Regenerative Fuel Cell System (SBIR Phase II)

pH Matter: **Paul Matter, Minette Ocampo, Chris Holt, Michael Beachy, Nora Shaheen, Monica Chan, and Jimmy Gaydos**

Giner: **Hui Xu, and Shuai Zhao**

NREL: **Shaun Alia, Andrew Park, and Bryan Pivovar**

June 7, 2017

Project ID: FC154

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Company Background

- Founded in 2010, located in Columbus, OH
- Mission: to develop and commercialize material-based products for alternative energy applications
- Primary focus on electrode materials
- Expertise in:
  - Catalyst synthesis, development, and scale-up
  - Fuel cell development
  - Commercialization of catalysts, advanced materials, and electrochemical devices

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Project Background

- Fuel cells are of interest for energy storage applications, such as grid load leveling and renewable integration.
- The fuel cells could potentially be operated in a reversible manner, allowing renewable energy to be stored in the form of hydrogen.
- When operating in regeneration mode, degradation is even more pronounced for conventional catalysts because of the high voltages required.
- In existing reversible systems, a separate electrode is typically used for oxygen evolution, adding to the already high system cost.
- If a low-cost reversible fuel cell could be developed, it would be a key breakthrough for energy storage.

Overview

Timeline and Budget

- Phase II SBIR Project
- Project Start Date: 04/11/2016
- Project End Date: 04/10/2018
- FY17 Project Budget: ~$500,000
- Total Budget: $1,000,000

Collaborators

- Giner, Inc.
- NREL

Barriers

- Barriers addressed:
  - Develop low-cost catalysts for reversible anion-exchange membrane fuel cells (oxygen and hydrogen electrodes)
  - Increase the durability/stability of catalysts with cycling
  - Integrate catalysts with membranes and GDLs into MEAs and stacks
- Targets:
  - 1,000 cycles above target operating efficiency and current density
  - 42% efficiency; >250 mA/cm^2 fuel cell; >50 mA/cm^2 electrolysis

Relevance

The DOE has a mission to develop lower cost and better performing fuel cell technologies, and develop technologies for energy storage. This project applies to both.

Project Objectives

- Demonstrate a reversible 25-cm^2 Anion Exchange Membrane Fuel Cell (AEMFC) for 1,000 cycles (42% round-trip efficiency; >250 mA/cm^2 power generation; >50mA/cm^2 energy storage).
- Incorporate Membrane Electrode Assemblies (MEAs) into regenerative stack.
- Perform economic analysis on reversible AEMFC system following DOE guidelines (Steward et al. NREL/TP-560-46719) for candidate grid energy storage technologies.

Approach

Tasks / Key Milestone	Quarter							
	1	2	3	4	5	6	7	8
Task 1. Hydrogen Electrode Development	■ ■	■ ■	■ ■	■				
Task 2. MEA and O_2 GDE Development								
Task 2.1 MEA Synthesis	■ ■	■ ■	■ ■	■ ■				
Task 3. Full Cell Testing								
Task 3.1 Performance Testing		■ ■	■ ■	■ ■				
> 250 mA/cm², >42% efficiency at 25-cm²				●				
Task 3.2 Load Cycle Testing				■ ■	■ ■	■ ■		
1,000 cycles demonstrated						●		
Task 3.3 Post-test Characterization					■ ■	■ ■	■ ■	
Task 4. Stack Testing (5-cell, 50-cm²)								
Task 4.1 Fabrication					■ ■	■ ■	■ ■	
Task 4.2 Stack Testing						■ ■	■ ■	■ ■
> 250 mA/cm², >42% efficiency, 500 hours								●
Task 5. Economic Modeling								
Task 5.1 Material Scale-up Projections	■ ■	■ ■	■ ■	■ ■				
Task 5.2 Delivered Electricity Projections				■ ■	■ ■	■ ■	■ ■	■ ■

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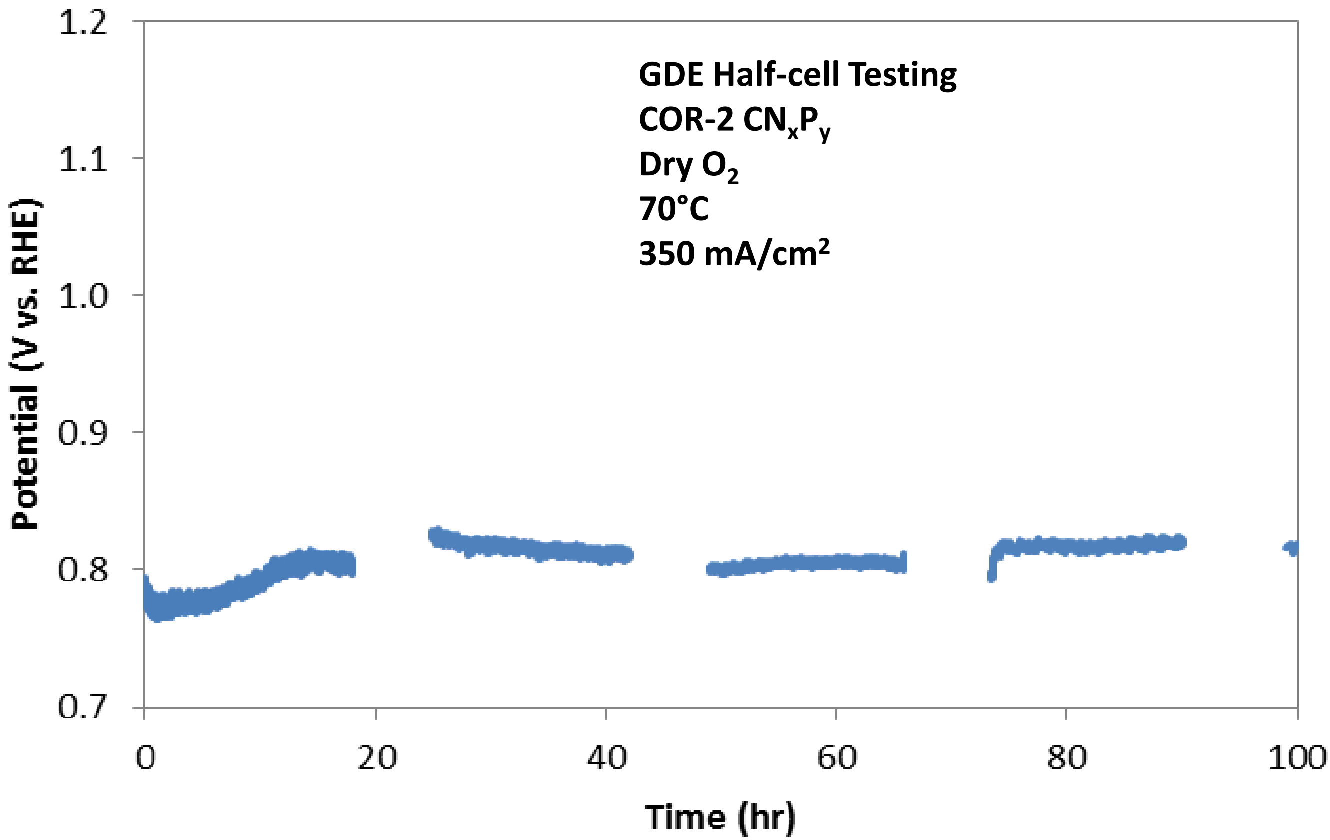
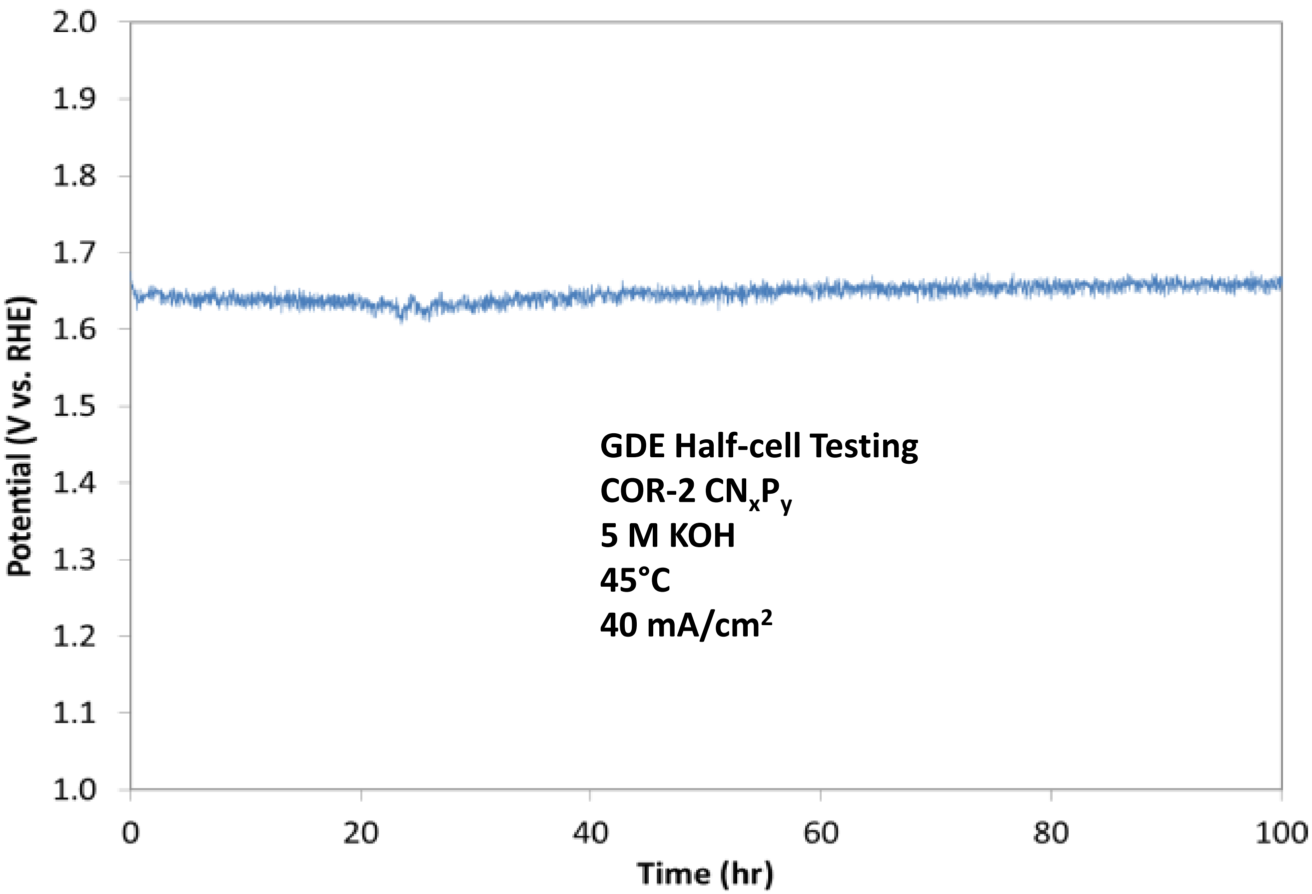
Accomplishments

- In Phase I SBIR demonstrated stable steady-state ORR performance over 100 hours in half-cell testing using patented PGM-free catalyst:

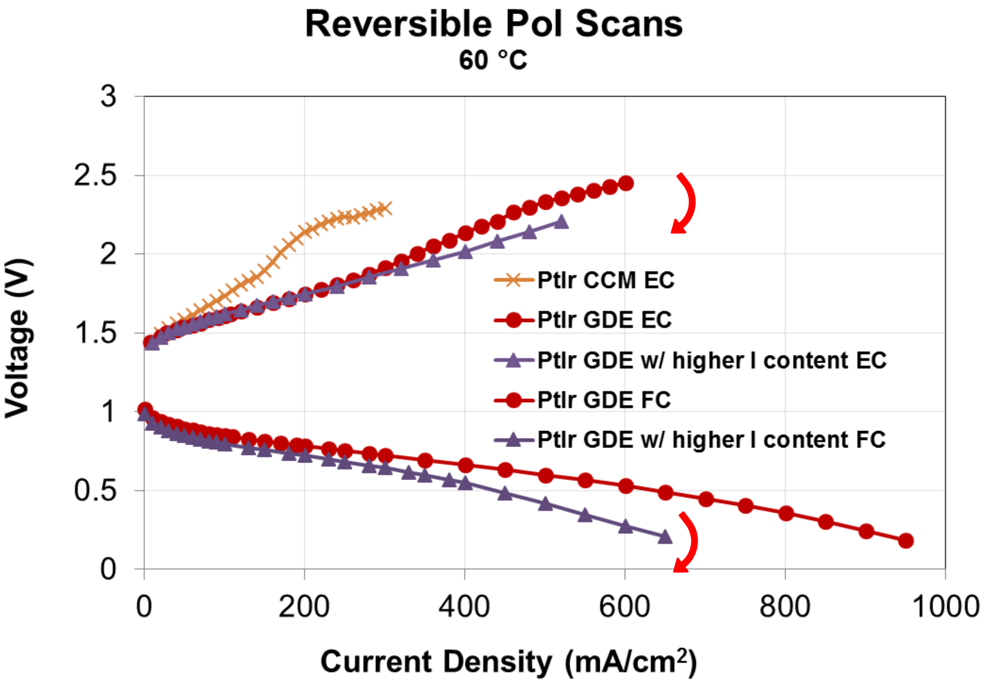


Accomplishments

- In Phase I SBIR demonstrated stable steady-state OER performance over 100 hours in half-cell testing using patented PGM-free catalyst:



Accomplishments: Baseline Catalyst Performance

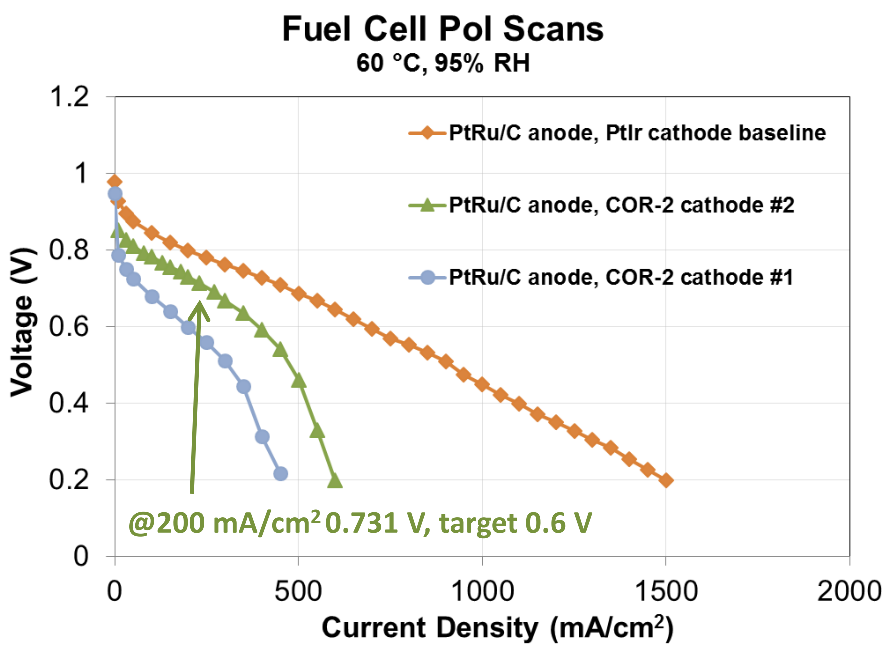


Cathode: PtIr ($0.75_{Pt}+0.75_{Ir}$ mg/cm^2, Ionomer=20%); Anode: PtRu/C (0.7 mg_{PtRu}/cm^2, I/C=0.8)

Fuel cell testing conditions: H_2/O_2 flowing at 1000 ccm/min, at the temperature of 60 °C (relative humidity of 95%), and H_2/O_2 backpressure of 30 psia

- Electrolyzer performance is much improved with GDEs vs. CCMs
- Higher ionomer content can further improve electrolyzer performance, but sacrifice fuel cell performance

Accomplishments: Gas Diffusion Electrode (GDE) Configuration



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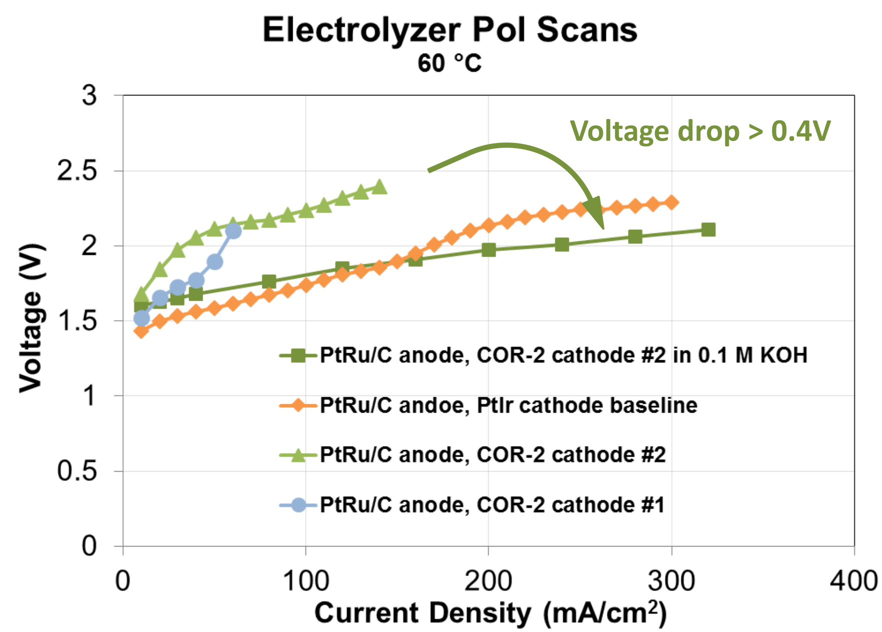


Cathode: COR-2 (2 mg/cm^2, Ionomer=20%);
Anode: PtRu/C (0.7 mg_{PtRu}/cm^2, I/C=0.8)

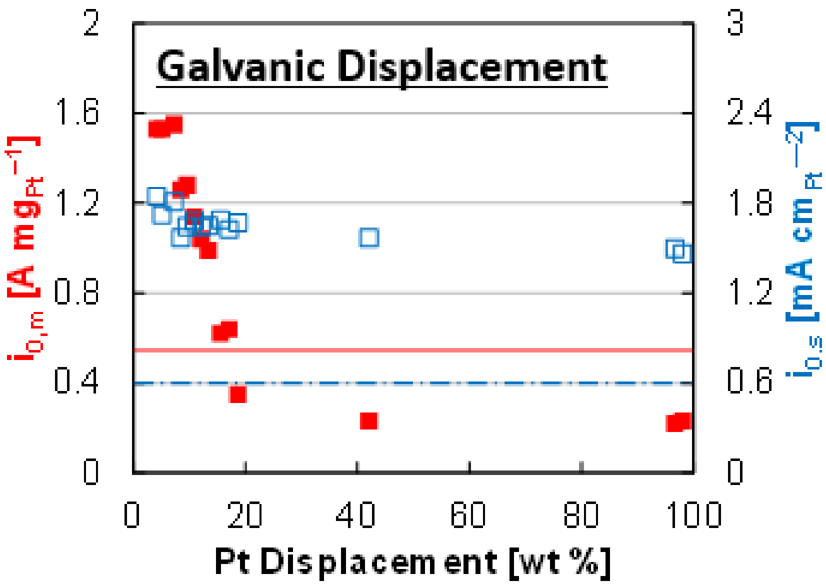
COR-2 #1: ionomer, no hot-press; COR-2 #2: ionomer, with hot-press

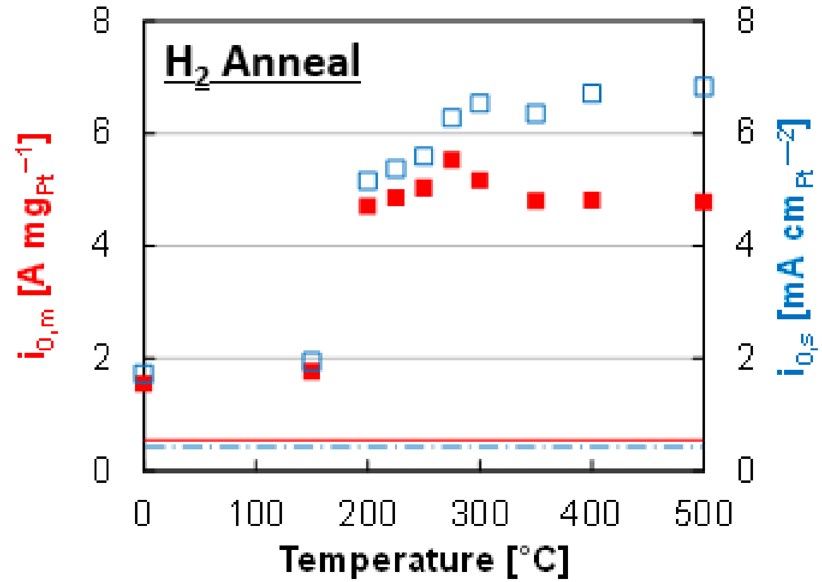
- Fuel cell performance using COR-2 (CN_xP_y) has reached the target
- Electrolyzer overpotentional decreased by 0.4 V by feeding 0.1 M KOH solution

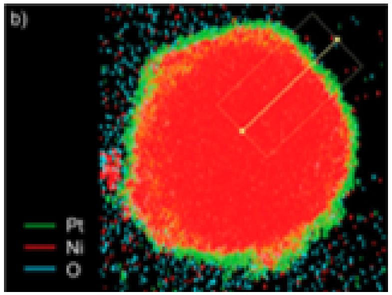
Accomplishments

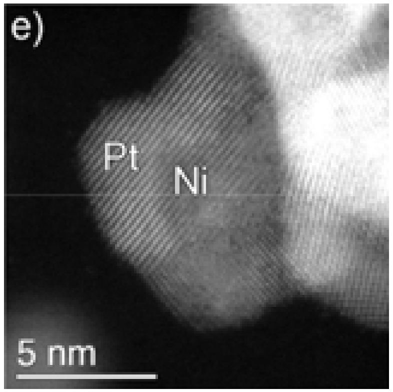
Platinum-Nickel Nanowires – Performance

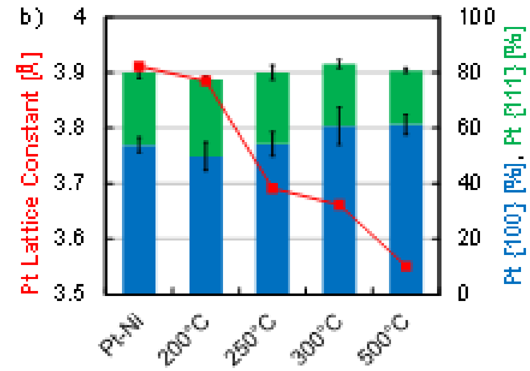
- As-synthesized – higher surface area, activity at low Pt composition
- Hydrogen annealing – lattice integration, higher specific activity
- **Mass activity 10 times greater than PGM baselines (Pt/HSC, PtRu/C)**











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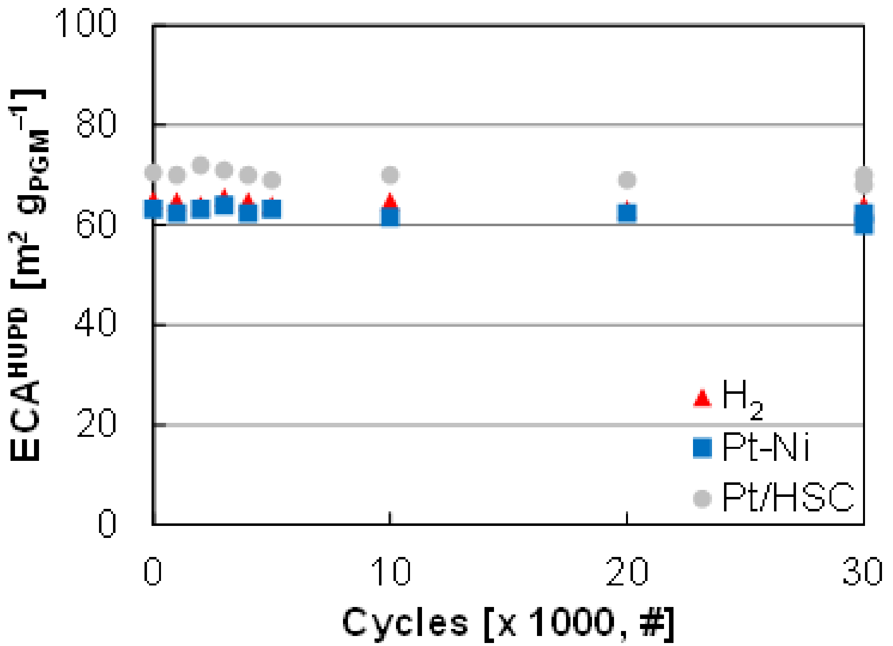
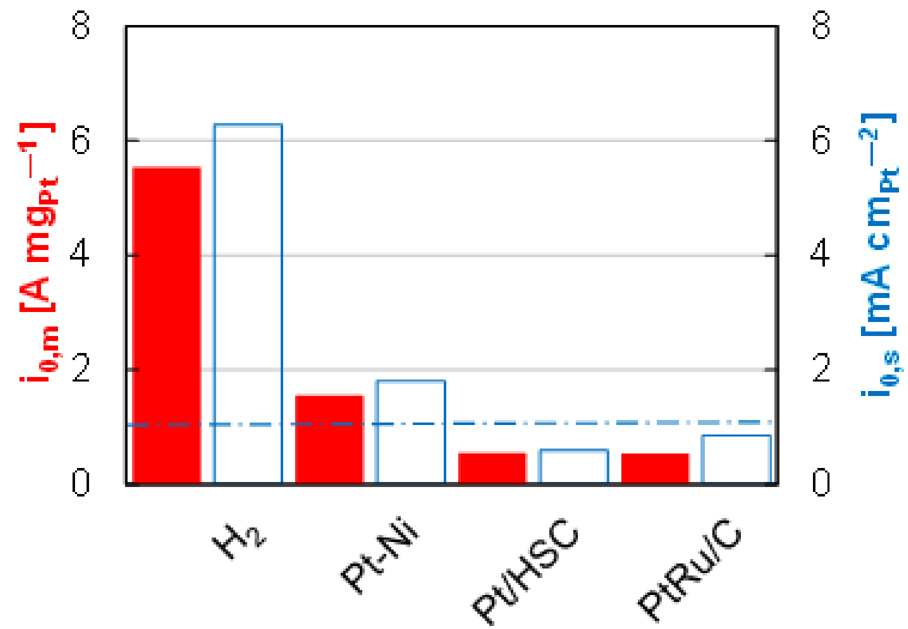
- Half-cell durability (30,000 cycles, -0.2 – 0.2 V versus RHE)
- No appreciable loss in activity
- **Mass activity 10 times greater than PGM baselines (Pt/HSC, PtRu/C)**



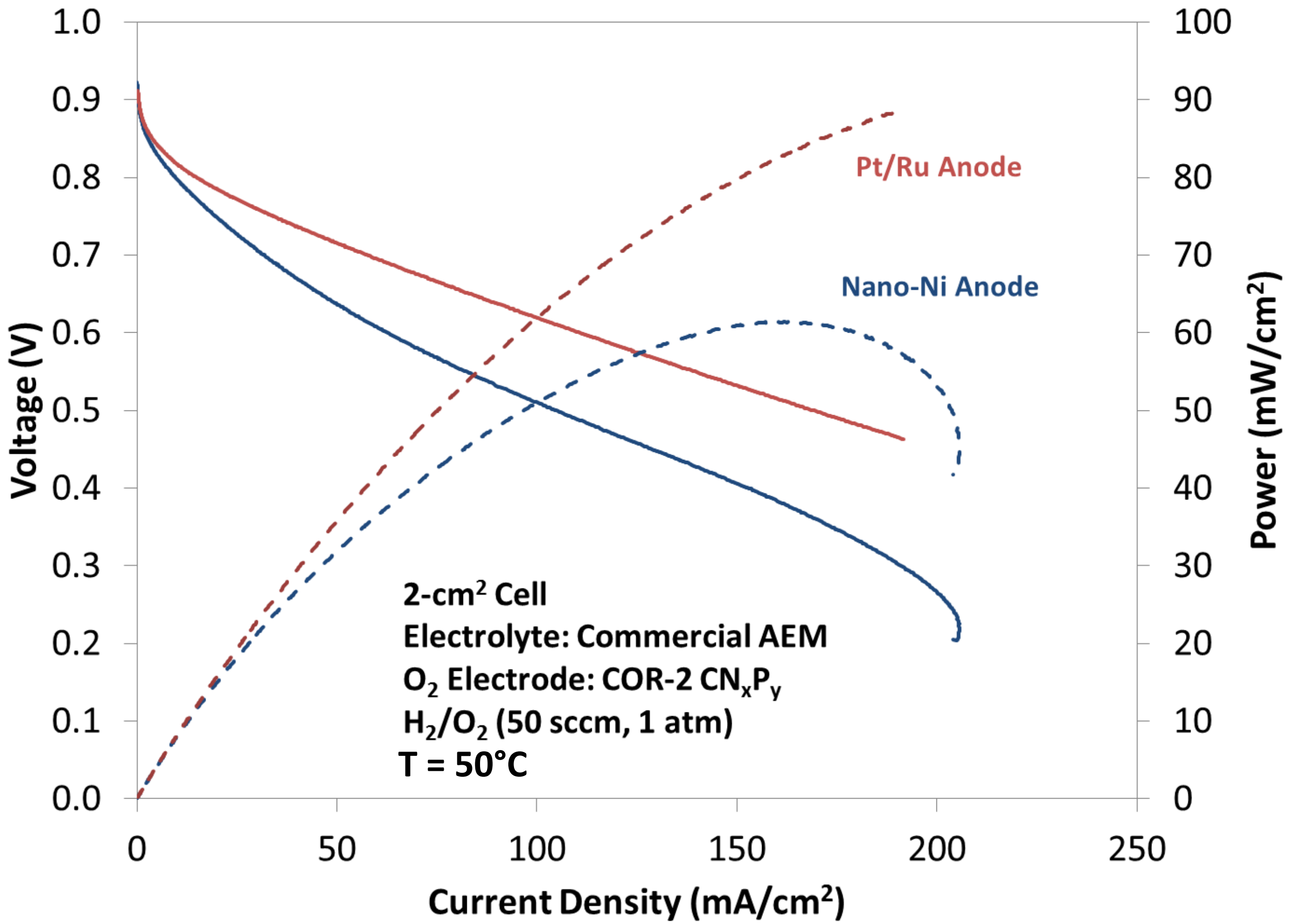


HER-HOR performance comparisons

- Mass exchange current densities (red) normalized to catalyst mass
- Specific exchange current densities (blue) normalized to surface area
- Dashed line – polycrystalline platinum

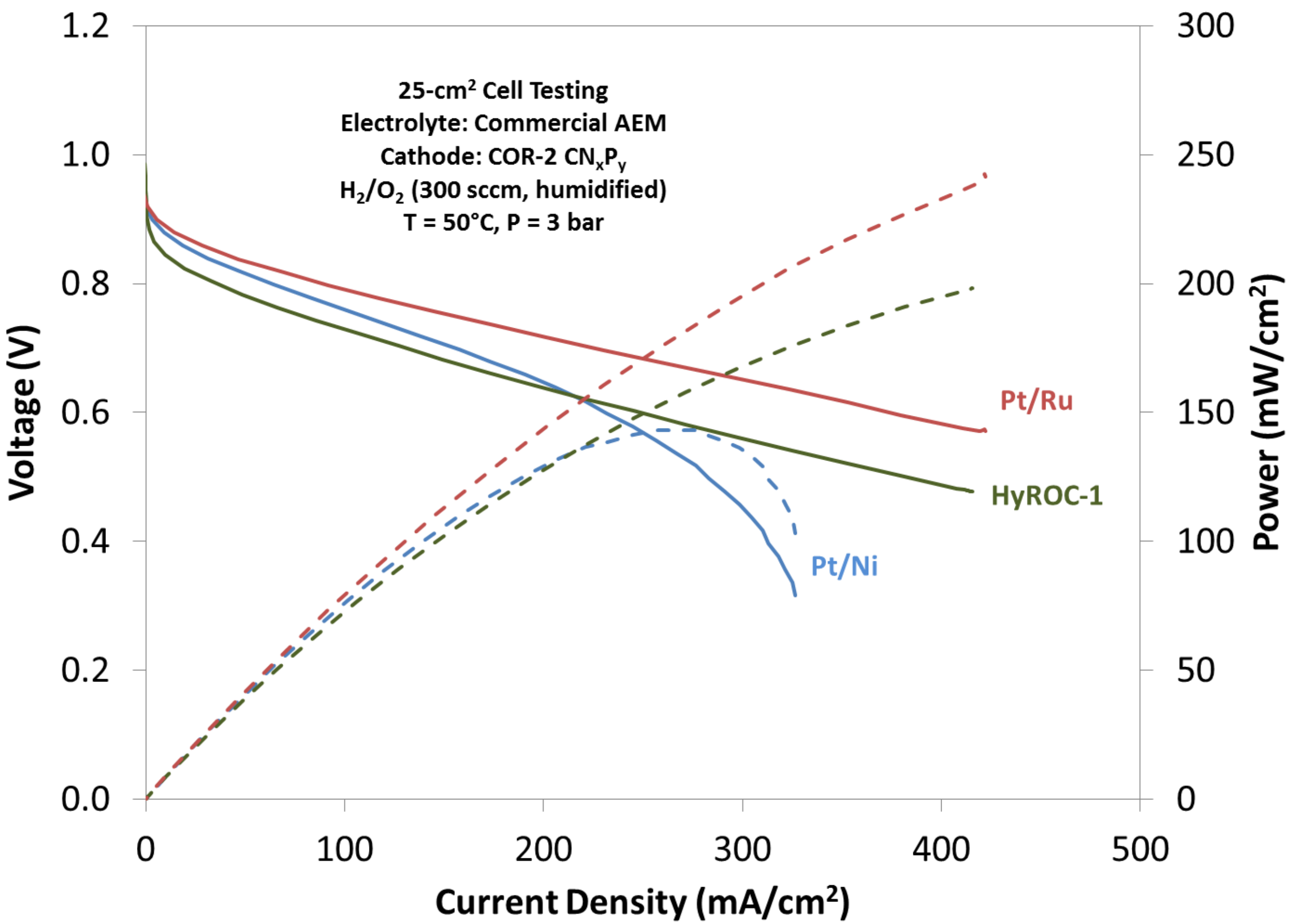
Accomplishments

- Screened catalysts for the hydrogen electrode:



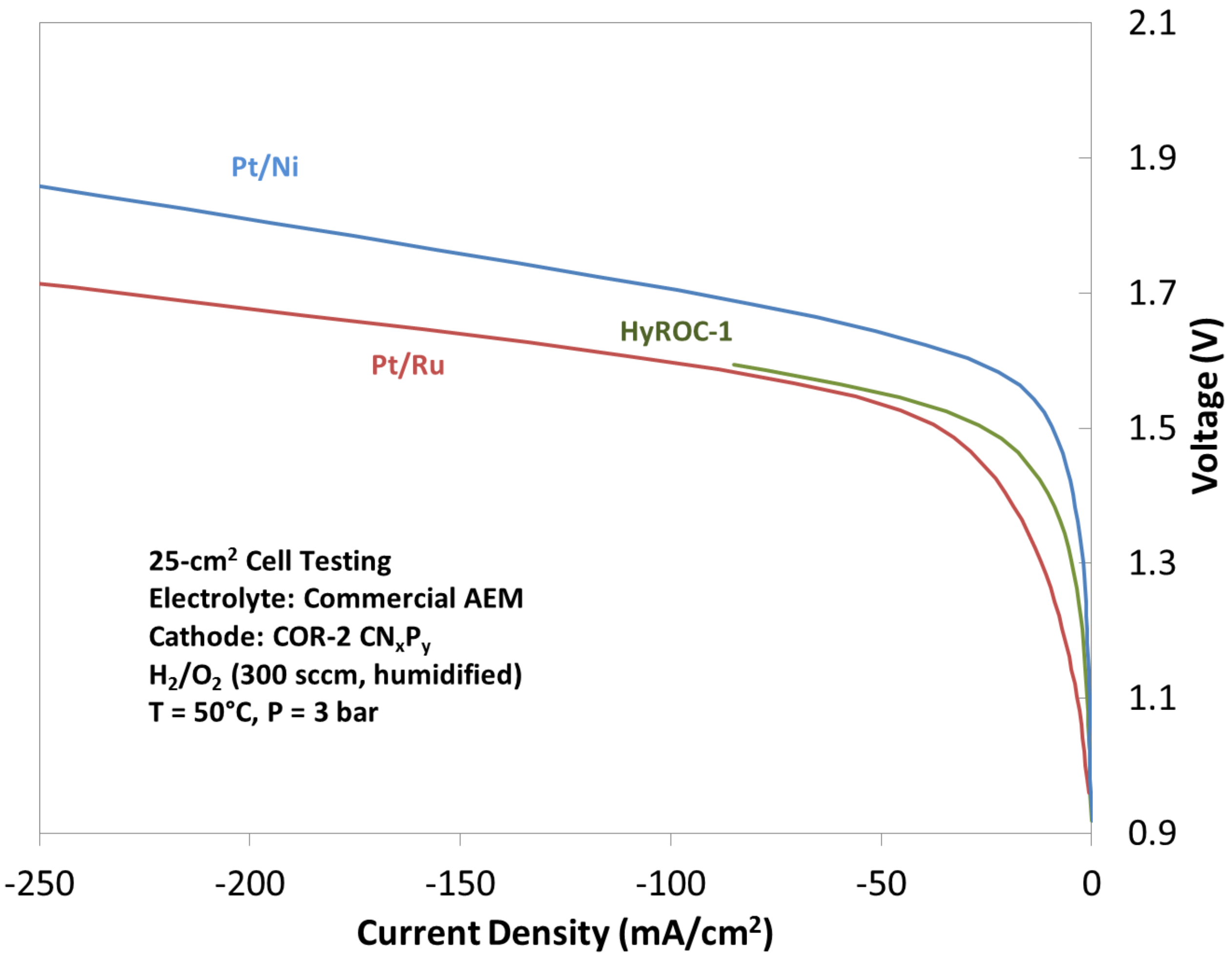
Accomplishments

- Identified low Pt and Pt-free compositions with excellent performance; tested fuel cell mode at 25-cm^2:



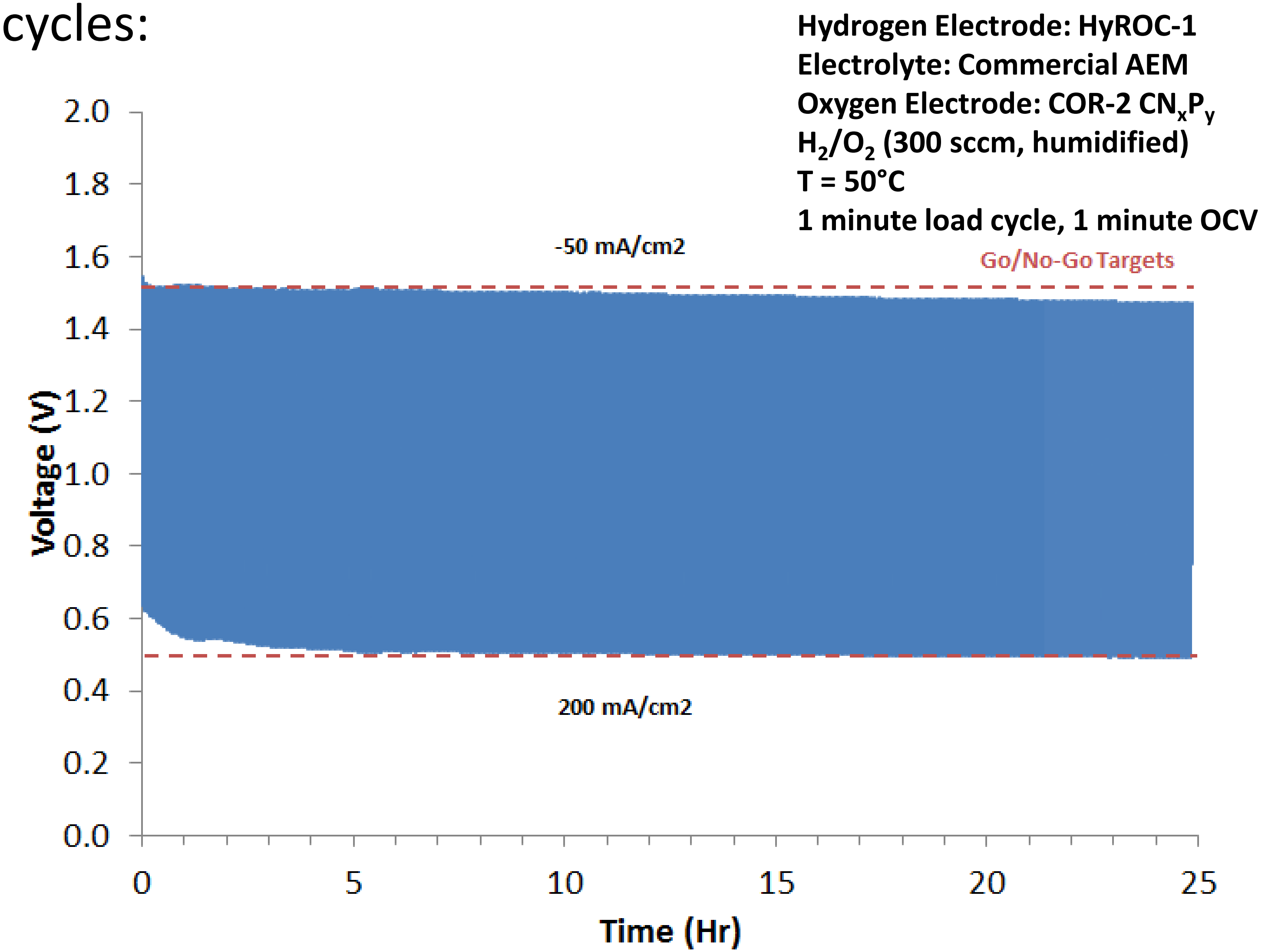
Accomplishments

- Identified low Pt and Pt-free compositions with excellent performance; tested electrolysis at 25-cm^2:



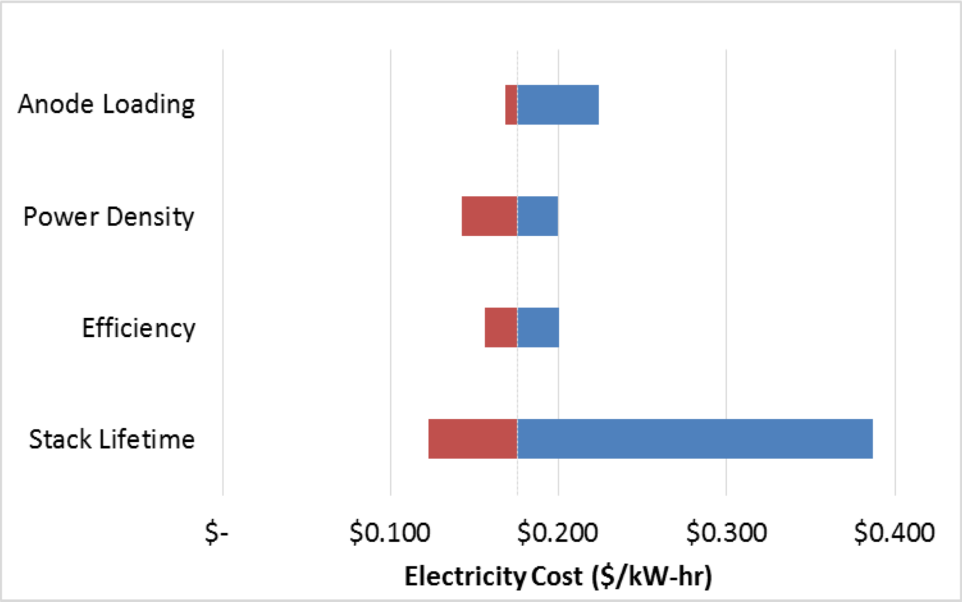
Accomplishments

- Developed Pt-free electrode with excellent durability for over 360 cycles:



Accomplishments

- Performed economic sensitivity analysis for grid storage applications; stack lifetime is the key unknown variable:



Variable	Low Value	Baseline	High Value
Lifetime	1 year	4 years	16 years
Efficiency	32%	42%	54%
Power Density	150 mW/cm^2	200 mW/cm^2	350 mW/cm^2
Anode Loading	3.0 mg/cm^2	4.9 mg/cm^2	16 mg/cm^2

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Collaborations

- Giner (sub-award):
  - Electrode processing optimization
  - Reversible stack design
  - Water management
- NREL (sub-award):
  - Patented Pt/Ni alloy catalyst
  - Advanced characterization techniques

Remaining Challenges

- Further improve economics with higher power, lower over-potential, and less ionomer
- Increase cell durability to over 1,000 cycles
- Demonstrate long-term operation over 1,000 hours
- Incorporate cells into regenerative stack with humidity control
- Reliability

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Proposed Future Work

- Characterize the electrodes before and after cycling to better understand degradation mechanisms
- Demonstrate durability over 1,000 cycles
- Demonstrate regenerative stack (5 cells, 500 hours, 250 mA/cm^2, 42% efficiency)
- Refine economic analysis for micro-grid applications

Any proposed future work is subject to change based on funding levels

Technology Transfer

- IP being used:
  - Licensed catalyst composition from Ohio State University
  - pH Matter's oxygen electrode and hydrogen electrode compositions
  - NREL's Pt/Ni electrode materials
  - Giner's reversible stack design

- Planning partnerships with strategic investors and system integrators for demonstration of 10-kW storage system

Presentations/Publications

- S.M. Alia, C. Ngo, S. Shulda, S. Pylypenko, B.S. Pivovar, *Platinum-Nickel Nanowires as Electrocatalysts in Alkaline Hydrogen Oxidation and Evolution*, 230th ECS Meeting 2016 (Honolulu, HI) 2787.
- S.M. Alia, C. Ngo, S. Shulda, S. Pylypenko, B.S. Pivovar, *Platinum-Nickel Nanowires as Electrocatalysts in Alkaline Hydrogen Oxidation and Evolution*, AIChE Annual Meeting 2016 (San Francisco, CA) 474452.

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Summary

- Reversible fuel cells are a potentially economical energy storage technology for a number of applications, including grid load-leveling and renewables storage.
- pH Matter, Giner, and NREL are developing a reversible AEMFC; the technology could be a breakthrough for energy storage applications.
- Stable 25-cm^2 cells have been demonstrated for over 300 cycles at target operating conditions.
- Future work aims to achieve performance and durability targets at the stack level.

Contact Info

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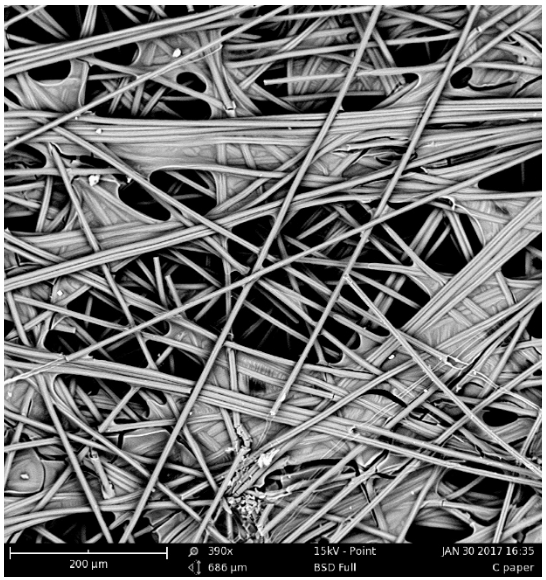
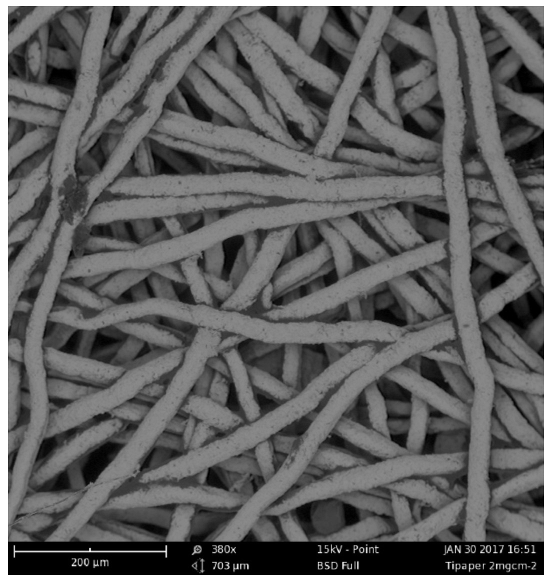
Supporting Info

GDE Optimization: Transfer from C Paper to Ti Sinters

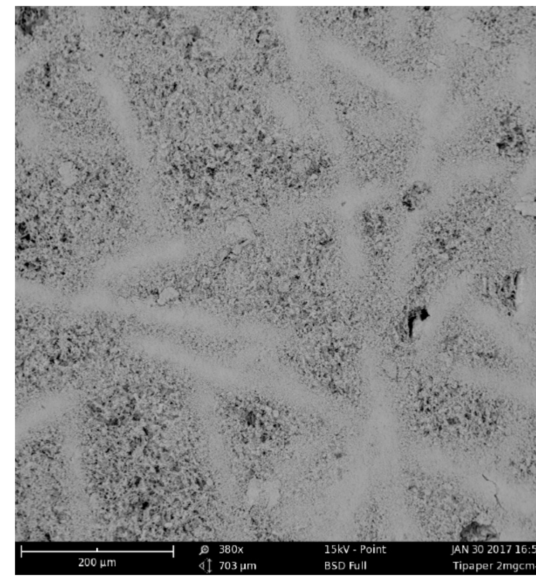
SEM images of gas diffusion layers:



C paper



Ti paper

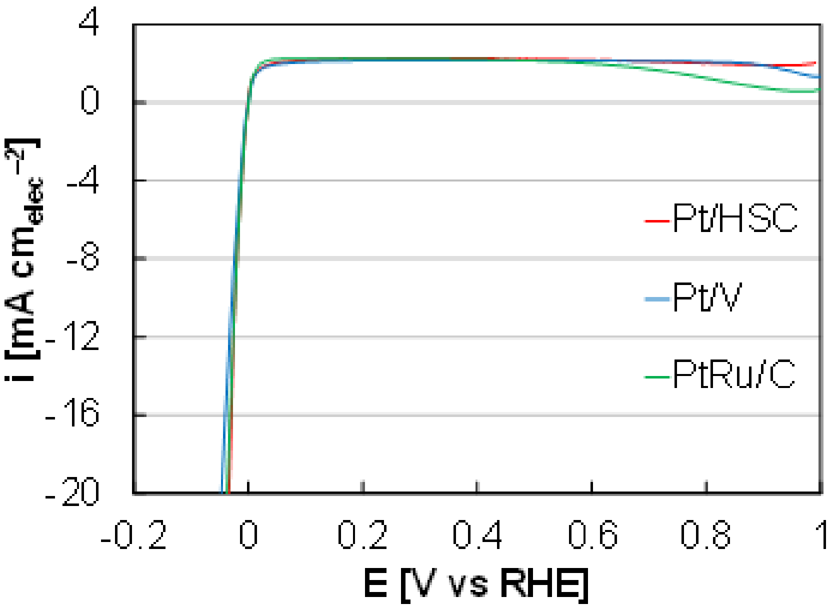


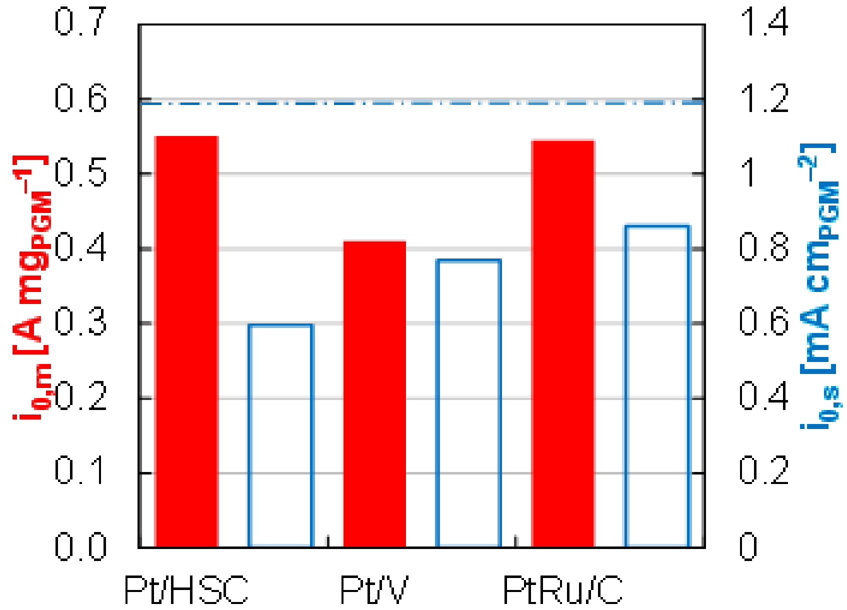
Mesoporous layer introduced onto Ti paper

- Ti paper will be used as the gas diffusion layer for durability test in electrolyzer mode
- The porous layer of Ti paper needs to be optimized for fewer porous layers than C paper
- Mesoporous layers is introduced onto Ti paper

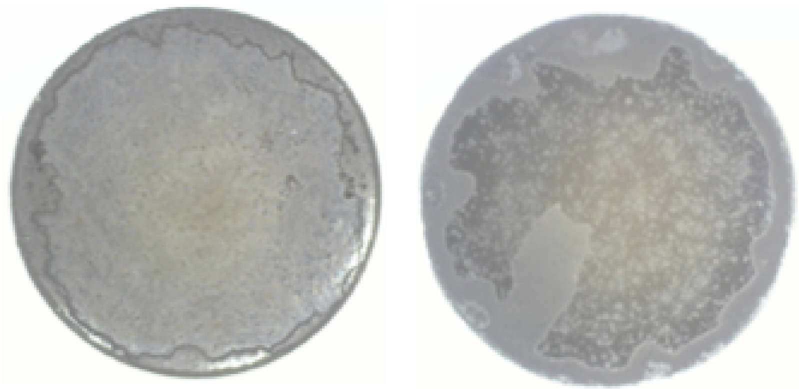
Half-Cell Testing
Established Performance Baselines

- Ink composition – loading, ionomer
- Half-cell experiments – glass, electrolyte purity, counter electrode





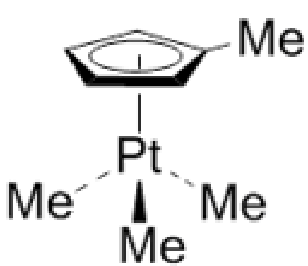
Robust baselines and durability protocols established

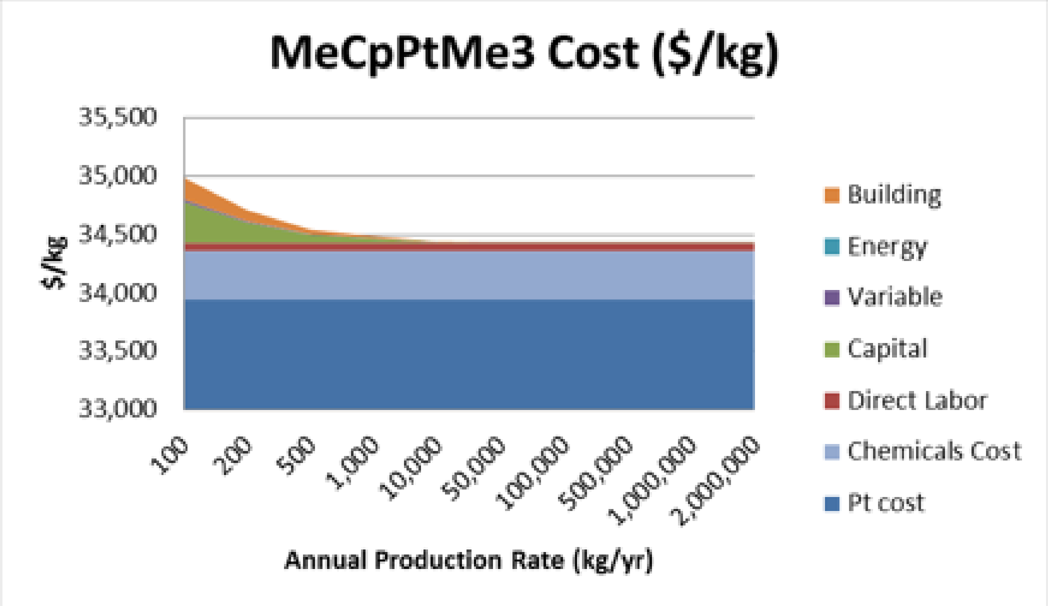


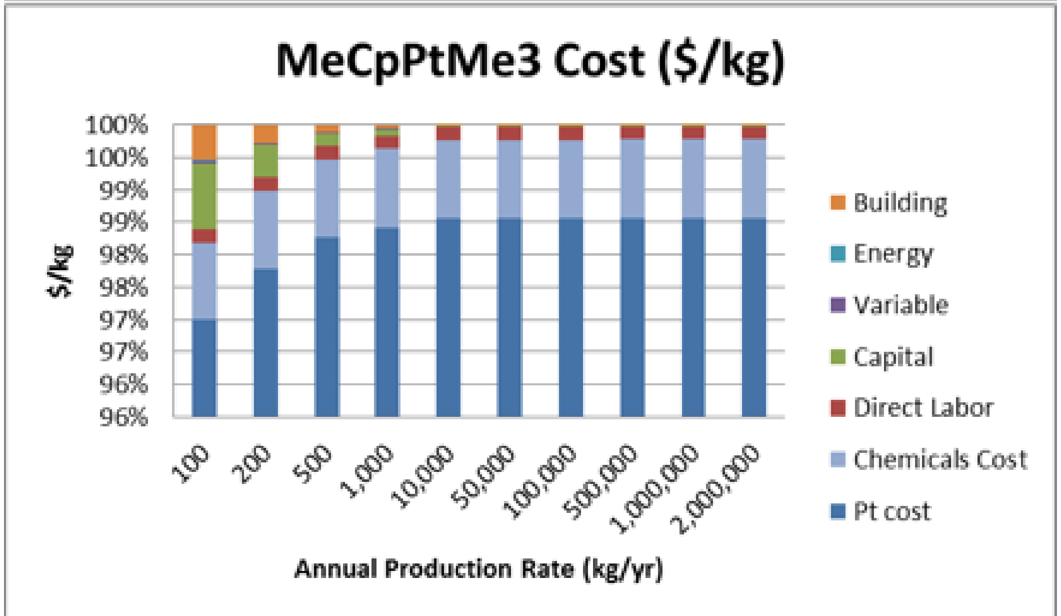
Nanowire Synthesis

Cost Analysis

- Nickel nanowires - cost approaches Ni cost at high volume
- SGD
  - Displacement by K_2PtCl_4 in water
  - Greater than 95% yield with small batches
- ALD – $MeCpPtMe_3$ deposition





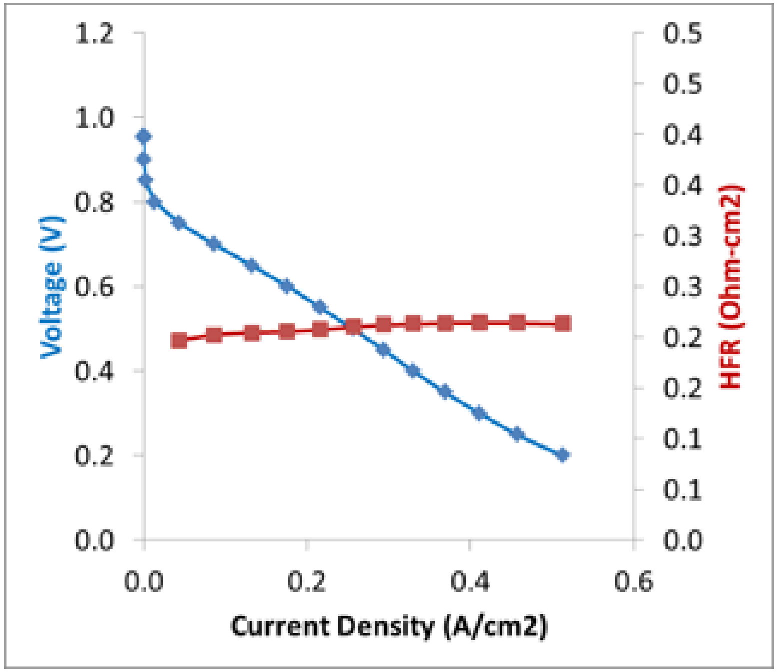


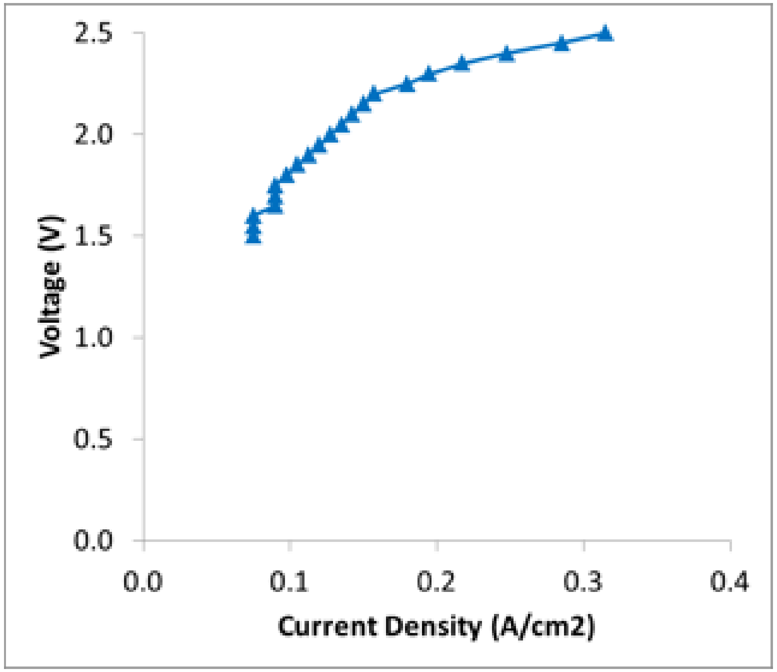
ALD Cost Analysis, courtesy of ETFECS
DOE/EERE, Contract No. DE-AC02-76SF00515

Membrane Electrode Assembly Testing

COR-2 Performance

- HFR consistent with PGM AEM Fuel Cells
- Performance within half of PGM O_2 electrodes





Achieved high MEA performance with COR/HCOR catalyst

MEA Details

- Membrane, Ionomer: Gen 2 PFAEM
- Cell: 5 cm², 60°C
- H_2 Electrode: 1 mg/cm² PtRu/Vu
- O_2 Electrode: 4 mg/cm² COR2/HCOR3