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U.S. Department of Energy

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Office of Science
U.S. DEPARTMENT OF ENERGY

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2009 DOE EERE Kick-off Meeting

Announcement No: DE-PS36-08GO98010 **Topic: 1A**

Nanosegregated Cathode Catalysts with Ultra-Low Platinum Loading

Argonne National Laboratory
Materials Science Division

PI: Nenad M. Markovic

Co-PI: Vojislav R. Stamenkovic

Subcontractors:

- **Oak Ridge National Laboratory** – Karren More
- **Jet Propulsion Laboratory** - NASA – S.R. Narayan
- **Brown University** – Shouheng Sun
- **Indiana University Purdue** – Goufeng Wang
- **3M Company** – Radoslav Atanasoski

Overview

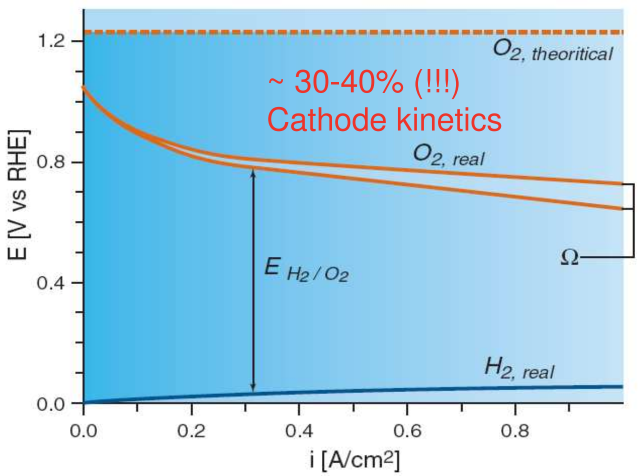
Timeline

- Project start: 9/2009
- Project end: 9/2012

Budget

- Total Project funding $ 6.5M
- Received in FY09: $ 300K

Barriers



- The main losses: CATHODE

1) High content of Pt

2) Poor activity: Pt/C = Pt-poly/10

3) Durability (Pt dissolves: power loss)

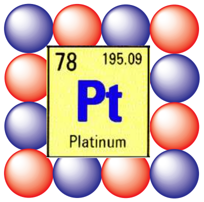
4) Carbon support corrosion

DOE Technical Targets

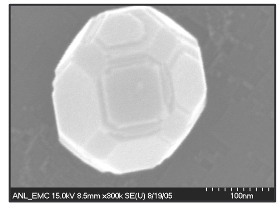
- Specific activity @0.9V$_{iR\text{-}free}$: 720 µA/cm^2
- Mass activity @0.9V: 0.44 A/mg$_{Pt}$
- Electrochemical area loss: < 40%
- Catalyst support loss: < 30%
- PGM Total content: 0.2 g/kW
- PGM Total loading: 0.2 mg/cm$^2_{electrode}$
- Cost*: $ 30/kW$_e$
- Durability w/cycling (80°C): 5000 hrs

*based on Pt cost of $450/troy ounce

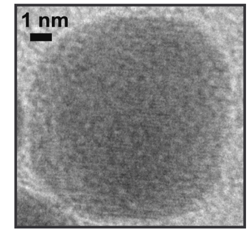
Project Approach



EXTENDED Multi-M SURFACES



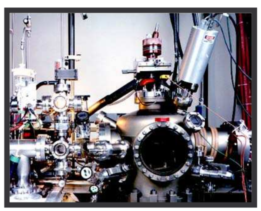
MODEL NANOPARTICLES



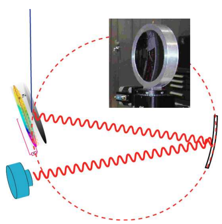
REAL NANOPARTICLES

Materials-by-design approach - developed by ANL will be utilized to design, characterize, understand, synthesize fabricate and test nanosegregated multi-metallic nanoparticles and nanostructured thin metal films

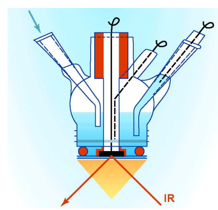
Surface Characterization



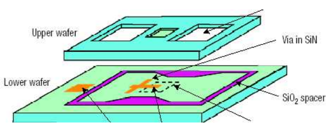
UHV (ANL)



HRDFS (ANL)

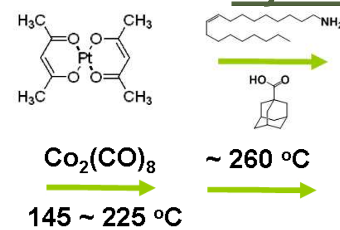


FTIR (ANL)



HRTEM (ORNL)

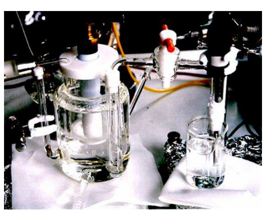
Synthesis



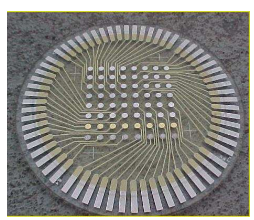
Colloidal (Brown)

Throughput (JPL)

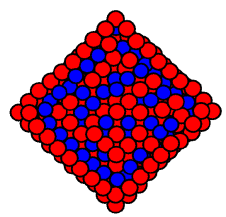
Electrochemical and theoretical screening



RRDE (ANL)

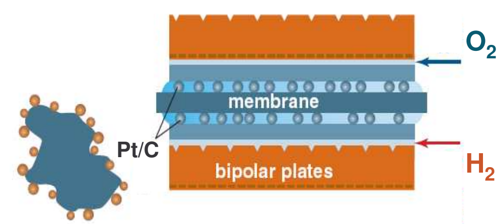


Throughput (JPL)



MC (IUPIU)

MEA fabrication-testing

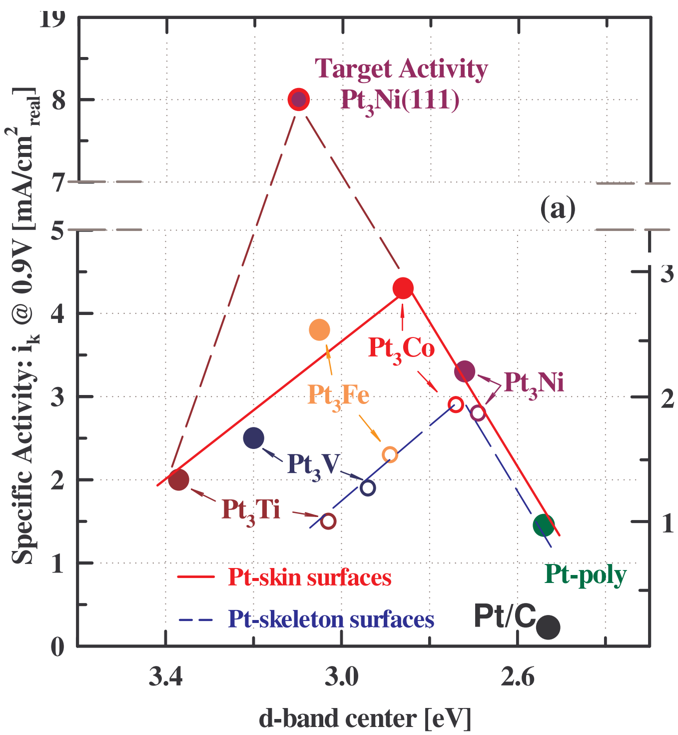


MEA (3M)

Project Objectives

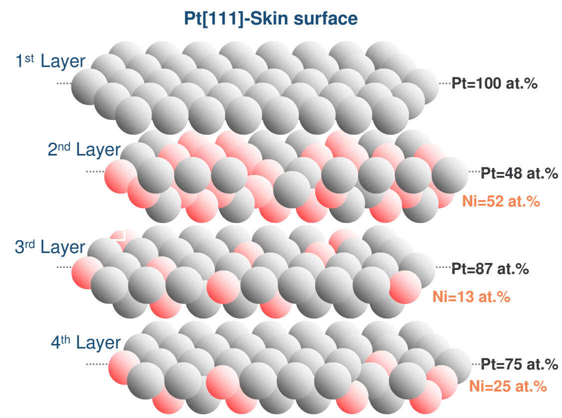
Fundamental understanding of the oxygen reduction reaction on PtM_1M_2 (M_1=Co,Ni; M_2=Fe, Mn, Cr, V, Ti etc) ternary systems that would lead to the development of highly-efficient and durable real-world nanosegregated Pt-skin catalysts with low-Pt content

Activity Map



V.Stamenkovic, B.S.Mun, M. Arenz, K.J.J.Mayerhofer, C.Lucas, G.Wang, P.N.Ross, N.M.Markovic
Nature Materials, 6(2007)241.

Nanosegregated Profile

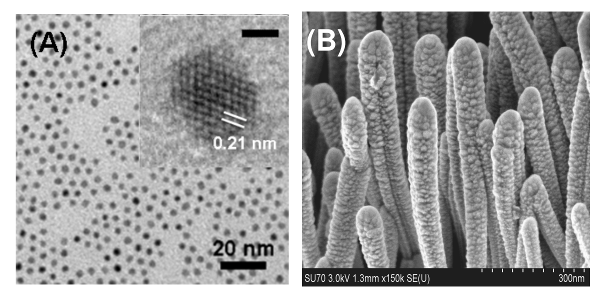


Pt(111)-Skin is the most active catalyst for the oxygen reduction reaction, and it is ~100 times more active than the state-of-the-art Pt/C catalysts

V.Stamenkovic, B.Flower, B.S.Mun, G.Wang, P.N.Ross, C.Lucas, N.M.Markovic
Science, 315(2007)493.

Technical Targets

- Specific activity @ $0.9V_{iR\text{-free}}$
  2015 DOE target x 3
- Mass activity @ $0.9V_{iR\text{-free}}$
  2015 DOE target x 3
- Electrochemical area loss
  2015 DOE target
- PGM Total content
  < 0.1g/kW



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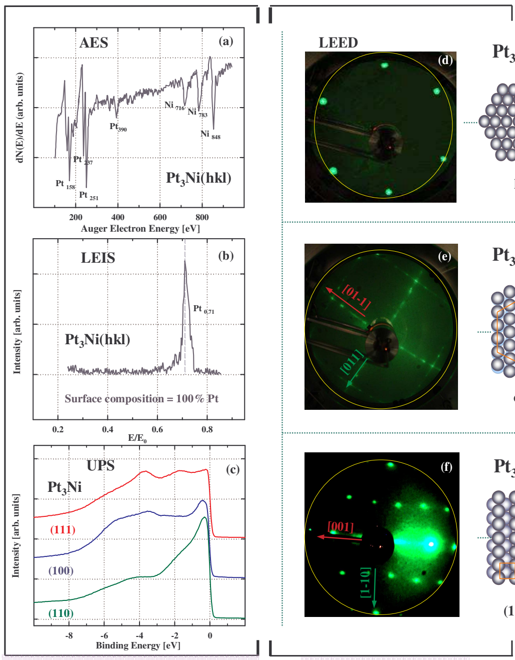
Relevant Prior Work

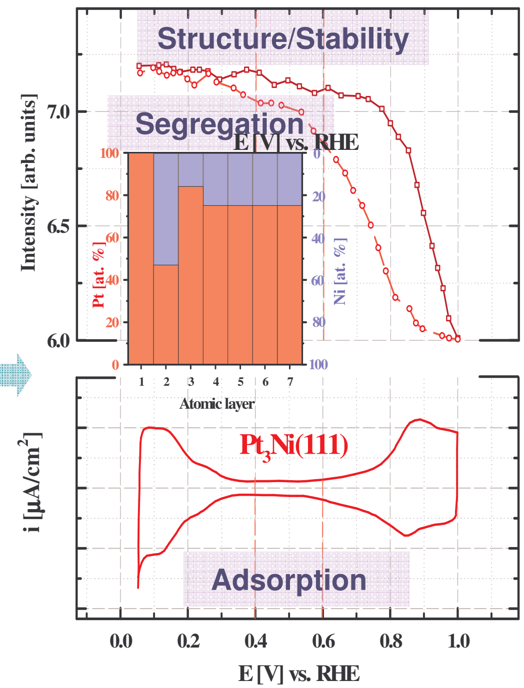
UHV



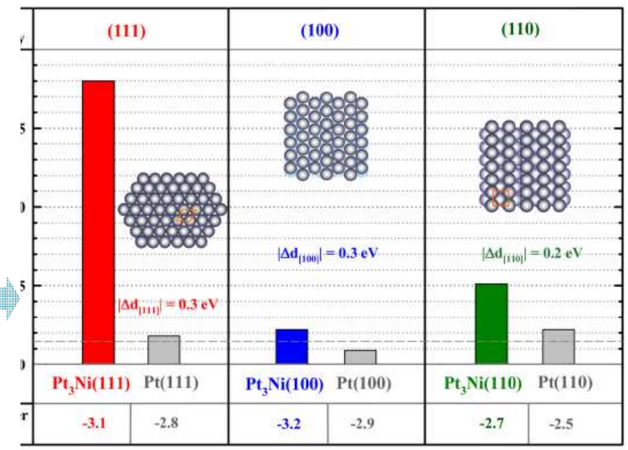
Composition

Structure

SXS-EC

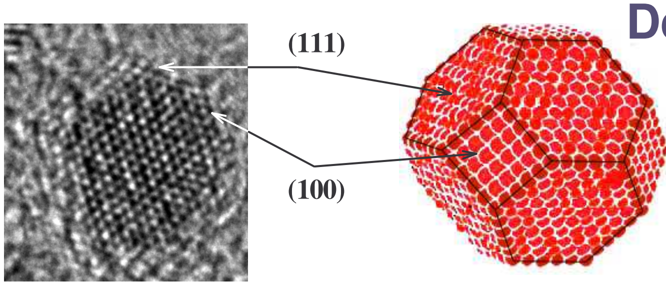


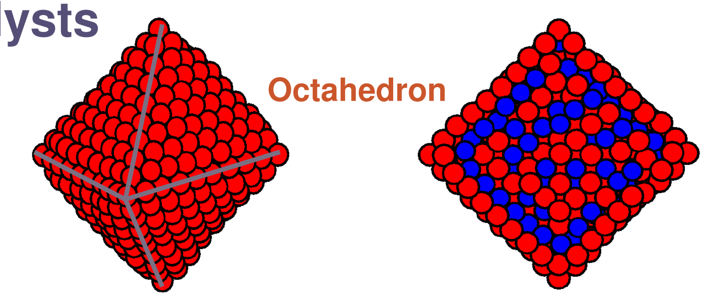
EC



The most active ORR catalysts

Design of real catalysts





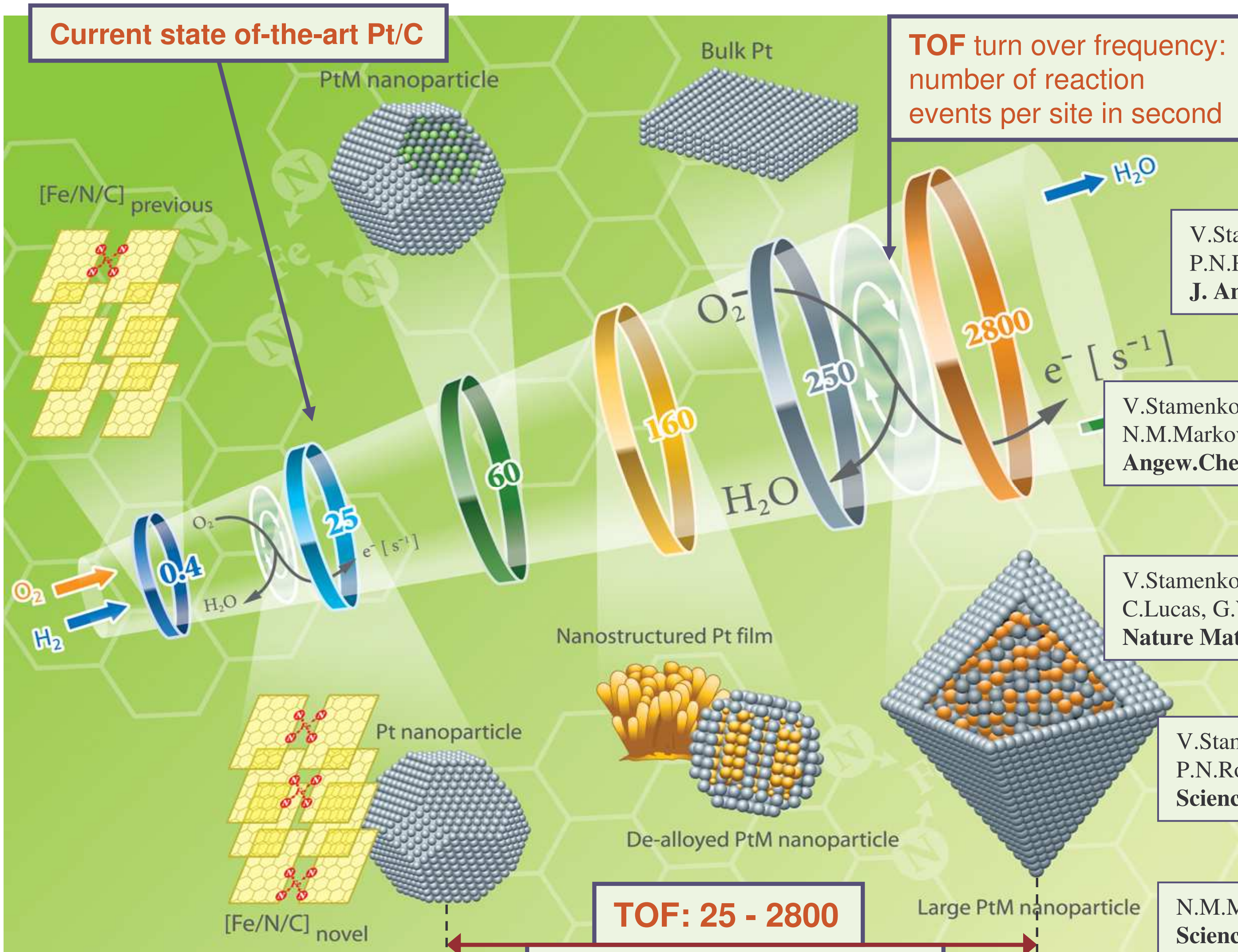
Conventional Catalysts

Tailored Nanoscale Catalysts

Relevant Prior Work

Current state of-the-art Pt/C

TOF turn over frequency: number of reaction events per site in second



TOF: 25 - 2800

Potential for improvements

V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic
J. Am.Chem.Soc., 128(2006)8813

V.Stamenkovic, B.S.Mun, K.J.J.Mayrhofer, P.N.Ross, N.M.Markovic, J.Rossmeisl, J.Greeley, J.K. Norskov
Angew.Chem.Int.Ed., 45(2006)2897

V.Stamenkovic, B.S.Mun, M. Arenz, K.J.J.Mayerhofer, C.Lucas, G.Wang, P.N.Ross, N.M.Markovic
Nature Materials, 6(2007)241

V.Stamenkovic, B.Flower, B.S.Mun, G.Wang, P.N.Ross, C.Lucas, N.M.Markovic
Science, 315(2007)493

N.M.Markovic, H.A. Gasteiger
Science, 3124(2009)48

Project Tasks

Task 1. Fundamental understanding

1.1 Resolving electronic/atomic structure and segregation profile

1.2 Understanding the reaction mechanism of the ORR

1.3 Mass activity and durability improvement

Task 2. Synthesis and characterization

2.1 Physical methods: TM films (5-10 layers), nanoparticles (5-300 nm)

2.2 Chemical methods: colloidal and impregnation methods

2.3 Characterization: Ex-situ (UHV, TEM) and in-situ (SXS, EC, Combinatorial)

2.4 Theoretical modeling (DFT, MC) methods

Task 3. Fabrication and testing

3.1 New PtM_1M_2 catalyst to increase catalytic activity and decrease dissolution

3.2 Carbon support vs. nanostructured thin film catalysts

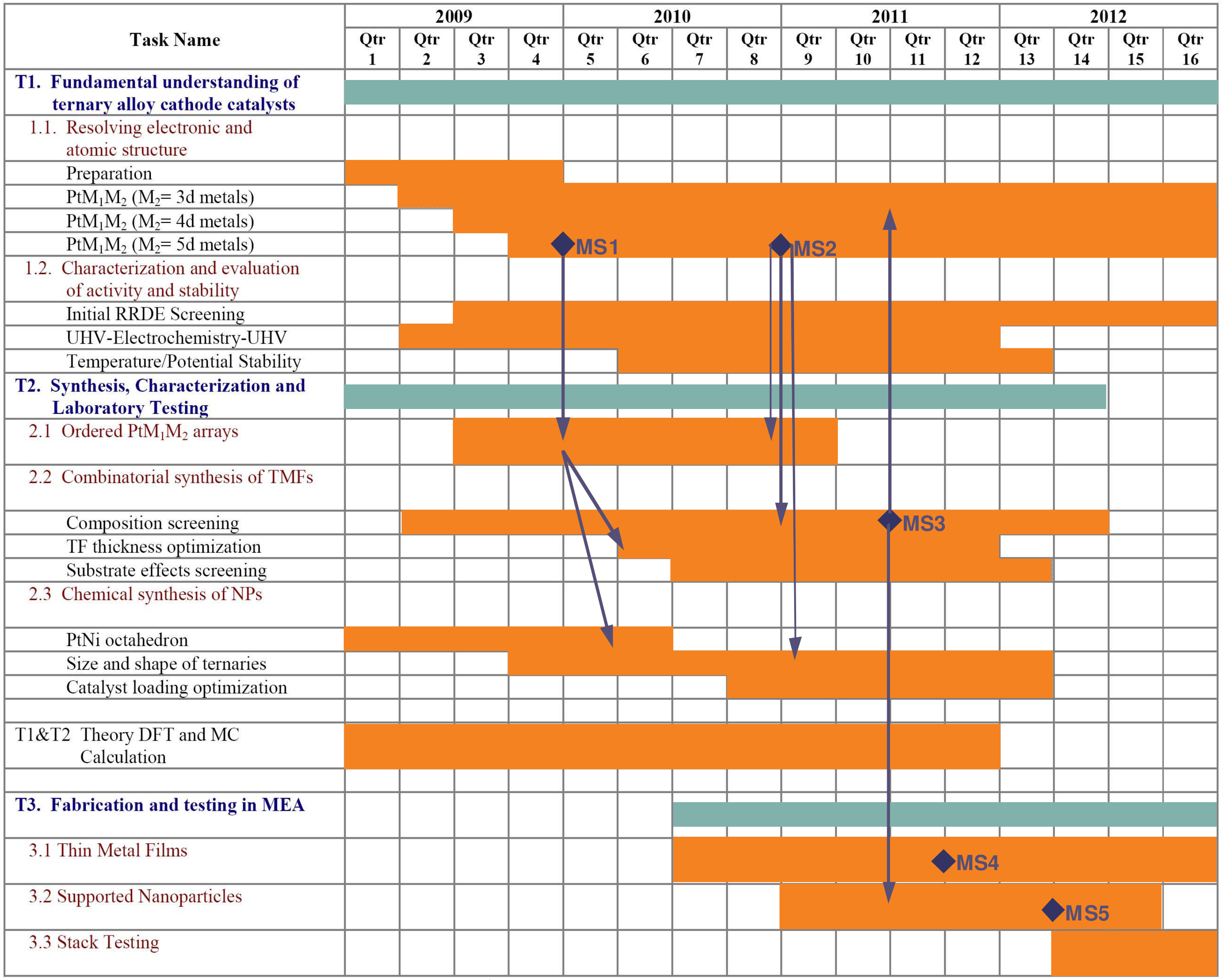
3.3 MEA testing (50 cm^2)

3.4 Short stack testing verification (>300cm^2)

Organization Responsibilities

Task / Lab	1.1	1.2	1.3	2.1	2.2	2.3	2.4	3.1	3.2	3.3	3.4
ANL	■	■	■	■	■	■	■	■	■	■	■
ORNL						■					
JPL				■		■				■	
Brown					■				■		
IUPIU							■				
3M				■					■		■

Project Timelines



◆MS – Mile Stones with corresponding Go – NoGo decision points described in text

Budget

In thousands $	FY09	FY10	FY11	FY12
ANL	865	858	884	781
ORNL	150	150	150	150
JPL	260	260	260	260
Brown University	120	125	131	136
Indiana Purdue U	80	82	85	87
3M	23	40	59	123
TOTAL	1,498	1,515	1,569	1,537