyst

    720 μA/cm², 0.44 A/mg (@900 mV$_{iR\text{-}free}$), 80°C, H_2/O_2, 2/9.5 stoichiometry, fully humidified, 150 kPa
  - Performance durability of ≥50-cm² MEAs containing newly-developed cathode catalyst

    Projected to meet or exceed 5,000 h at ≤80°C

Project budget and acknowledgements

	Funding in $K		
Fiscal Year	DOE	Cost-Share	Total
2007	920	29	949
2008	1,309	45	1,354
2009	1,409	43	1,452
2010	1,436	43	1,479
2011	359	13	372
Total '07-'11	**5,434**	**172**	**5,606**

- Financial support from DOE, Hydrogen, Fuel Cells & Infrastructure Technologies and the universities
- Nancy Garland, DOE Project Manager