High-Efficiency Reversible Alkaline Membrane Fuel Cells

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2019 DOE Hydrogen and Fuel Cells Annual Merit Review

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Project ID
FC315

Overview

Timeline
- Project Start Date: October 1, 2018
  Actual start date: January 1, 2019
- Project End Date: December 31, 2020

Barriers Addressed
A: Cost
B: Durability
C: Performance

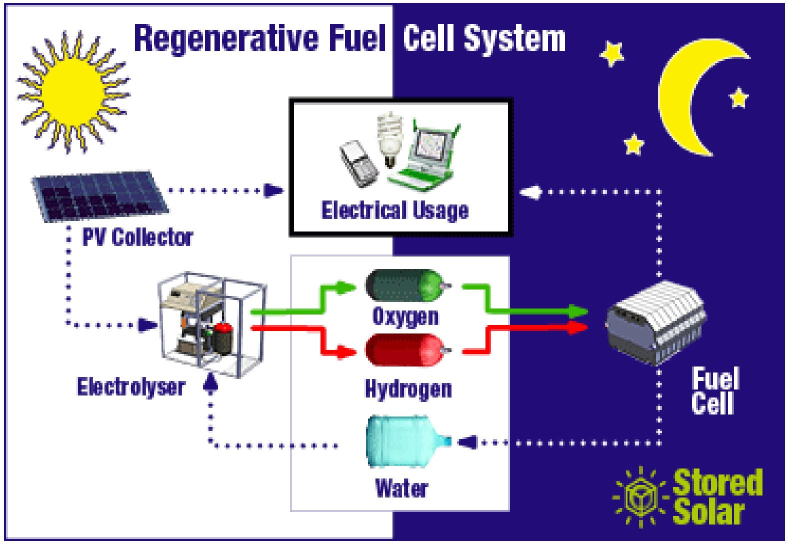
Budget
- Overall $1,250.139
  - DOE share $799,503
  - Cost share $250,636
  - FFRDC $200,000 to NREL
- $9089 spent as of 3/1/2019

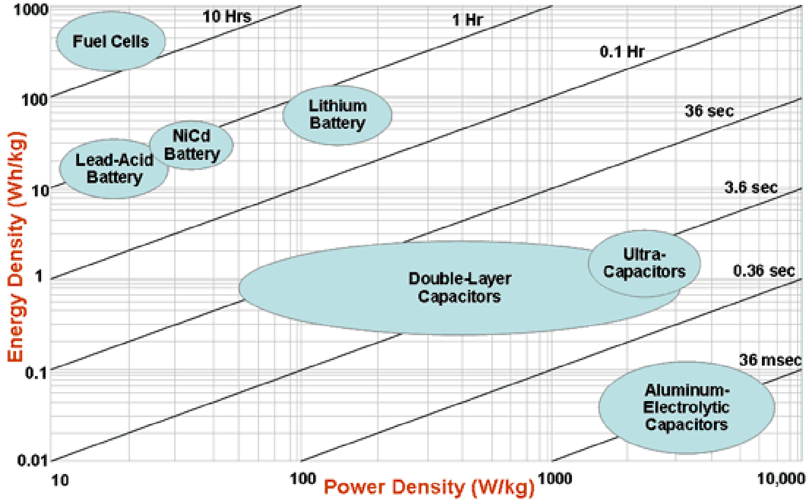
Partners
- Giner, Inc. Project lead
- Collaborations:
  - University at Buffalo (UB)
  - University of Delaware (UD)
  - National Renewable Energy Lab (NREL)

Relevance

Overall objectives:

- Explore oxidation-resistant anion exchange membranes/ionomers and corrosion-resistant bifunctional catalysts
- Demonstrate prototyped reversible alkaline membrane fuel cell with >50% round trip efficiency at 1000 mA/cm^2





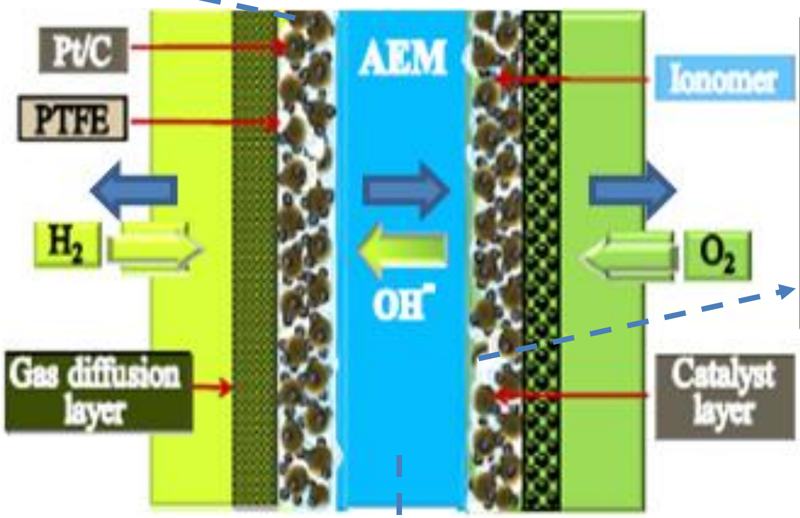
Source US Defence Logistics Agency

- ❑ Reversible fuel cells can store renewable energy like batteries, but with much higher energy density
- ❑ Alkaline membrane system may lead to low capital cost due to adopted cheap materials (catalysts, bipolar plates)

Technical Approaches

Reversible Anion Exchange Membrane (AEM) Fuel Cells

Bifunctional catalysts for hydrogen oxidation reaction (HOR) /hydrogen evolution reaction (HER)



Bifunctional catalysts for oxygen reduction reaction (ORR) /oxygen evolution reaction (OER)

High-performance Membrane
- High OH^- conductivity
- Oxidative resistance
- Mechanical stability

Performance Tasks

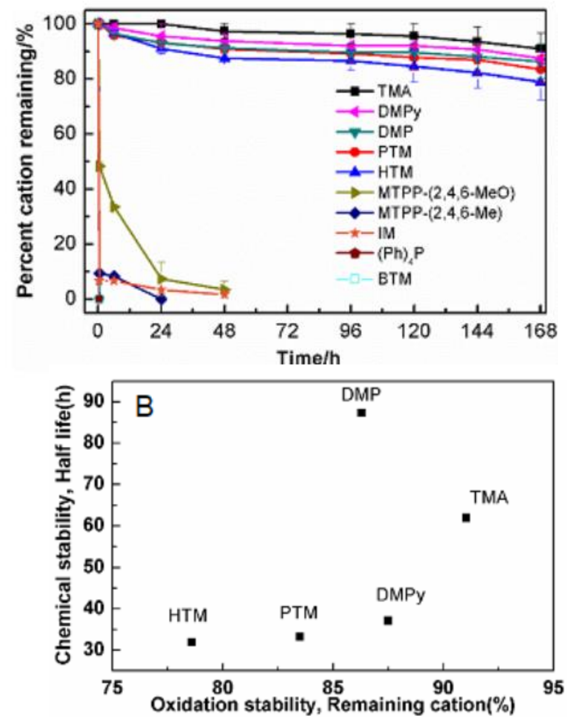
- **Task 1 Membrane and Ionomer Development**
  - Develop alkaline ionomers
  - Impregnate ionomers into dimensionally-stable membranes (DSM)
- **Task 2 Catalyst Preparation**
  - Prepare bifunctional HOR/HER and ORR/OER catalysts
  - Low PGM (baseline) and PGM-free catalysts
- **Task 3 MEA Design and Fabrication**
  - Optimize interactions of catalyst, ionomer and membrane
  - MEA water management
- **Task 4 Reversible Fuel Cell Test**
  - Charge-discharge operations
  - Salt addition Impact
- **Task 5 Techno-economical Analysis**
  - Capital cost
  - Operation efficiency and cost

Task 1: AEM Preparation

- Current commercial alkaline membranes cannot sustain electrolysis conditions due to possible degradation under high oxidative voltage
- A family of poly(aryl piperidinium) (PAP) membranes has been developed at the University of Delaware
  - Highly conductive for hydroxide ions
  - Chemically stable
  - Mechanically robust

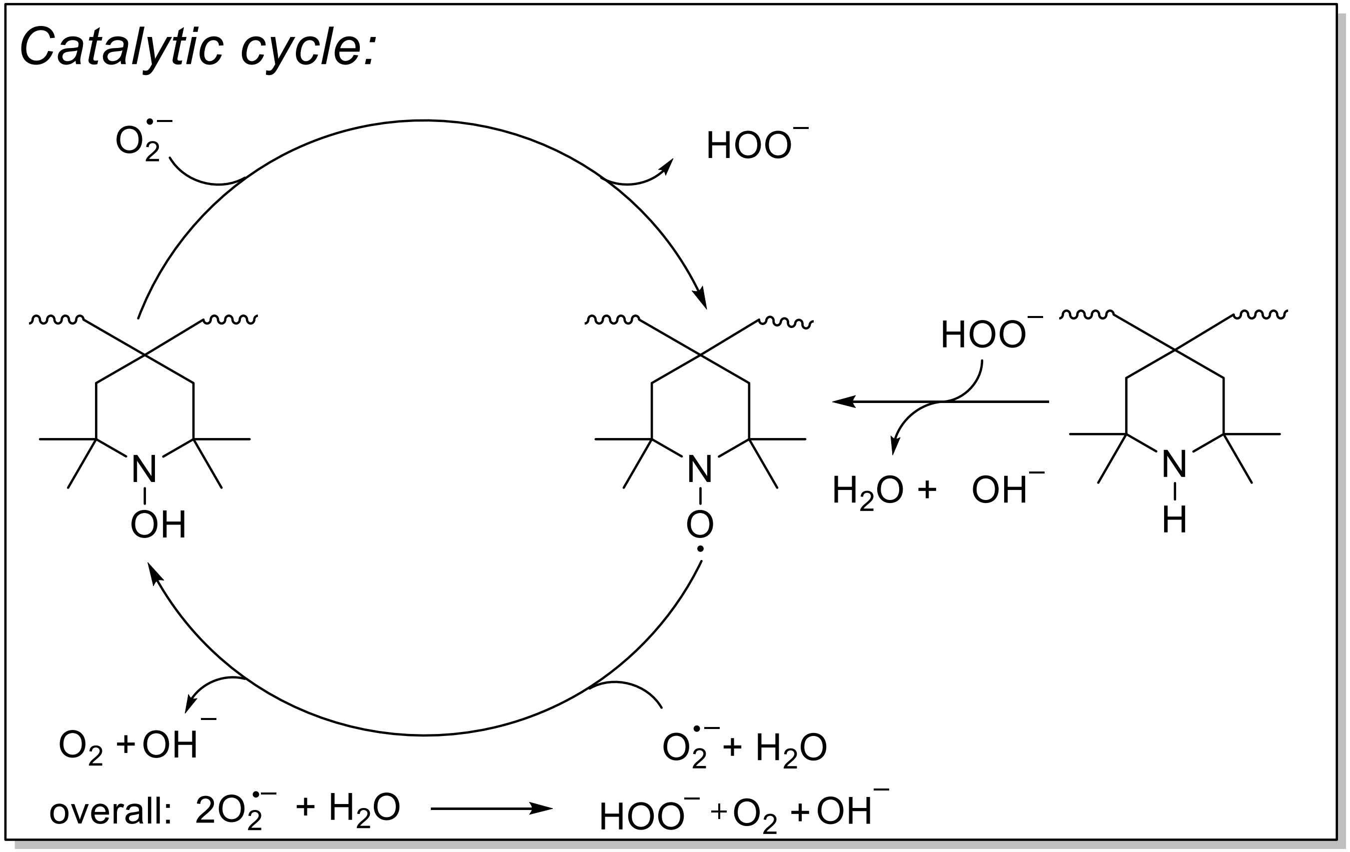
Work plan for this task:

- Prepare and characterize benchmark PAP membranes with varying IEC
- Synthesize piperidinium monomers and PAP-TP-TMP polymer
- Oxidation resistance study
- Prepare and characterize reinforced membranes



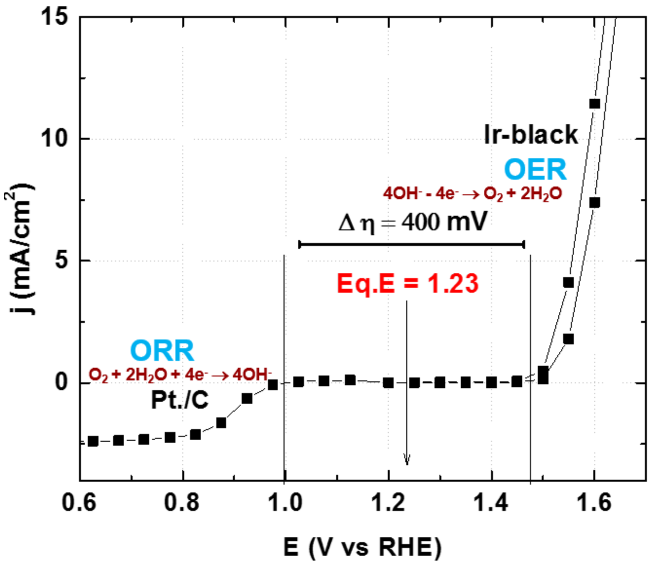
TMA = tetramethylammonium DMPy = dimethylpyrrolidinium
DMP = dimethylpyrrolidinium PTM = propyltrimethylammonium
HTM = hexytrimethylammonium MTPP = trimethyphenylphosphonium
IM = imidazolium $(Ph)_4P$ = tetraphenylphosphonium
BTM = benzyltrimethylammonium

Redox cycle to scavenge super oxide free radicals



GINERLABS | University at Buffalo | NREL NATIONAL RENEWABLE ENERGY LABORATORY | UNIVERSITY OF DELAWARE

Task 2-1: Bifunctional Oxygen Catalysts



Nanocarbon		Metal Oxides
✓	Electronic Conductivity	✗
✓	Surface Area	✗
✓	Cost	✗
✓	Easy of Functionalization	✗
✗	Stability	✓

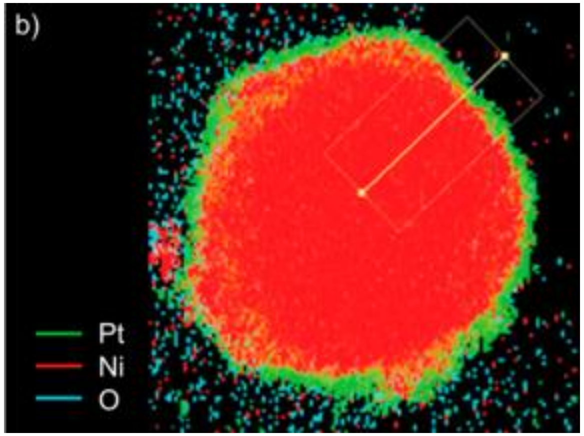
Challenges of bifunctional catalysts:

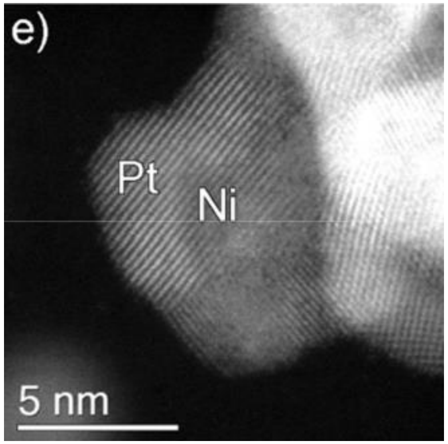
- Theoretically, no single type of active site for both ORR and OER
- Overcome large overpotential for both reactions simultaneously
- Instability of most carbon based ORR catalysts in OER potential regime

Previously, $NiCo_2O_4$ with nanoflower morphology showed best ORR-OER activity and good stability

Task 2-2: Bifunctional Hydrogen Catalysts

- Investigating several low-PGM HER/HOR routes
- Work at NREL has shown increased mass activity through galvanic displacement, hydrogen annealing of Pt-Ni materials
- Nano-particulate molybdenum disulfide (MoS_2) has also demonstrated remarkable HER activity
  - By ball-milling with small amounts of platinum for hydrogen oxidation, a low-PGM bifunctional HOR/HER catalyst can be synthesized

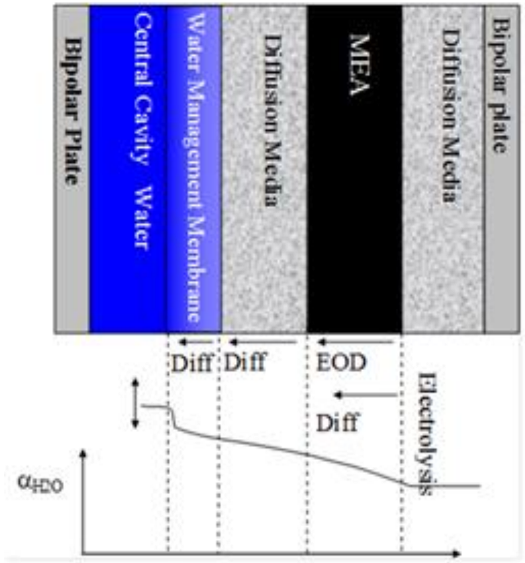


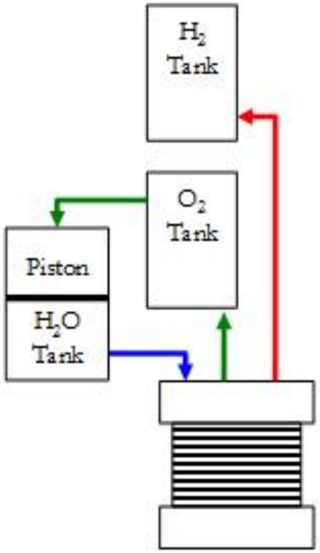


S. M. Alia, B. A. Larsen, S. Pylypenko, D. A. Cullen, D. R. Diercks, K. C. Neyerlin, S. S. Kocha and B. S. Pivovar, ACS Catalysis, 4, 1114 (2014). DOI:10.1021/cs401081w

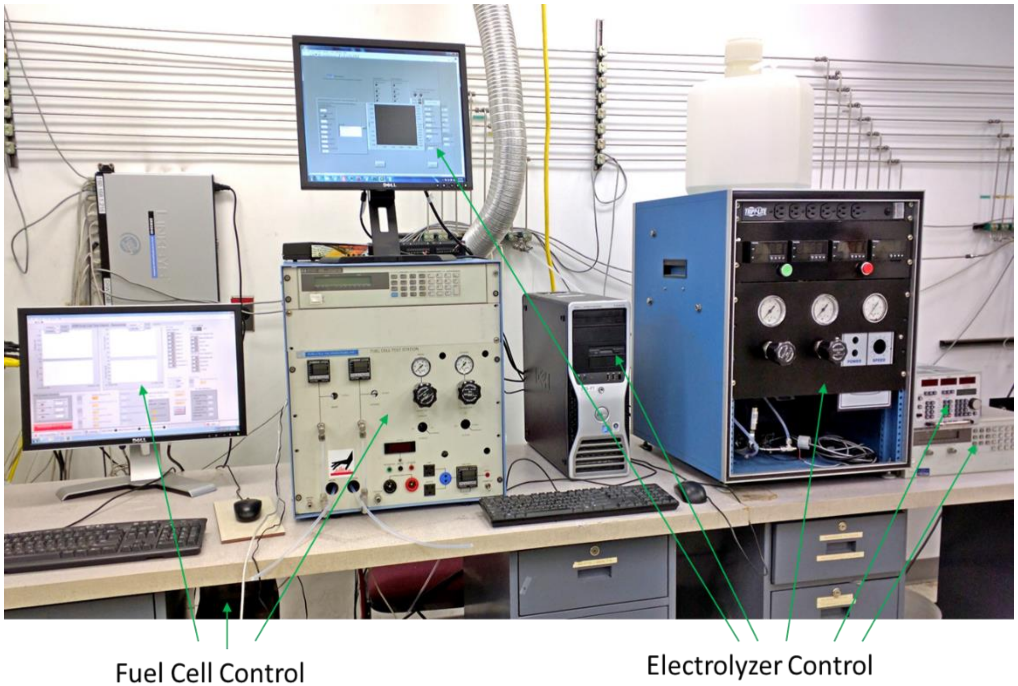
Task 3: MEA Design and Fabrication

- Interactions between catalyst, membrane and ionomer need to be optimized
- Water management is a concern with AEMs; slight adjustments to reactant gas dew points can drastically affect performance
- The application of Giner's proprietary Water Management Membrane (WaMM) technology be investigated to build vapor-feed reversible AMFCs
- High temperature AEM can enable high temperature (>100 ℃) operation thus easing water management

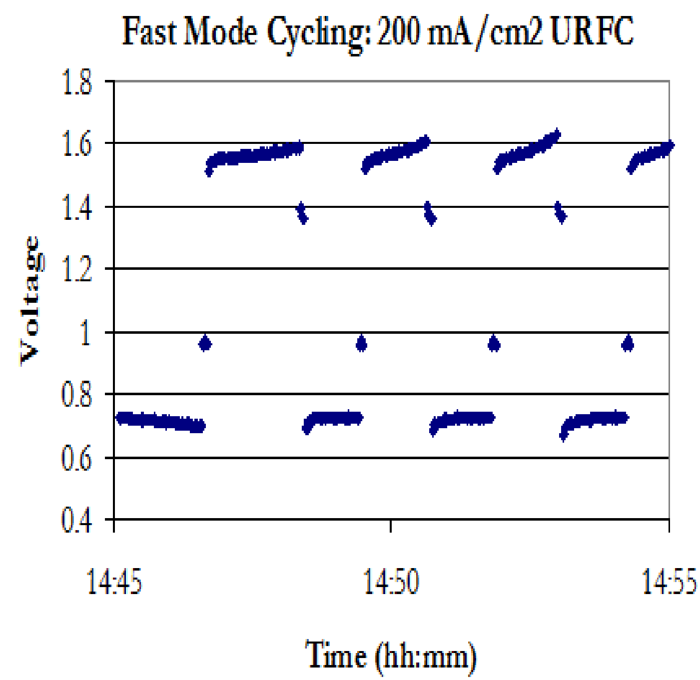




Task 4: Reversible Fuel Cell Test



Giner unitized reversible fuel cell

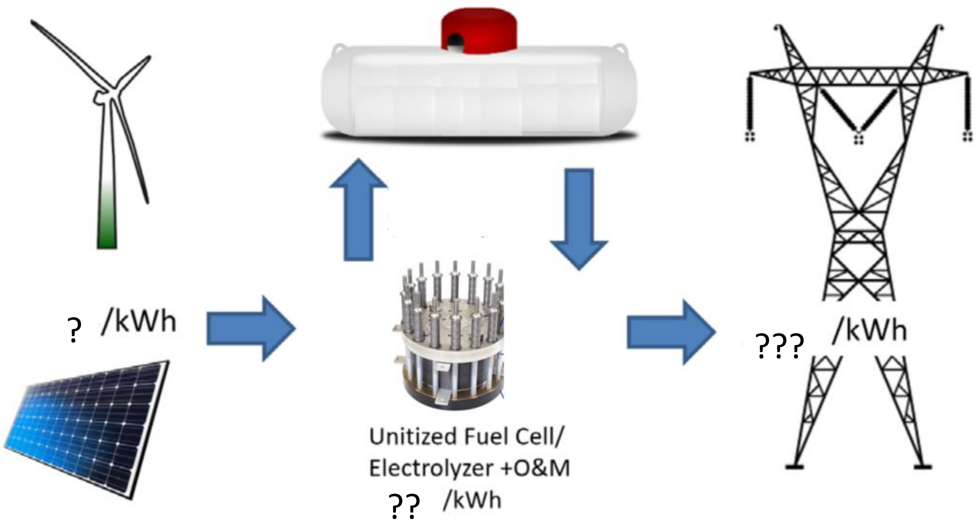


- ❑ Impact of the addition of diluted salts
- ❑ Impact of cell cycling frequency and current density

Task 5: Techno-economical Analysis

- ❑ Capital Cost
  - Catalysts, AEMs, ionomer, and bipolar plates
  - Size decided by current density

- ❑ Operating cost
  - Round trip efficiency
  - Electricity cost



Technical Approach: Milestones

- **Milestone 1.1** Demonstrate 30-50 µm self-supporting membranes with conductivity >100 mS/cm (80 °C), tensile strength > 50 MPa, elongation at break > 100% **June 2019**
- **Milestone 1.2** Deliver 400 cm^2 of PAP-TP-TMP membranes w/ superoxide disproportionation activity and 50 % improved oxidation resistance **December 2019**
- **Milestone 1.3** Demonstrate PAP membranes and ionomers w/ half-life in KO_2/DMSO/D_2O 10x longer than commercial ionomer **June 2020**
- **Milestone 1.4** Prepare reinforced PAP membranes with through-plane ASR < 0.15 Ohm cm^2, ≥60 MPa tensile strength, ≥150% elongation at break **September 2020**
- **Milestone 2.1** 15 g $Co3O_4$ or $NiCoO_4$ ORR/OER catalyst **March 2019**
- **Milestone 2.2** Produce 5 g MoS_2/RGO HER catalyst **September 2019**
- **Milestone 2.3** 5 g chevrel-phase $NiMo_3S_4$ HER catalyst **December 2019**
- **Milestone 3.1** Identify three most impactful parameters for reversible fuel cell electrode design and fabrication **December 2019**

Technical Milestones (Cont'd)

- **Milestone 4.1** **GO/NO GO** Achieve a round trip efficiency of 50% at 500 mA/cm^2 in both fuel cell and electrolyzer modes **December 2019**
- **Milestone 4.2** Achieve a degradation rate <1 % over 200 hours with operation in both fuel and electrolyzer modes **March 2020**
- **Milestone 4.3** With a reversible AEM fuel cell MEA, achieve round trip efficiency of 40% at 400 mA/cm^2 with pure water as feedstock **June 2020**
- **Milestone 4.4** With a low-PGM reversible AEM fuel cell MEA:
  - Achieve round trip efficiency of 45% at 500 mA/cm^2 with pure water as feedstock, or
  - Achieve round trip efficiency of 50% at 600 mA/cm^2 with allowed salts in water feedstock **September 2020**

- **Overall project goal** Obtain reversible AEM fuel cell round trip efficiency of 50% @ 1000 mA/cm^2 **December 2020**

Collaboration & Coordination

Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Zach Green	Prime, oversees the project; MEA design, optimization and fabrication; reversible fuel cell design; cost analysis
University of Delaware (UD) Yushan Yan	Anion exchange membrane and ionomer development
University of Buffalo(UB) Gang Wu	Bifunctional OER/ORR catalyst development
National Renewable Energy Laboratory (NREL) Bryan Pivovar and Shaun Alia	Bifunctional HOR/HER catalyst development

Proposed Future Work

Next steps for FY 2019

- ❑ Optimize electrode coating on AEMs
- ❑ Prepare HER/HOR and OER/ORR bifunctional catalysts
- ❑ Modify existing test instrumentation at Giner to enable reversible testing with dilute hydroxide solutions

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

Summary

- Oxidation-resistant alkaline membranes and ionomers will be synthesized and characterized at the University of Delaware
- AEM materials will be integrated with bifunctional catalysts from SUNY Buffalo and NREL to enable reversible AEMFCs
- Giner's water management membranes will be used to mitigate flooding concerns during long-term AEM operation
- A reversible AMFC with >50% RTE at 1000 mA/cm^2 will be demonstrated without introducing any salts or bases in the aqueous feed

Acknowledgements

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