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Low-Noble-Metal-Content Catalysts/Electrodes for Hydrogen Production by Water Electrolysis

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Organization: Proton OnSite

Date: June 18th, 2014

Project ID: PD098

Overview

Timeline

- Project Start: 28 June 2012
- Project End: 13 Aug 2015
- Percent complete: 45%

Budget

- Total Funding Spent*
 - \$413,000
- Total Project Value
 - \$1,150,000
- Cost Share Percentage
 - 0% (SBIR)

Barriers

- G. Capital Cost

Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis
Hydrogen Protoduction ^{a, b, c}

Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost ^d (Production Only)	\$/kg	4.2 ^d	3.9 ^d	2.3 ^d
Electrolyzer System Capital Cost	\$/kg	0.70	0.50	0.50
	\$/kW	430 ^{e, f}	300 ^f	300 ^f
System Energy Efficiency ^g	%(LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency ^h	%(LHV)	74	76	77
	kWh/kg	45	44	43

2012 MYRDD Plan

Partners

- Brookhaven National Lab

Relevance: Leveraging Fuel Cell Advancements in Electrolyzers

- Significant investment made in PEM fuel cells
- Electrolyzer platform can benefit with incremental investment
 - Similar chemistry but different operating requirements
 - Not always a drop in but shows promise – need some adaptation
- Core-shell catalysts: developed by various groups including BNL/Adzic group
 - High activities and durability demonstrated
 - Even more benefit in reduction of electrolyzer loadings

Relevance: Renewable Fuels

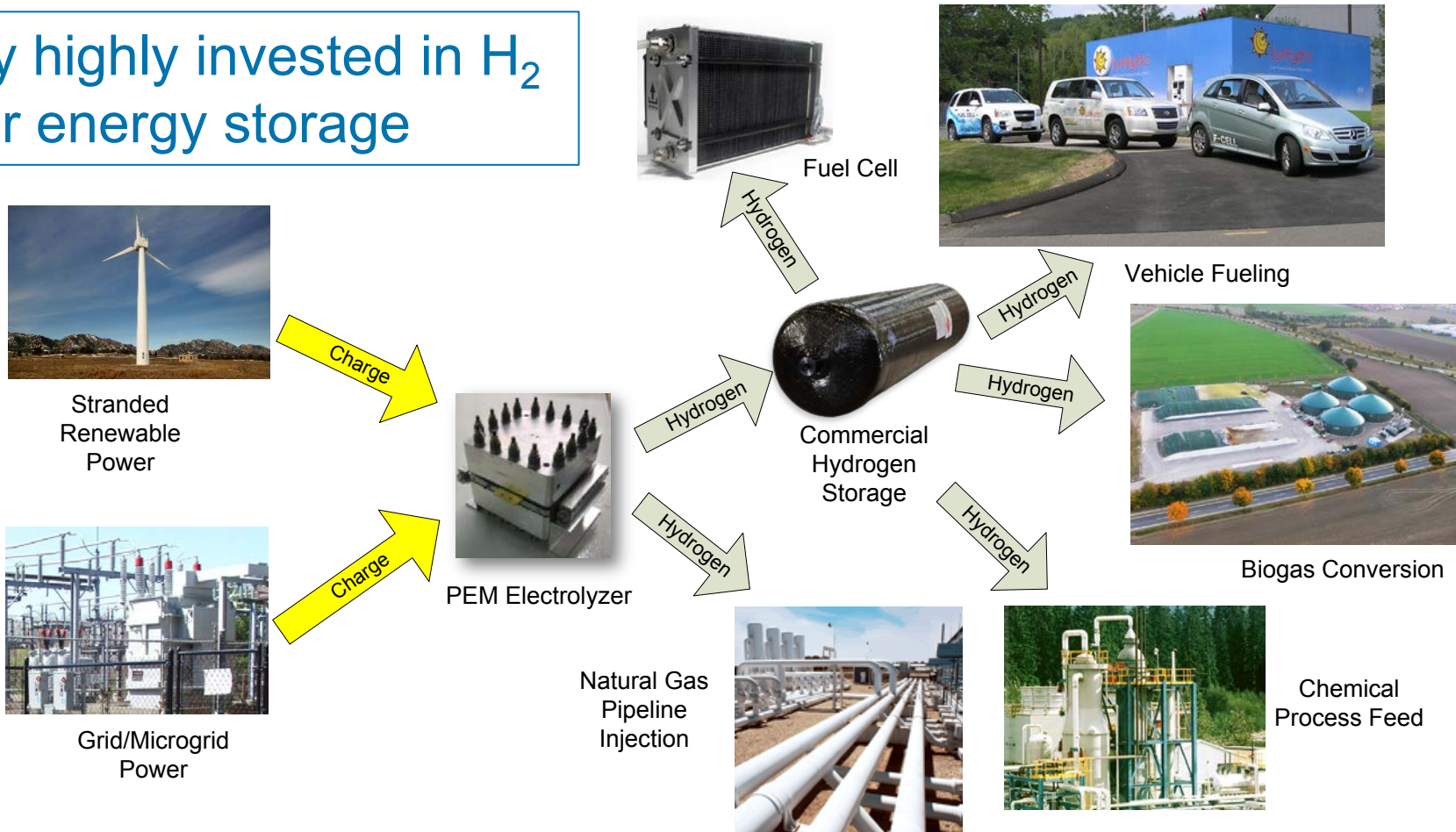
- Hydrogen from electrolysis is the carbon-free solution
- Germany already at 20-40% stranded wind power
 - Changes economics for \$/kg production



Relevance: Hydrogen Energy Storage

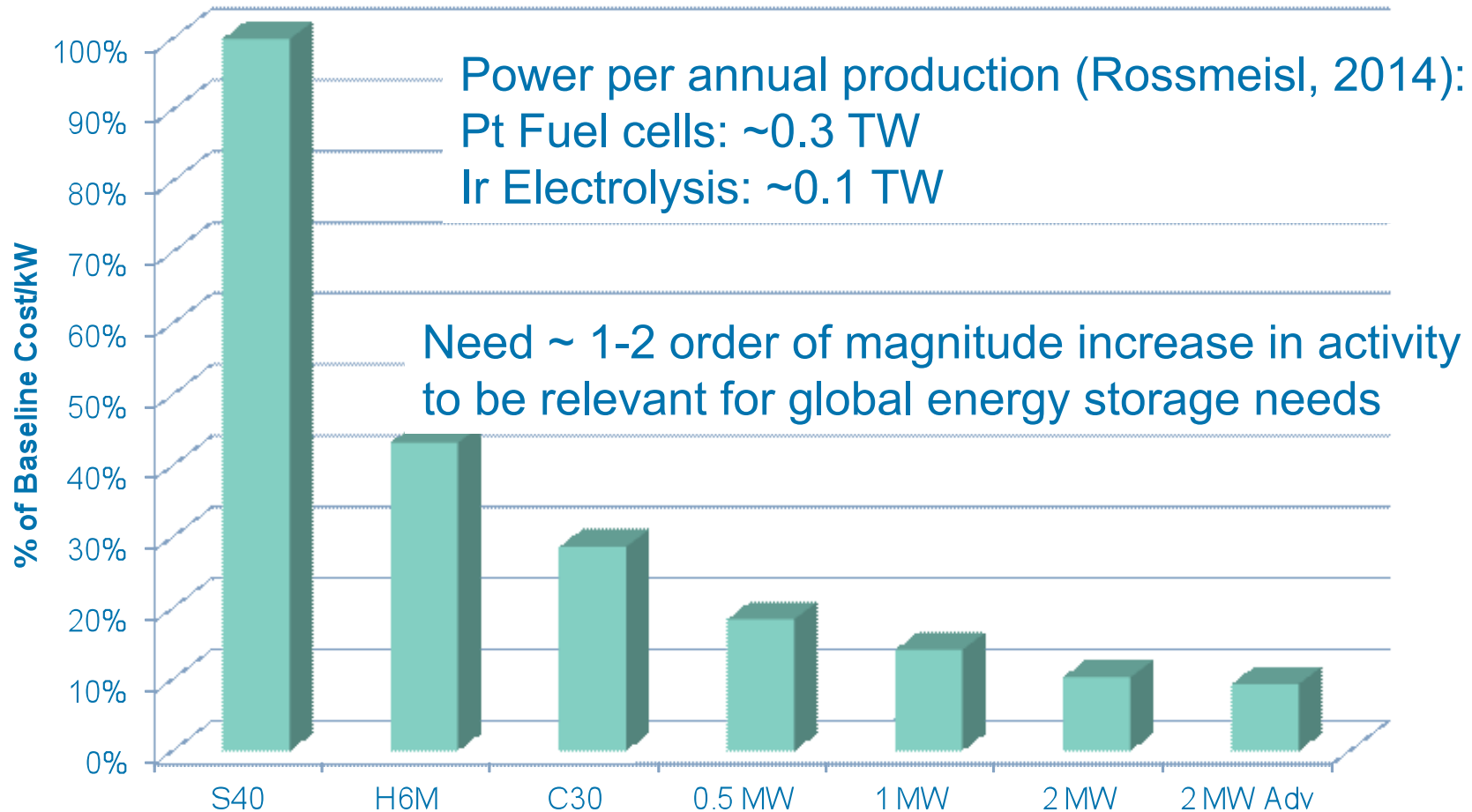
- Flexibility of hydrogen enables additional options for lower cost across applications
 - Also impacts fueling through biogas applications

Germany highly invested in H₂ option for energy storage



Relevance: System Scale-Up Needs

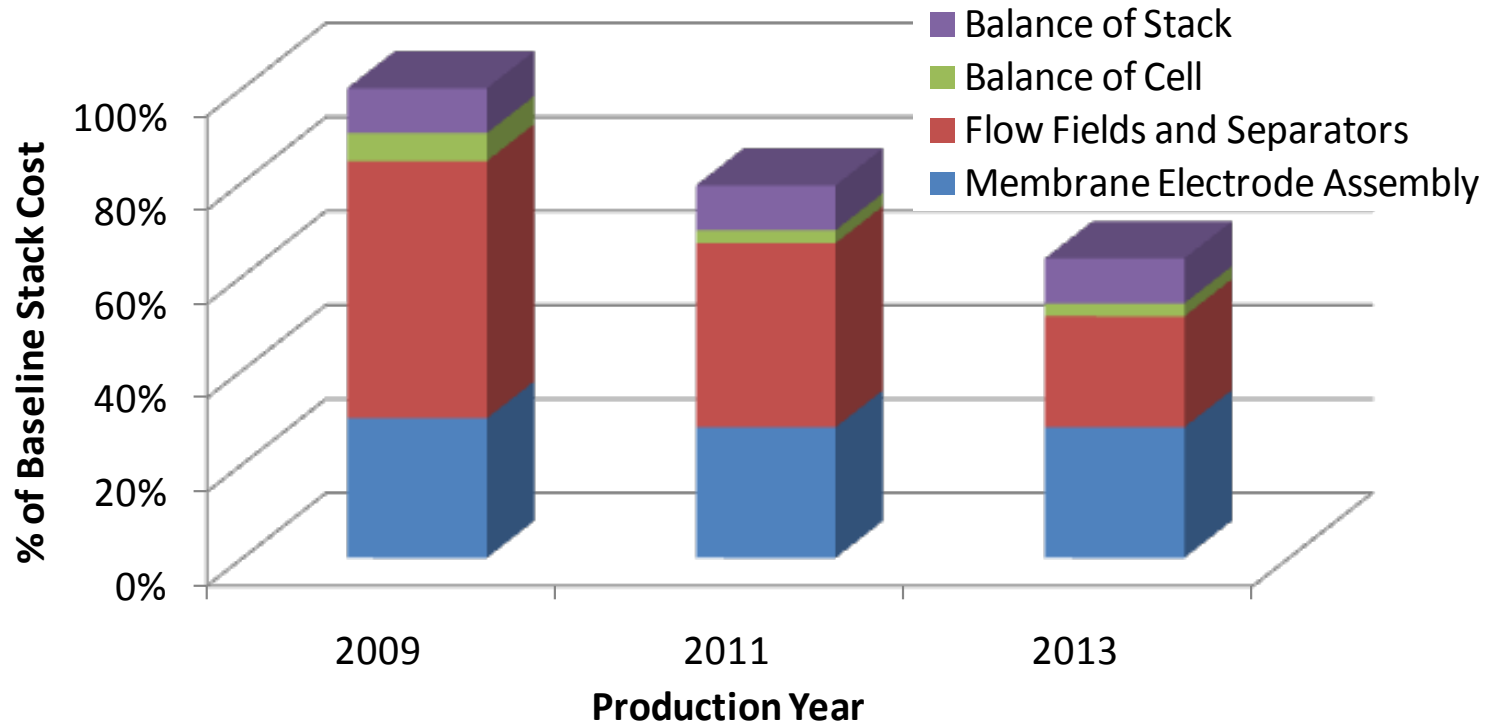
MW Cost Trajectory



- System cost improves considerably with scale
- Reduction of PGM content needed to manage price volatility and high volume needs

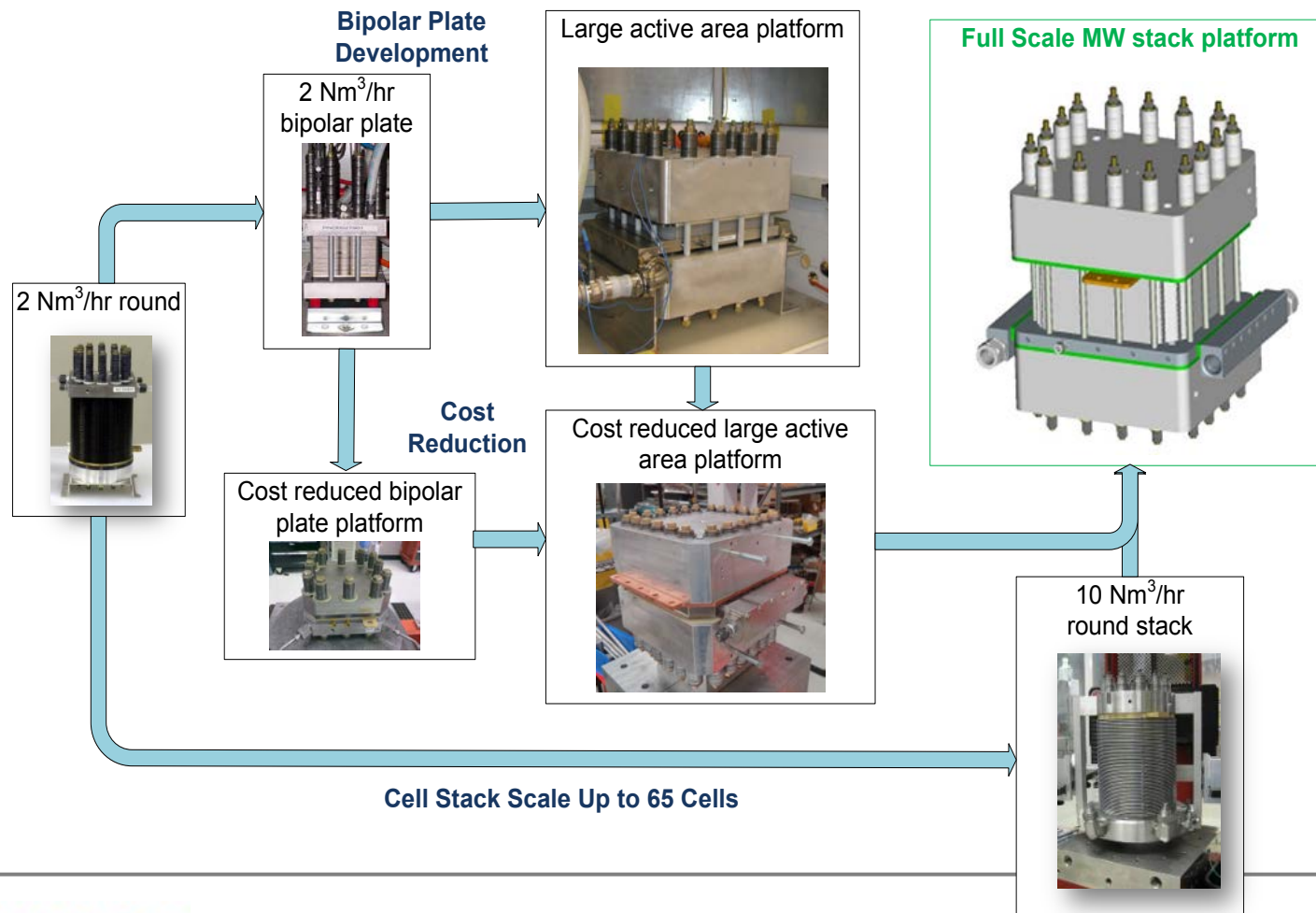
Relevance: Capital Cost Reduction

- MEA is a large fraction of overall stack cost
- Current cost roughly equivalent between membrane, catalyst, and manufacturing/labor
- New manufacturing methods and ultra-low PGM loading will reduce capital costs significantly and enable scale



Insertion to MW Scale

- Stack platform already in verification stages
- Manufacturing processes must be scalable to required active area



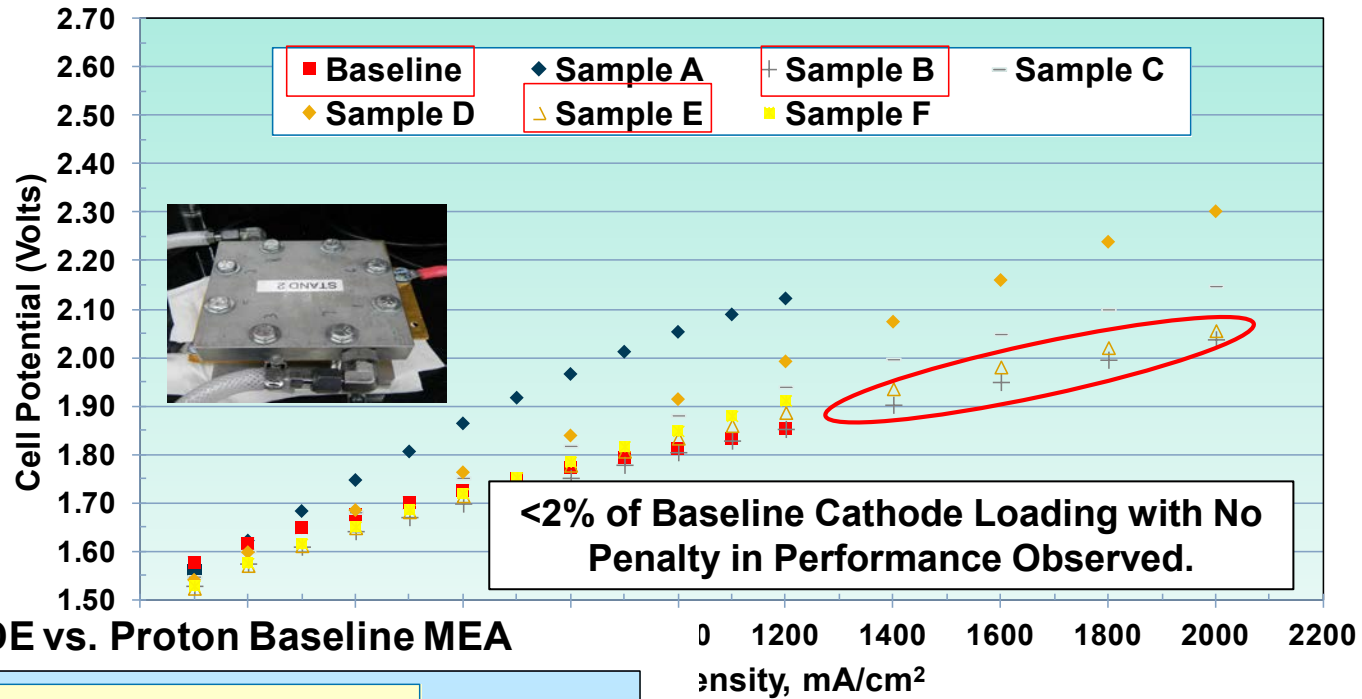
Top Level Approach

- Task 1.0 Cathode Catalyst
 - Technology transfer
 - Scale-up
- Task 2.0 Cathode Manufacturing
 - Deposition verification
 - Manufacturing development
- Task 3.0 Anode Catalysts
 - Synthesis of Ru nanoparticles on TiO_2
 - Coating Ir metal/metal oxide on Ru cores
 - Evaluation of synthesized catalysts
- Task 4.0 Anode Electrode
 - Ink formulation for anode catalysts
 - Anode GDE fabrications
 - Structural and component characterization
- Task 5.0 Cell Development and Testing
 - Anode GDL development
 - Cathode GDE incorporation
 - Durability and post-operation assessment
- Task 6.0 Cost Analysis

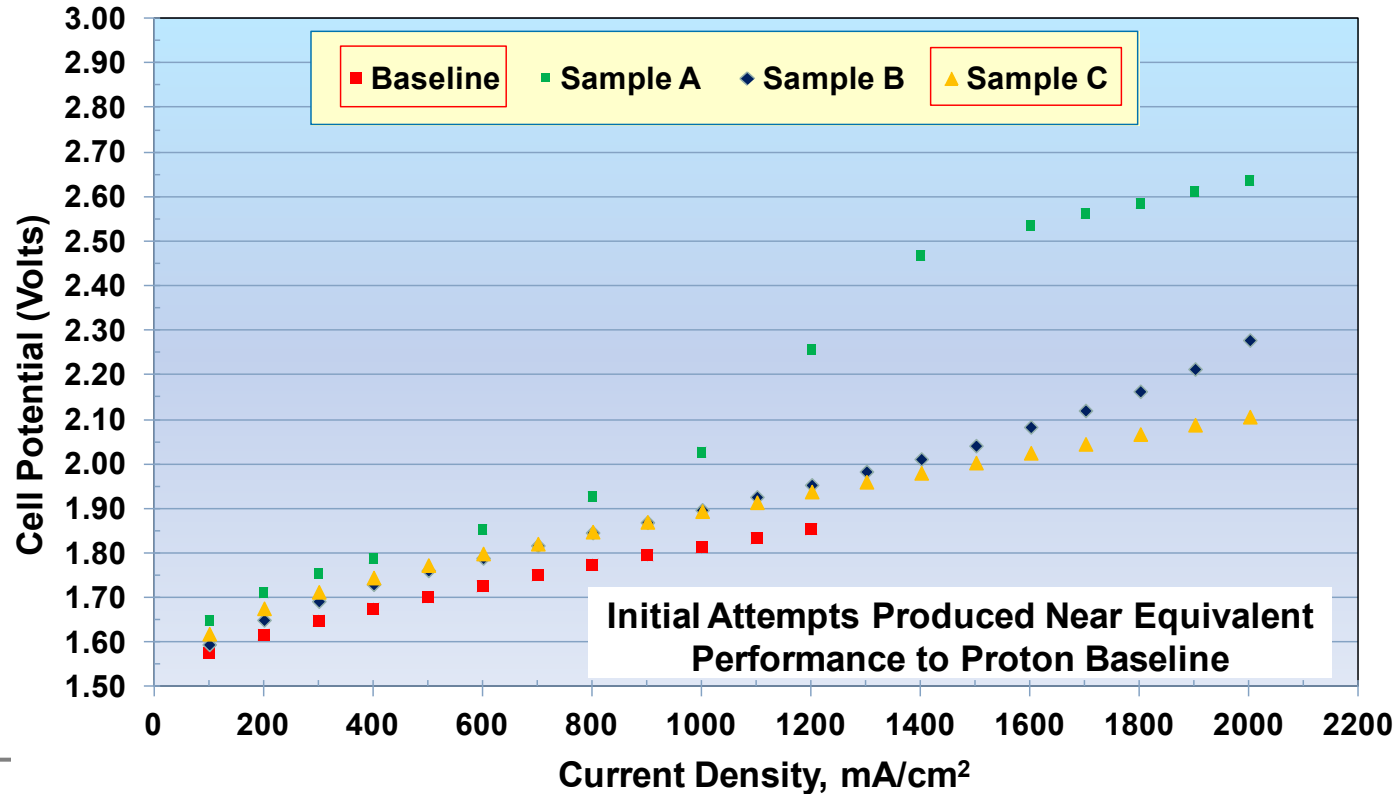
Phase I Summary

- Equivalent cathode performance at low loadings (<0.1 mg/cm²)

Brookhaven Cathode GDE vs. Proton Baseline MEA



Brookhaven Anode GDE vs. Proton Baseline MEA



- Reduction on anode to <0.5 mg/cm²
- Manual application processes used in Phase 1

Approach: Phase II Project Objectives

- Translate catalyst synthesis to a manufacturable process at Proton.
- Develop technique for manufacturable electrodes.
- Demonstrate feasibility for 80% cost reduction in OER catalyst.
- Downselect promising anode electrode configurations to achieve >100 hrs durability.
- Achieve 500 hours of operation with cathode GDE.
- Evaluate the cost benefits of new materials.

Approach: Year 1 Project Milestones

Task #	Milestone Description	Due Date / Completion
6	Project Kick-off: Proton, BNL	8/30/2013 (100%)
1	Demonstrate successful cathode catalyst synthesis and electrode manufacture at Proton	12/31/2013 (100%)
3	Complete study of TiO_x -supported Ru@Ir catalysts in solution electrochemical cells.	12/31/2013 (100%)
4	Demonstrate uniform and robust catalyst layer on Ti GDLs	4/30/2014 (20%)
1	Complete scale up synthesis of cathode catalysts to 10 – 100 g batch level	6/30/2014 (20%)
5	Complete cell design analysis for cathode configuration	7/15/2014 (0%)

Cell design analysis shifting due to resource availability and priority of task

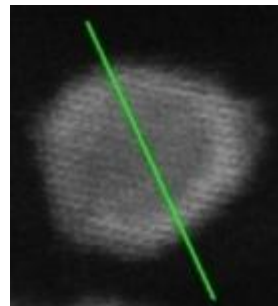
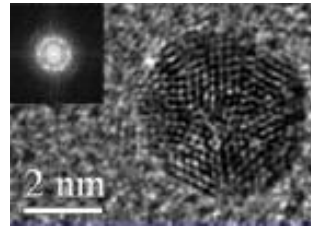
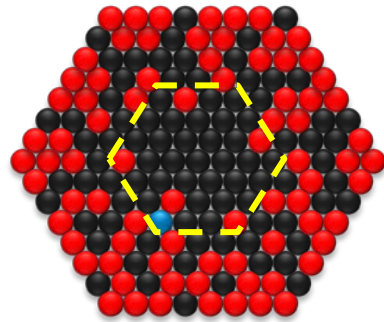
Approach: Year 2 Project Milestones

Task #	Milestone Description	Due Date / Completion
2	Downselect optimal cathode material and process for reliable production	8/30/2014 (20%)
4,5	Demonstrate improved activity and durability of selected anode GDE samples in cell	8/30/2014
6	Provide initial cost assessment via H2A model	8/30/2014
2,4,5	Identify key issues for enhancing durability	11/30/2014
4,5	Achieve >100 hours durability of developed anode catalyst/GDE	4/30/2015
2,4,5	Demonstrate process capability for large active area electrodes	6/30/2015
2,4,5	Achieve 500 hours of operation at 89 cm ² cell level	7/30/2015 (50%)
6	Evaluate the benefits of selected anode catalysts/electrodes over the baseline in cost reduction or efficiency boost.	8/30/2015
6	Complete Final Reporting	8/30/2015

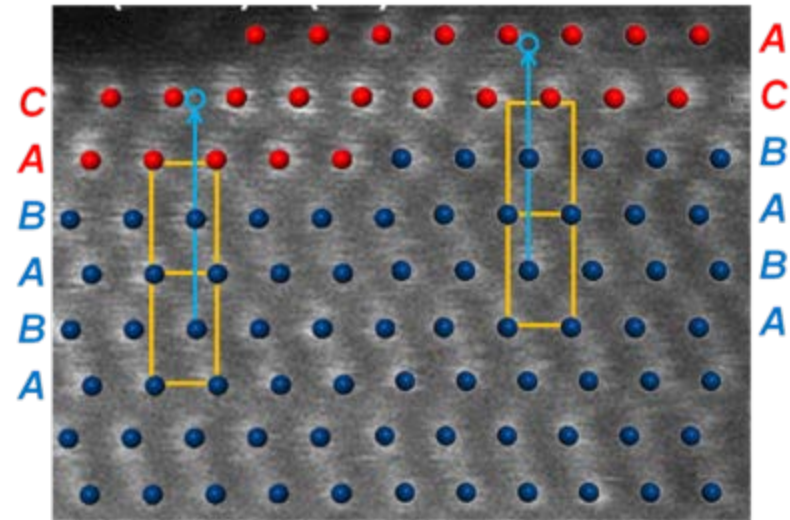
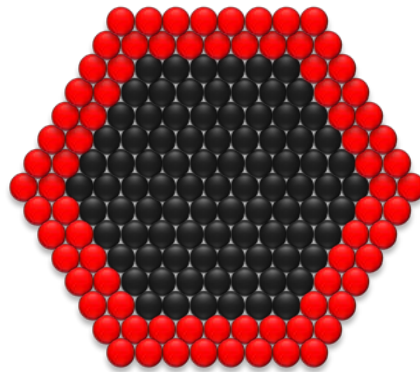
Approach: Low Catalyst Loading Concept

- Increase the Pt specific surface area by synthesizing sized-controlled, core-shell nanocatalysts
- Translates into a >98% reduction of Pt
- Strategy: translate and scale up process for manufacturing

Previous methods produced imperfect structure and mixing



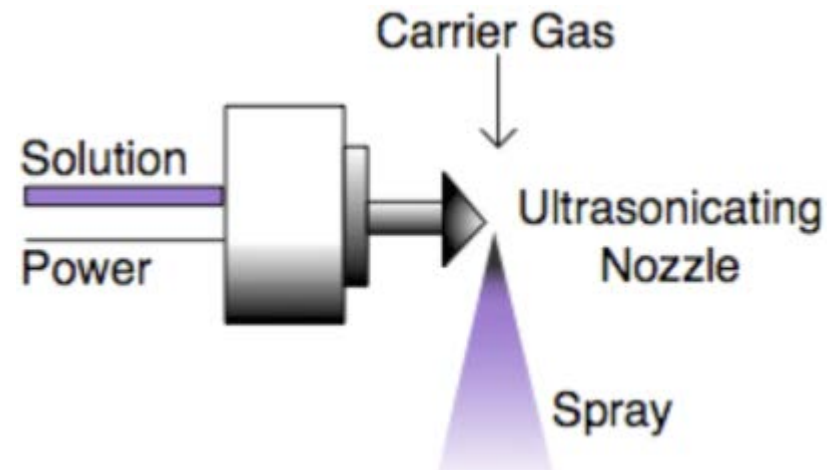
Defect-induced partial alloying eliminated.



Atomically coated structures process shown by TEM (right) using a simple process.

Approach: Manufacturing and GDL Selection

- Ultrasonic spray deposition identified as possible approach for high-throughput and low labor
- Phase 1: MPLs result in better distribution of catalyst near membrane
- Stable anode supports need to be identified
- Strategy:
 - optimize deposition technique and GDL selection
 - explore TiO_2 as initial anode support



Ultrasonic spray deposition¹

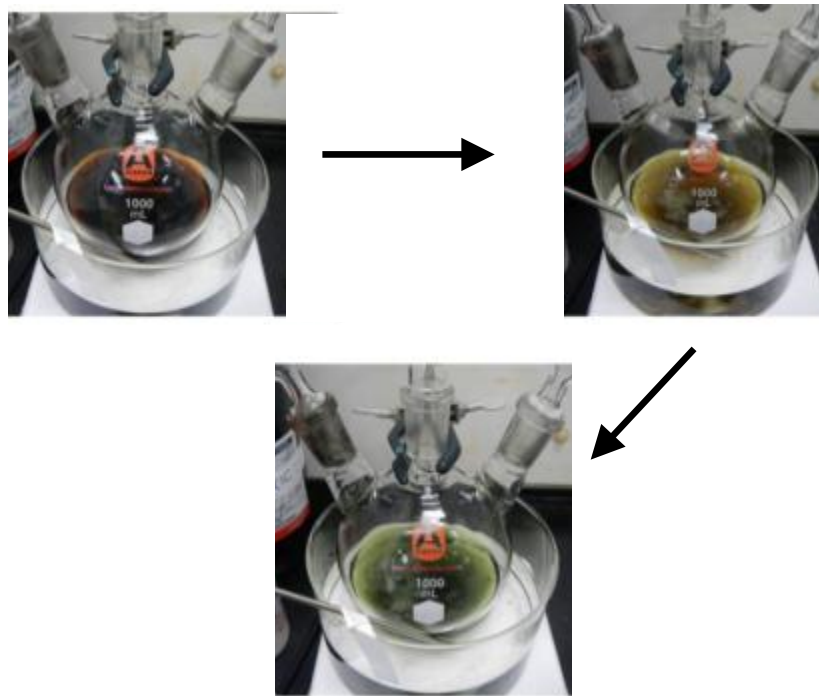
¹SPIE Newsroom. DOI: 10.1117/2.1200903.1555

Technical Accomplishments

- Demonstrated successful cathode catalyst synthesis and electrode manufacture at Proton
- Completed study of TiO_x -supported Ru@Ir catalysts in solution electrochemical cells
- Downselect optimal cathode material and process for reliable production
 - Showed feasibility for ultrasonic spray deposition for cathode manufacturing
- Showed > 500 hrs durability with ultra-low loaded Proton-made cathode in production quality hardware

Technical Accomplishments

- Task 1.0 Cathode Catalyst Development
 - Installed safety-qualified equipment and procedures
 - Established quality metrics at critical process points: solution color, pH, and product weight



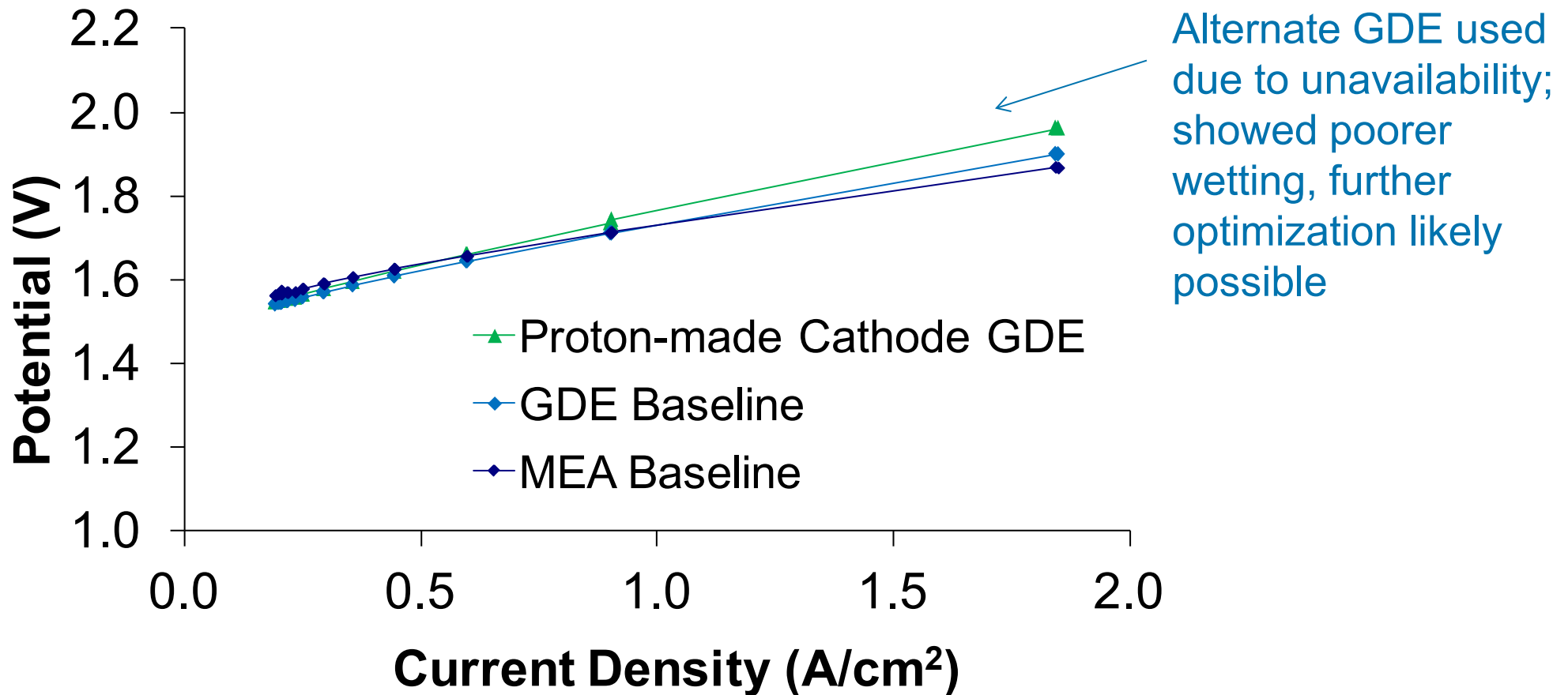
Color transformation of solution should proceed from dark brown to green



Safety-qualified hydrogen reducing furnace

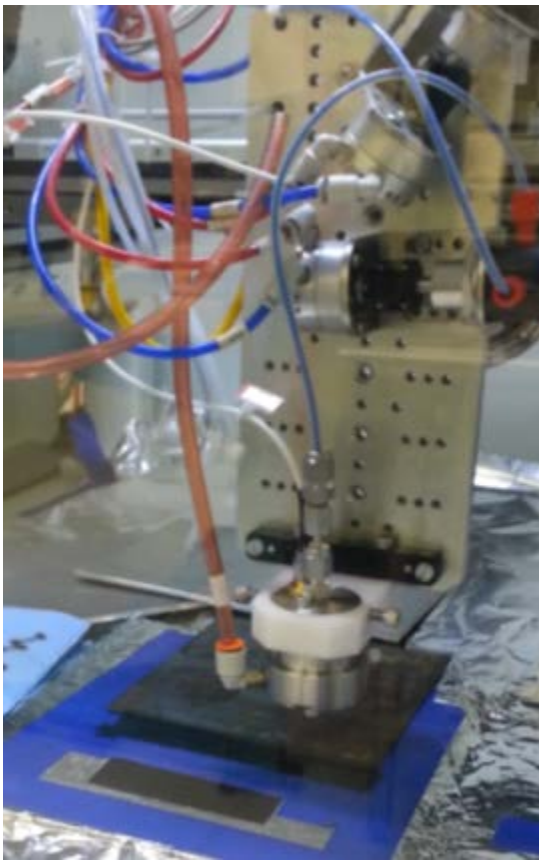
Technical Accomplishments

- Task 1.0 Cathode Catalyst Development
 - Achieved equivalent cathode performance at 1/10 the loading using Proton-made catalyst and GDE

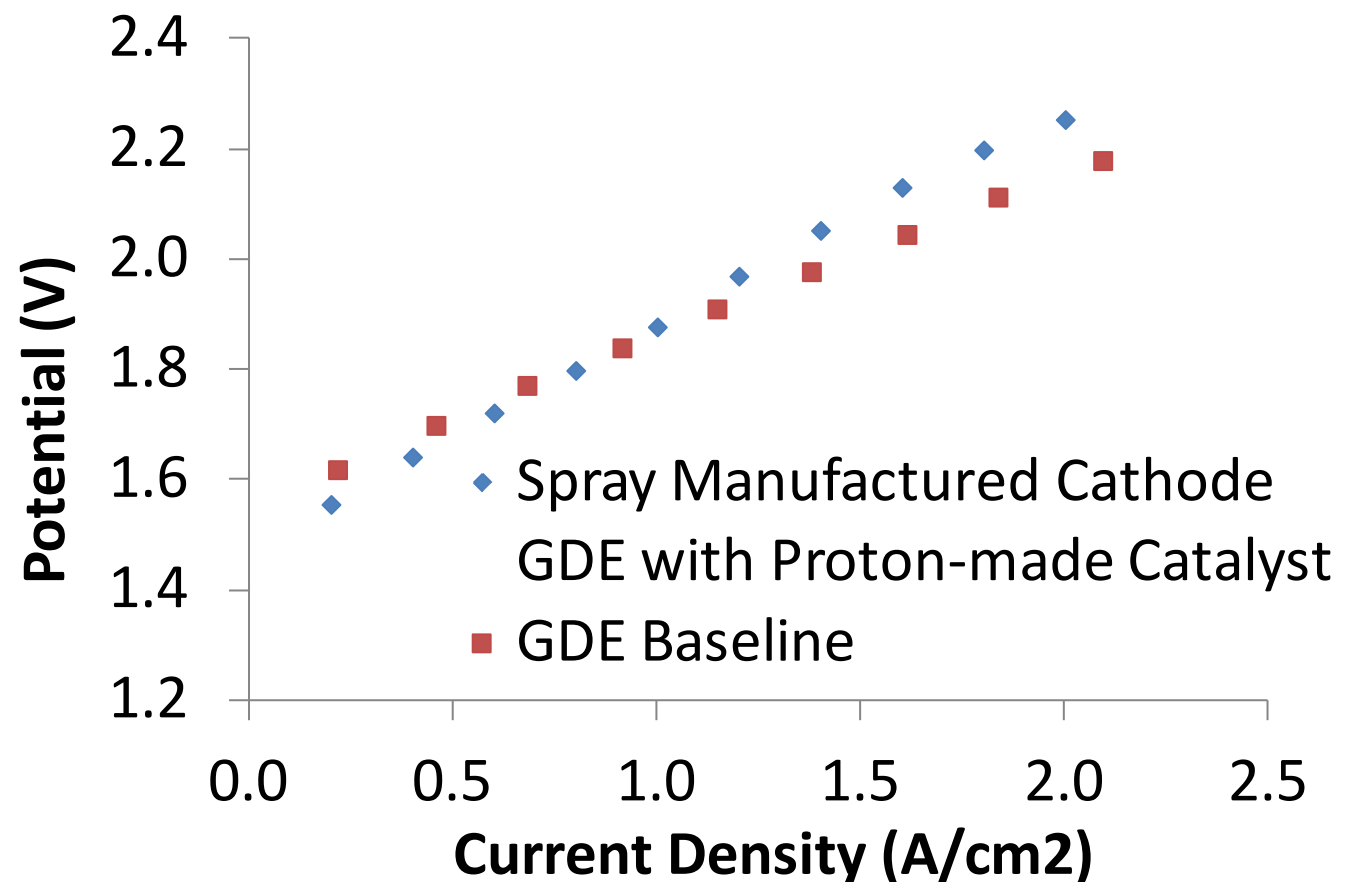


Technical Accomplishments

- Task 2.0 Cathode Manufacturing Development
 - Achieved nearly equivalent performance using a spray-deposited cathode ($<0.15 \text{ mg/cm}^2$)

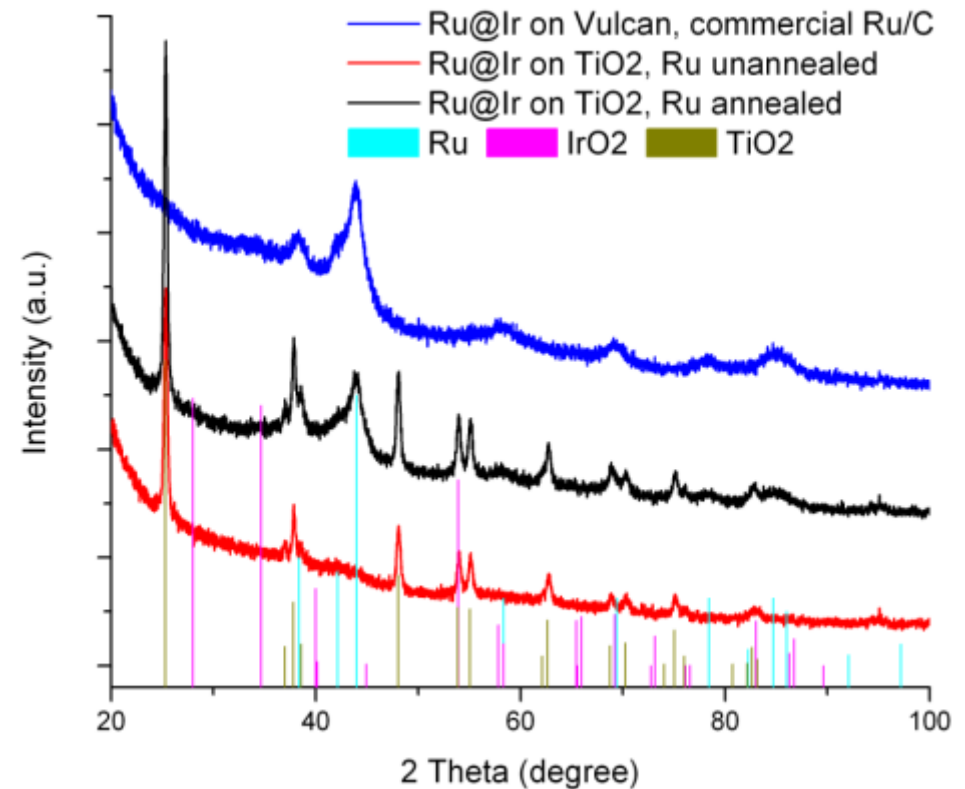


Ultrasonic printer used to make GDE.



Technical Accomplishments

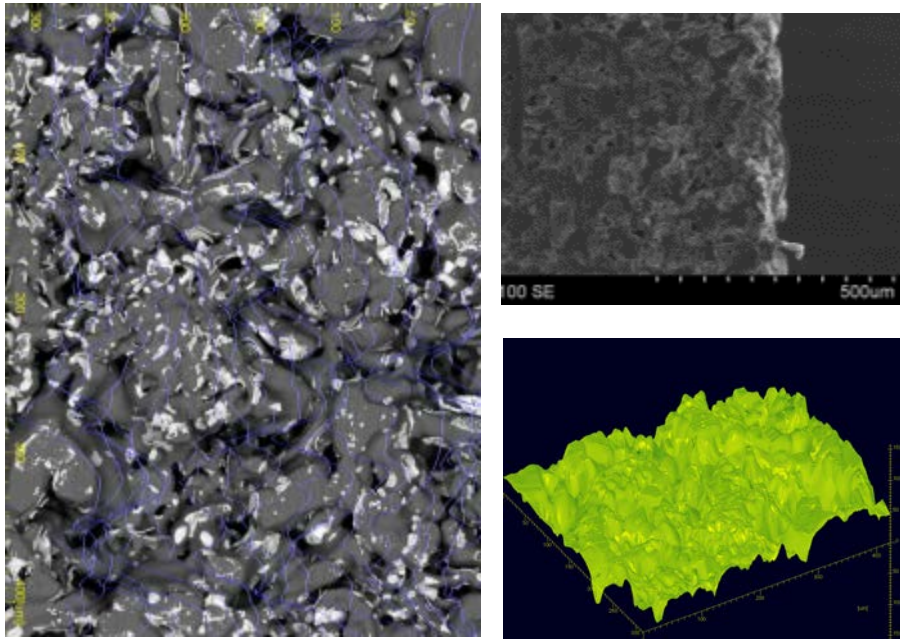
- Task 3.0 Develop Anode Catalysts
 - BNL synthesized and characterized Ru-Ir “core-shell” nanocatalysts on TiO_2 supports
- Ru-Ir particles were 2.4 and 6.8 nm in diameter respectively before and after annealing, while TiO_2 particles are ~30 nm.
- Performances were similar to unsupported catalysts.
- Interaction with Ti GDL may be more important.



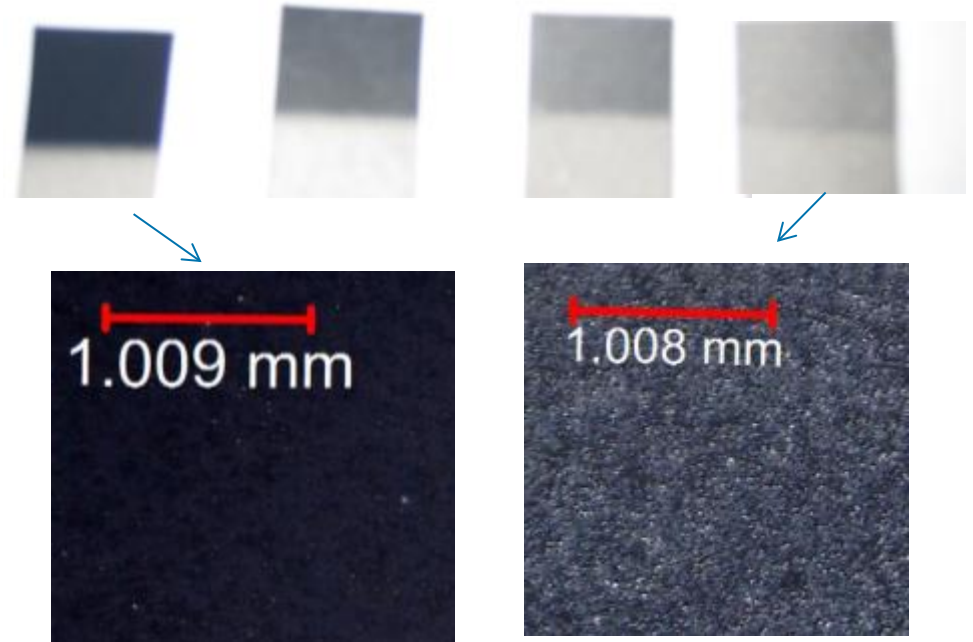
XRD measurements confirm nanocatalyst synthesis

Technical Accomplishments

- Made uniform and stable catalyst coating on Ti GDL and OER catalyst for anode



3D SEM image of a Ti GDL
average roughness 20 μm

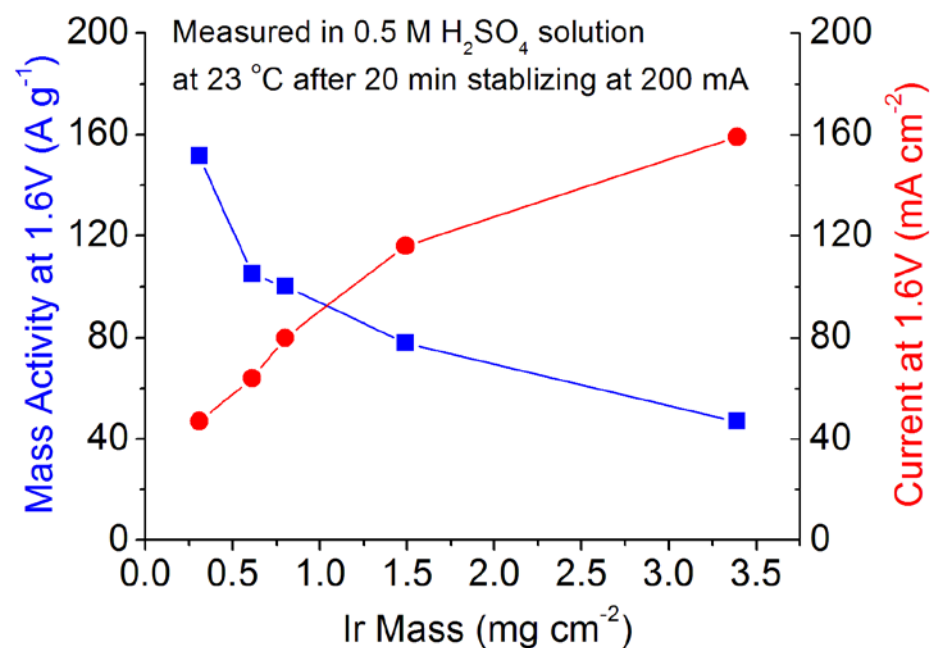
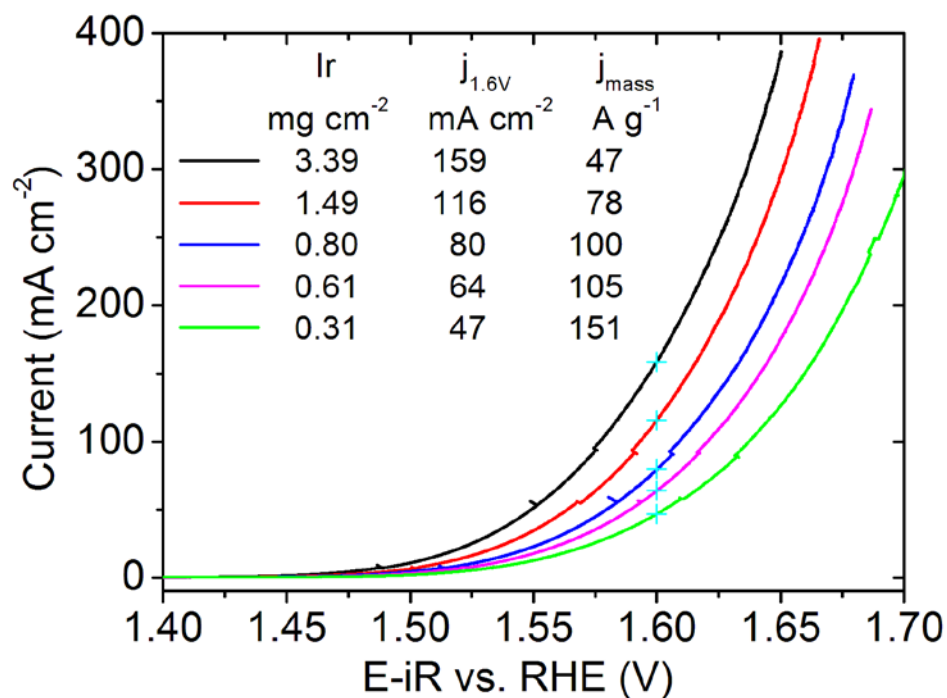


Photos and optical images of catalyst-coated Ti GDLs with 3.4, 1.5, 0.8, and 0.3 mg cm^{-2} IrOx

- Uniform change in catalysts' loading by ten-fold.

Technical Accomplishments

- Established IrOx baseline measured in solution electrochemical cell using standalone GDE strips.

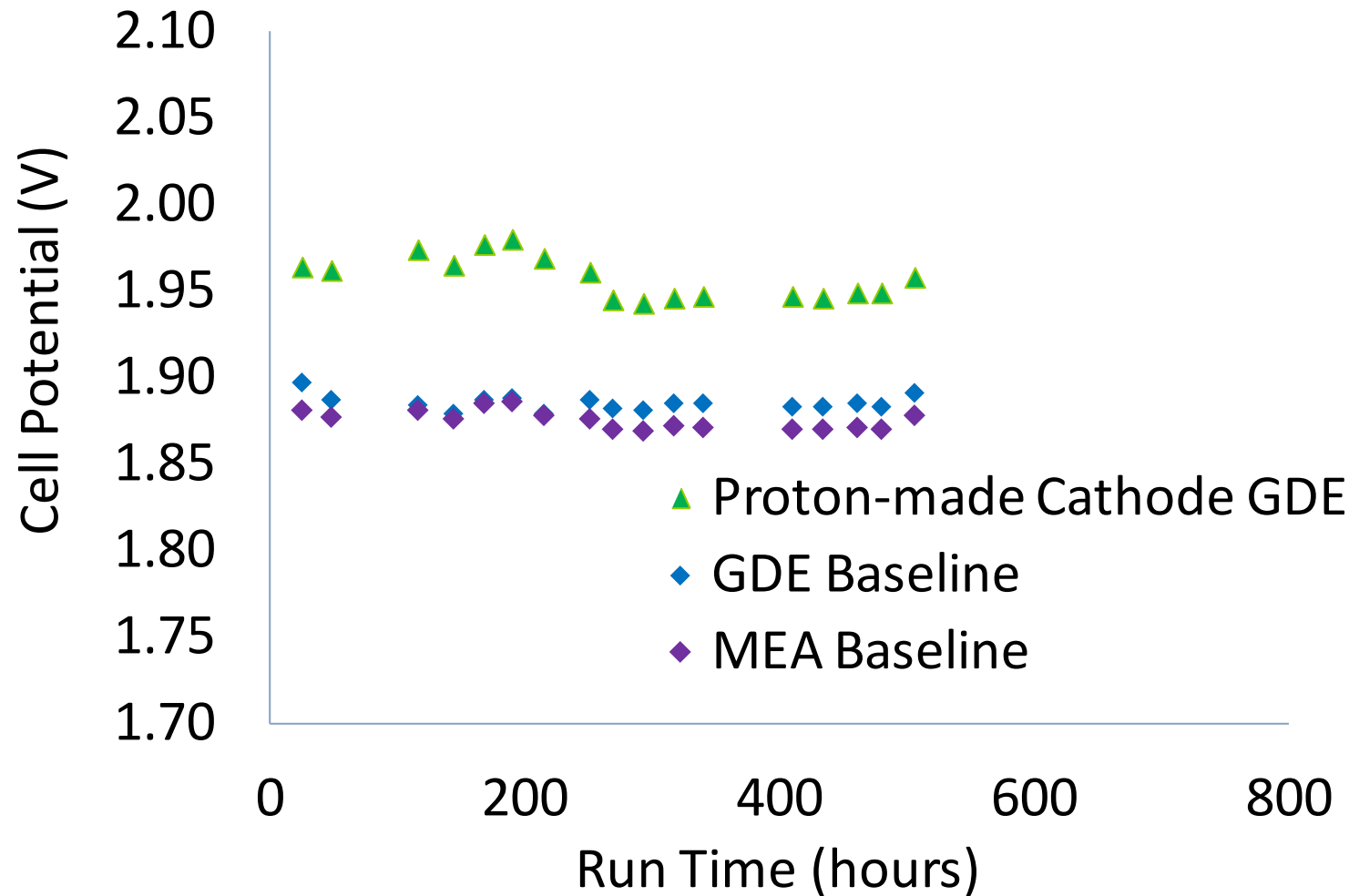


iR-corrected polarization for IrOx on Ti measured after 20 min stabilization at 200 mA cm⁻² in 0.5 M H₂SO₄ solution.

Kinetic current at 1.6 V (right axis) and mass activity (left axis) as a function of IrOx loading.

Technical Accomplishments

- Task 5.0 Cell Development and Testing
 - Proton-made cathode shows durability for >500 hr



Future Work

- **Task 1: Cathode Development**
 - Scale up process to relevant production lot quantity
- **Task 2: Cathode Manufacturing**
 - Identify optimum spraying parameters and equipment
- **Task 3: Develop Anode Catalysts**
 - Improve the durability of Ru-Ir core-shell catalysts or leverage new approach being explored in parallel by BES-supported research project
- **Task 4: Anode Electrode Fabrication**
 - Explore and develop ways to enhance catalyst-Ti interaction
 - Study the impact of Ti GDLs on OER performance

Future Work

- **Task 5: Cell Development and Testing**
 - Identify optimum cathode GDL material to increase efficiency and maintain durability
 - Identify promising anode GDL materials and test performance/durability
- **Task 6: Cost Analysis**
 - Utilize H2A model and Proton's electrochemical interface model to refine the impact of design changes developed in Tasks 1-5 on the \$/kg of H₂

Collaborators

- Brookhaven National Lab
 - Synthesis and characterization of core shell catalyst materials
 - Development of electrode formulations and application methods on gas diffusion layers for low catalyst loading



Summary

- **Relevance:** Reduces stack capital cost for lower hydrogen production cost
- **Approach:**
 - Optimize anode catalyst utilization for >80% reduction in PGM loading
 - Identify optimum configuration for manufacturable, ultra-low loaded cathode
- **Technical Accomplishments:**
 - Achieved equivalent cathode performance at <1/10 loading
 - Showed feasibility for ultrasonic spray deposition for cathode manufacturing
 - TiO_x-supported Ru@Ir catalysts manufactured and characterized
 - Showed > 500 hrs durability with ultra-low loaded Proton-made cathode
- **Collaborations:**
 - Brookhaven National Labs – catalyst and formulation development
- **Proposed Future Work:**
 - Scale up cathode manufacturing
 - Identify optimum ultrasonic spraying parameters and equipment
 - Carry out MEA tests to identify key issues for anode catalyst durability
 - Identify optimum anode and cathode GDL materials for final design
 - Perform cost analysis

Acknowledgments

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