Lab Call FY18 (Reversible FC): Technology-Enabling Materials and Cell Designs for Reversible PEM Fuel Cells

LBL: **Nemanja Danilovic**, Yagya Regmi, Adam Weber

ANL: Debbie Myers, Jeff Elam

5/1/19

Project ID#: FC183

Overview

Timeline

- Project Start Date: 01/01/2018
- Project End Date: 12/31/2019
- Percent complete: 58%

Budget

- Total Project Budget: $ 400K
  - Total Recipient Share: $ 0K
  - Total Federal Share: $ 400K
  - Total DOE Funds Spent*: $ 223 K

* As of 2/28/19

Partners

- Project lead: Danilovic, Weber (LBNL)
- Co-PI: Debbie Myers (ANL)
- Interactions/collaborations:
  - 3M
  - Proton OnSite

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

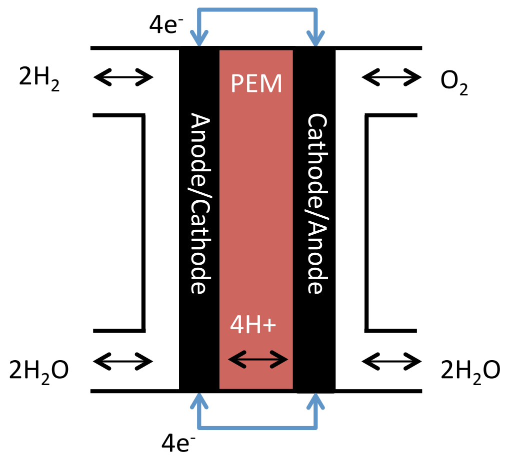
Relevance – Energy Storage

- An URFC is an energy storage device which stores electricity in the form of H_2 & O_2 gas and producing electricity
- Advantages:
  - Combine balance of plant and cell, and MEA materials of discrete systems
  - Energy density (>400 kWh/kg)
  - Scalable storage (H_2, w/ or w/o O_2)
  - High current density (up to 2A/cm^2)
  - No corrosive or toxic substances
- Disadvantages:
  - Durability
  - Performance and cost
  - Technical maturity vs discrete counterparts
  - Switching time

Approach - Objectives

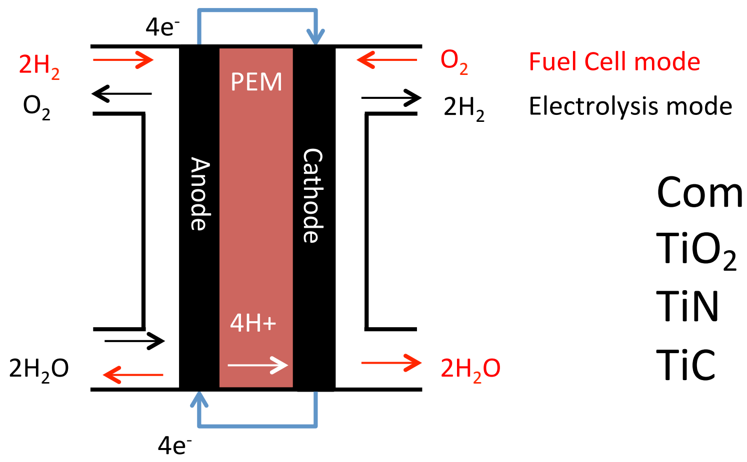
Show feasibility of fixed polarity unitized regenerative fuel cell (URFC) and engineered bifunctional OER/HOR catalyst

Traditional URFC



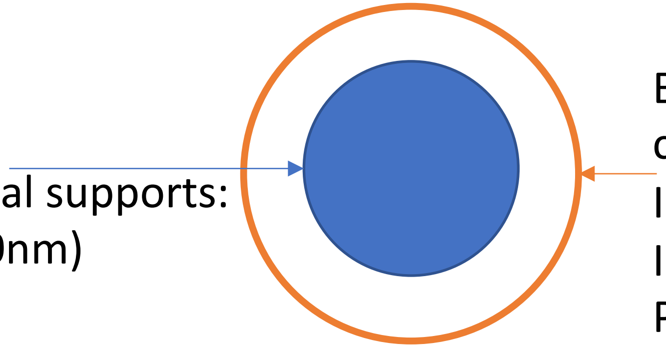
"Fixed Gas"

Proposed URFC



"Fixed Polarity"

Commercial supports:
TiO_2 (5, 40nm)
TiN
TiC



Bifunctional HOR/OER catalyst:
Ir rich, Pt-Ir alloys
Ir skin decorated with Pt

Electrode	Fuel Cell Mode	Electrolyzer mode
Anode	Hydrogen oxidation reaction (HOR) $H_2 \rightarrow 2H^+ + 2e^-$	Oxygen evolution reaction (OER) $H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$
Cathode		

LBNL/ANL Targets

Specification	Baseline FC	Baseline Electrolyzer	Baseline URFC	Proposed URFC
Membrane thickness (microns)	25	125	125-175	50-60
Total cell Pt catalyst loading (mg/cm²)	0.4	1	6	0.8
Ir catalyst loading (mg/cm²)	n/a	2	4	1
Fuel cell stack efficiency	>50%	n/a	<40%	>50%
Electrolysis stack efficiency	n/a	~65%	<55%	>75%
Round trip electrical efficiency (%)	n/a	n/a	<25%	>45%

Approach

LBNL

Show feasibility of URFC approach in MEA testing

- Use state of the art PEM fuel cell and electrolysis materials
  - N212 <-> N117
  - Pt/C: HER/ORR
  - Pt and Ir black: HOR/OER
- Develop application relevant cycling protocol and AST

ANL

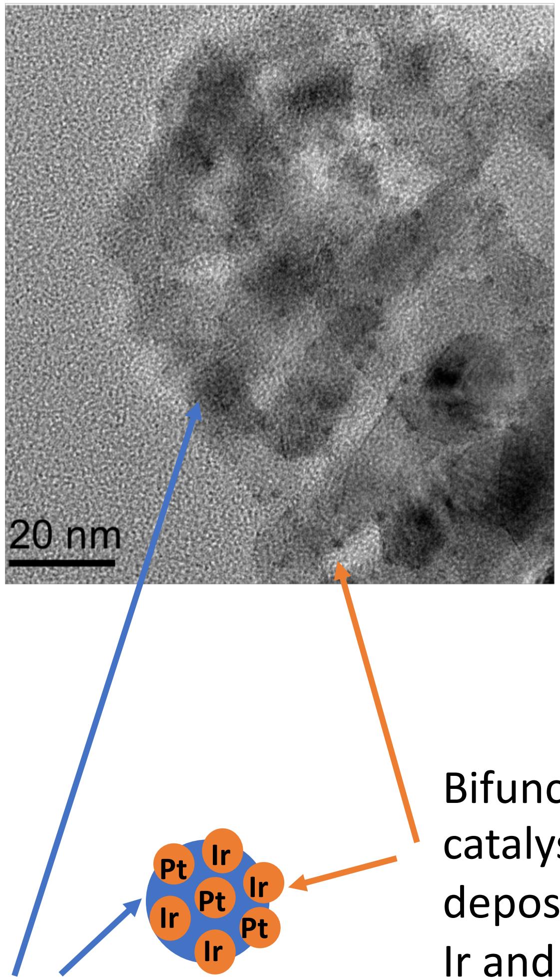
Show feasibility of engineered supported catalyst approach

- Develop ALD deposition process
- Characterize *activity* and *stability* of supported bifunctional catalyst vs baseline materials for HOR, OER and cycling

Approach - Milestones

Quarter	Type	Deliverable	Status
Q1-3/31/2018		Definition of technical targets, and parameters for techno-economic tracking	Complete
Q2-6/31/2018	Progress measure	Flow battery station modified to operate between fuel cell and electrolysis modes using LabView software	Partially Complete. Test stand operational but manual cycling.
Q3-9/30/2018	Progress measure	Pt, IrO2 and Pt-IrO_2 coatings on high-surface-area carbide or nitride supports evaluated for OER and HOR activity in aqueous electrolyte testing	Complete
Q4-12/30/2018		Pt, Ir and Pt-Ir alloy catalysts baselined under RDE and MEA experimental conditions in discrete fuel cell (HOR) and electrolysis (OER) modes	Complete
		Baseline URFC MEA consisting of Pt-IrO2 blacks, demonstrates discrete performance in FC and EC mode within 200 mV of baseline FC (Pt/C) and EC (IrO2 black) MEAs in their respective modes of operation at 1 A/cm^2 using the same membrane.	**Complete**
Q1-3/31/2019	Progress measure	Using the baseline URFC MEA, three different modes of URFC operation will be evaluated fixed polarity, fixed gas and vapor feed under cycling operation. The most stable and the most efficient ones will be identified and downselected	On track
Q2-6/31/2019	Progress measure	The baseline URFC MEA under the downselected mode of operation will be evaluated under cycling conditions under 0.5hr (8hr day, 3 days total), 1 hr (8hr day, 3 days total), 2hr (8hr day, 3 days total), 4hr (8hr day, 3 days total) and 8hr (24hrs day, 3 days total). Degradation rates and efficiencies will be compared.	On track
Q3-9/30/2010	Progress measure	The thin film on non-carbon support catalyst will be incorporated into a ionomer ink vehicle for ultrasonic spray deposition and demonstrated by fabricating and testing MEAs. MEAs will be sent to ANL for testing at the APS.	On track
Q4-12/30/2019		URFC MEA containing down-selected thin film anode catalyst demonstrates discrete performance in FC and EC mode within 100 mV of baseline FC (Pt/C) and EC (IrO_2 black) MEAs in their respective modes of operation at 1 A/cm^2	

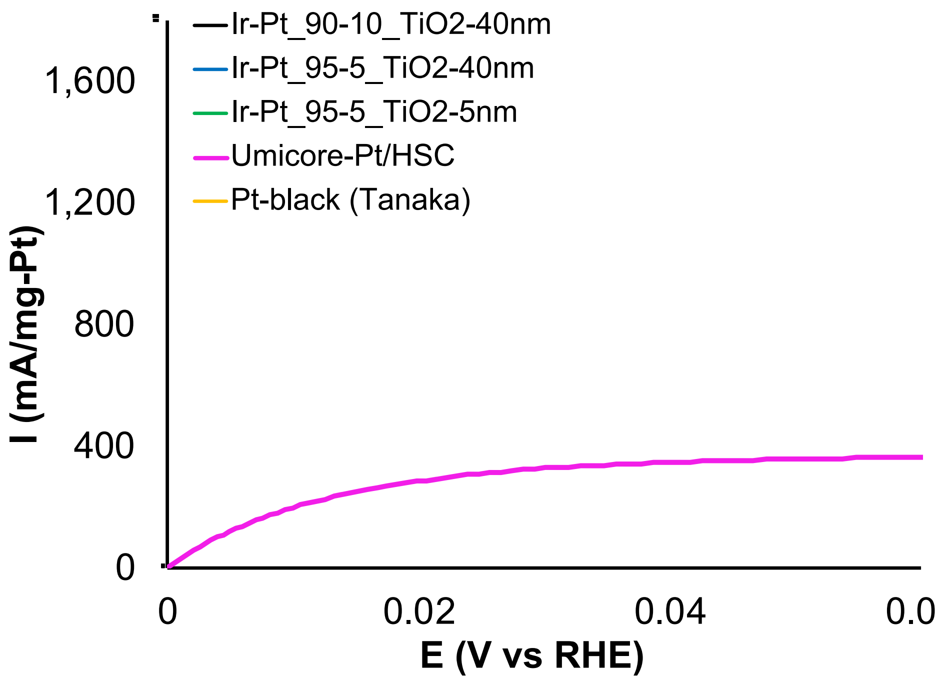
Accomplishment
HOR/OER Catalyst Development



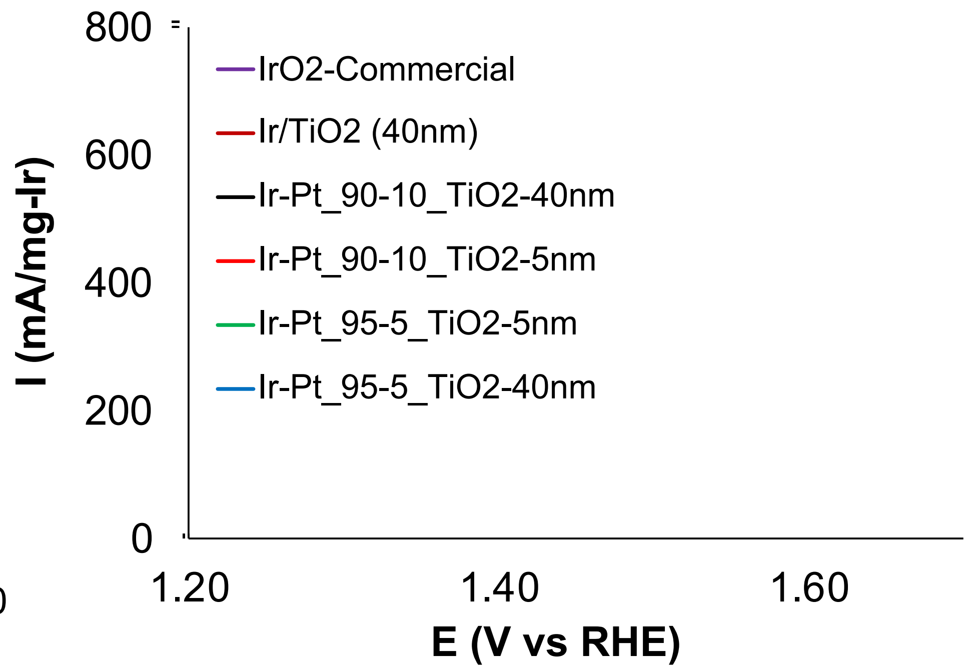
Commercial supports: TiO_2 (5, 40nm)

Bifunctional HOR/OER catalyst: ALD deposited Ir and Pt nanoparticles 1-2 nm

Hydrogen Oxidation
Hydrogen-saturated 0.1M $HClO_4$, 10 mVs^{-1}, 3600 rpm



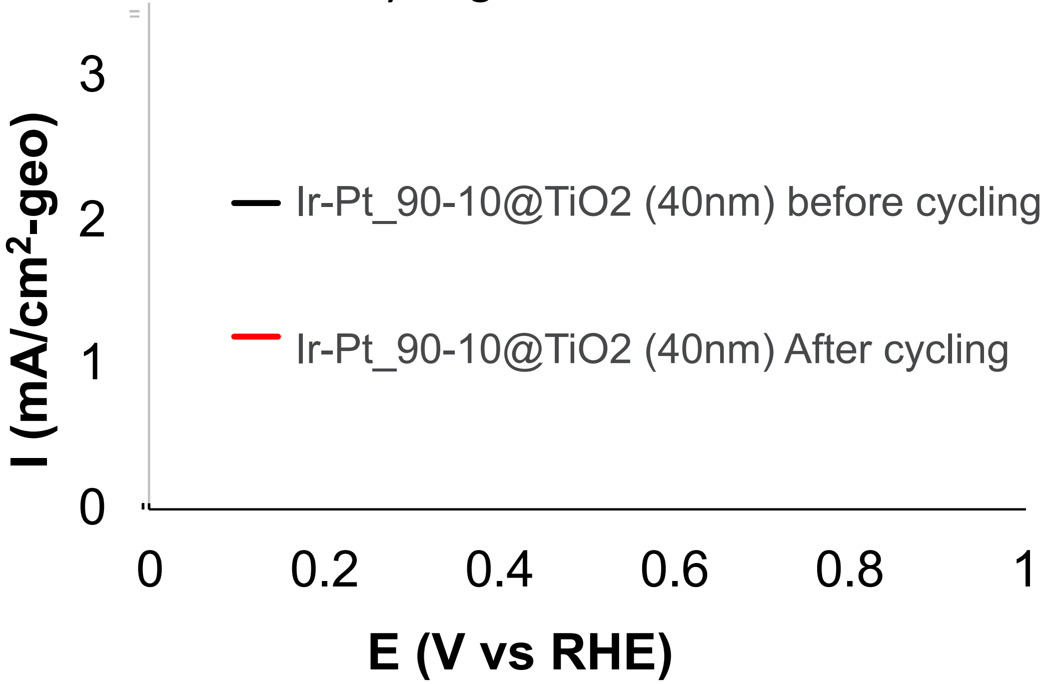
Oxygen Evolution
Deaerated 0.1M $HClO_4$, 10 mVs^{-1}, 3600 rpm



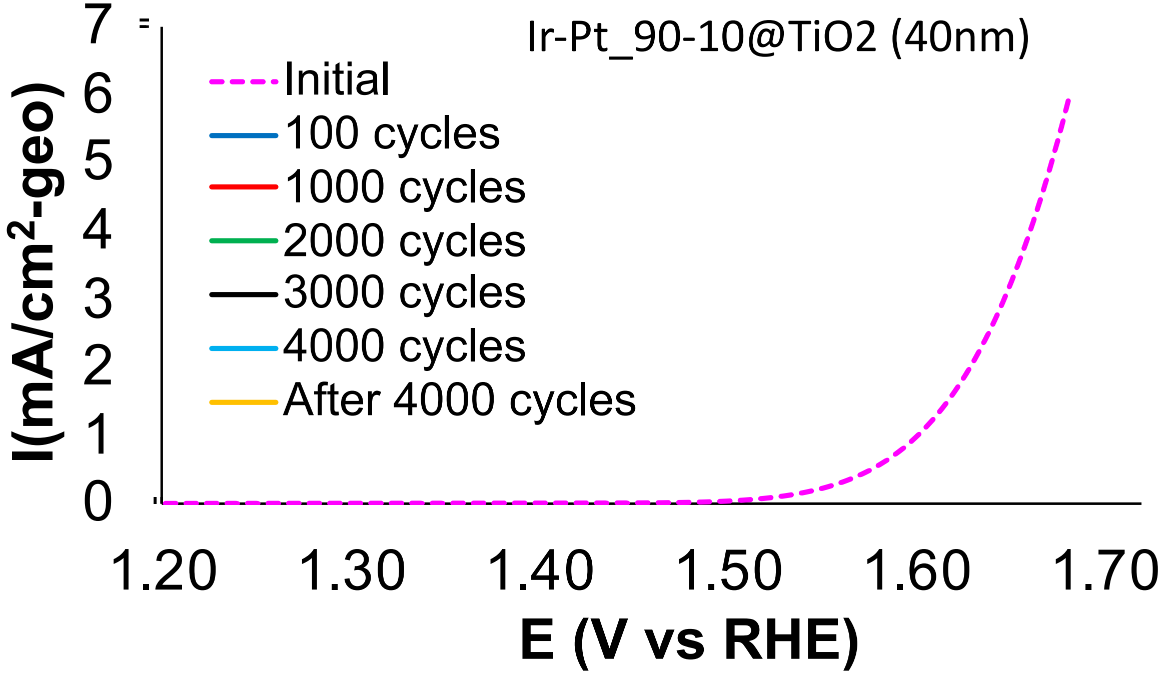
- Pt and Ir are deposited by atomic layer deposition (ALD) onto TiO_2
- Total metal loading on TiO_2 of ~24wt% in optimal 90-10 Ir-Pt ratio
- Ir-Pt_90-10@TiO_2 has higher mass activity than Pt black and Pt@C
- Compared to commercial Ir black
  - Ir-Pt_90-10@TiO2 has 46mV higher overpotential at 100mA/mg-Ir
  - Ir@TiO2 has 38mV higher overpotential at 100mA/mg-Ir
- *Ir-Pt_90-10@TiO_2 meets our ANL-RDE target performance target*

Accomplishment
HOR/OER Catalyst Development

Hydrogen Oxidation



Oxygen Evolution

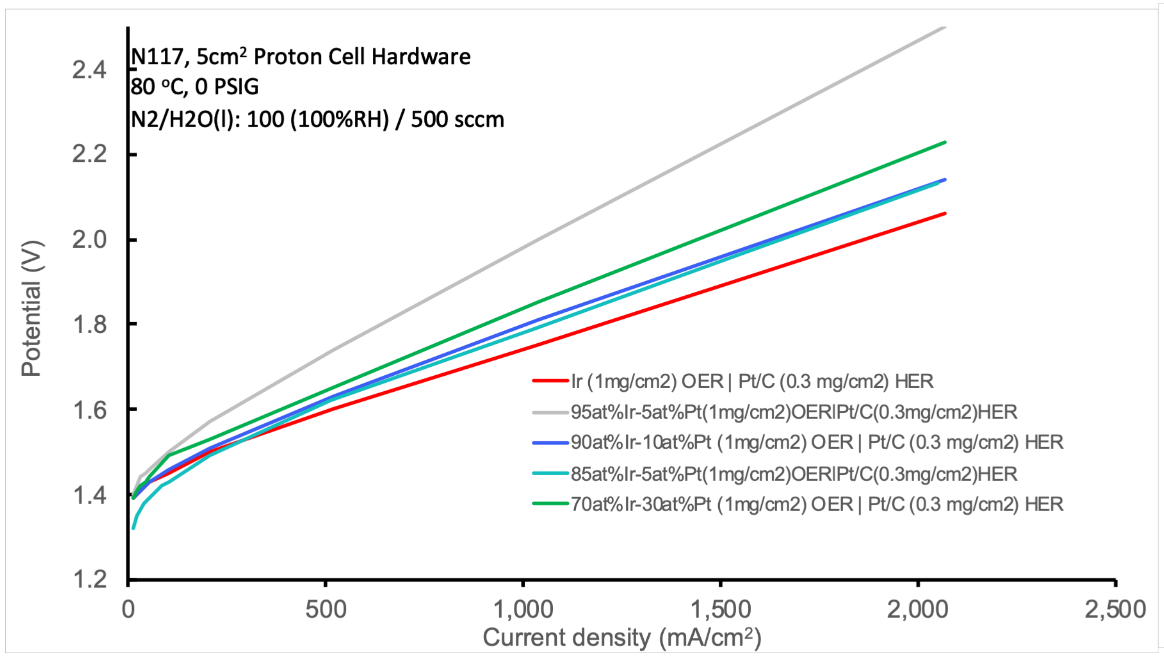


Deaerated 0.1 M $HClO_4$; Potential window: 0.05 V to 1.6 V Scan rate: 50 mV s^{-1}

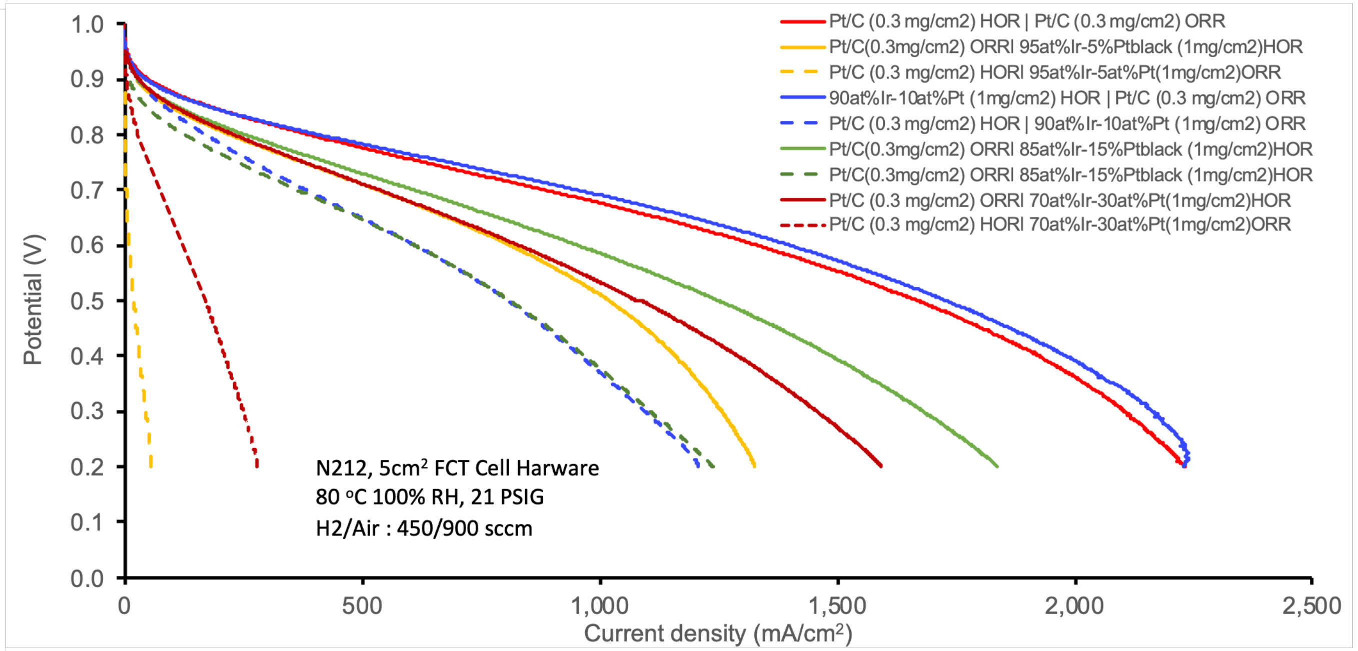
- Evaluating durability by cycling catalyst from 0.05V to 1.6V (vs RHE) to simulate voltage swing for bifunctional HOR/OER catalyst
- At 2 mA/cm^2 OER current density, Ir-Pt (90-10)@TiO_2 catalyst exhibits <**50mV increase** in overpotential after **4,000** cycles between OER and HOR modes.
- Surface Pt is lost during electrode cycling between OER and HOR potentials: shown by absence of H_{upd} feature in the background CV and dramatic **loss of HOR activity**
- *Ir-Pt_90-10@TiO_2 meets the ANL-RDE OER durability target, but not the HOR durability target*

Accomplishment
Pt/Ir Ratio Optimization

URFC MEA in EC mode



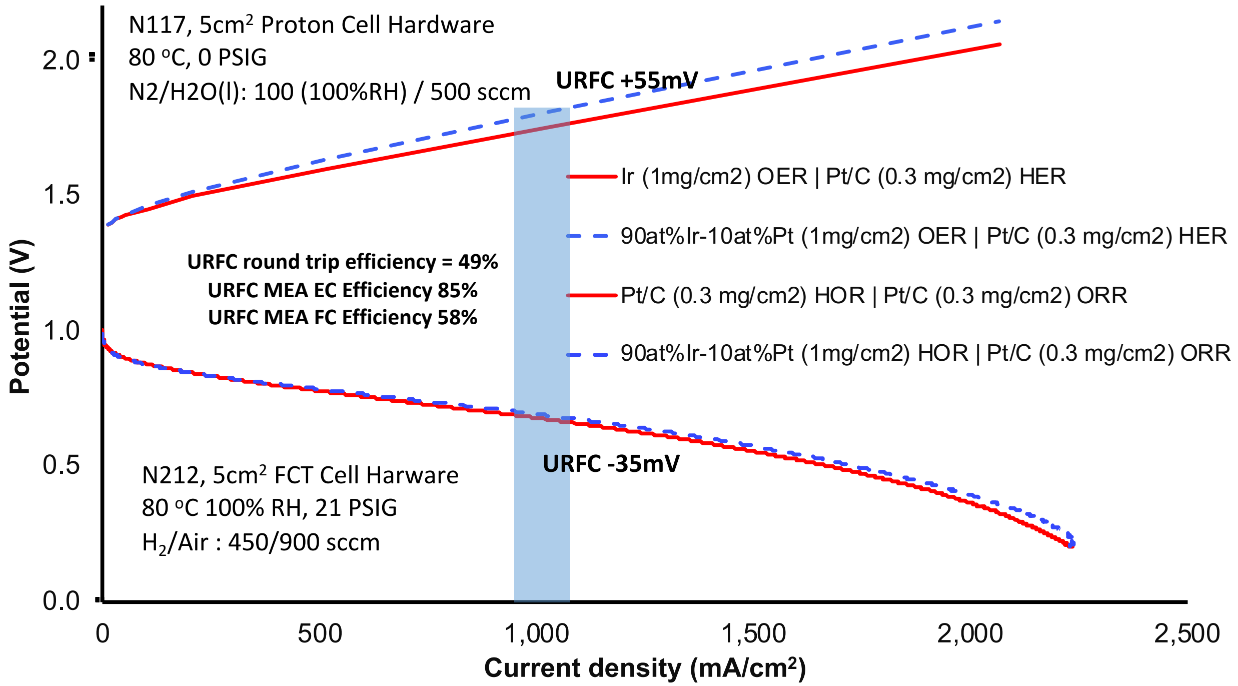
URFC MEA in FC mode



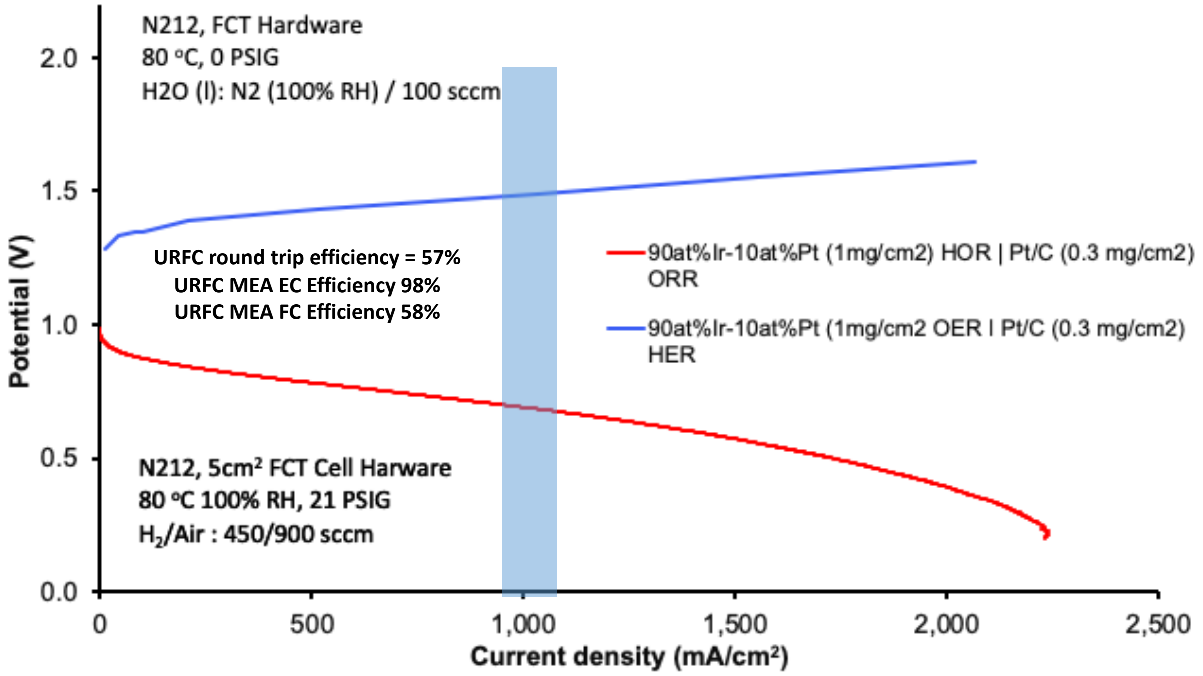
- Varied ratio of Pt and Ir in HOR/OER bifunctional electrode
- Fixed total PGM loading at 1 mg/cm^2 PGM loading on N212 for FC and N117 for EC tests
- **Downselect 90at%Ir- 10at%Pt ratio as most optimal in EC and FC mode**
- Poor results in fixed gas mode even at higher Pt loadings, most likely due to use of Pt black versus supported Pt catalyst
  - Validates approach of fixed polarity

Accomplishment
MEA development and testing

URFC MEA vs Discrete FC and EC MEAs



URFC MEA on N212



- Downselected Ir/Pt black physical mixture at 90/10 at% as baseline bifunctional HOR/OER catalyst
- Showing the same URFC bifunctional catalyst layer with 1 mg/cm^2 PGM loading on N212 for FC and N117 for EC tests
- Total PGM loading 1.3mg/cm^2 < total of two discrete systems (EC+FC)
- Round trip efficiency is increased with N212 URFC MEA approaching 60%
- Further optimization of catalyst layer, gas diffusion layer and incorporating ANL supported catalysts to maximize performance
- *Q4 Go/No Go met*

Accomplishments and Progress
Response to Previous Years Reviewers' Comments

- Project not reviewed last year

Collaboration & Coordination

Entities	Role	Type	Relationship with FCTO	Extent of collaboration
LBNL	Prime	Federal Lab	Within	TEA analysis
ANL	Sub	Federal Lab	Within	Catalyst development and design
Proton OnSite	In kind	Industry	Within	Materials supplier
3M	In kind	Industry	Within	Materials supplier

Remaining Challenges and Barriers

- Water management
  - Challenges of water management remain
  - Need to focus on treatments of the PTL (Teflon treatment)
  - Flowfields are a factor as well that needs to be looked at
- Stability of Pt and Ir under cycling between operating modes
  - Ir handles the voltage cycling better than Pt, while Pt poisons Ir OER
  - Will explore structural approaches and discrete Pt@TiO_2 and Ir@TiO_2 to offset this
- TEA analysis to inform cycle lengths between modes
  - We will be doing cycling from 0.05 to 1.6 V in MEA and RDE testing for ASTs
  - For cycle testing we will settle on 4 hr cycles most likely

Proposed Future Work

- LBL:
  - Evaluate diffusion layer and flowfields
  - Evaluate vapor feed, fixed gas and fixed electrode stability under URFC testing
  - Incorporate ANL catalyst for further PGM reduction and efficiency improvement
  - Evaluate durability and cycling
  - Track performance and cell costs for TEA
- ANL:
  - Increase metal loading to 50wt%
  - Evaluate Pt-Ir alloy vs Pt and Ir particles on TiO_2
  - Evaluate in situ SAXS at APS

Technology Transfer Activities

- Tech to market plans
  - Coordinate with TEA analysis team at LBL
  - Determine best market and performance requirements for URFCs
- Feed knowledge gained within this project to FC313 for advanced URFC development
- Evaluate URFC IP portfolio potential
- Seek commercialization partners and demonstration funding

Summary

- Relevance
  - URFCs energy storage devices that decouple storage from conversion, are are enablers for intermittent renewable energy
  - Proposed URFC design could enable active and durable energy storage at low cost
- Approach
  - Address barriers to URFC deployment: Durability and Cost
  - The main focus of this project is to demonstrate a highly efficient and stable URFC achieved through novel cell operation and engineered supported catalysts
    - LBNL: Focus on showing feasibility of the MEA and proposed constant polarity URFC cell vs discrete and traditional cells
    - ANL: Focus on showing feasibility of Pt-Ir coated supports with ALD
- Technical Accomplishments
  - ALD grown bifunctional catalysts achieve activity targets at reduced loading
  - Fixed polarity URFC mode of operation achieved over 50% round trip efficiency
- Proposed Future Work
  - ANL: Optimize Pt/Ir ratio and structure of catalyst on support
  - LBNL: URFC durability and cycle testing. Integration of ANL catalyst into MEA

Acknowledgments

Department of Energy for support