Novel Bifunctional Electrocatalysts, Supports and Membranes for High Performing and Durable Unitized Regenerative Fuel Cells

LBL: **Nemanja Danilovic**, Yagya Regmi, Adam Weber
WUSTL: Vijay Ramani
Proton: Chris Capuano, Kathy Ayers
Ballard: Rajesh Bashyam, Shanna Knights
Pajario Powder: Barr Zulevi
04/29/19

Project ID#: FC313

Overview

Timeline

- Project Start Date: 10/01/2018
- Project End Date: 09/30/2020
- Percent complete: 20%

Budget

- Total Project Budget: $ 1,250K
  - Total Recipient Share: $ 250K
  - Total Federal Share: $ 1,000K
  - Total DOE Funds Spent*: $ 10,101

* As of 02/28/19

Partners

- Project lead: Danilovic (LBNL)
- Subs:
  - Proton
  - WUSTL
  - Ballard
  - Pajarito Powder (added post FOA award)

Barriers

- Barriers addressed
  - No *regenerative* fuel cell specific barriers, optimization between fuel cell and electrolyzer barriers:
  - Fuel cells
    - Catalyst, Catalyst support and Membrane electrode assembly:

      A: Durability; B: Cost; C: Performance
  - Hydrogen Production
    - Catalyst, Catalyst support and Membrane electrode assembly:

      F: Capital cost; G: System efficiency and electricity cost

Relevance - Objectives

BERKELEY LAB

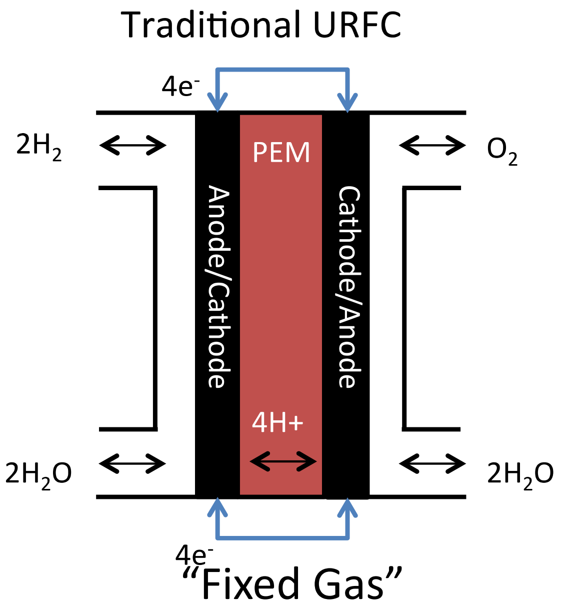
- The main focus of this project is to demonstrate a highly efficient and stable unitized regenerative fuel (URFC) achieved *through novel membrane and supported electrocatalysts*

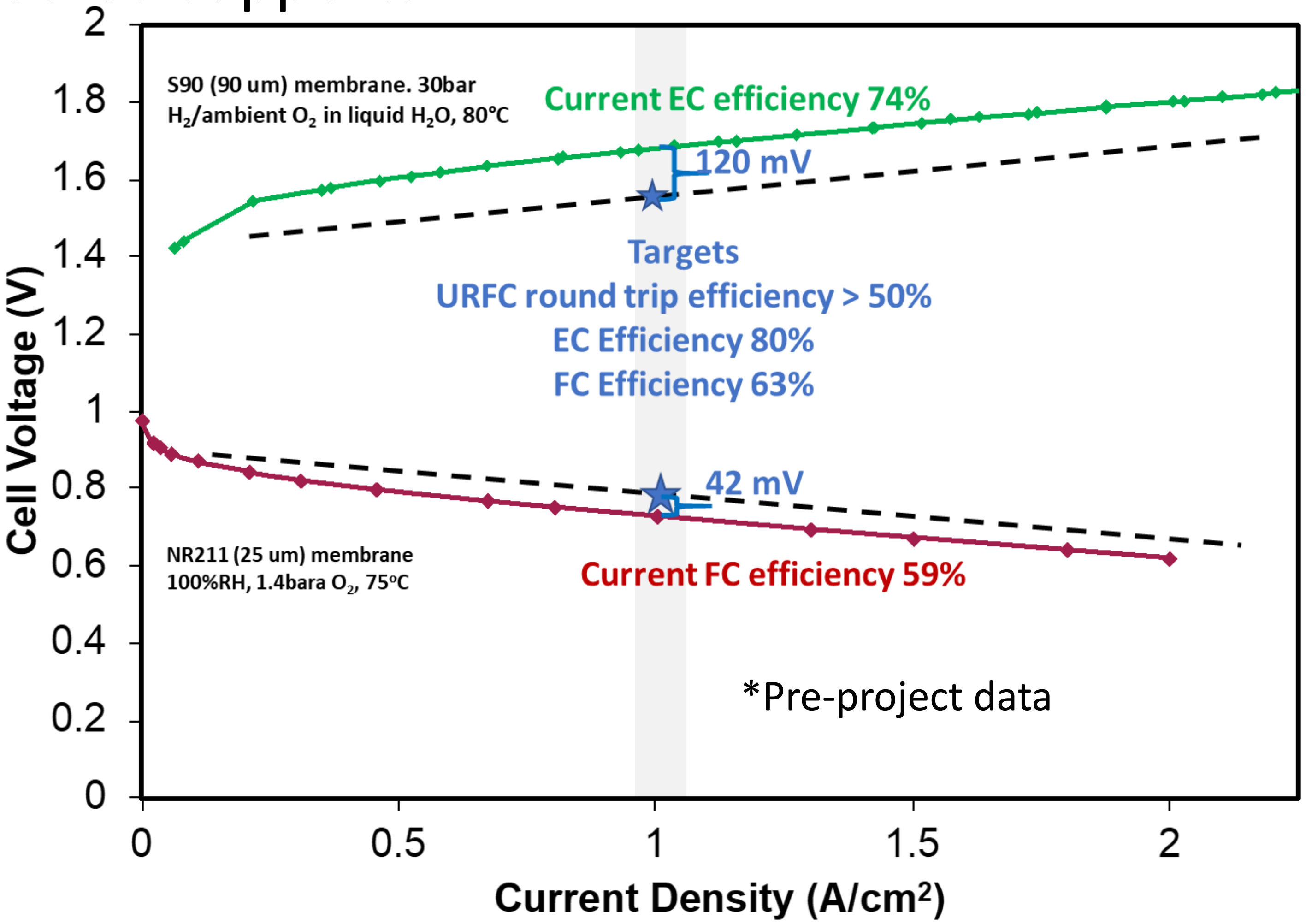
Project Targets

Specification	Baseline FC	Baseline Electrolyzer	Baseline URFC	Proposed URFC
Membrane thickness (microns)	25	90	125-175	**15-30**
Total cell Pt loading (mg/cm^2)	0.3	1	6	**0.55**
Ir catalyst loading (mg/cm^2)	n/a	2	4	**0.6**
Fuel cell stack efficiency (%)	>40% (@2 A/cm^2)	n/a	<40%	**>63% (@1 A/cm^2)**
Electrolysis stack efficiency (%)	n/a	>60% (@2 A/cm^2)	<55%	**>80% (@1 A/cm^2)**
Round trip efficiency (%)	n/a	n/a	<25%	**>50% (@1 A/cm^2)**
Durability	5,000 auto 28,000 bus	50,000 steady state	n/a	**100 hrs cycling URFC 1000 hrs discrete < 100 ∝V/hr**

Relevance - Project Goal

- Show feasibility of fixed gas unitized regenerative fuel cell (URFC) to achieve 50% round trip efficiency utilizing advanced membranes and bifunctional OER/ORR catalysts on engineered supports





Approach

WUSTL

Develop membrane/ionomer and catalyst supports

- Develop and characterize membrane and ionomer for URFC operation
- Develop and characterize engineered catalyst supports

LBNL/Pajarito Powder

Integrate WUSTL membrane into MEA, integrate bifunctional catalyst onto WUST supports

- Deposit bifunctional catalyst onto supports and evaluate properties
- Fabricate and test MEAs at up to 25cm^2 under discrete and URFC conditions
- Determine if support interactions stabilize bifunctional catalyst

Approach

Proton

Demonstrate MEA performance and durability in electrolysis testing at >50 cm^2

- Baseline performance of SOA membrane and catalysts
- Evaluate WUSTL membrane properties
- Fabricate MEAs from WUSTL materials
- Demonstrate > 100hrs durability at 50 cm^2

Ballard

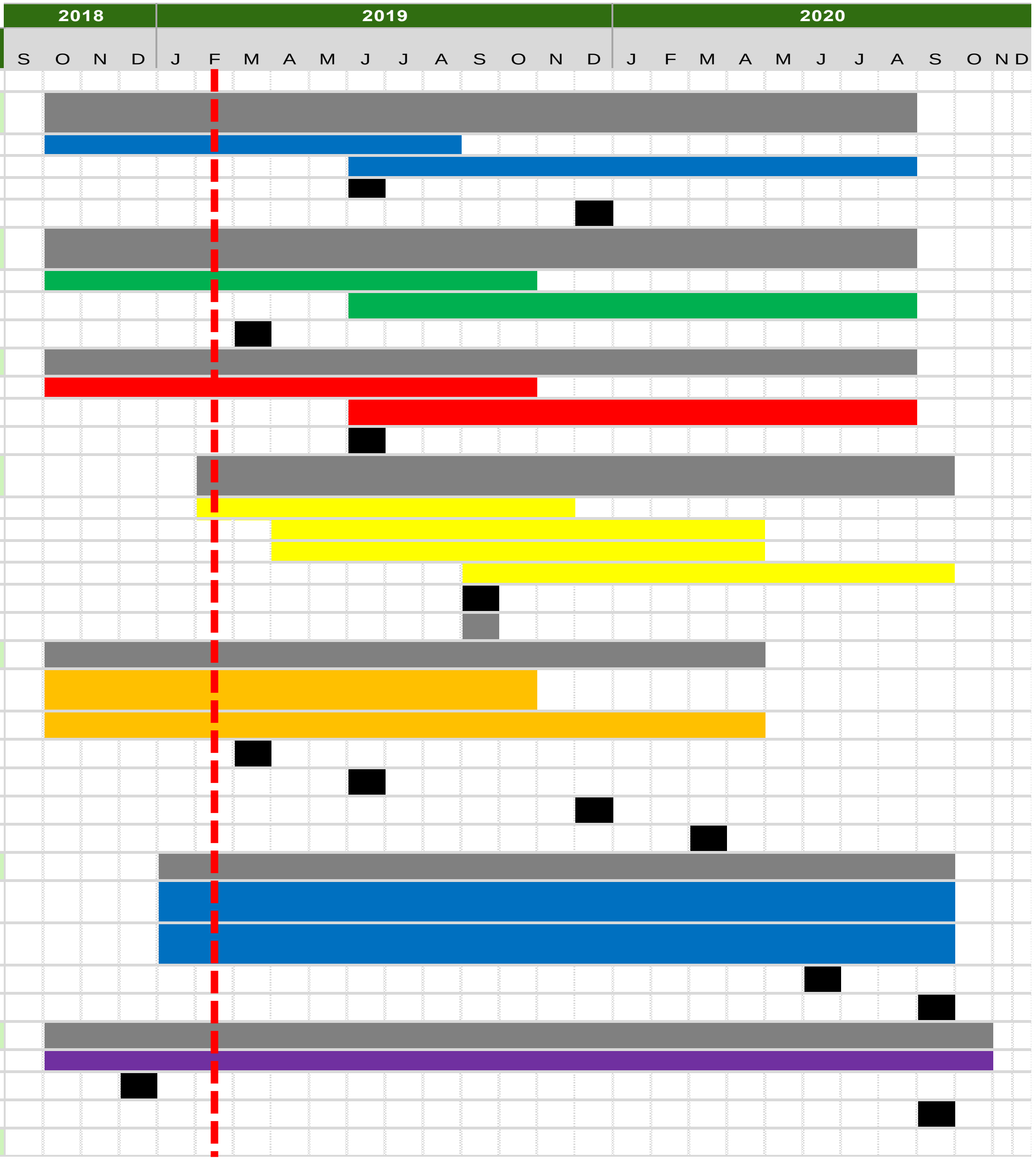
Demonstrate MEA performance and durability in fuel cell testing at >50 cm^2

- Baseline performance of SOA membrane and catalysts
- Evaluate WUST catalyst support durability
- Fabricate MEAs from WUSTL materials
- Demonstrate > 100hrs durability at 50 cm^2

Approach - Tasks

BERKELEY LAB

TASK DESCRIPTION	PLAN START	PLAN END
Task 1 Membrane Development (WUSTL)	10/1/18	8/1/20
Subtask 1.1 Membrane Syn and Char.	10/1/18	8/1/19
Subtask 1.2 Membrane Scale-Up	6/1/19	8/1/20
Milestone 1.1	6/30/19	6/30/19
Milestone 1.2	12/30/19	12/30/19
Task 2 Support Development (WUSTL)	10/1/18	8/1/20
Subtask 2.1 Support Syn and Char.	10/1/18	10/1/19
Subtask 2.2 Support Scale-Up	6/1/19	8/1/20
Milestone 2.1	3/30/19	3/30/19
Task 3 Catalyst Development (LBL)	10/1/18	8/1/20
Subtask 3.1 Catalsyt Syn and Char.	10/1/18	10/1/19
Subtask 3.2 Catalyst Scale-Up	6/1/19	8/1/20
Milestone 3.1	6/30/19	6/30/19
Task 4 MEA Integration and Optimization (LBL)	2/1/19	9/1/20
Subtask 4.1 Ink Development	2/1/19	11/1/19
Subtask 4.2 MEA Fab.	4/1/19	4/1/20
Subtask 4.3 MEA Char.	4/1/19	4/1/20
Subtask 4.4 URFC Modeling	9/1/19	9/1/20
Milestone 4.1	9/30/19	9/30/19
Go/No Go 1	9/30/19	9/30/19
Task 5 Subscale Testing (LBL)	10/1/18	4/1/20
Subtask 5.1 5 and 25cm2 EC and FC testing	10/1/18	10/1/19
Subtask 5.2 5 and 25cm2 URFC	10/1/18	4/1/20
Milestone 5.1	3/31/19	3/31/19
Milestone 5.2	6/30/19	6/30/19
Milestone 5.3	12/30/19	12/30/19
Milestone 5.4	3/30/20	3/30/20
Task 6 Validation	1/1/19	9/30/20
Subtask 6.1 25 and 50 cm2 FC testing (Ballard)	1/1/19	9/1/20
Subtask 6.2 25 and 50 cm2 EC tsting (Proton)	1/1/19	9/1/20
Milestone 6.1	6/30/20	6/30/20
Milestone 6.2	9/30/20	9/30/20
Task 7 Project Management (LBL)	10/1/18	10/1/20
Subtask 7.1 Proj. Mng. and Track.	10/1/18	10/1/20
Milestone 7.1	12/31/18	12/31/18
Project Goal	9/30/20	9/30/20



Approach - Milestones

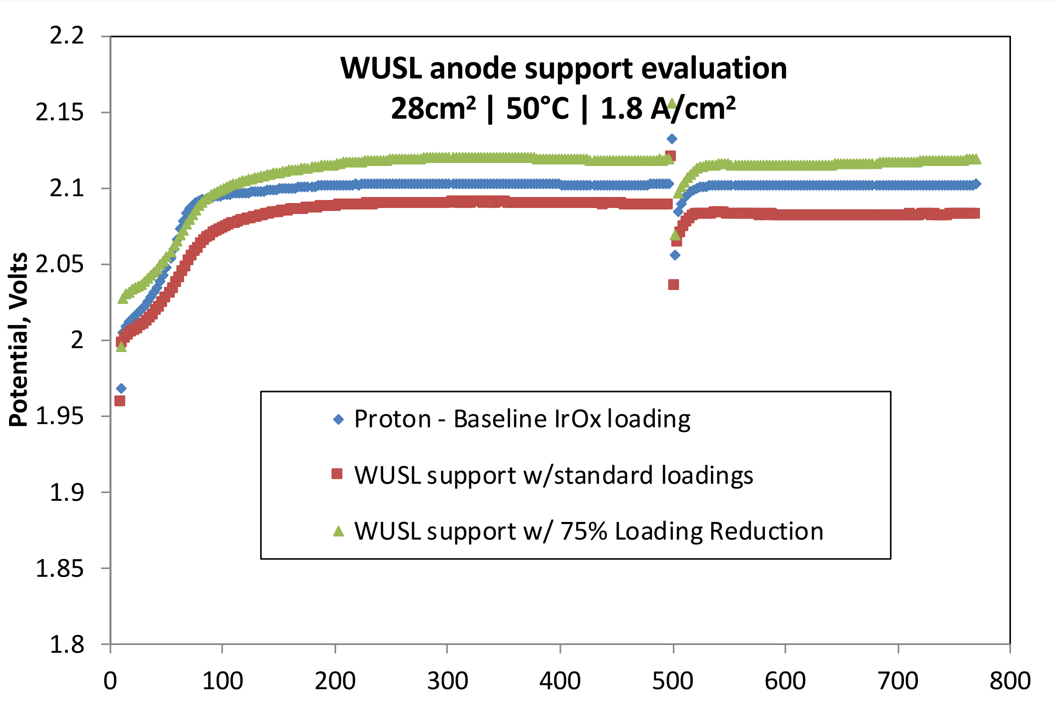
Progress measures	Type	Deliverable	Status
Q1-12/31/2018	Milestone 1	Common set of baseline materials testing protocols set and agreed upon, data management plan executed.	Complete
Q2-3/31/2019	Milestone 2	Baseline MEA baselined under MEA experimental conditions in discrete fuel cell (ORR) and electrolysis (OER) modes at LBL, Proton and Ballard in order to standardize performance.	On Track
Q3-6/30/2019	Milestone 3	Pt, Ir and Pt-Ir alloy catalysts baselined under RDE and MEA experimental conditions in discrete fuel cell (ORR) and electrolysis (OER) modes at LBL.	On Track
Q4-9/30/2019	Milestone 4	Down-select membrane and ionomer, and supported catalyst based on MEA performance at the 25 cm^2 level, showing potential to meet 1A/cm^2 currents at >43% round trip efficiency.	On Track
	Go/No Go 1	Demonstrate MEA performance at the 25 cm^2 level, showing potential to meet 1A/cm^2 currents at >43% round trip efficiency.	On Track
Q5-12/31/2019	Milestone 5	Optimized MEA meets or exceeds project PGM loading target at and demonstrated at 25 cm^2 active area while achieving 1A/cm^2 currents at >40% round trip efficiency	On Track
Q6-3/31/2020	Milestone 6	Membrane and electrocatalyst fabricated at scale enabling > 50 cm^2 active area MEA fabrication at Proton and Ballard.	On Track
Q7-6/30/2020	Milestone 7	Optimized MEA meets or exceeds project PGM loading target at and demonstrated at >50 cm^2 active area while achieving 1A/cm^2 currents at >45% round trip efficiency.	On Track
Q8-9/30/2020	Milestone 8	Down-selected MEA operated at 50 cm^2 at Ballard and Proton for 1000 hrs (exceeding 1 A/cm^2 and mV/1000hrs< 100).	On Track
	Project Goal	The end of project goal is a URFC that can achieve performance in Table 1 and validated in URFC operation at 25 cm^2 as well as discrete testing for 100 hrs (exceeding 1A/cm^2 and round-trip efficiency of 50%) and at 50 cm^2 at Ballard and Proton for 1000 hrs (exceeding 1 A/cm^2 and mV/1000hrs< 100).	On Track

Task 1: Membrane Development

- Development of ionomers and membranes
  - Targeting stability under liquid water operating conditions while maintaining high conductivity and mechanical integrity
  - Targeting reduced crossover for high system efficiency
- Developed and characterized at WUSTL
  - Delivered to LBL for 25cm^2 MEA integration and testing
  - Delivered to Ballard and Proton for MEA fabrication and scale up
    - Proton to perform membrane characterization

Task 2: Support Development

- Development of conductive/stable catalyst supports
  - Delivered to LBL for catalyst deposition

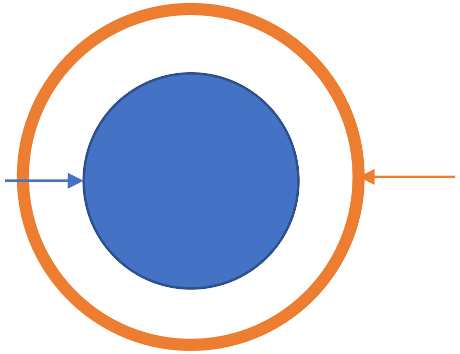


*Pre-project data

Task 3: Catalyst Development

- OER/ORR catalysts deposited onto WUSTL supports
  - Vary Pt/Ir ratios using scalable wet synthesis methods
  - Initial activity and durability evaluated in rotating disk electrode experiments at WUSTL

WUSTL supports:
Ru doped TiO_2 (RTO)
Nb doped TiO_2 (NTO)
Sb doped SnO_2 (ATO)



Bifunctional ORR/OER catalyst:
Pt + Ir nanoparticles 5-10 nm
*Adopt Pt/Ir ratio from Lab call

Task 4: MEA Integration

- Ink formulation development with supported catalysts, baseline ionomer and WUSTL ionomer
  - Catalyst inks and ink recipes delivered to Ballard and Proton for MEA synthesis
- MEA fabrication by spray deposition and casting

Task 5. Subscale Testing

- 5-25cm^2 active area MEA testing under discrete and URFC conditions
  - Cycling between fuel cell and electrolysis up to 1A/cm
  - Voltage efficiency and initial durability
- URFC model development

Task 6: Validation

- Proton and Ballard to evaluate discrete operation >50cm^2
  - Stability under discrete conditions
  - Accelerated stress testing

Accomplishments and Progress

- Defined baseline set of materials and testing protocols

Material	Fuel Cell MEA	Electrolyzer MEA	URFC MEA
ORR catalyst	0.3 mg/cm^2 Pt/C	n/a	0.3 mg/cm^2 Pt black (JM)
HOR catalyst	0.3 mg/cm^2 Pt/C	n/a	0.3 mg/cm^2 Pt/C (JM)
OER catalyst	n/a	1.5 mg/cm^2 Ir black (JM)	1.5 mg/cm^2 blak (JM)
HER catalyst	n/a	0.3 mg/cm^2 Pt/C (JM)	0.3 mg/cm^2 Pt/C (JM)
Membrane	Solvay 50um-boiled	Solvay 50um-boiled	Solvay 50um-boiled
GDL	Sigracet 29BC	Sigracet 29BC	Sigracet 29BC
PTL	n/a	Sintered titanium	Sintered titanium
Flowfield cathode	Serpentine graphite	Serpentine graphite	Serpentine graphite
Flowfield anode	Serpentine graphite	Parallel channel titanium	Parallel channel titanium

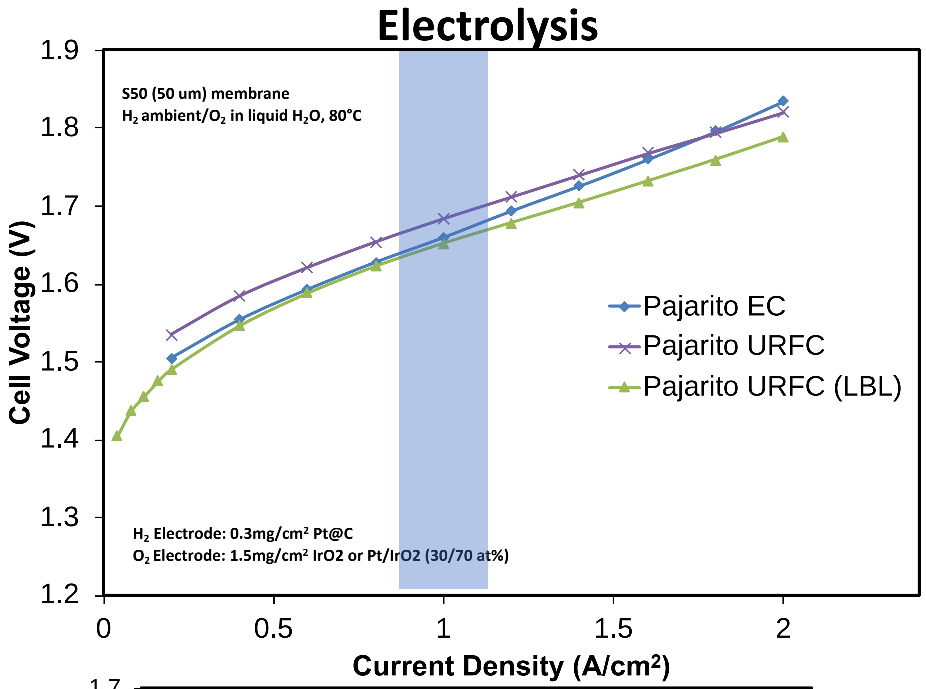
Accomplishments and Progress

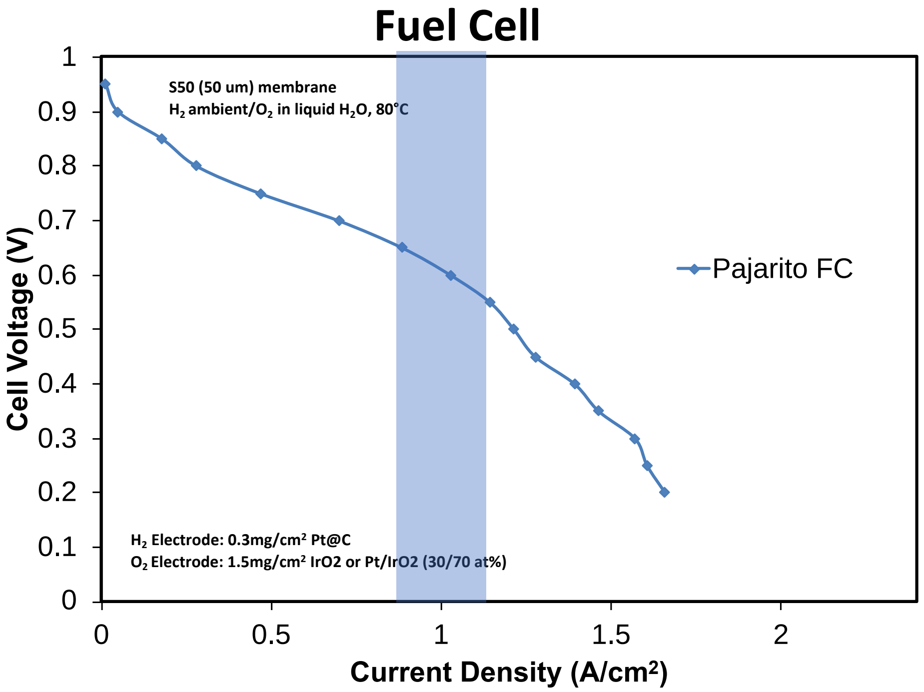
- Risks and Mitigations

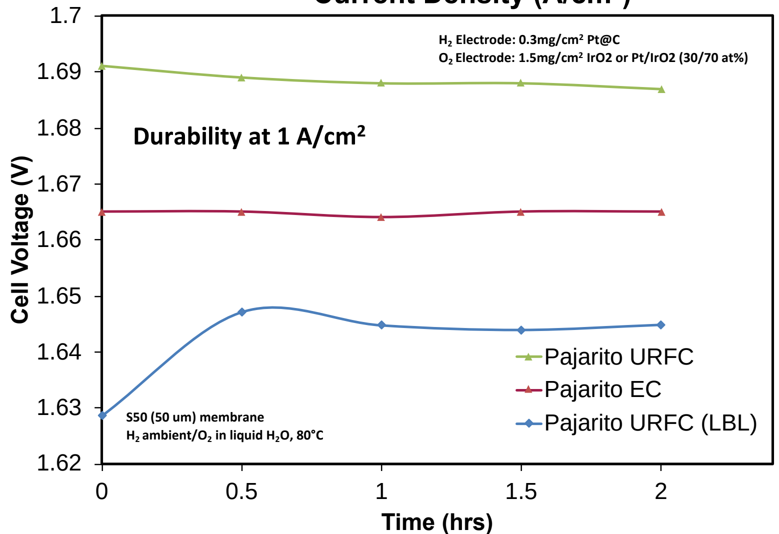
RISKS	Mitigations
Fixed gas mode is not able to reach desired efficiency targets	Operate in fixed polarity mode for high efficiency
Insufficient mechanical robustness for differential pressure operation:	Mitigated by using mechanical reinforcements (thin porous PTFE or other supports) to prepare the membranes
Low intrinsic support surface area:	Mitigated by using aerogel synthesis methods to enhance pore volume and surface area.
Support chemistry will not be compatible with Pajaritos catalyzation process.	Pajarito has a more costly thermal catalyzation process demonstrated in 10gr scale
Catalyst scale-up will be hindered by chemistry of supports	Preliminary work at Pajarito shows compatibility of Ir and Pt depositions method with Ti, Sb, and Nb

Accomplishments and Progress

- Baseline MEA Fabrication and Baselining







- Electrolysis and URFC MEAs in Electrolysis testing have satisfactory performance and durability for baseline materials for project
- FC performance needs to be improved

Collaboration and Coordination

- Collaborations
  - Pajarito Powders
    - Added to project post FOA award
    - Collaboration turned into subcontract on project
    - Leverages Pajaritos catalyst experience and worldwide supply base for materials
  - Solvay
    - Aquivion chosen as baseline membrane/ionomer material
    - Direct supply by lots
- Coordination
  - Benchmarking and AST development
    - Crosscuts with HydroGEN and FCPAD
  - URFC Targets
    - Max Wei at LBL

Remaining Challenges and Barriers

- Non-technical
  - Complete subcontracting and adjust affected milestones
- Technical
  - Gas Diffusion Layer/Porous Transport Layer
    - Bifunctional OER/ORR electrode requires GDL/PTL that can manage liquid water and water vapor
  - Advanced Baseline Bifunctional Supported Catalysts
    - Identify next gen material for ink and catalyst layer development
    - To be synthesized by Pajarito Powder
  - Accelerated Stress Tests
    - What is the main degradation mechanism, how to accelerate/characterize
  - Duty Cycle
    - What is the competitive URFC duty cycle

Proposed Future Work

- YR1:
  - Supported Catalyst
    - Fabricate and test supported catalysts on commercial supports as "advanced baselines"
    - Develop and incorporate WUSTL supports with catalysts
  - Membrane Electrode Assembly
    - Use advanced baseline catalyst to develop ink and catalyst layers
    - Optimize MEA to extract best discrete and reversible performance
    - Incorporate WUSTL supported catalysts into MEA
  - AST
    - Develop AST for durability and degradation mechanism identification
- YR2:
  - MEA optimization
  - Cycle testing
  - Scale up and discrete testing

Technology Transfer Activities

- IP Management Plan
  - Being developed to protect existing IP
    - WUSTL: V, Ramani patents on supports
    - Pajarito
    - LBNL
  - To protect IP generated within project between partners

Summary

- Project start and progress delayed due to contracting delays
  - Contracting language
- Baseline material set and testing protocols established
  - Unsupported bifunctional catalyst and mechanically robust thin membrane
- Baseline MEAs and testing initiated on schedule
  - EC results are on target
  - FC results rquire more FC MEA refinement
- Further progress enabled by identified advanced baseline materials
  - Pajarito supported bifunctional catalysts

Acknowledgments

- Department of Energy for support