PROTON ON SITE
nel number one by nature
YOUR SOURCE FOR ALL THINGS HYDROGEN

P.I. Name: Kathy Ayers
Presenter: Christopher Capuano

ARPAe: Dual Mode Energy Conversion and Storage Flow Cell

Date: June 14, 2018

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Project Overview

Overview

Timeline

- Project Start: 6 May 2016
- Project End: 5 May 2019
- Percent complete: 66%

Budget

- Total project funding
  - ARPAe: $2,500,000
  - Cost-share: $277,777

Barriers

- Barriers addressed
  - F: Capital Cost
  - H: Stack Energy Efficiency

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 [e]	3.9 [e]	2.3 [e]
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

Partners

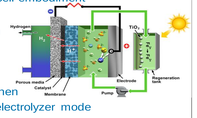
- Pacific Northwest National Labs

Program Overview

- ARPA-e Contract: DE-AR0000686
- Period of Performance: 5/6/16-5/5/19, 36 months
- Description:
  - Development of a hydrogen-iron flow cell in partnership with PNNL, capable of two operating modes:
    - As a pseudo-electrolyzer for hydrogen generation
    - As a hydrogen-iron redox flow cell, capable of high efficiency and low-cost grid scale energy storage
- Partners:
  - Wei Wang (PNNL): Catholyte and non/low PGM catalyst development. Proof of concept regeneration cell

Background: Flow Battery Technology

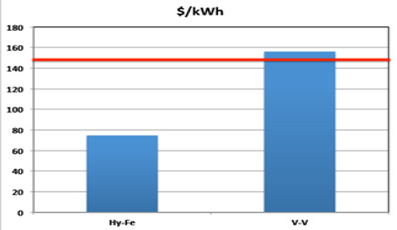
- Leverage existing PEM cell stack architecture
  - Iron electrolyte allows for production of hydrogen at lower voltage, higher efficiency vs. water electrolysis
  - Enables non/low-PGM catalysts for hydrogen half-cell
  - No catalyst for iron half-cell - potentially
  - Enables cheaper materials for cell embodiment
- Main challenges:
  - Electrolyte cross-contamination
  - Shunt currents
  - Metal ion impact on membrane performance
  - Regeneration of iron species when using the hydrogen in pseudo electrolyzer mode



Project Objectives

- Develop electrolyte concentration and composition through structure, property, and performance studies
- Develop mitigation strategies for cross-over (H_2 and Fe)
- Refine electrode manufacture for loading reductions and scale-up
- Develop electrode materials for porosity, conductivity, surface area, and redox activities
- Evaluate Fe^{n+} poisoning tolerance
- Conduct CFD modeling to determine optimal flowfield/shunt design
- Operate a 28 cm^2 stack in pseudo-electrolysis and flow battery mode
- Technoeconomic analysis

Problems Addressed and Targets

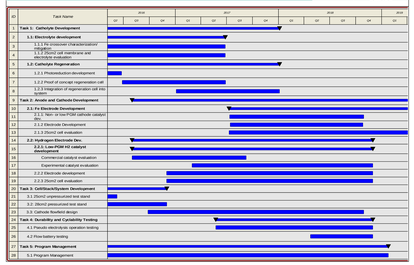


Program Targets

- Shunt currents losses <2% operating current
- < 0.6 mg/cm^2 total PGM content in hydrogen and iron electrodes
- 5-cell, 28 cm^2 stack cycle operation
  - 750 mA/cm^2 with 75% efficiency
- Show improvements in cell design resulting in a 25% reduction versus state of the art electrolysis

Approach: Overall

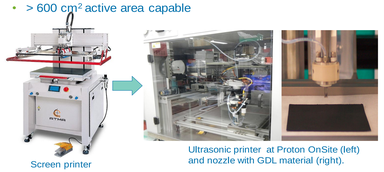
Milestone	Date	Status
Cost model Development	8/5/2016	Complete
Complete chemical compatibility analysis to support stack development and define cell stack materials that reduce cell cost by 25% compared to PEMWE	11/5/2016	Complete
Down-select catholyte that achieves low Fe permeation, and meets regenerative conversion efficiency to support 500 mA/cm^2	2/5/2017	Complete
Identify and evaluate 3 alloy catalysts for HER/HOR activity that have capability of <0.1mg/cm^2 Pt content.	8/5/2017	Complete
Identify and evaluate 3 experimental catalysts for $Fe^{2+/3+}$ activity that have capability of <0.075mg/cm^2 Pt content.	8/5/2018	Complete
Demonstrate shunt current reduction by 25% using computationally derived flowfield design.	11/5/2018	In-Progress
Demonstrate 3-cell 28cm^2 test stand operation in pseudo electrolysis mode; <.6mg/cm^2 Pt content in hydrogen and iron electrodes and optimized cathode flowfield. (1000hr test)	2/5/2019	In-Progress
Final Report Completion and Submission	5/5/2019	Not Yet Started



Approach: Low Loaded HER Electrode Development

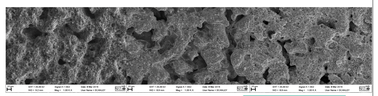
Electrode Manufacture: Options

- Ultrasonic spray deposition and screen printing MEA fabrication
- High throughput, manufacturing friendly techniques
- > 600 cm^2 active area capable



Ultrasonic printer at Proton OnSite (left) and nozzle with GDL material (right).

Deposition Improvements (GDE)

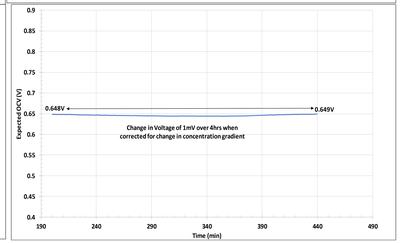


Initial Testing → Process Iteration → Ink/Process Iteration

Loading Held Constant

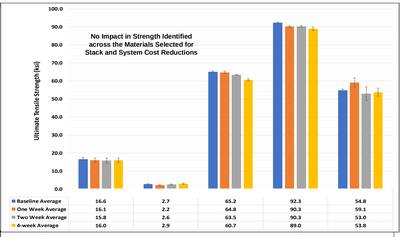
- Degradation of electrochemical surface area (ECSA) after testing in the Fe^{2+} electrolyte was observed for all PGM catalysts
- ECSA losses on Pt-based catalysts were 7~25%
- Pd/C catalyst ECSA loss was 93%

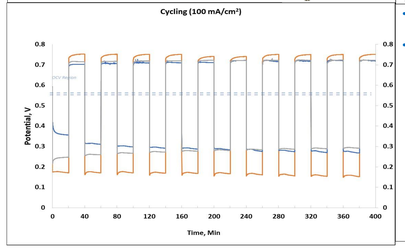
Catalyst	ECSA (m^2 g^{-1})		Loss (%)
	Before Fe^{2+} test	After Fe^{2+} test	
20% Pt/C	51.9	45.8	12%
50% Pt/C	65.1	60.8	7%
Pt-Black	6.8	5.1	25%
Pd/C	16.1	1.2	93%



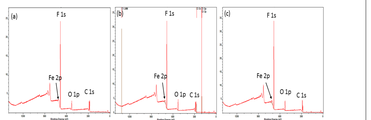
Approach & Accomplishments: Material Compatibility Membrane & Stack Hardware

- Materials selected for cost-reduction were exposed to the electrolyte solution for compatibility
  - Wetted components were the focus
- Dog bone samples were prepared in accordance with material testing lab dimensional requirements





- Analysis conducted at PNNL using XPS to measure iron content in cycles membrane samples
- Intended to look for differences in uptake of iron for materials with different equivalent weights
  - Attempt to correlate to performance stability or loss



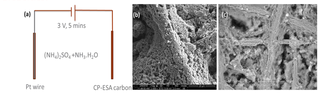
- Iron ions trapped inside the membrane after cycling is at a minimal level, with no significant difference between membranes used in the test

Accomplishments: Acid Electrode and Catholyte Development

- Development focused on electrolyte composition
  - Targets of >150 mS/cm
  - >1M active material concentration
  - Stability up to 60C
  - 750 mA/cm^2 electrolyzer operation
- Catholyte composition evaluation assessed acid concentration/type on conductivity
- Evaluate carbon electrode and activity improvements through electrochemical post-processing

- **High electrochemical performance carbon electrode:**
  - High porosity and tortuosity for mass transfer;
  - High hydrophilic properties for liquid access;
  - High active surface for iron redox reaction (catalytic properties)

What is the method which can:
(1) maintain porosity and tortuosity; (2) enhance hydrophilicity; (3) increase catalytic properties?



The schematic description of electrochemical modification process of CP-ESA **(a)**; The SEM image of electrochemical modified CP-ESA carbon electrode **(b)** and the pristine CP-ESA **(c)**.

Results: No morphology change is observed before and after electrochemical modification process

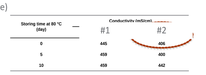
Electrolyte conductivity (Room Temperature)

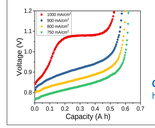
Electrolyte composition	Conductivity (mS/cm)
Iron Electrolyte #1	294
Iron Electrolyte #2	548

The conductivity of electrolyte #2 is almost two times higher than that of electrolyte #1

Electrolyte conductivity (Room Temperature)

Electrolyte composition	Conductivity (mS/cm)
Electrolyte #1	294
Electrolyte #2	548

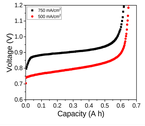




Test condition:
N211 membrane
Proton GDE and Electrochemical modified CP-ESA
Flow rate: 120 ml/min
Proton serpentine flow field (9 cm^2)
Temperature : 22 °C

Conclusion: High conductivity of electrolyte can support high current density of 1000 mA/cm^2

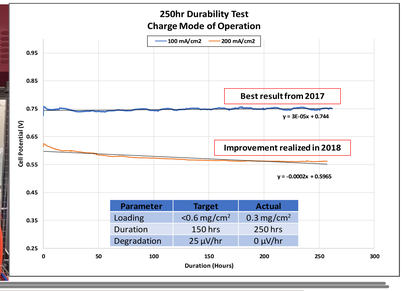
Solution : 1M $FeSO_4$ +2.5 M H_2SO_4



Test condition:
N211 membrane
Proton GDE and Electrochemical modified CP-ESA (9 cm^2)
Flow rate: 120 ml/min
Proton serpentine flow field
Temperature : 40 °C

Conclusion: The voltage plateau at current density of 750 mA/cm^2 with 9 cm^2 serpentine flow field is around 0.9 V, validating that the improved conductivity of iron solution is an important factor to benefit the charge process.

Accomplishments: Full System/Stack Testing



Project Summary

- All program milestones completed to date
- Full-system developed with automated cycling capability
  - 30 bar hydrogen generation pressure
  - Configured for multi-cell support
  - Up to 80°C operation for improved efficiency
- Testing has shown stability in charge mode of operation for 11 days of continuous operation
- Testing at PNNL has developed an acid electrode and electrolyte solution capable of 750 mA/cm^2

- **Principal Investigator (PI):** Kathy Ayers, customer interface, high level oversight
- **Program Manager:** Chris Capuano, subcontract management of PNNL, program technical oversight, government reporting, budget tracking, and resource planning
- **Chemical Engineer:** Luke Wiles, characterize catalyst formulation and deposition techniques. Perform materials operational characterization
- **Systems Engineer**: Andrew LaMarche, system development
- **Engineering Technician**: Ed Demarest, system fabrication
- **Mechanical Engineer**: Eric Scheuing, support cell design
- **Principal Engineer**: Andy Roemer, cell architecture and system component analysis
- **PNNL Principal Investigator**: Wei Wang