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Polymer Electrolyte Fuel Cell Electrocatalysis

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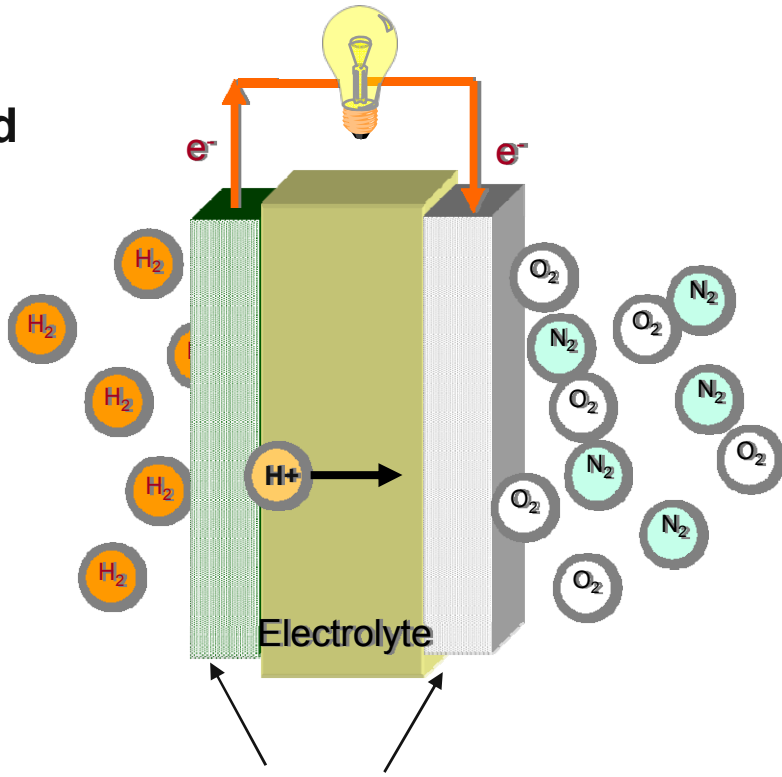
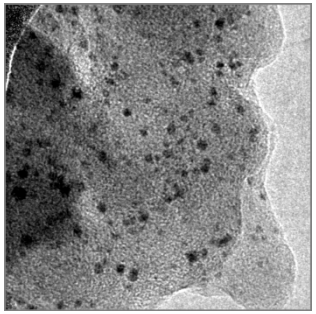
The Oxygen Reduction Reaction (ORR) is the key catalytic challenge for hydrogen/air fuel cell vehicles

- **State-of-the-art fuel cell anode and cathode catalysts are platinum nanoparticles supported on high surface area carbon (Pt/C)**
- Nanoparticles maximize Pt surface area for catalysis per gram of Pt
- **Anode**
  - Kinetics are fast on Pt – seven orders of magnitude faster than cathode reaction
  - Low Pt loadings (0.05 mgPt/cm^2) work well on anode
- **Cathode**
  - Kinetics are slow on Pt ⇒ high voltage losses
    - *400 mV out of 560 mV total loss at 1.5 A/cm²*
  - High Pt loadings necessary (~0.4 mg pure Pt/cm^2)
    - *Pt/C ORR activity of 0.11 A/mg Pt*
    - *0.5 g Pt/kW is state-of-the-art for stacks with Pt/C cathode catalyst*

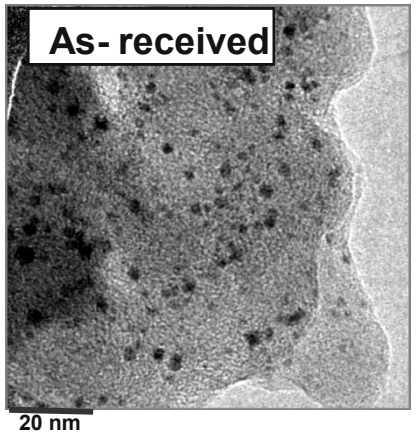


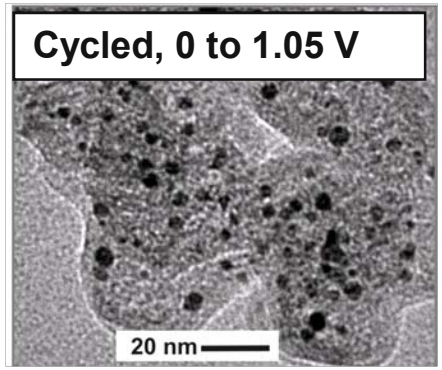


20 nm

Pt cathode catalyst durability limits PEMFC lifetime

- Automotive fuel cell stack operating conditions promote materials degradation
  - Polymer electrolyte is very acidic
  - 300,000 large load cycles
    - *~1/3 loss of Pt surface area loss over 1000 hours at constant current and after 1000 voltage cycles (2.5 nm to 3.5 nm particle growth)*
  - 30,000 shutdown/startups
    - *Can result in very corrosive conditions (high voltages)*
    - *Corrodes catalyst and carbon support*
  - ~2500 subfreezing starts
    - *Transition through frozen and liquid water product*
- Must last for 5,000 operating hours with less than 50 to 75 mV voltage loss
  - Less than 5 to 12-fold loss of catalyst activity
- Current durability status with conventional Pt/C materials is 2,000 hours with cycling





U.S. Department of Energy Catalyst Technical Targets

Characteristic	Units	Stack Targets	
		2010	2015
Platinum group metal total content (both electrodes)	g/kW (rated)	0.3	0.2
Platinum group metal (PGM) total loading	mgPGM/cm² electrode area	0.3	0.2
Cost	$/kW	5[a]	3[a]
Durability with cycling Operating temp ≤80°C Operating temp >80 °C	 h h	 5,000[b] 2,000[b]	 5,000[b] 5,000[b]
Electrochemical area loss[c]	%	<40	<40
Electrocatalyst support loss[c]	mV after 100 h@ 1.2V	<30	<30
Mass activity[d]	A/mgPt @ 900 $mV_{iR\text{-}free}$	0.44	0.44
Specific activity[d]	$\mu A/cm^2$ @ 900 $mV_{iR\text{-}free}$	720	720
Non-PGM catalyst activity per volume of supported catalyst	A/cm^3 @ 800 mV (IR-free)	>130	300

[a] Based on 2002 dollars, platinum cost of $450/troy ounce = $15/g, loading <0.2 g/kW and cost projected to high volume production (500,000 stacks per year)

[b] Includes typical driving cycles.

[c] Tested per GM protocol (Mathias, M.F., et al., Interface, Electrochemical Society, Fall, 2005, p. 24.)

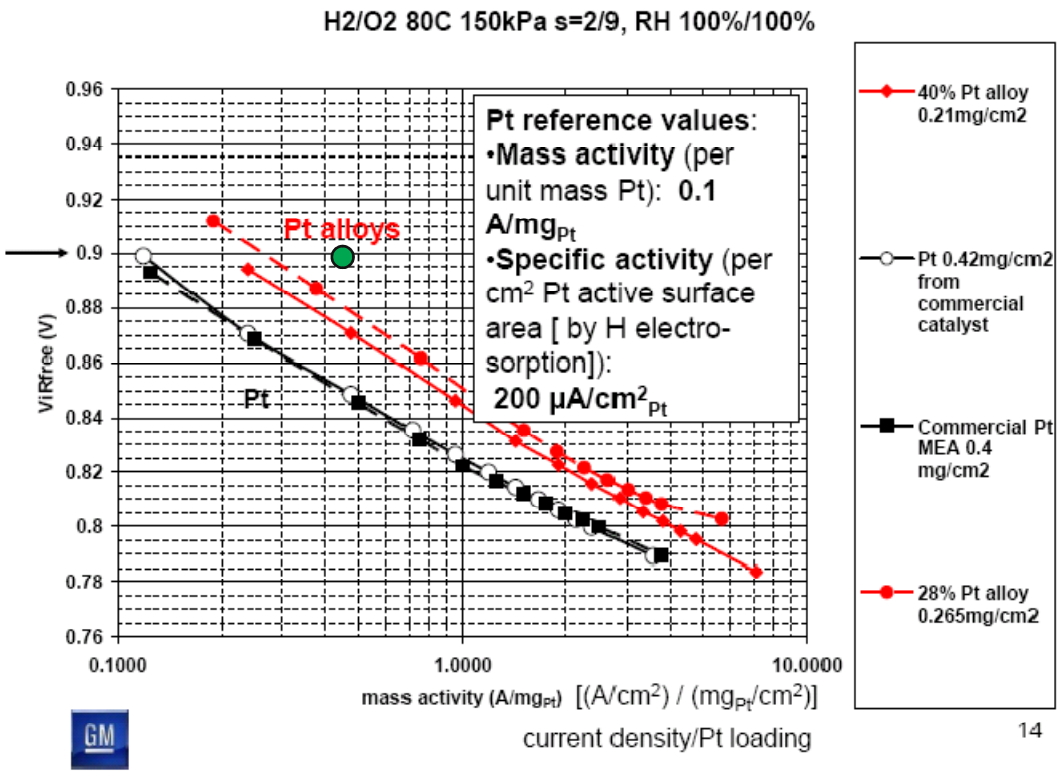
[d] Test at 80°C/120°C H2/O2 in MEA; fully humidified with total output pressure of 150 kPa; anode stoichiometry 2; cathode stoichiometry 9.5

Approaches to developing lower cost and more durable cathode catalysts

- **Platinum group metal (PGM) alloys**
  - Changing electronic properties/bonding characteristics of PGM
- **Ultra-low Pt loading by "nano-engineering" of particles**
  - Core-shell structures
- **Novel support and catalyst structures**
  - Organic "whiskers"
  - Carbon nanotubes
  - Mesoporous carbon supports
  - Conductive oxide supports
- **Non-PGM catalysts**
  - Fe and Co complexed with carbon-nitrogen molecules/polymers
    - *not pyrolyzed, pyrolyzed, and acid-leached*
  - Chalcogenides
  - Carbides, oxides, oxynitrides, and oxycarbonitrides

Alloying Pt with base metals enhances ORR activity by 2x

- Many researchers over several decades have shown that Pt alloys have higher ORR activities than Pt alone.
  (P. Ross, M. Watanabe, K. Kinoshita, R. Adzic, N. Markovic, V. Stamenkovic, D. Landsman, F. Luczak, and many others)
- Nanoparticles do not achieve the high levels of enhancement (4-10x) seen with bulk alloys, but enhancements of 1.5 to 4x are observed.

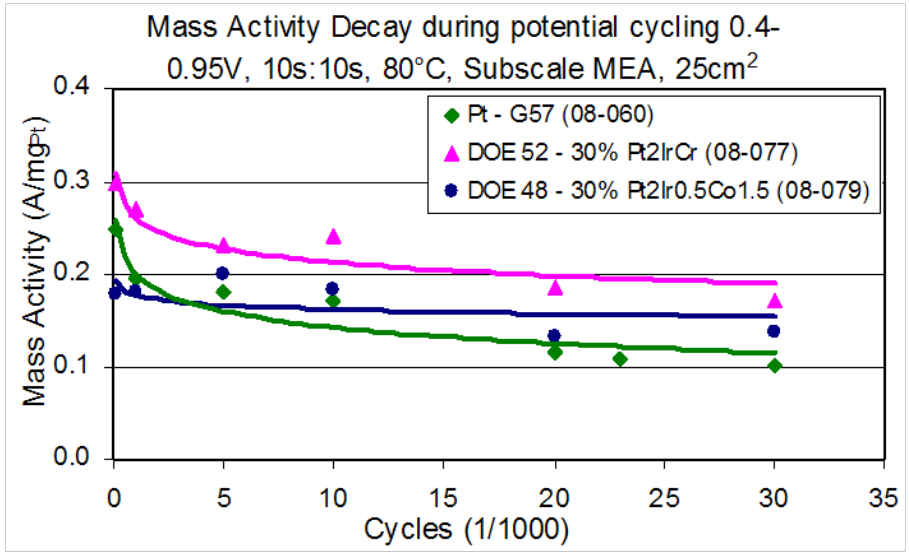


Short stack data from General Motors

Reference: F. Wagner, General Motors, Progress MEA 2008 Conference, La Grande Motte, France, Sept., 2008.

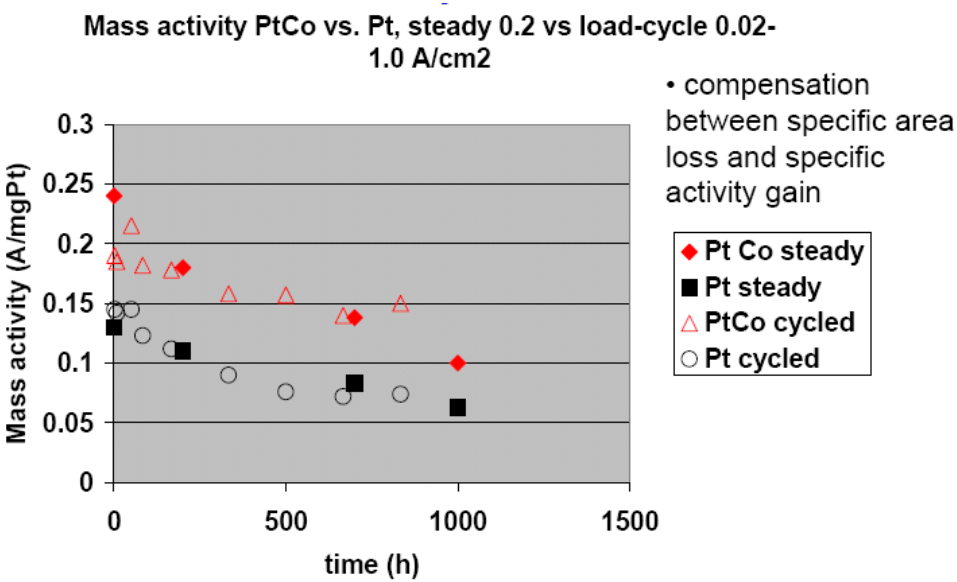
Pt alloys also show superior resistance to surface area loss and maintain activity advantage over time

- UTC Power PtIrCr alloy



Source: S. Motupally, UTC Power, Jan., 2009.

- Platinum alloy particles lose activity with time, however
  - activity benefit of alloys still retained after 1,000 hours of operation
  - base metal lost immediately from alloy surface, but maintained in core

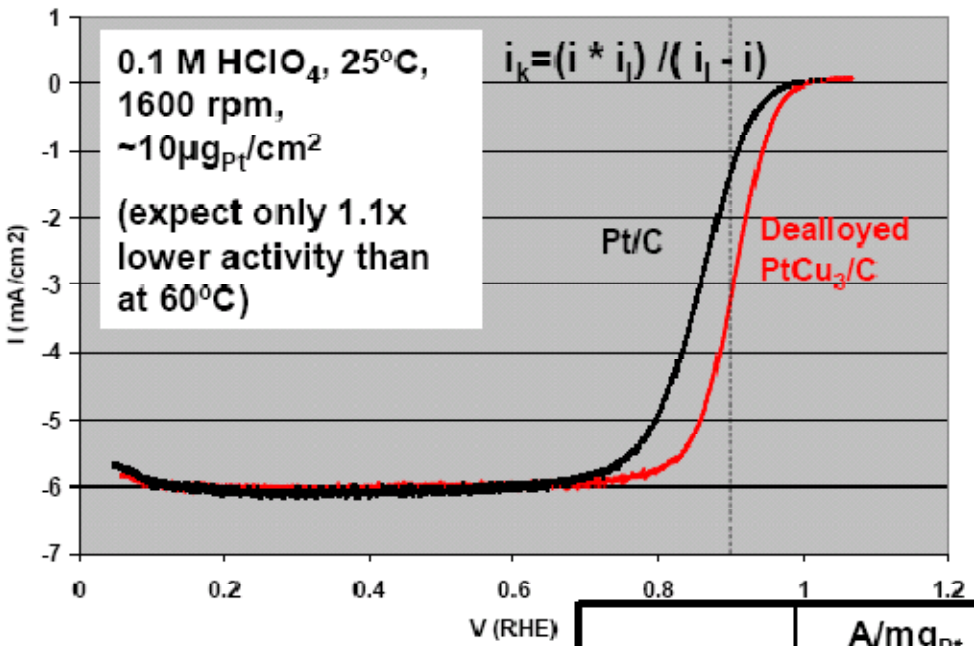


• compensation between specific area loss and specific activity gain

Source: F. Wagner, General Motors, Progress MEA 2008, La Grande Motte, France, Sept., 2008.

De-alloyed $PtCu_3$ exceeds Pt mass activity targets in liquid electrolyte tests

- P. Strasser, University of Houston
- Activity and durability need to be confirmed in fuel cell tests



N. Hahn, S. Koh and P. Strasser, ECS Trans. 3(1), 2006, 139.

- activating pretreatment removes most copper
- but Pt-Pt XRD spacing still that of a PtCu alloy (smaller)

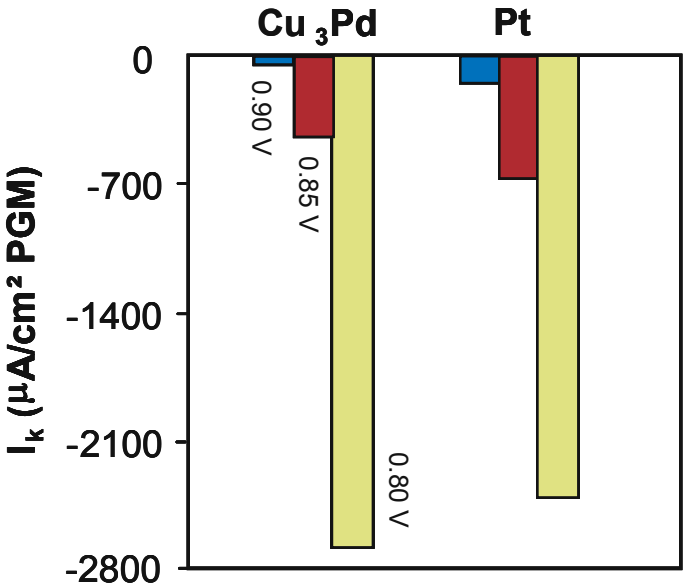
	A/mg$_{Pt}$	m²/g$_{Pt}$
Dealloyed $PtCu_3$/C	0.52	88
Pt/C	0.12	77

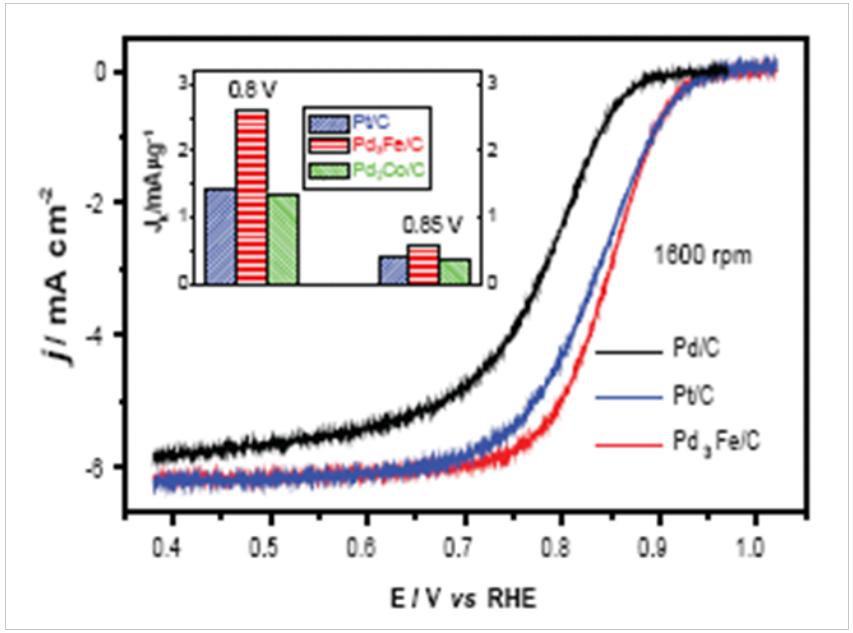
29

Source: Fred Wagner, General Motors, Progress MEA 2008 Conference, La Grande Motte, France, Sept., 2008.

Alloying palladium with base metals also enhances Pd's activity

- Brookhaven National Laboratory; Argonne National Laboratory; University of Texas; Ecole Polytech, Canada; and others.
- Activity of Pd_3Fe exceeds that of Pt, but does not achieve DOE target

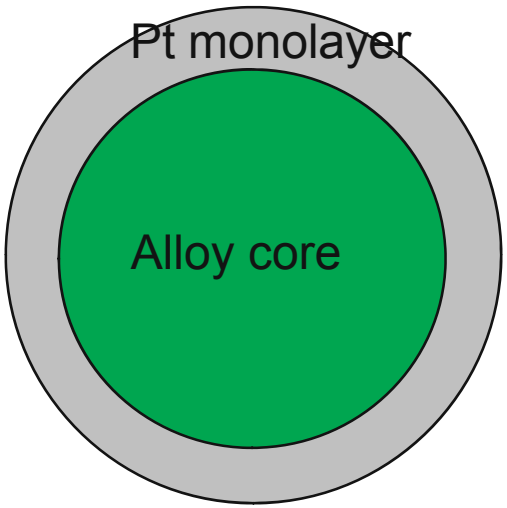


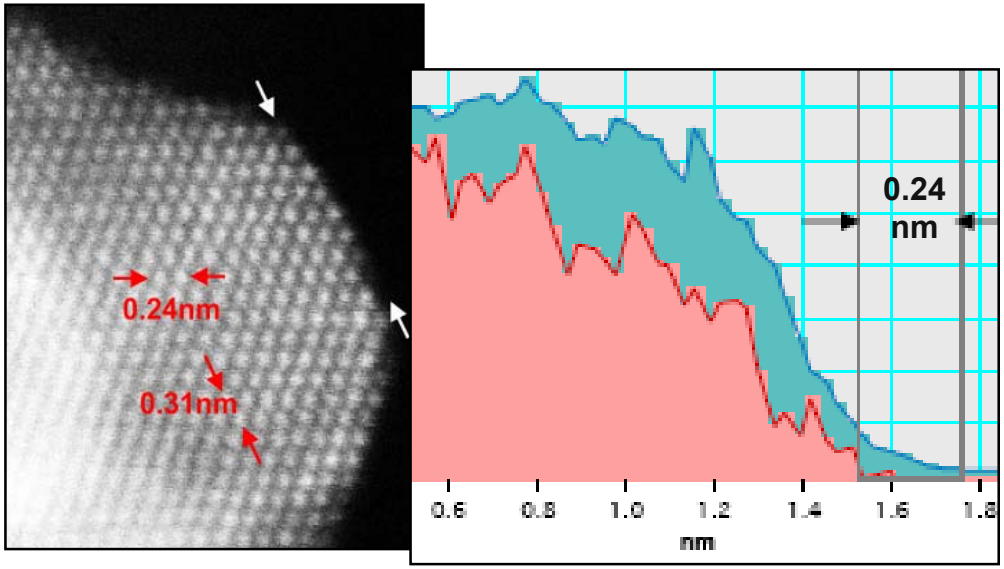


Source: R. Adzic, 2006 DOE Annual Report.

Core-shell structures improve Pt utilization

- Only Pt atoms on the surface of nanoparticles are active for ORR
  - For 3-5nm nanoparticles ~25% of atoms are on the surface, ~75% are not available for catalysis
- Core-shell catalysts with thin (monolayer) shells of Pt and cores of less expensive metals maximize Pt utilization and reduce cost
- Core metals or alloys modify the electronic structure of the Pt shell to enhance its ORR activity

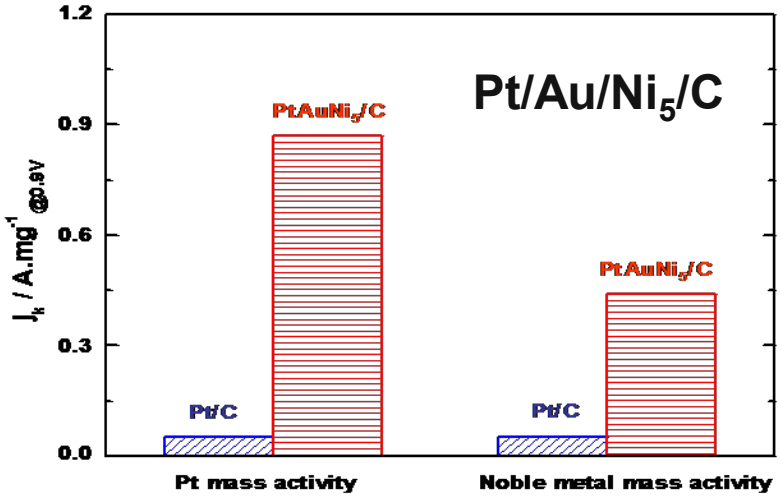


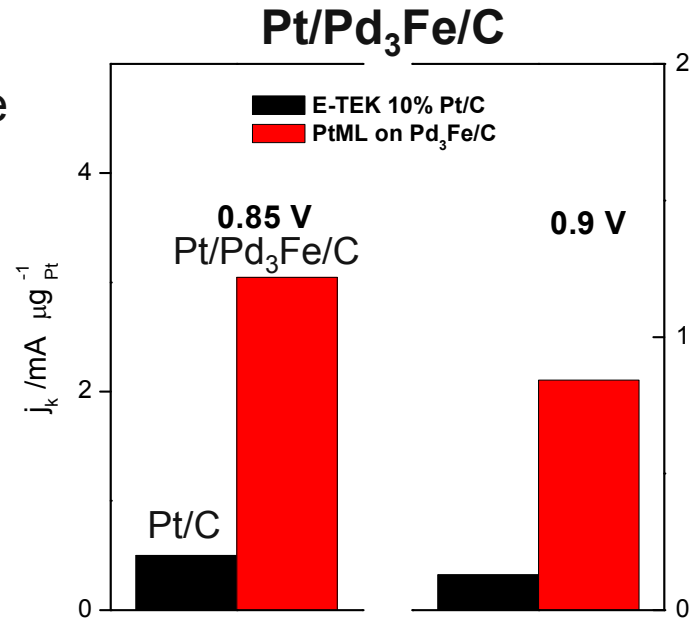


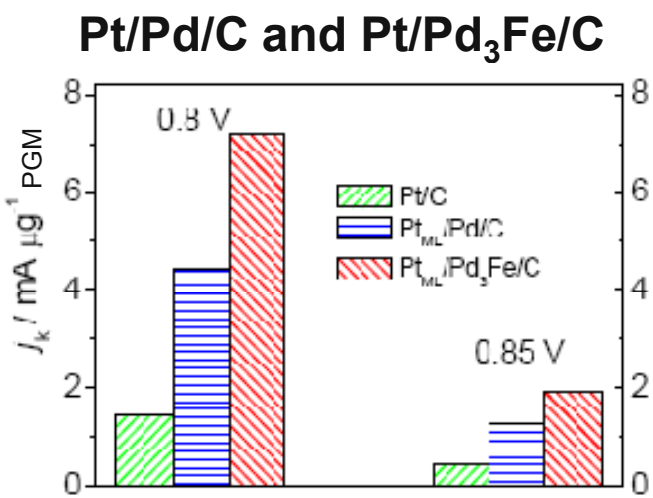
Source: P. Zelenay, FC-3, 2008 DOE Hydrogen Program Review.

Pt monolayers on alloy cores exceed DOE activity targets in liquid electrolyte tests

- Brookhaven National Laboratory
- Pt on Pd core; Pt on Pd_3Fe; Pt on Au/Ni_5 core





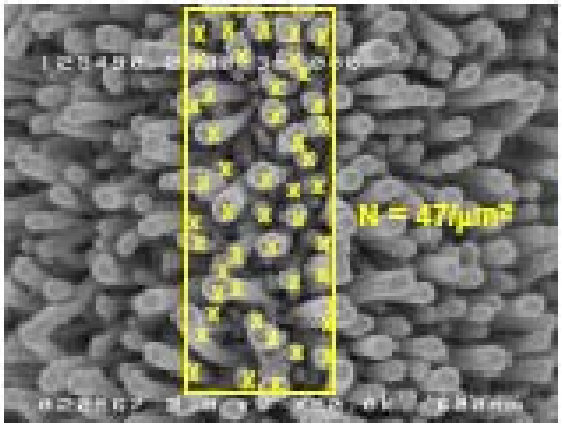


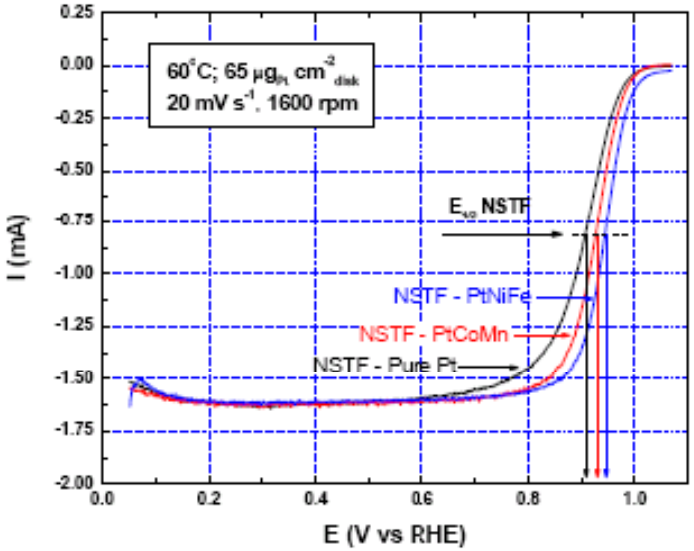
- Pt on Pd shows 2.5 times activity of Pt
- Pt on Pd_3Fe shows 5 times activity of Pt
- Pt on Pd core shows perfect core-shell structure with complete layer-by-layer shell formation
- Incomplete shell formation with other catalysts

Source: R. Adzic, Brookhaven National Laboratory.

Novel support structures - organic "whiskers"

- 3M's nanostructured thin film (NSTF) electrodes are formed from an organic pigment
- Pt and Pt alloys are vapor-phase deposited on aligned whiskers
- Catalyst forms continuous thin layer over whiskers
- Catalyst has high activity and stability due to thin film rather than nanoparticle structure
- Best NSTF-supported Pt alloy catalyst shows 4x activity of state-of-the-art nanoparticle Pt (Source: V. Stamenkovic, Argonne National Laboratory, Feb., 2009)

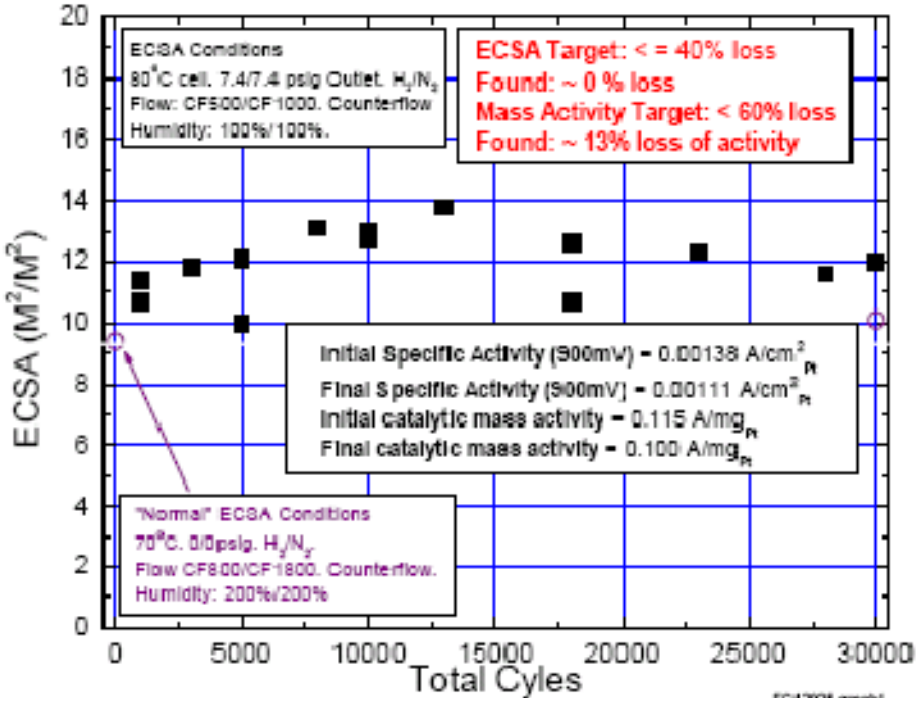




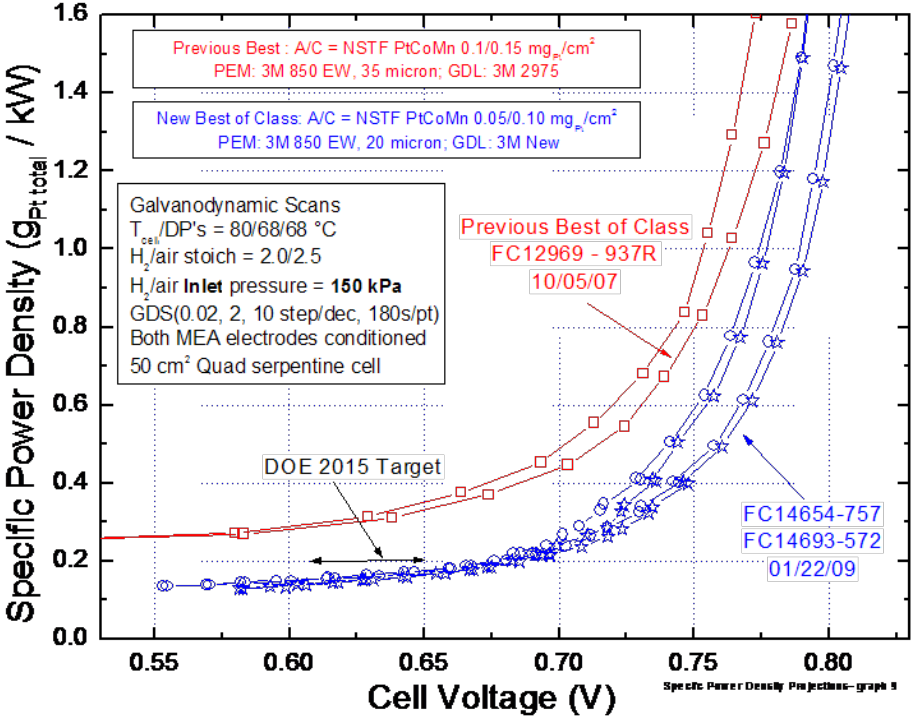
Source: M. Debe, FC-1, 2008 DOE Hydrogen Program Annual Merit Review.

3M NSTF catalyst shows the potential to exceed the 2010 catalyst durability and 2015 Pt loading targets

- 3M NSTF catalyst showed no surface area loss and low mass activity loss (13%) over 30,000 voltage cycles in a single cell (must be demonstrated in a stack)
- <0.2 g Pt/kW achieved with 0.05/0.10 mgPt/cm^2 on anode/cathode in a single cell (shows the potential to exceed DOE's 2015 0.2 g/kW peak power stack target)
- Challenge with NSTF architecture is preventing "flooding" of catalyst layer



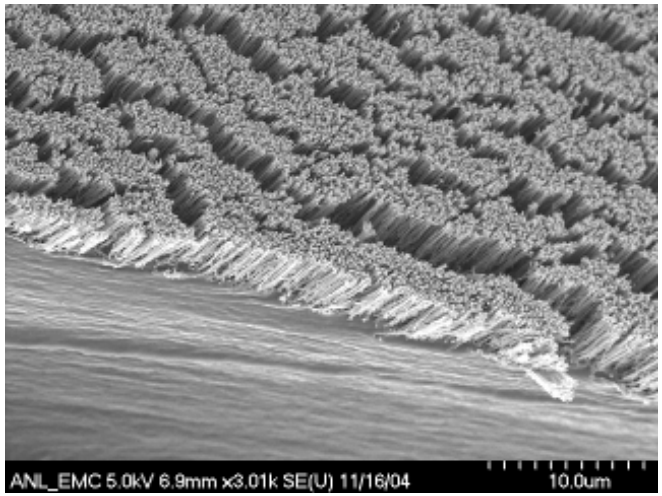
Source: M. Debe, FC-1, 2008 DOE Hydrogen Program Annual Merit Review.



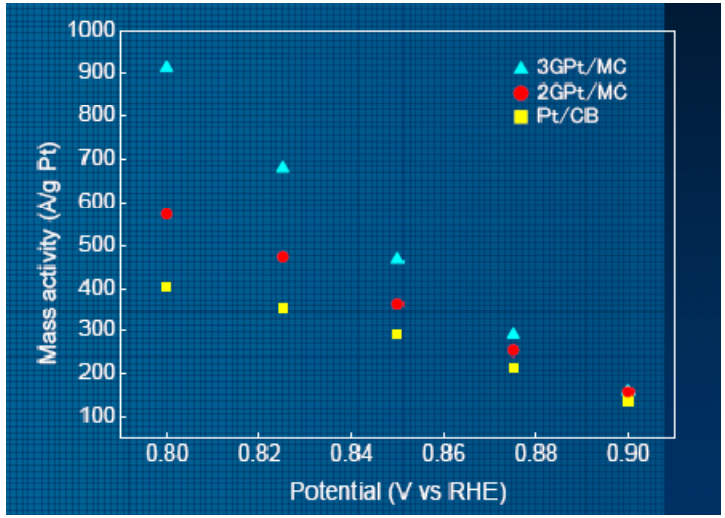
Source: M. Debe, 3M, Jan., 2009.

Carbon nanotubes and mesoporous carbon supports

- Argonne National Laboratory; U. California-Riverside; U. New Mexico, U. Dayton; FC-Cubic, Japan; ECN, Netherlands; others
- Well-controlled electrode architecture can improve platinum utilization and reactant access to catalyst
- Carbon nanotubes and mesoporous carbon show higher stability than traditional carbons
- Mesoporous carbon support improves mass activity of platinum
- Very small (<1 nm) Pt particles are encapsulated and stabilized by mesopores
- Mesoporous carbons have issues with poorer conductivity than traditional carbon



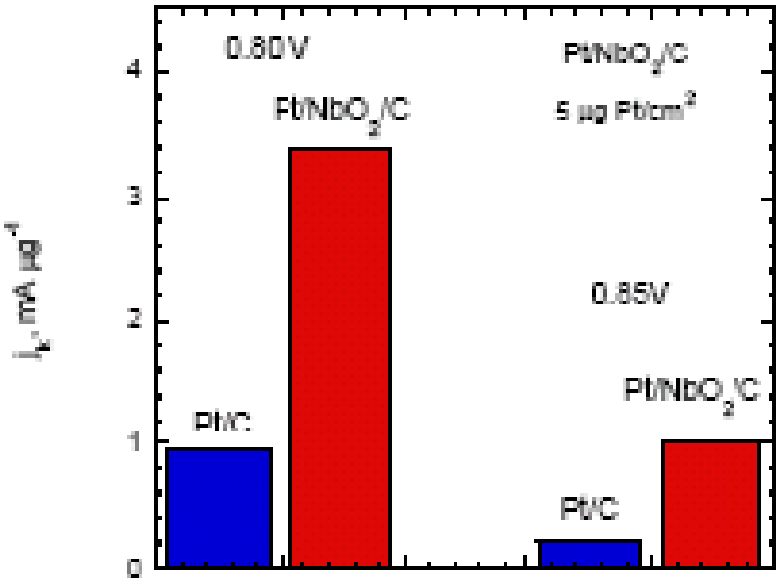
Source: D.J. Liu, Argonne National Laboratory



Source: H. Notsu, T. Kitamura,A. Hayashi, I. Yagi, FC-Cubic, Japan,3rd LANL-NEDO-AIST Workshop, San Diego, CA, Sept., 2008.

Oxide supports and additives improve Pt ORR activity

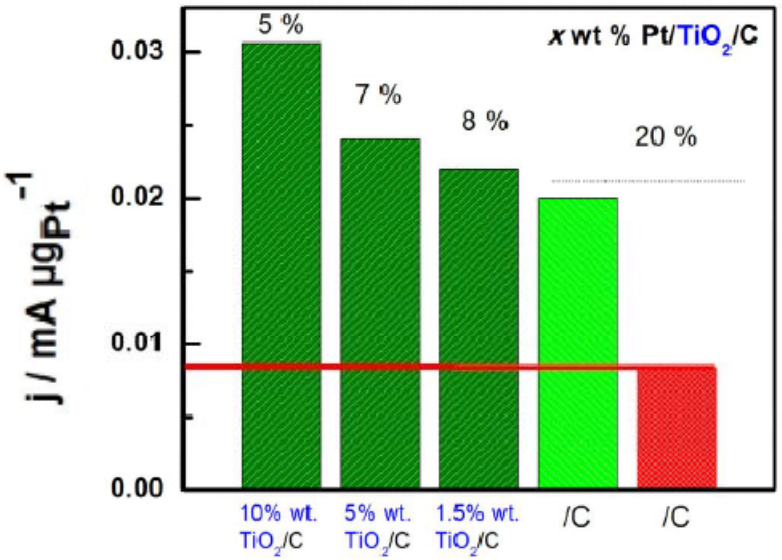
- NbO_2 (Brookhaven NL); TiO_2 (U. Poitiers, France); $NbTi_4O_9$ (AIST, Japan)



- $Pt/NbO_2/C$: Three times the activity of Pt on carbon alone

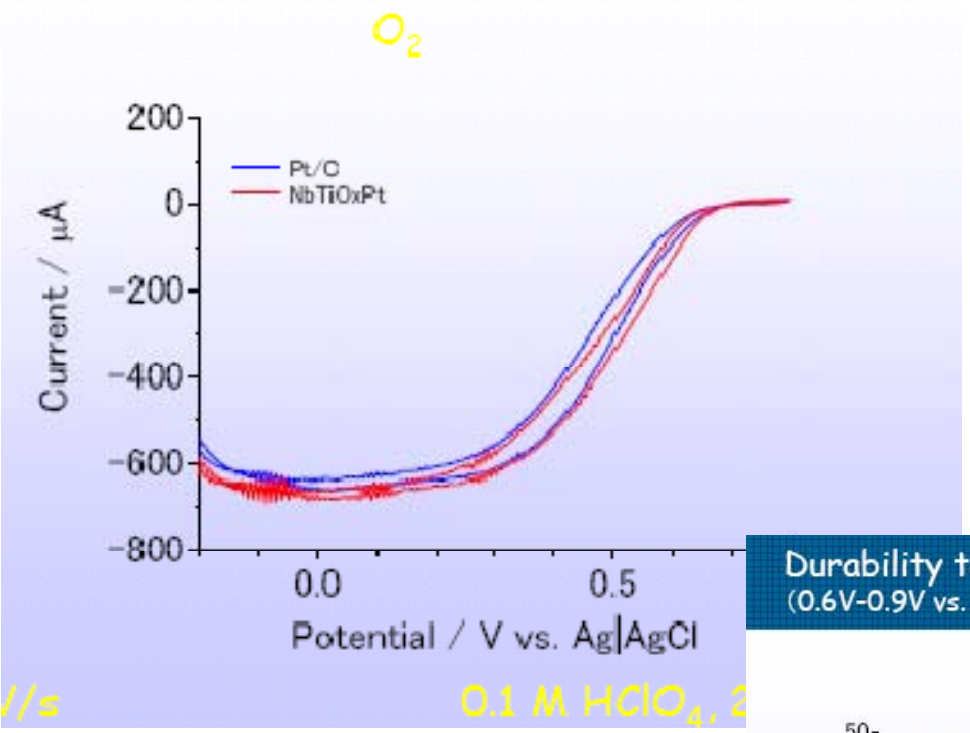
Source: R. Adzic, J. Zhang, K. Sasaki, M. Vukmirovic, J. Wang, M. Shao, FC-09, DOE Hydrogen Program Review, May 16-19, 2006.

- $Pt/TiO_2/C$: Three times the activity of Pt on carbon alone

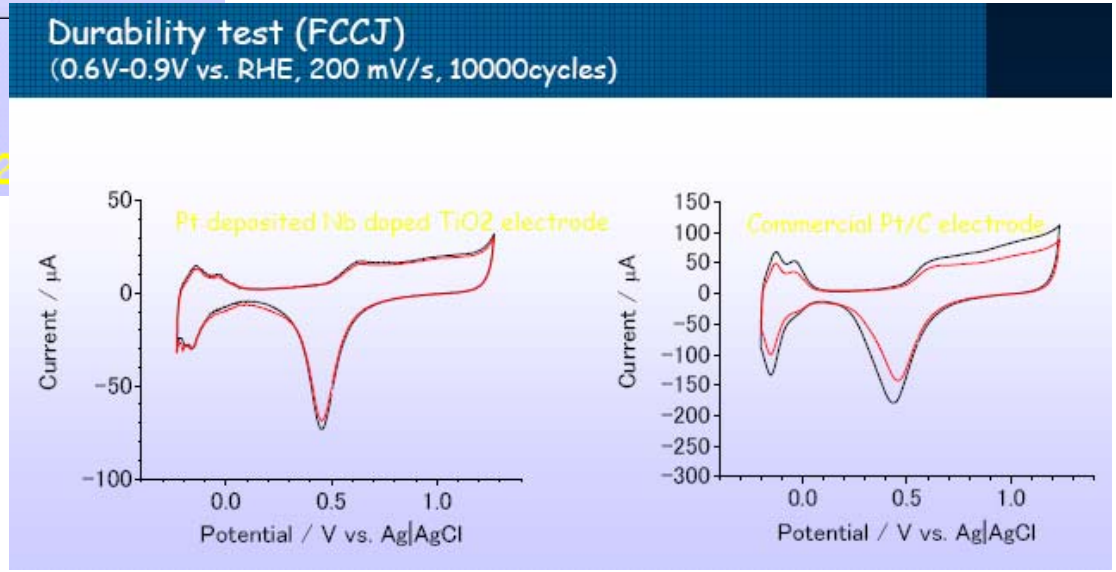


Source: N. Alonso-Vante, Progress MEA 2008 Conference, La Grande Motte, France, Sept, 2008.

Niobium-doped titanium oxide supports improve Pt-based electrode durability



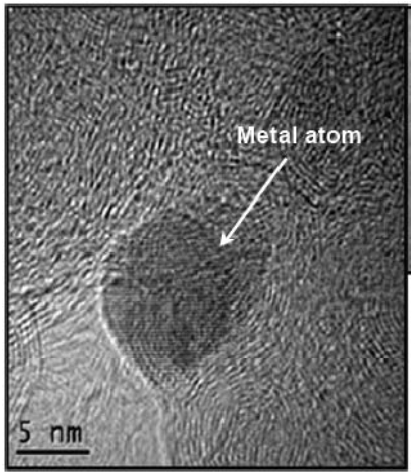
- $NbTi_4O_9$ (AIST, Japan)



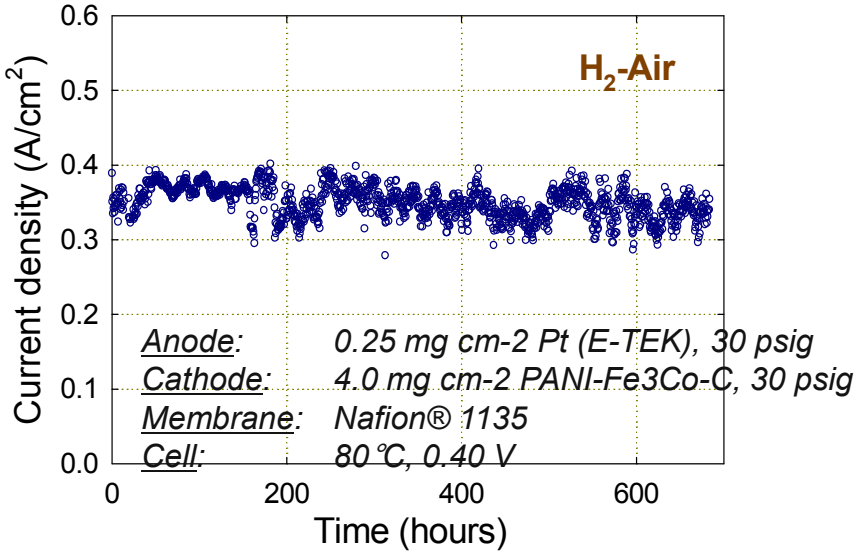
Source: H. Notsu, T. Kitamura,A. Hayashi, I. Yagi, FC-Cubic, Japan,3rd LANL-NEDO-AIST Workshop, San Diego, CA, Sept., 2008.

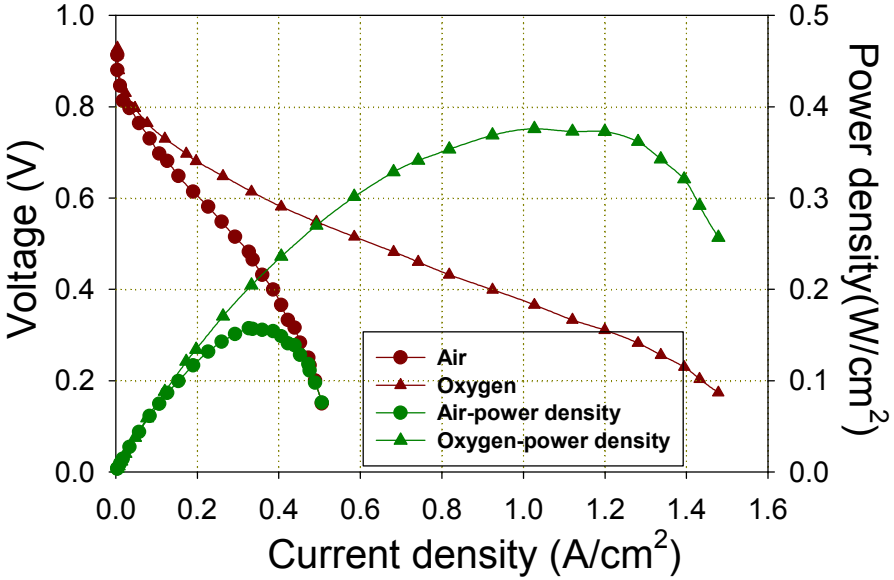
Transition metal-carbon-nitrogen complex catalysts offer potential for PGM-free catalysts

- Los Alamos NL, 3M, and South Carolina have demonstrated improved activity and lifetime for Fe and Co-containing pyrolyzed catalysts
- Activity still lags that of PGM catalysts and needs improvement
- Identity of the active site is not known – encapsulated metal catalyzes site formation?

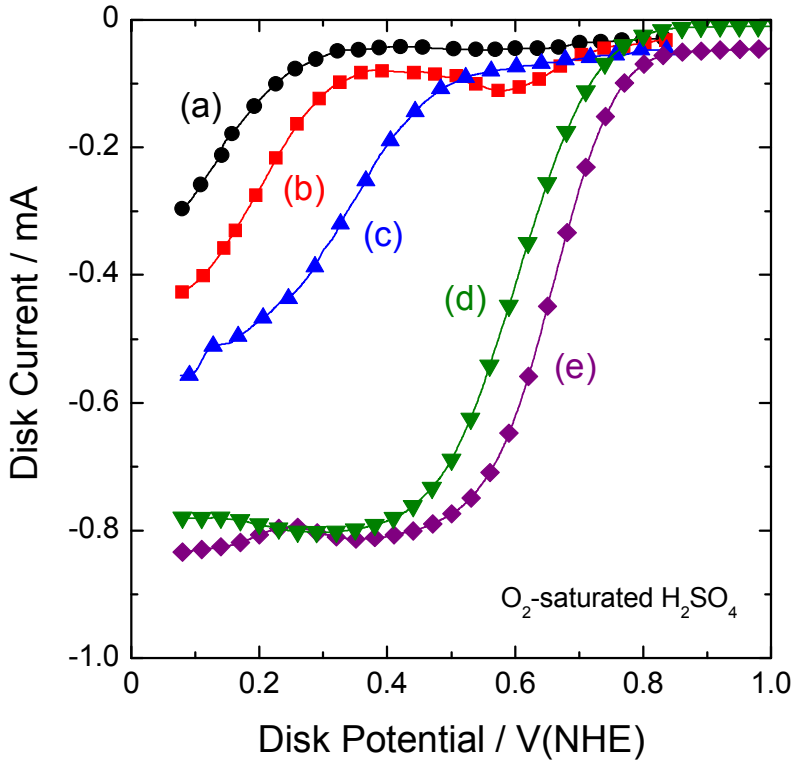


Pyrolyzed Fe_3Co-polyaniline cathode catalyst fuel cell performance

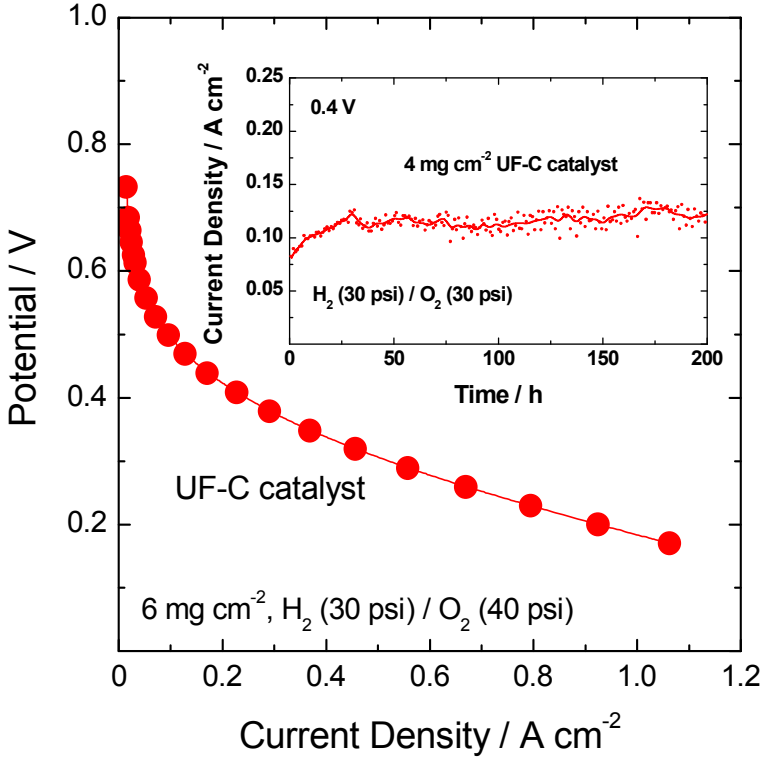




Nitrogen-modified carbon-based catalysts show ORR activity



- University of South Carolina
- Metal-free nitrogen-modified carbon
- Activity lags that of metal-containing catalysts
- Identity of the active site is not known

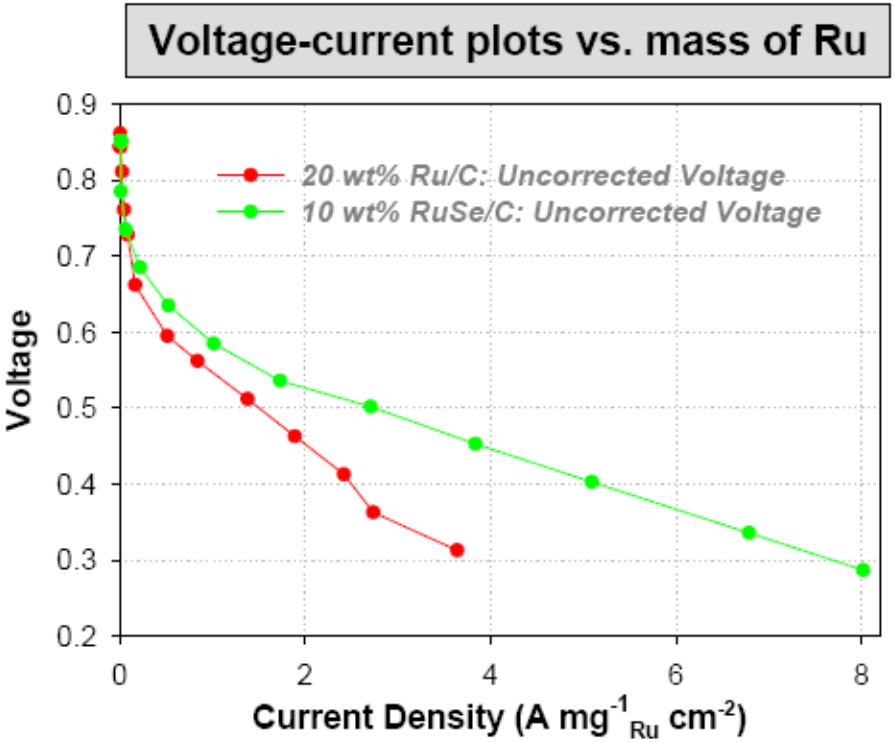


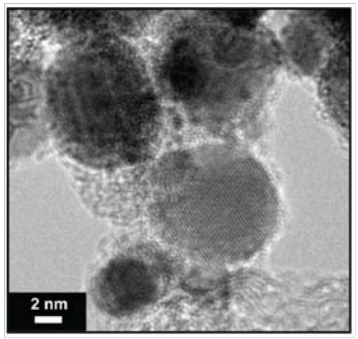
(a) C
(b) HNO_3-treated C,
(c) NH_3-treated C
(d) urea-formaldehyde-modified C
(e) selenourea-formaldehyde-modified C

Source: B. Popov, U. South Carolina, Jan., 2009.

Chalcogenide catalyst activity is improving, but still relatively low

- University of Illinois, University of Poitiers, France, and others
- Chalcogenides are metal selenides or sulfides
- PGM chalcogenides have been found to be more active than non-PGM chalcogenides
- Current focus is to form shells of PGM selenides on less expensive cores (e.g., iron)

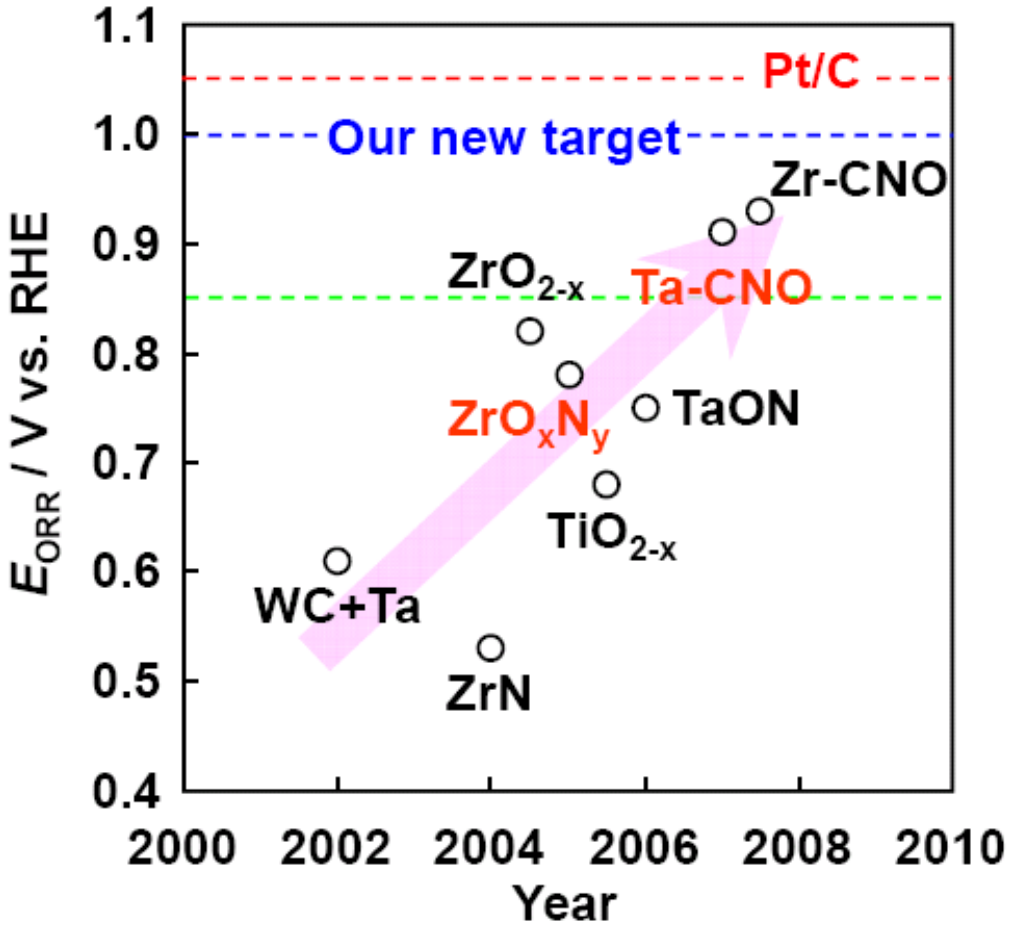




Sources: A. Wieckowski, University of Illinois, and P. Zelenay, Los Alamos National Laboratory

Tantalum oxycarbonitride shows promising ORR activity

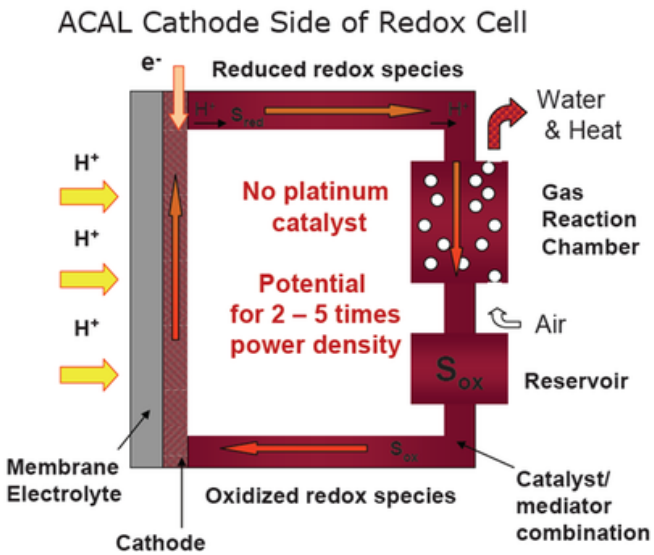
- Yokohama National University, Japan
- High performance, but still approximately 100 mV voltage loss compared to Pt



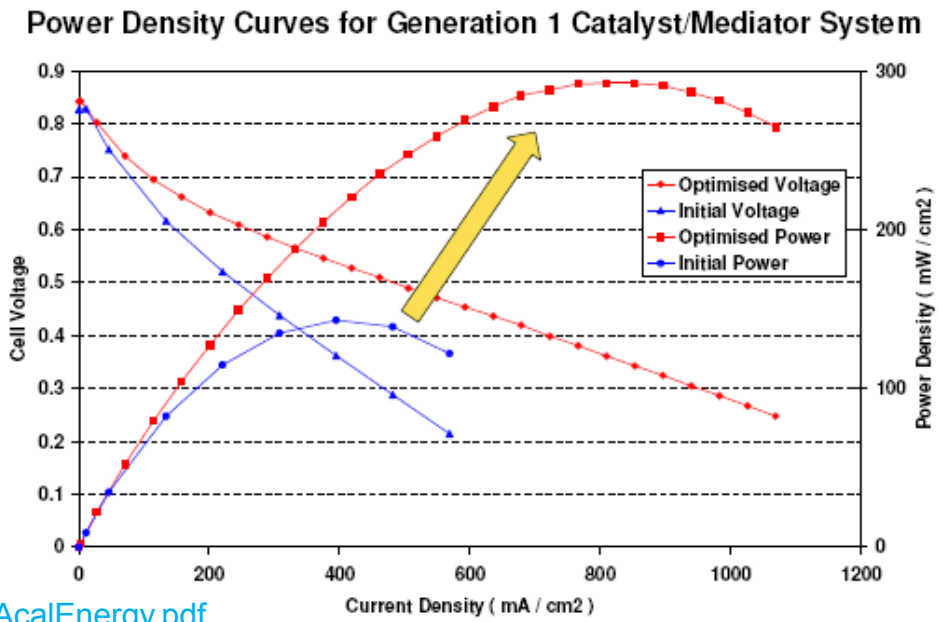
Source: K. Ota, 3rd LANL-NEDO-AIST Workshop, San Diego, CA, Sept., 2008.

Alternative oxidants

- Acal Energy liquid re-circulating oxidant, polyoxometallate



- Acal Energy's business plan based on a 10+ year timeframe for automotive applications



- Recent claims of 570 mW/cm², published power density of ~300 mW/cm²
- Power density does not currently meet DOE target of >1 W/cm²
- System-level issues with a re-circulating aqueous-based reactant

Source: http://ukinjapan.fco.gov.uk/resources/en/pdf/5608783/6_AcalEnergy.pdf

Summary and future directions

- Pt-based catalysts
  - Conventional supports and architectures:
    - *Pt core-shell catalysts and de-alloyed catalysts show the most promise for meeting or exceeding performance and cost targets for PGM-based catalysts*
    - *Long-term durability in a fuel cell under load cycling conditions* ***must*** *be demonstrated*
  - Novel architectures and supports:
    - *3M NSTF architecture shows great promise for meeting performance, cost, and durability targets (simultaneously and in a stack)*
    - *Water management is a challenge and is being addressed by 3M*
    - *NSTF-based fuel cell must be demonstrated in a real-world environment*

- Non-Platinum electrocatalysts
  - Enormous progress has been made in improving activity, however activity still falls short of targets
  - Identification of active site in C-N-containing catalysts is necessary to improve number of active sites and reduce electrode layer thickness
  - Novel electrode architectures will most likely be needed for non-PGM catalysts to facilitate reactant access to all active sites within the electrode volume

DOE's catalyst R&D strategy to address cost and durability issues

- Continue to carry out Pt, PGM, and non-PGM studies in parallel
- Increase open circuit voltage and performance of non-PGM catalysts
- Identify catalyst degradation mechanisms and mitigate effects
- Test catalysts in fuel cells under load cycling and start-stop conditions
- Develop an accelerated durability test protocol which mimics real-world conditions, but shortens analysis time

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