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Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation

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U.S. Department
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Objective and Technical Targets

■ Objectives

- Understand the role of cathode electrocatalyst degradation in the long-term loss of PEMFC performance,
- Establish dominant catalyst and electrode degradation mechanisms,
- Identify key properties of catalysts and catalyst supports that influence and determine their degradation rates,
- Quantify the effect of cell operating conditions, load profiles, and type of electrocatalyst on the performance degradation, and
- Determine operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime targets.

■ Technical Targets

- Durability with cycling 5,000 hours ($\leq 80^{\circ}\text{C}$) and 2,000 hours ($> 80^{\circ}\text{C}$)
- $\leq 40\%$ loss of initial catalytic mass activity; < 30 mV loss at 0.8 A/cm^2

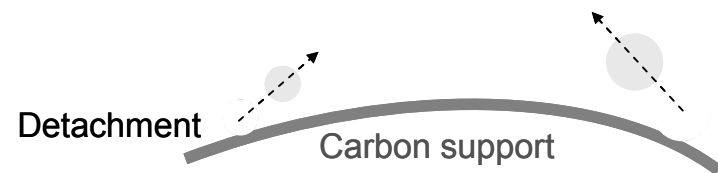
Pt catalyst degradation mechanisms

- Proposed mechanisms inferred from *ex situ*, pre- and post-mortem TEM and XRD analyses:
 - Pt coalescence *via* migration across support (2D)
 - Erosion of carbon support
 - Pt dissolution of smaller particles and re-deposition onto larger particles (3D)
 - Pt dissolution and precipitation in ionomer/membrane

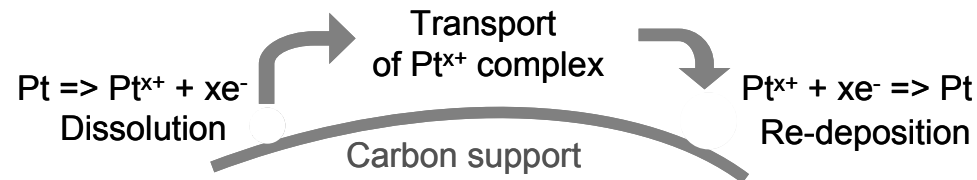
(1) Coalescence via Crystal Migration



(2) Detachment from carbon support



(3) Growth via Modified Ostwald Ripening



(4) Dissolution and Precipitation in the Ion Conductor

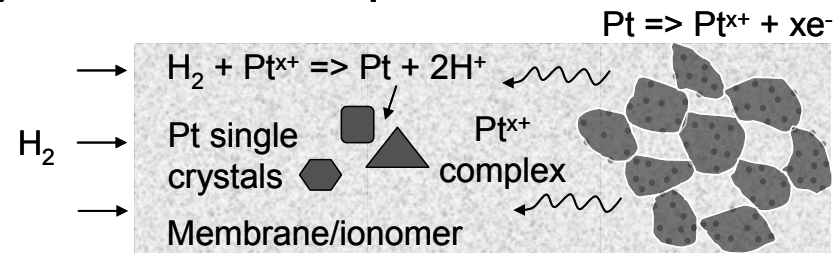
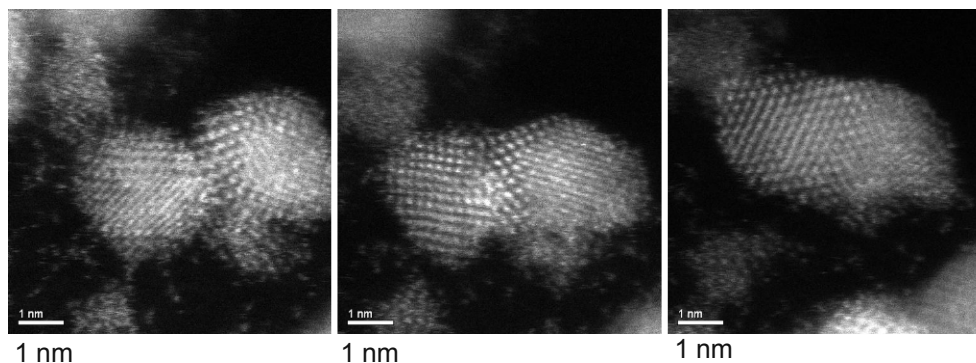


Figure adapted from: Y. Shao-Horn et al., *Topics in Catalysis*, **46** (2007) 285–305.

Particle migration and coalescence

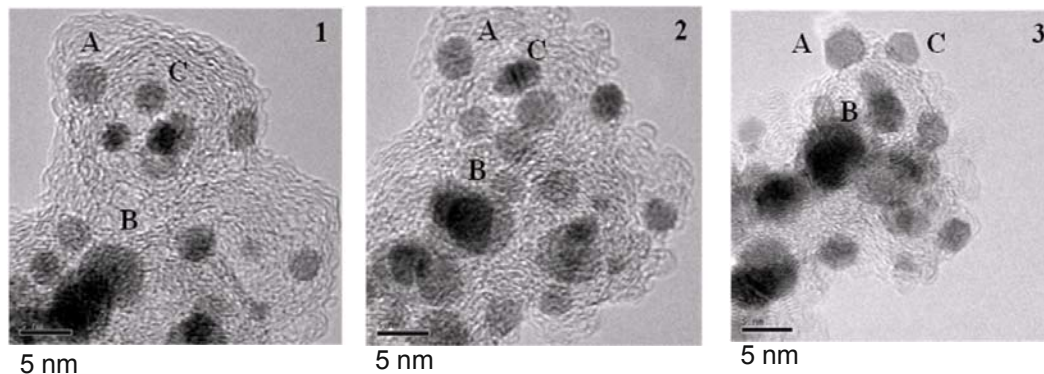
- May dominate at low cell voltages where Pt dissolution and carbon corrosion rates are slow
- Predominance of this mechanism is indirectly supported by *ex situ* analysis of particle size distributions
- Defects on carbon support may trap the Pt particles and limit their mobility
- Further work is necessary to:
 - determine realistic trapping models
 - determine support properties mitigating this degradation mechanism
 - quantitatively describe Pt particle motion in an electrolyte environment
 - assess the conditions under which particle migration and coalescence are active



Source: M. Asoro, D. Kovar, L.F. Allard, Y. Shao-Horn, and P.J. Ferreira (MIT, ORNL, UT-Austin)

Detachment of catalyst particles from the carbon support

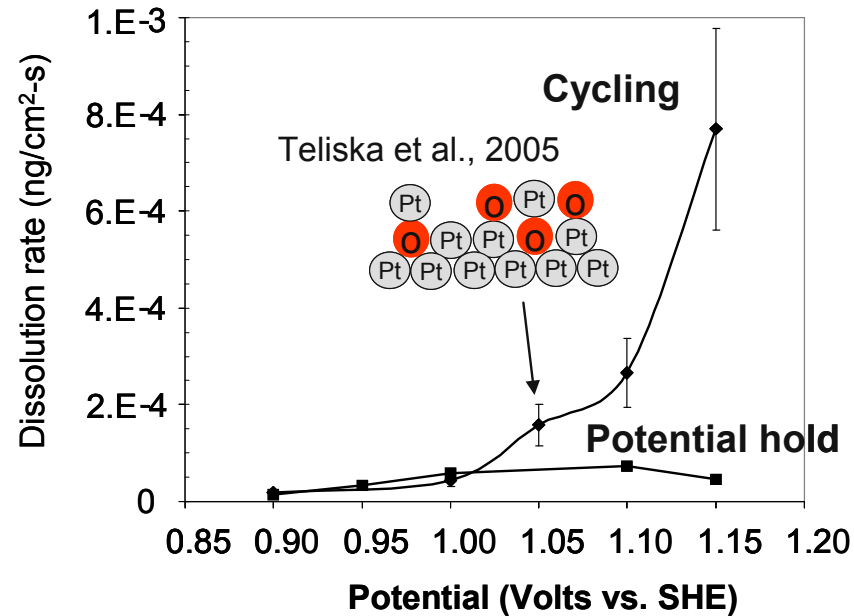
- Generally believed to be linked with carbon corrosion
- Debate as to whether the presence of Pt accelerates carbon oxidation
- Electrochemically-active surface area (ECA) loss is slower on lower surface area carbons, with graphitized carbon showing the slowest rate of ECA loss
- Further work is necessary to determine:
 - if lower ECA loss rates are due to larger initial Pt particle on lower surface area carbons or lower rates of carbon corrosion
 - the extent to which carbon-support interactions, temperature, and relative humidity contribute to carbon corrosion-related ECA loss



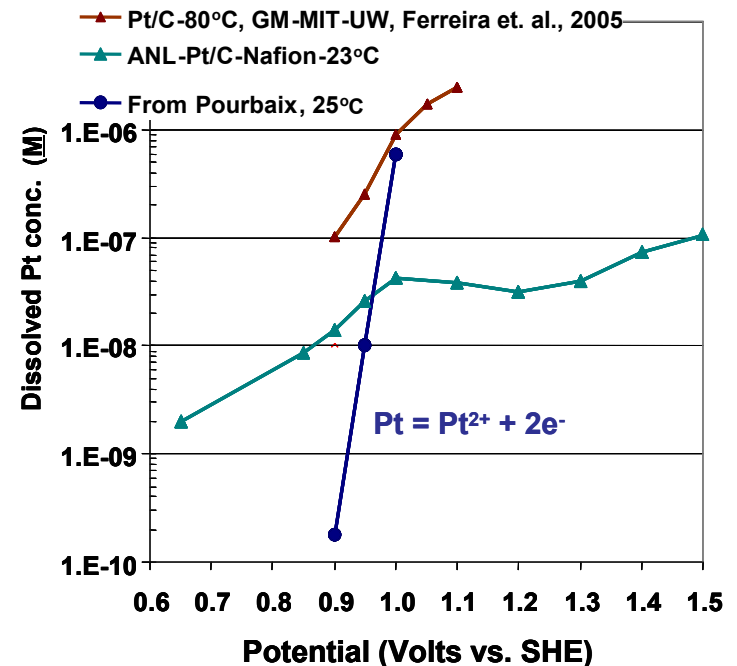
Source: M. Asoro, D. Kovar, L.F. Allard, Y. Shao-Horn, and P.J. Ferreira (MIT, ORNL, UT-Austin)

Pt dissolution and re-deposition

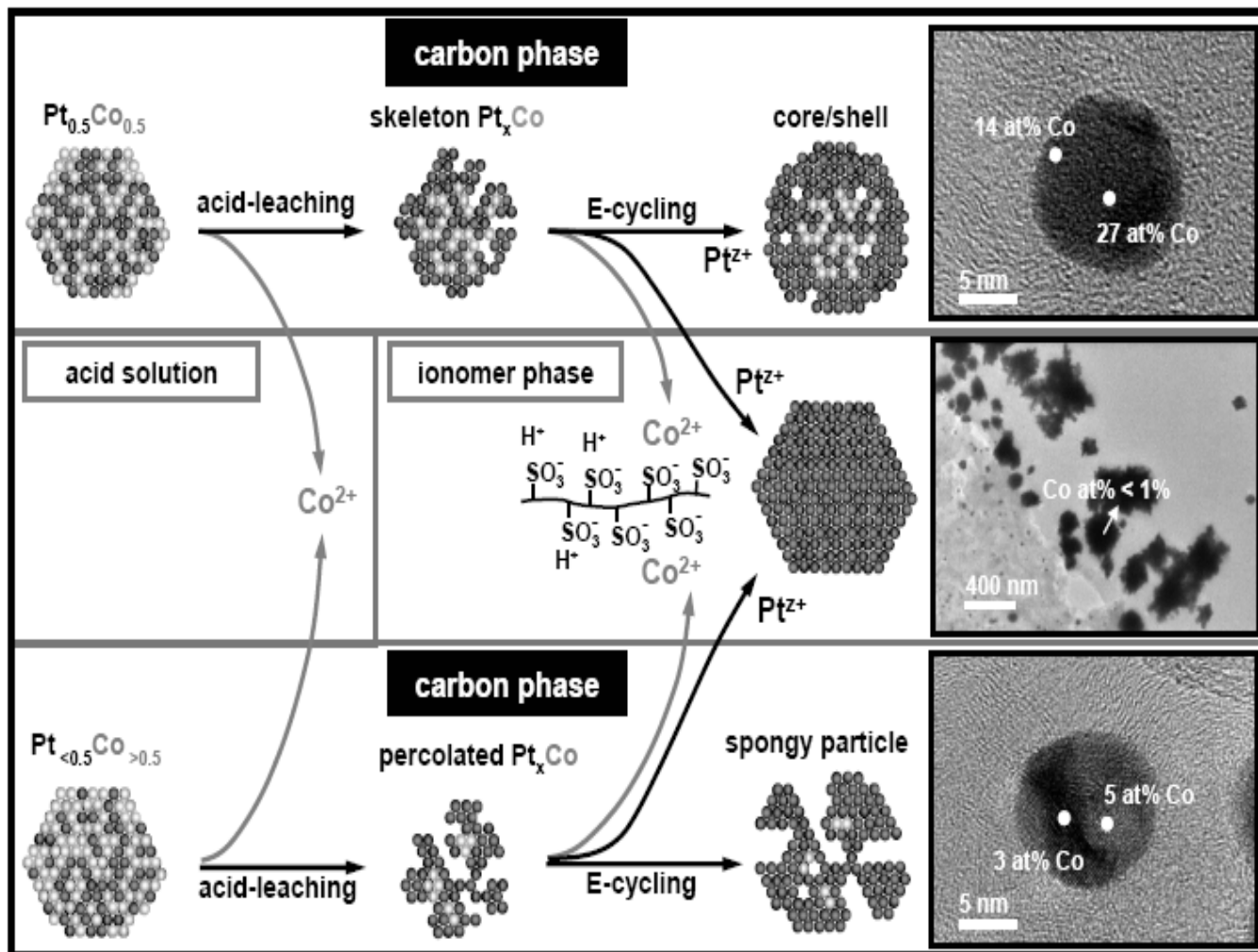
- Evidence for dominance of this mechanism at >0.8 V
- Pt dissolves and re-deposits on existing particles and in membrane (TEM, EDX, UV-VIS)
- ECA loss and coarsening increase with increasing potential and with cycling
- Secondary damaging effects on membrane and proton transport



- Further work is necessary to determine:
 - Soluble Pt species
 - Dissolving species (e.g., oxide or metal)
 - Role of oxide formation and structure of oxide
 - Cause of potential dependence of eq. conc.
 - Cause of potential and potential profile dependence of dissolution rate
 - Effects of particle size, temperature, anionic impurities, alloying metal, and catalyst structure



Non-noble metal is leached from Pt alloy catalysts



Yang Shao-Horn et al., JES, accepted.

Research needs for elucidation of catalyst degradation mechanisms

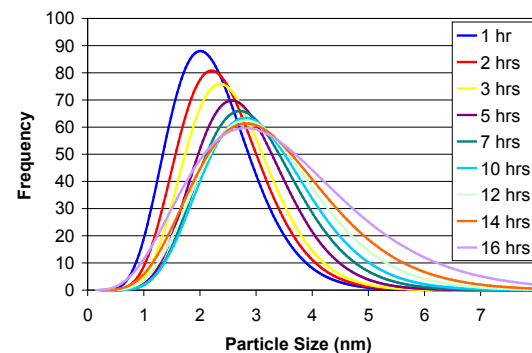
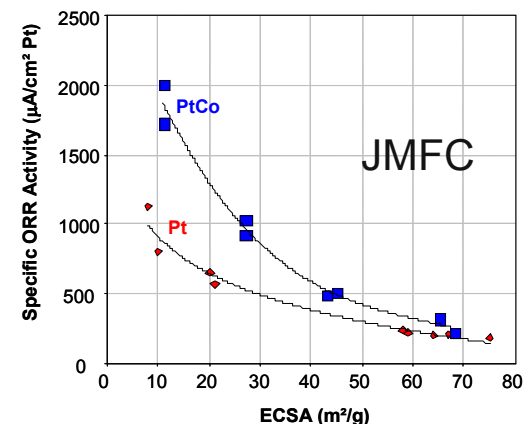
- Particle migration and coalescence
 - Realistic trapping models using *ab initio* energetics for binding
 - *In situ* TEM studies of Pt particles on carbon supports with systematically varied degrees of graphitization, surface area, pore size, and pore size distribution
 - Careful and systematic SEM and TEM characterization of aged MEAs
- Detachment of catalyst particles from the carbon support
 - Systematic variations in the carbon support properties
 - Assessment of the impact of the carbon surface area, porosity, and functionality
 - Assessment of the impact of the contact area of the Pt with the carbon on the stability of the carbon itself and its effect on the platinum loss
- Pt dissolution and re-deposition
 - Systematic variations in particle size, independent of heat treatment
 - Systematic studies of Pt dissolution rates, alloying metal dissolution rates, and equilibrium dissolved concentrations of catalyst components
 - Simultaneous determination of extent of oxidation and structure of oxide

Approach

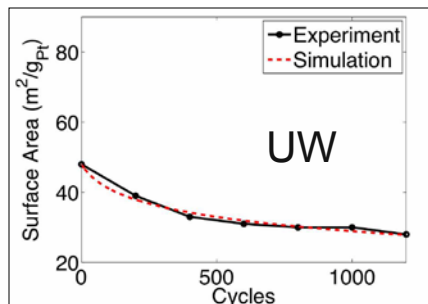
- Identify the degradation modes and factors contributing to degradation, using
 - Systematic cell degradation tests
 - *In situ* structural characterization of the catalyst
 - Fundamental out-of-cell studies
 - Theoretical modeling
- Variables
 - Catalyst type and oxophilicity
 - *Pt, Pt alloys, acid-leached Pt alloys, core-shell*
 - Catalyst particle size
 - Catalyst impurities
 - Type of carbon support
 - *varied surface area, pore size, and relative proportions of micro- and mesopores*
 - Cell operating parameters
 - *Potential cycling profile, upper potential limit, cell temperature, RH on cathode*

Project tasks and roles of team members

- Catalyst synthesis, membrane-electrode assembly (MEA) fabrication, and aqueous studies of carbon corrosion (JMFC)
- MEA testing, on-line diagnostics, and post-test characterization of MEAs, including electrode porosity (UTRC)
- *In situ* and *ex situ* microscopic characterization of the MEAs and catalysts (UT-Austin-Ferreira)
- *In situ* and *ex situ* X-ray spectroscopic and scattering studies of catalyst degradation (ANL)
- Aqueous electrochemical studies of catalyst dissolution and oxygen reduction reaction (ORR) activity (ANL and MIT)



ANL



- *Ab initio*-based modeling of Pt, Pt alloy, and core-shell dissolution (UW)
- Catalyst degradation models (UW)
- Cell kinetic and transport modeling incorporating degradation effects and kinetics (UT-Austin-Meyers)



Intended results of this project

- Relative lifetimes of platinum, platinum alloys, acid-leached alloys, and core-shell catalysts in the MEA, independent of particle size and support effects
- Effect of MEA operating conditions, such as voltage cycling protocols, cell temperature, and cathode relative humidity on MEA performance degradation
- Relationship between catalyst particle size and degradation rates and mechanisms
- Effects of catalyst precursor impurities on the catalyst degradation rate
- Role of carbon support properties and carbon support degradation in cathode performance loss
- Cathode catalyst atomic structure and oxidation state in the MEA environment and how these are affected by cell conditions
- Roles of the extent of oxide formation, catalyst oxophilicity, and oxide structure in catalyst degradation and relationship to ORR activity
- Mechanisms and rates of catalyst dissolution as a function of potential and temperature and effect of extent of dissolution (i.e., sub-monolayer to multi-monolayer) on this mechanism
- Loss of non-noble alloying or core metals as a function of catalyst structure (e.g., core-shell, acid-leached, ordered vs disordered)
- Impact of catalyst component dissolution on cathode performance

Project timeline

Project Schedule	Year 1 1				Year 2 2				Year 3 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1. Catalyst and Membrane-Electrode Assembly Fabrication												
1.1 Benchmark Pt and one Pt alloy with varying particle sizes	■	■	■									
1.2 Pt alloys, acid-leached alloy, core-shell on standard support		■	■							■	■	
1.3 Pt alloy catalysts with varying degrees of oxophilicity										■	■	■
1.4 Pt on supports with varying surface area, pore size, and pore size distribution				■	■	■	■	■				
1.5 Catalysts with post-doping of catalyst precursor impurities					■	■	■	■	■	■		
Task 2. Cell degradation studies/single cell cycling/parametric aging studies												
2.1 Accelerated stress testing of baseline MEAs and impact of operating conditions	■	■	■	■	■	■	■					
2.2 Advanced catalyst degradation mode identification		■	■	■	■	■	■	■	■	■	■	■
2.3 Effect of carbon support on MEA electrode performance loss					■	■	■	■	■	■	■	■
2.4 Effect of catalyst impurities on MEA electrode performance loss						■	■	■	■	■	■	■
Task 3. Mechanisms of catalyst degradation and underlying physicochemical catalyst properties responsible for degradation									□			
3.1 Roles of catalyst oxophilicity, extent of oxide formation, and structure of oxide in catalyst degradation	■	■	■	■	■	■	■	■	■	■	■	■
3.2 Influence of potential, temperature, and physical properties of catalyst on the rates and mechanisms of catalyst component dissolution		■	■	■	■	■	■	■	■	■	■	■
3.3 Role of catalyst-support interactions and support degradation			■	■	■	■	■	■	■	■	■	■
3.4 Effect of particle size and catalyst type on ORR activity			■	■	■	■	■	■	■	■	■	■
Task 4. Ex situ microscopic and X-ray scattering characterization of catalysts and MEAs												
4.1 Optical microscopy, aberration-corrected STEM and high-resolution TEM w/ EDAX, EELS, XPS	■	■	■	■	■	■	■	■	■	■	■	■
4.2 Small angle X-ray scattering		■	■	■	■	■	■	■	■	■	■	■
Task 5. Modeling												
5.1 Ab initio based modeling of Pt, Pt alloy, and core-shell dissolution	■	■	■	■	■	■	■	■	■	■	■	■
5.2 Catalyst degradation models including nature and role of oxide formation in catalyst degradation		■	■	■	■	■	■	■	■	■	■	■
5.3 Cell kinetic, transport model incorporating degradation effects/kinetics	■	■	■	■	■	■	■	■	■	■	■	■

1 Milestone 1 (Y1-Q4): Development of initial macroscopic-based CV model plus ORR catalyst layer performance model, identification of parameters still needed. *In situ* and *ex situ* characterization of three classes of catalysts

2 Milestone 2 (Y2-Q4): Development of macroscopic model of platinum dissolution and place exchange and completion of CV and ORR catalyst performance models. Determination of effect of carbon support properties and on cathode degradation rates and mechanisms.

3 Milestone 3 (Y3-Q4): Integration of catalyst layer morphological evolution with ORR catalyst layer performance model. Performance degradation and comparison of pristine, as-received MEA to degraded as function of potential, oxide coverage, operating conditions

□ Go/No-Go Decision Point (Y2-Q4): Demonstrated link between aqueous electrolyte studies of degradation mechanisms of three classes of catalysts and degradation observed in MEA tests.

Project deliverables

- Integrated model of the loss of PEMFC performance relating to catalyst degradation that can be used as a predictive tool for estimating the lifetime of PEMFCs under a variety of operating conditions
- Identification of performance degradation mechanisms for different catalyst types and operating conditions
- Definition of catalyst and support physicochemical properties that influence or determine catalyst degradation
- Definition of the operating conditions and catalyst properties that will allow automotive PEMFC power systems to achieve or exceed the DOE lifetime targets, while also meeting activity targets

Project budget and acknowledgements

	Funding in \$K		
Fiscal Year	DOE	Cost-Share	Total
2010	1,238	177	1,415
2011	1,251	182	1,433
2012	1,265	185	1,450
Total '10-'12	3,754	544	4,298

- Financial support from DOE-EERE, Fuel Cell Technology Program
- Nancy Garland, DOE Project Manager