Engineered Nanostructured MEA Technology for Low Temperature Fuel Cells

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Overview

- **Timeline**
  - Project start date – 8/1/08
  - Project end date – 7/31/09
  - Percent complete – 100%
- **Budget**
  - Total project funding: $1,230 K
  - DOE share: $ 984 K
  - Contractor share: $ 246 K
  - Funding received to date: $ 900 K
- **Barriers addressed**
  - Power density
  - Durability
  - Cost
- **Interactions**
  - Vendors
    - GDLs
    - PEMs
    - Ionomers
  - End Users

Project Objectives

The US DOE four strategies to address challenges in catalysts & support materials are:

1. Lower PGM content: improved Pt utilization and durability
2. Pt alloys: maintain/improve performance and reduce cost
3. **Novel support structures: Non-carbon supports** and alternative carbon structures
4. Non-Pt catalysts: maintain performance and durability

– For this project, Nanosys focused on strategy #3

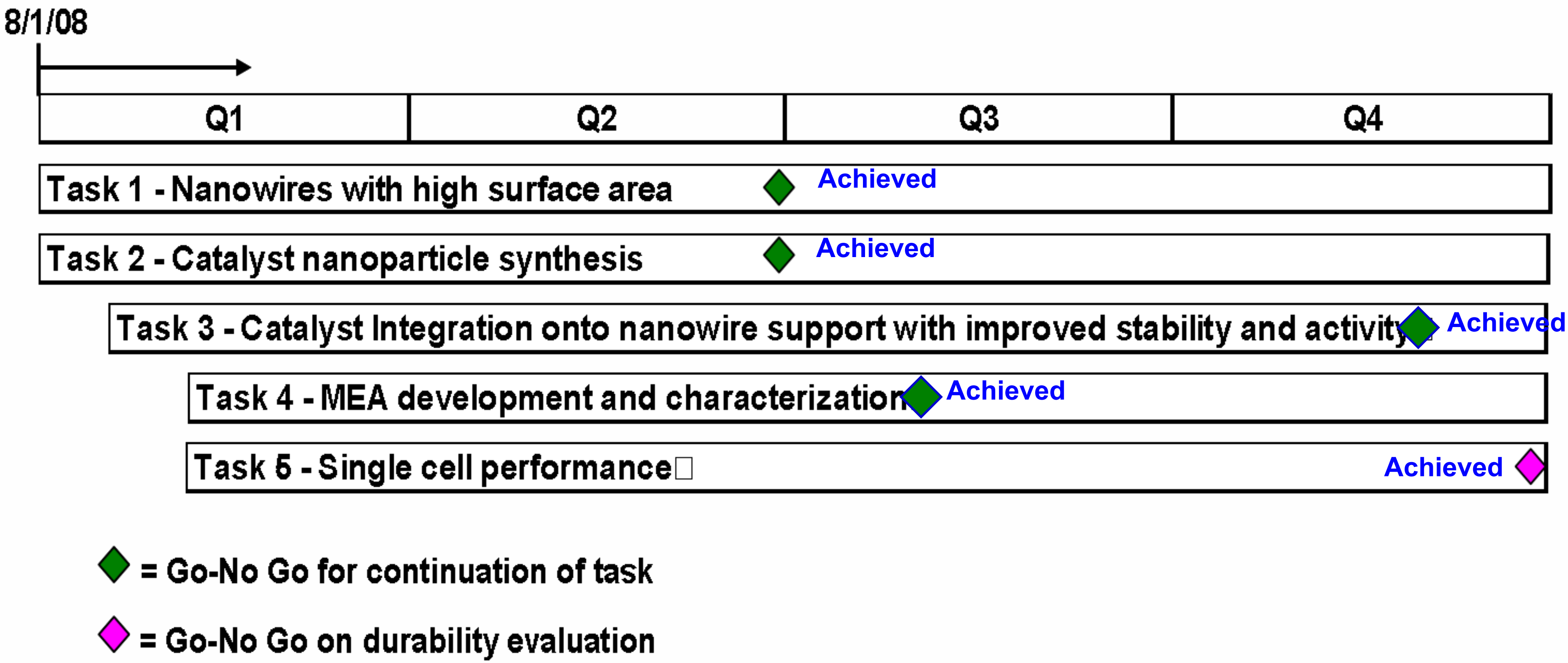
The objective of this project is to developed a novel catalyst support technology based on unique engineered nanostructures for low temperature fuel cells which

- Achieves high catalyst activity and performance
- Improves catalyst durability over current technologies
- Reduces catalyst cost

We have developed novel inorganic, nano-technology support structures using *Functionalized Silicon Nanowires* which

- Are highly durable, have high conductivity and large surface area
- Have controlled porosity which improves catalyst utilization
- Have improved Pt alloy catalyst particle dispersion on the support
- Maintain well controlled catalyst loading characteristics
- In the course of this work, we also:
  - Studied the novel support structure catalyst activities, e.g. for methanol oxidation reaction
  - Optimizing the MEA fabrication process using the novel support material and catalysts

Project Milestones and Timing



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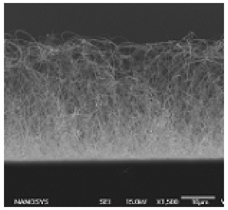
Plan and Technical Approach

Plan: Develop inorganic nanowire support with high surface area and electrical conductivity to improve catalyst utilization, activity and stability.

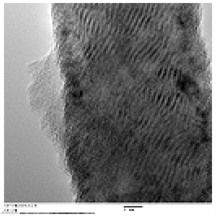
Task Number	Task	Approach
1	Create nanowires with high surface area and conductivity	- VLS synthesis method for Si Nanowires. - Si nanowire carburization and SiC/nano-graphite core/shell structure formation
2	Create catalyst nano-particles with a size range of 1 to 5 nm	- Colloidal method to synthesize catalyst nano-particles - Optimize particle size and composition
3	Integrate catalyst onto nanowire support with improved stability and activity	- Nanoparticle catalysts deposition process - Process optimization for distribution of nanoparticles and control of catalyst loading - Process optimization to Improve the activity and stability for methanol oxidation versus commercial PtRu/C supported catalysts
4	Build MEA using above materials	- Fabricate catalyst coated membrane with nanowire supported PtRu catalysts - Process optimization to control the porosity of nanowire supported catalyst layer as well as catalyst and ionomer distribution in MEA
5	Optimize and test cell performance improvement	- Improve anode and fuel cell polarization performance - Complete durability evaluation

Technical Accomplishments Overview: From Novel Nanowire to MEA

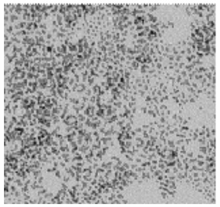
Produced Si nanowire with a diameter as small as 30nm



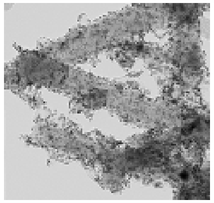
Converted Si nanowire to graphite/SiC nanowire with high surface area of 125 m^2/g (BET)



Controlled Pt alloy particle size in the range of 1.5 ~ 3nm, average 2nm



Uniformly deposited Pt alloy nanoparticles on nanowire support



Achieved >110 mW/cm^2 with nanowire catalysts-based MEA at ambient condition & 40^oC

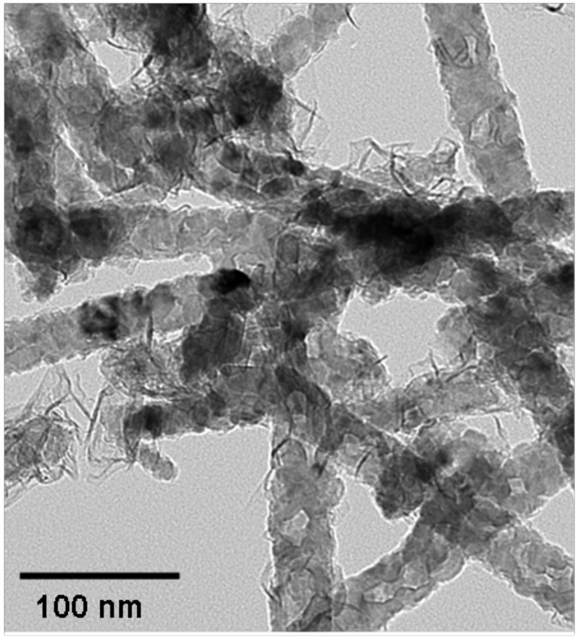
Catalyst Support Development

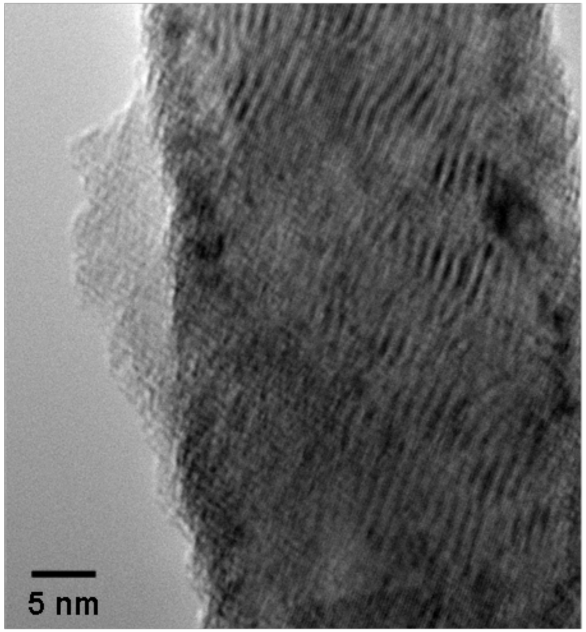
- **Nanosys Technology Provides Superior Performance Through:**
  - Advanced Support Structure
    - Corrosion resistant inorganic SiC nano wire support
      - Enables operation at wide operating window
      - Provides excellent durability without sacrificing initial performance
  - Superior Electrochemical Catalysts
    - High performance nano structured Pt alloys
      - Improved mass activity
      - Low precious metal loading
      - High absolute performance

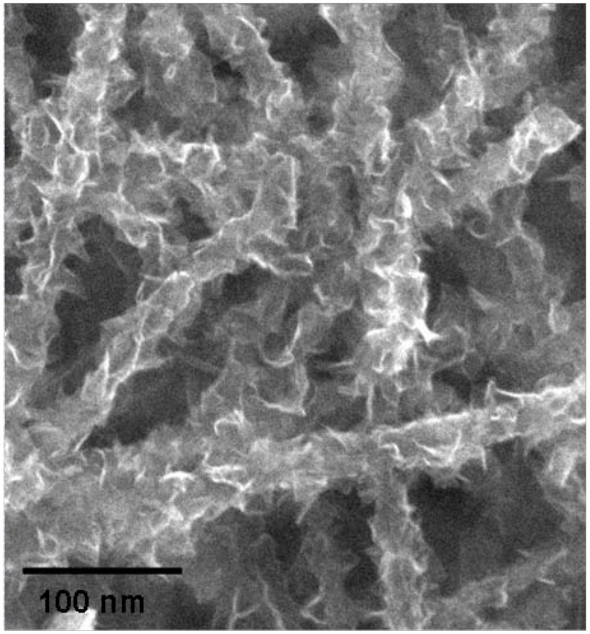
- **To Meet Ideal Specifications for Catalyst and Support Materials**

Surface area:	> 100 m^2/g
Porosity:	Meso-porosity 40 nm -100 nm, matched to ionomer dimensions
Acid Media Stability	No solubility at pH 1-2; Low impurities and poisonous species
Electro-Chemical Corrosion Stable	Inert surface chemistry; Inert core material
Electronic conductivity:	Very High

Advance Inorganic Nano Wire Material Development Process







- Core-shell nano wires grown using VLS method with diameter distribution between 30nm and 40nm, aspect ratio ~100:1

- Carburized silicon core-shell nano wires bonded with the nano-graphite shell
- Crystallinity and integrity of the nano wire structure is maintained

- Final birds nest structure formation
- High conductivity and stability achieved due to high crystallinity & covalent bonding
- Surface area BET $\geq$ 125 m^2/g achieved with nano - graphite shell with barbs

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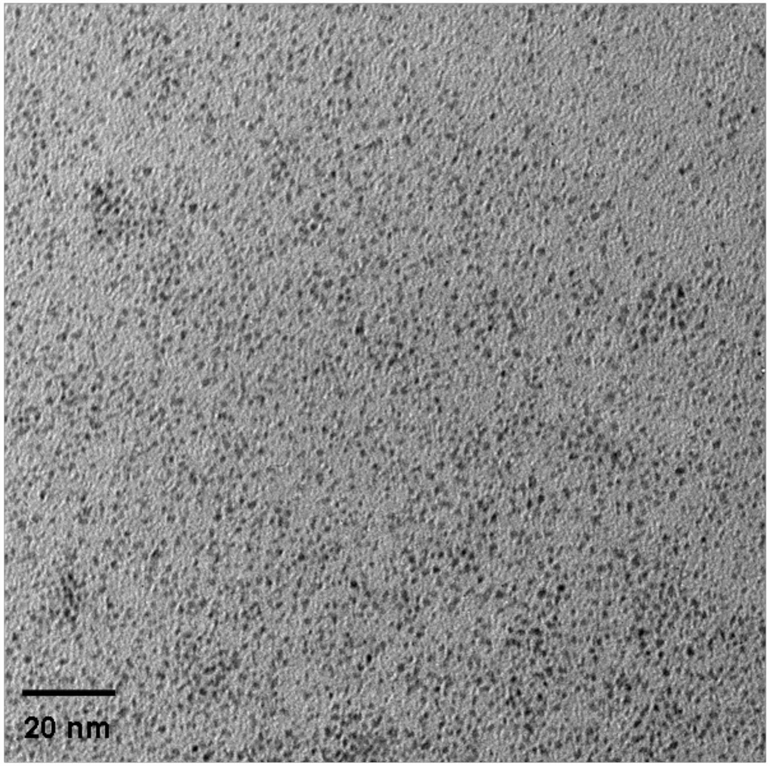
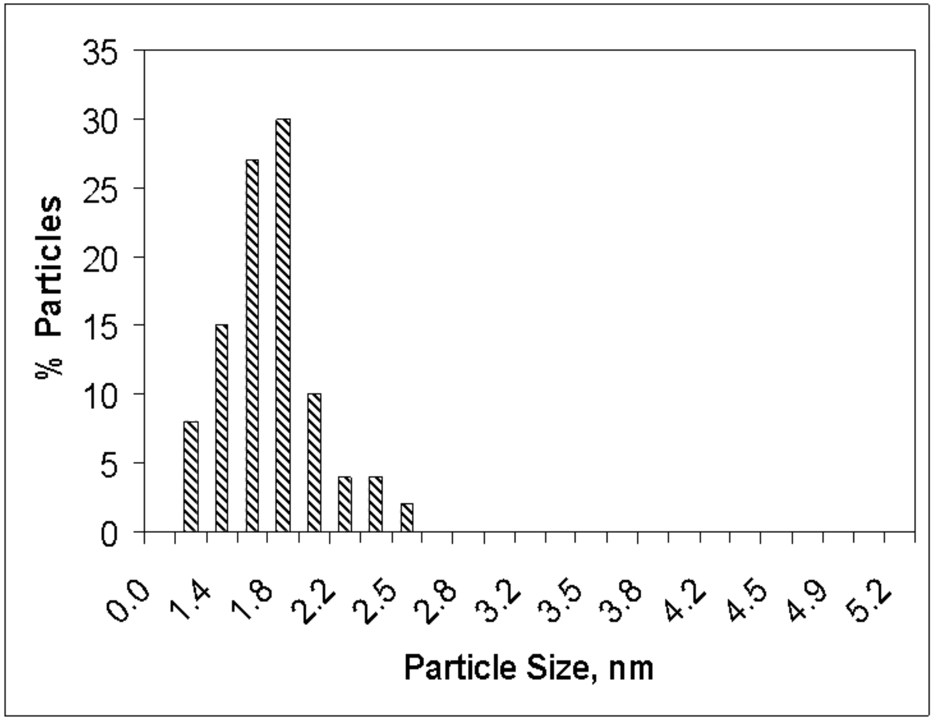
Catalyst Nano-Particle Formation

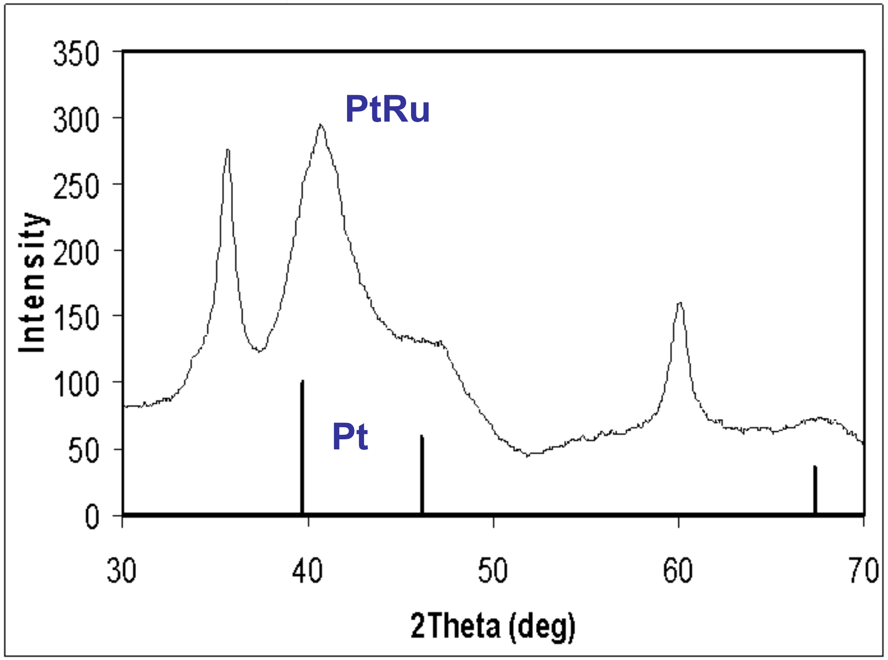




Unique Catalyst Nanoparticles

- Well-dispersed nanoparticles (TEM images)
- Particle size, size-distribution and composition have been tuned independently
- EDX analysis indicated the ratio of Pt and Ru of 1:1
- PtRu particles controlled from 1 to 3 nm, average. 2 nm

Catalyst Nano-Particle Characteristics

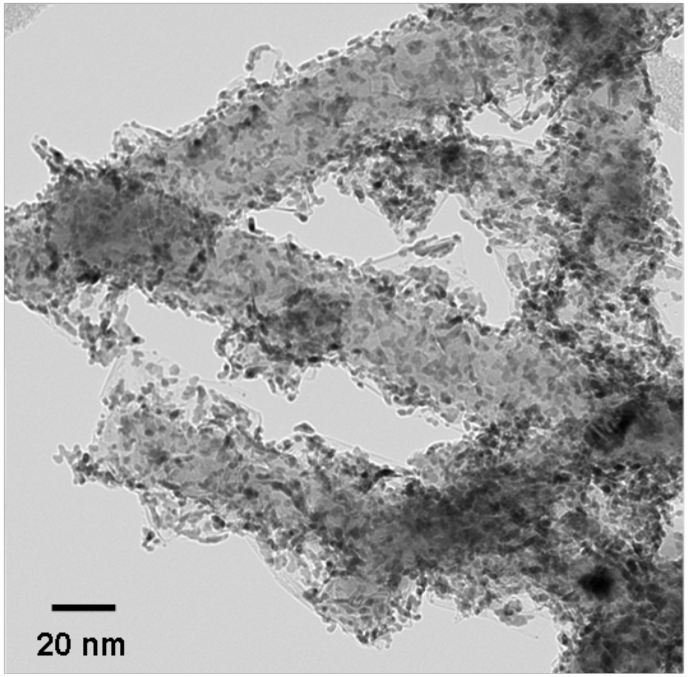


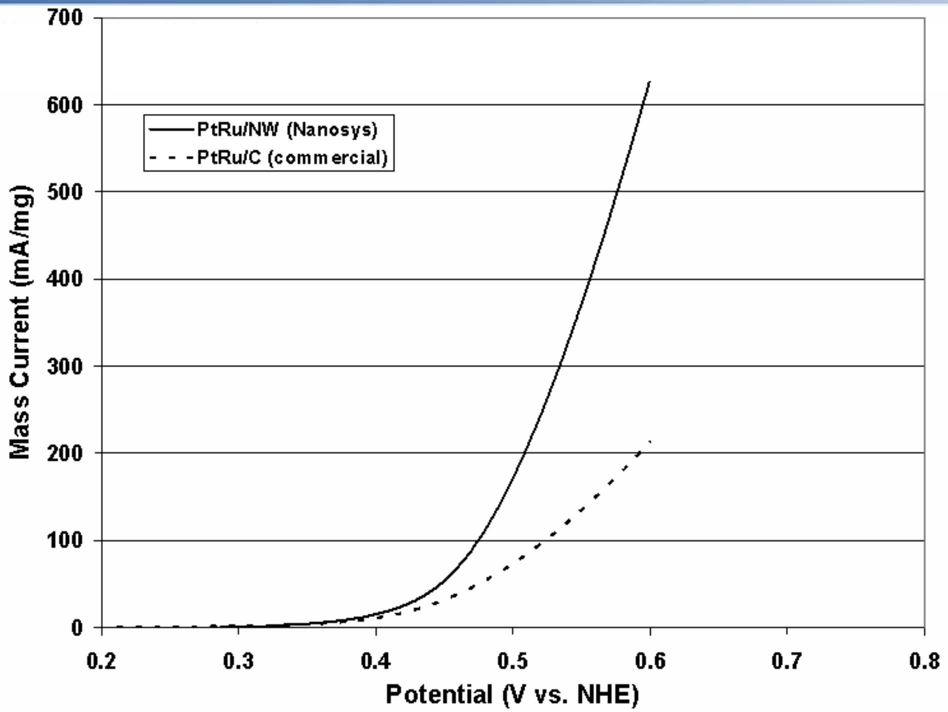
	Dia. nm XRD	Dia, nm TEM	d spacing nm
PtRu/NW	2.7	2.1	0.236
Pt/C ref.	3.2	3.0	0.241

Catalyst Nanoparticle – XRD Characterization

- Obtained the metallic PtRu particles and particle size: 2.7nm (XRD) > 2.1nm (TEM)
- The *d*-spacing of reflexion (index) decreased with increasing Ru content and annealing temperature, resulting from the replacement of Pt atoms on the lattice points of the f.c.c. by the smaller Ru atoms.

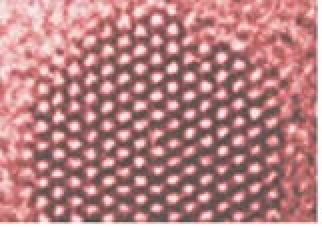
Nano wire deposited nano-catalyst activity





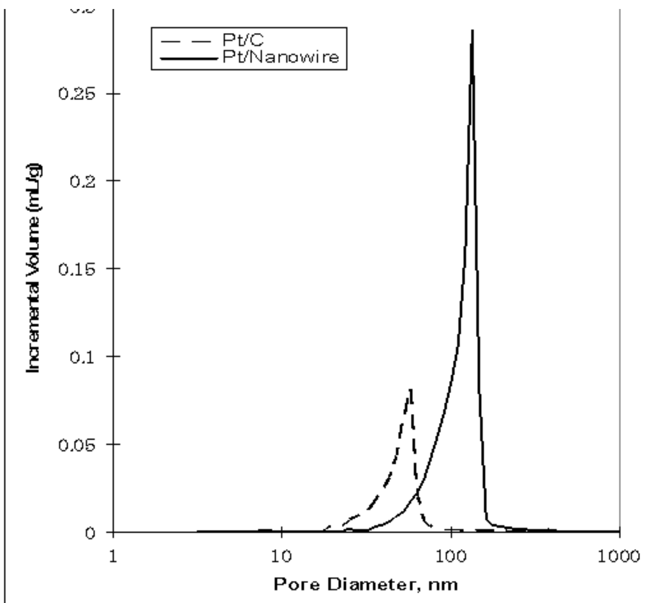
Nanowire supported PtRu and activity for methanol oxidation

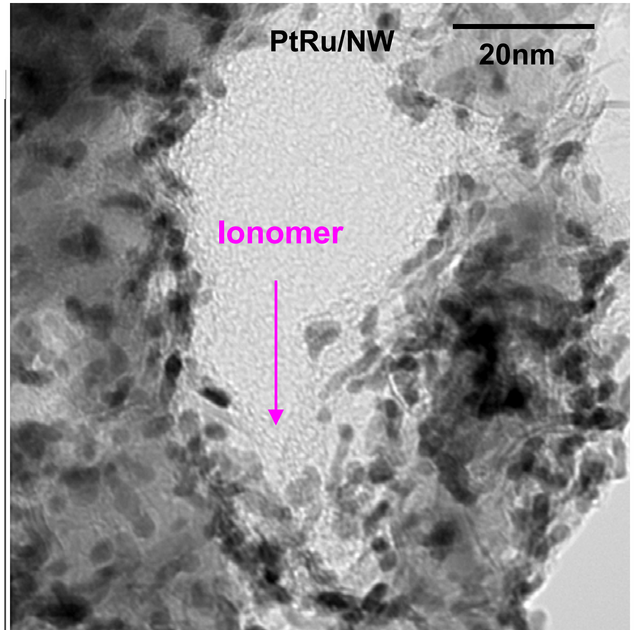
- Small PtRu particle size maintained on nanowire support
- Controlled catalyst metal content, typically 30% PtRu on nanowire support
- Uniform distribution of nanoparticles on nanowire support (TEM)
- High mass activity for MOR using the nanowire supported PtRu catalyst at 40^{o}C: At 0.5V, PtRu/NW 2.5x > PtRu/C

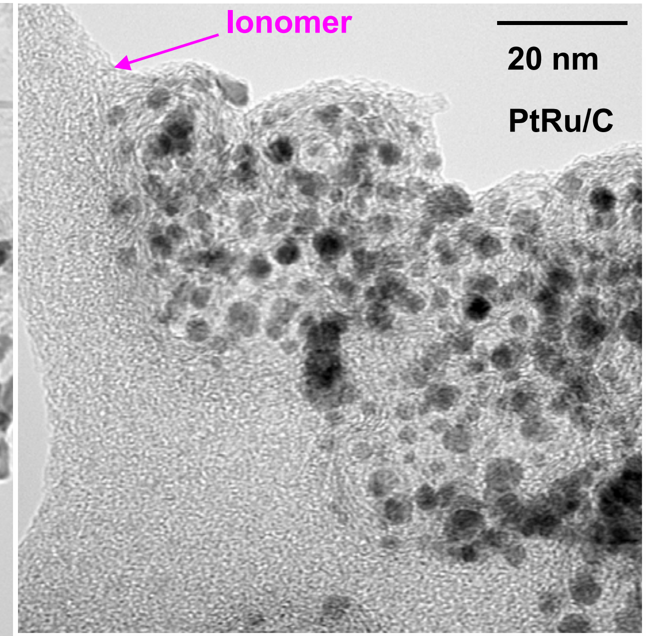


MEA Development

Porosity for catalyst layer with carbon supported catalyst (dash) or nanowire supported catalyst (solid)







Better-performaing MEA with high catalyst utilization

- The porosity of nanowire supported catalyst layer is relatively larger than that of carbon supported catalyst layer in MEAs. Average pore size for nanowires: 160nm, no pore < 30nm; average pore size for carbon black: 36nm, no pore > 50nm.
- Ionomer uniformly distributed in the catalyst layer with nanowire supported catalysts. In contrast, large ionomer agglomerates observed in the catalyst layer with carbon supported catalysts.
- These features result in a higher triple-phase boundary area and hence higher catalyst utilization for the nanowire supported catalysts over the carbon supported catalysts.

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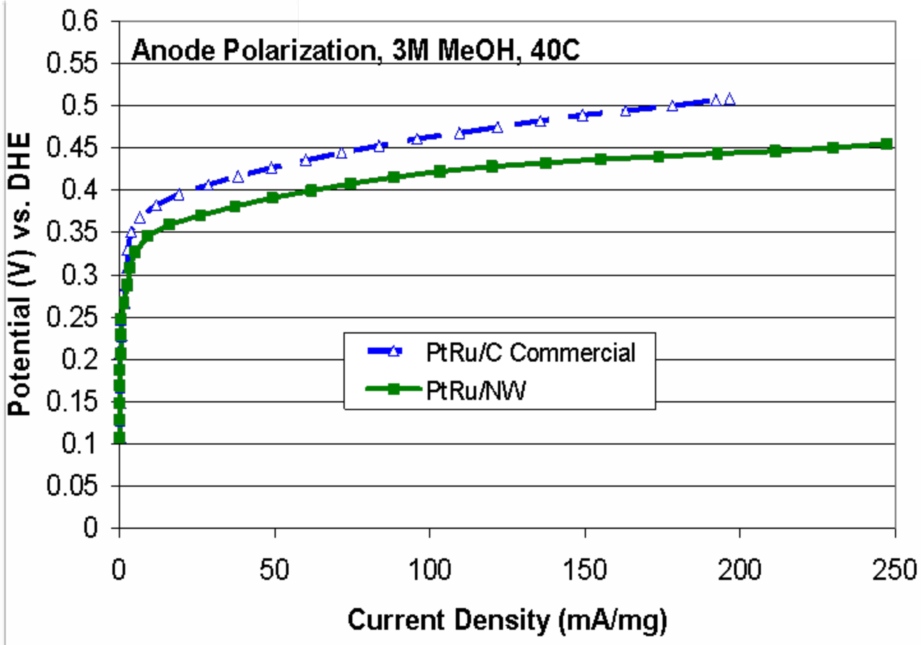
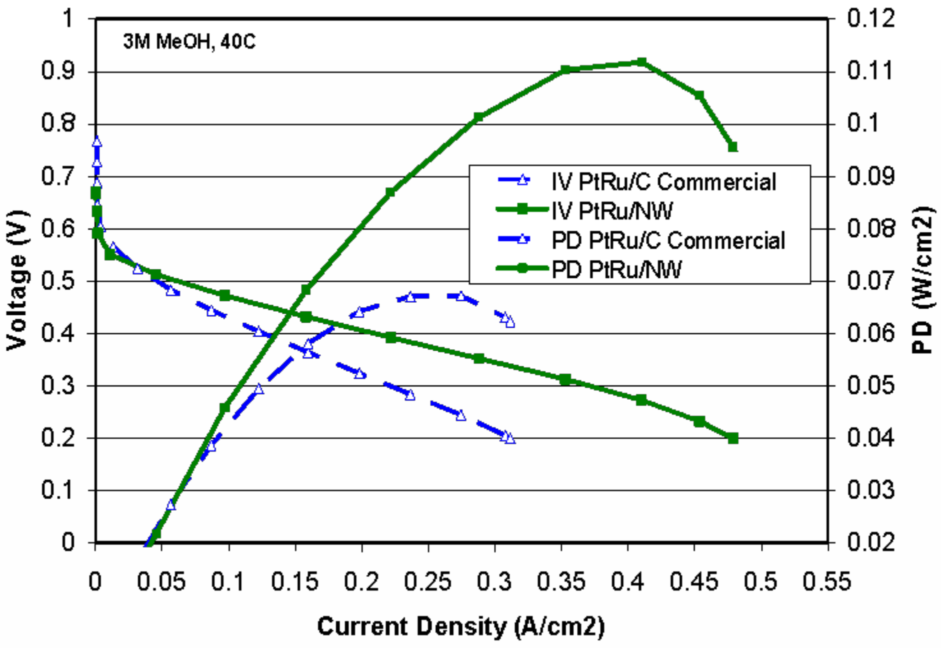
Fuel Cell and Anode Polarization





Fuel Cell Performance and Anode Performance

- Improved anode performance by PtRu/NW over PtRu/C, 47mV at 100mA/mg-PtRu and 71mV at 200mA/mg-PtRu
- Achieved a maximum power density of **112mW/cm^2** with PtRu/NW and 3M methanol at 40^{o}C, 45mW/cm^2 > that with commercial PtRu/C
- High Efficiency of 86mW/cm^2 achieved at 0.4V

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Nano wire supported catalyst advantages

- High catalyst utilization, activity, accessibility, and stability/durability differentiate nanowire based catalyst from carbon supported catalyst

	TPB Area (m^2/g)	Catalyst Utilization (%)	AP, I (mA/mg) @ 0.45V, 40ºC	AP, I (mA/mg) @ 0.3V, 40ºC
Nanosys PtRu/Nanowire	47	61	260	9.8
Commercial PtRu/Carbon	23	39	76	3.8
Nanosys Advantage	***2x***	***1.6x***	***3.4x***	***2.6x***

3.4x (activity + accessibility) > 2.6 (activity dominant)
Difference in mass current gain between 0.45V and 0.3V is attributed to improvement in accessability

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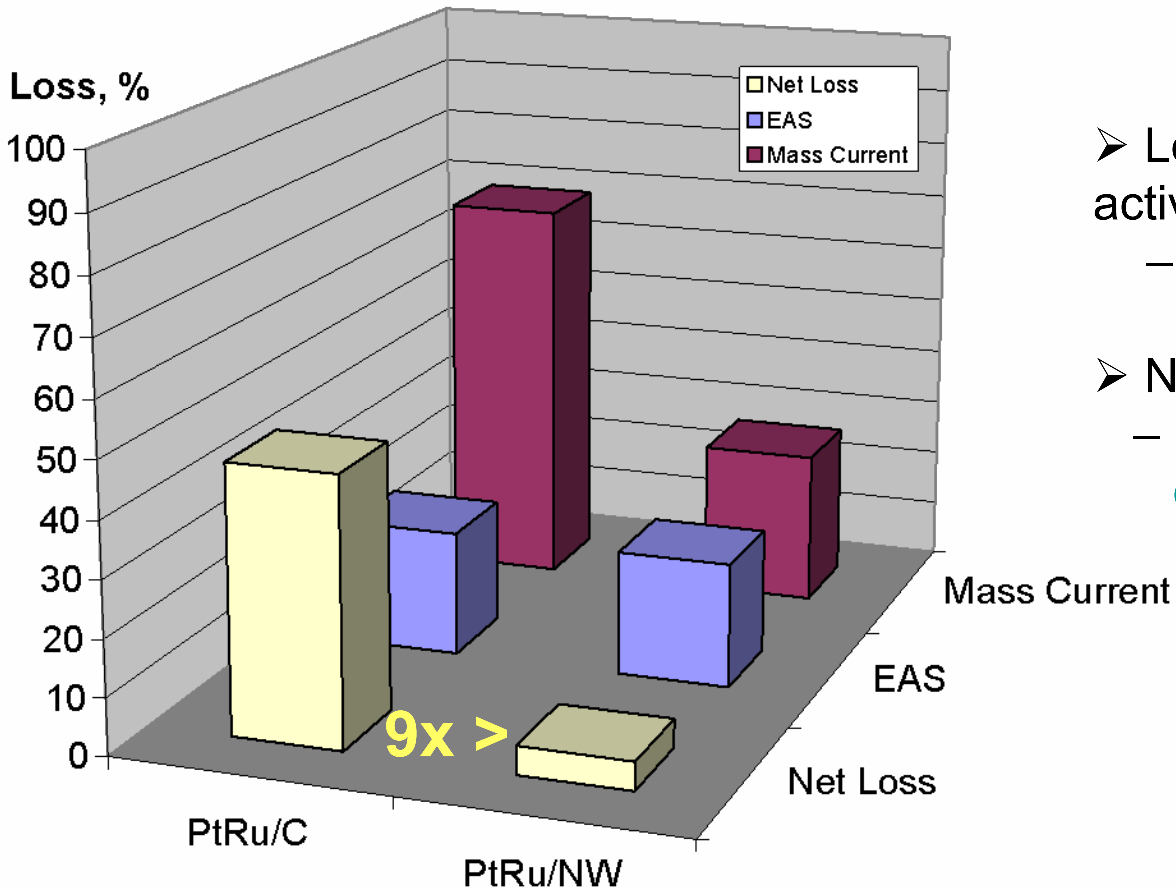
Stability of PtRu/NW catalysts

Potential Cycling from 0.05 – 0.6V > 3200 cycles



- Loss in Mass Current @ 0.5V
  - Activity for methanol oxidation reaction
- Loss in Electrochemically active surface area (EAS)
  - defoliating; coalescing
- Net Loss
  - Net activity loss corrected by defoliating/coalescing

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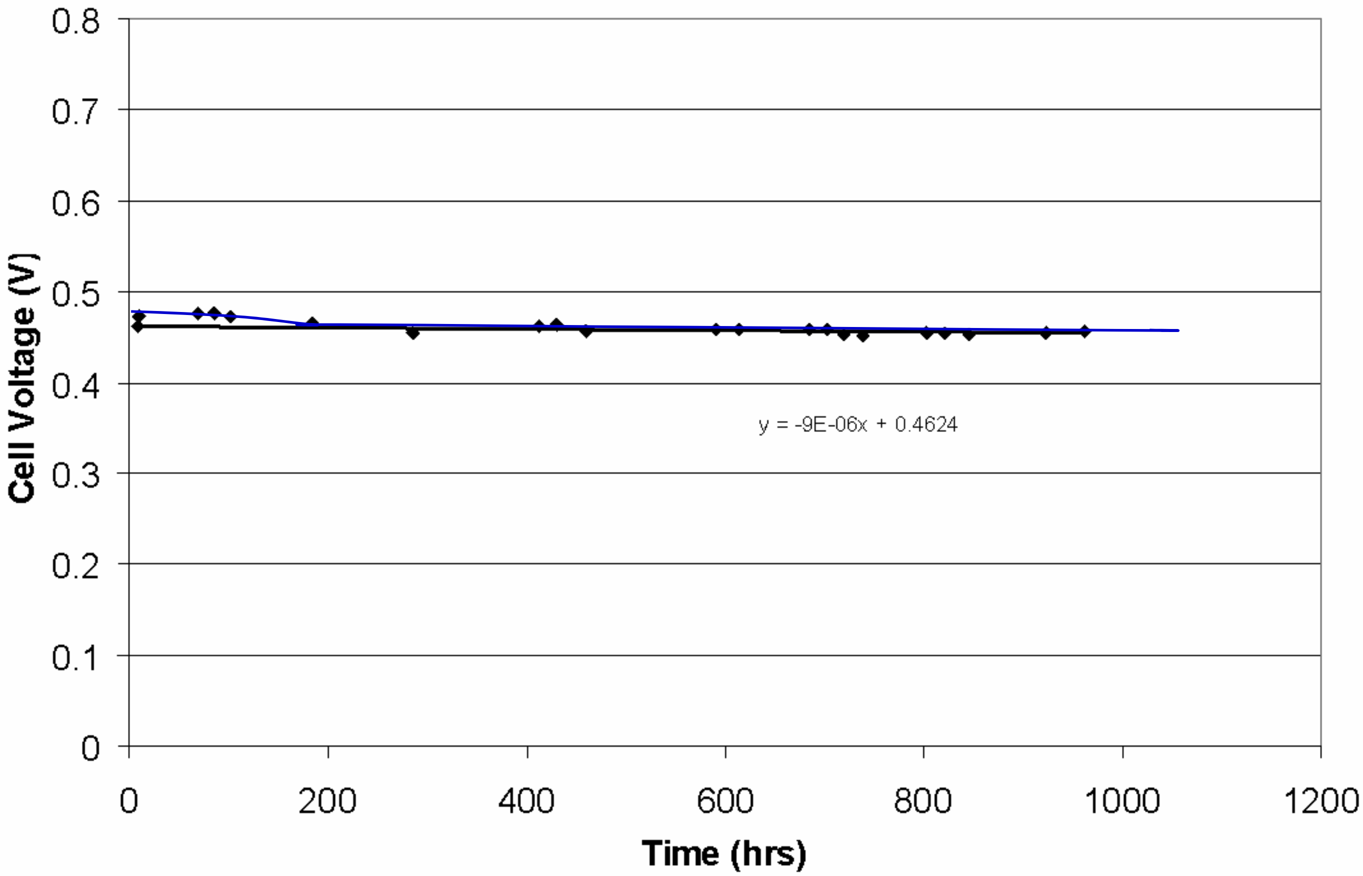
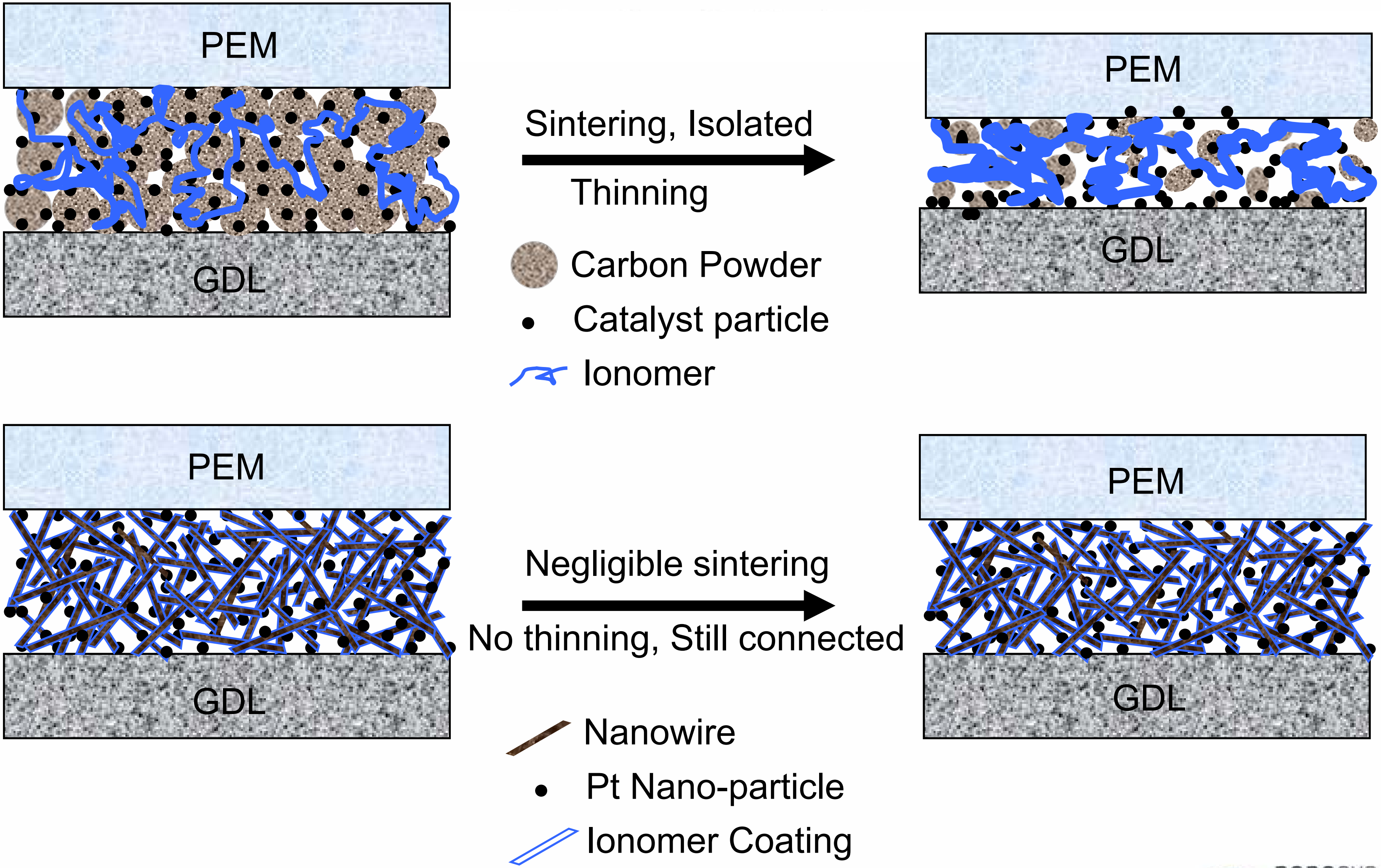
Nano wire MEA Durability

DMFC with Ambient Air @ 40ºC



- In 1000 hours life test, ~ 9uV/hr loss was observed at 100mA/cm^2
- Stability was achieved after 200hr initial operation

Catalyst Durability Mechanism



Project Summary of Achievements

- Developed novel inorganic support materials and processes for durable catalyst support with high conductivity and surface area (125 m^2/g, BET). The resulted core-shell nanowires have diameter in the 30~40 nm and aspect ratios of ~100:1; the SiC core is bonded with crystallized nanographite shell.
- Controlled porosity of the nanowire support networks facilitate ionomer and PtRu particle distribution and hence improve catalyst utilization.
- PtRu particle size, size-distribution and composition have been tuned independently. Well dispersed PtRu (1:1) alloy catalyst particles deposit on the support. PtRu particles controlled from 1 to 3 nm, average. 2 nm.
- Unique features of the nanowire supported catalysts are firstly demonstrated for methanol oxidation reaction: higher activity, utilization and accessibility over commercial PtRu/C catalysts.
- In particular, nanowire supported catalysts have superior stability over carbon supported catalysts.
- The mass activity for MOR at the nanowire supported PtRu catalyst at 40^{o}C: PtRu/NW 2.5x > PtRu/C
- Achieved a maximum power density of **112W/cm^2** with PtRu/NW and 3M methanol at 40^{o}C, 45mW/cm^2 better than that with commercial PtRu/C.

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