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Technology-Enabling Materials and Cell Designs for Reversible PEM Fuel Cells

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6/13/18

Project ID #: FC183

Overview

Timeline

- Project Start Date: 01/01/2018
- Project End Date: 12/23/2020
- Percent complete: 12.5%

Budget

- Total Project Budget: $ 400K
  - Total Recipient Share: $ 0K
  - Total Federal Share: $ 400K
  - Total DOE Funds Spent*: $ 33K

* As of 3/31/18

Partners

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

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

- The main focus of this project is to demonstrate a highly efficient and stable unitized regenerative fuel (URFC) achieved through novel cell operation and engineered supported catalysts

DOE Targets from MYRD&D

Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2015 Status	2020 Targets
Platinum group metal total content (both electrodes)[a]	g / kW (rated,[b] gross) @ 150 kPa (abs)	0.16[c,d]	0.125
Platinum group metal (pgm) total loading (both electrodes)[a]	mg PGM / cm^2 electrode area	0.13[c]	0.125
Mass activity[e]	A / mg PGM @ 900 mV$_{IR\text{-}free}$	>0.5[f]	0.44
Loss in initial catalytic activity[e]	% mass activity loss	66[c]	<40
Loss in performance at 0.8 A/cm^2[e]	mV	13[c]	<30
Electrocatalyst support stability[g]	% mass activity loss	41[h]	<40
Loss in performance at 1.5 A/cm^2[g]	mV	65[h]	<30
PGM-free catalyst activity	A / cm^2 @ 0.9 V$_{IR\text{-}free}$	0.016[i]	>0.044[j]

Table 3.1.5 Technical Targets: Central Water Electrolysis[a,b]

Characteristics	Units	2011 Status[c]	2015 Target[d]	2020 Target[e]
Hydrogen Levelized Cost (Plant Gate)[f]	\$/kg H_2	4.10	3.00	2.00
Total Capital Investment[b]	\$M	68	51	40
System Energy Efficiency[g]	%	67	73	75
	kWh/kg H_2	50	46	44.7
Stack Energy Efficiency[h]	%	74	76	78
	kWh/kg H_2	45	44	43
Electricity Price[i]	\$/kWh	From AEO '09	\$0.049	\$0.031

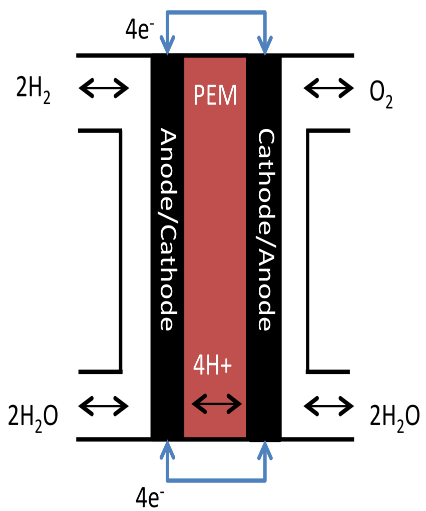
LBNL/ANL Targets

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

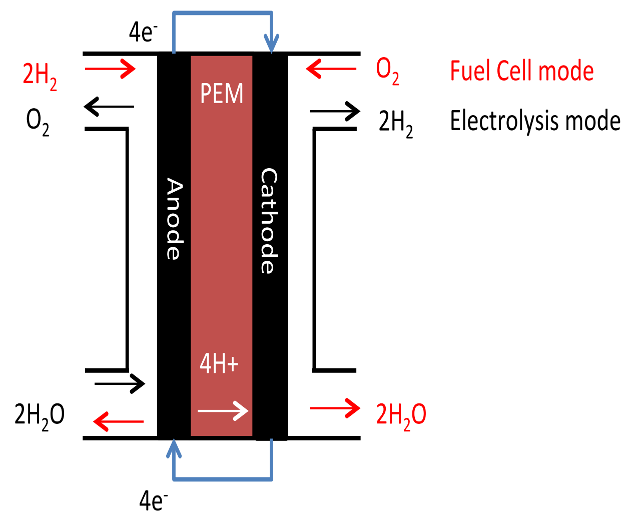
Relevance - Project Goal

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

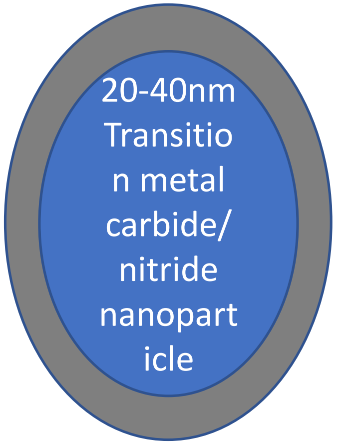
Traditional URFC



Proposed URFC



1-2 nm ALD Pt & Ir



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	Oxygen reduction reaction (ORR) $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	Hydrogen evolution reaction (HER) $2H^+ + 2e^- \rightarrow H_2$

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

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
- Track technoeconomics of device

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 - Tasks

- Task 1: Oxygen evolution reaction/ Hydrogen oxidation reaction catalyst development
- Task 2: Membrane electrode assembly development and testing
- Task 3: Cyclability and durability (Phase 2)
- Task 4: Cost analysis (Phase 2)

Task	Lead	Y1 Q1	Y1 Q2	Y1 Q3	Y1 Q4	Y2 Q1	Y2 Q2	Y2 Q3	Y2 Q4
Task 1	ANL		X	X	X	X	X	X	X
Task 2	LBL	X	X	X	X	X	X	X	X
Task 3	LBL					X	X	X	X
Task 4	LBL/ANL	X				X	X	X	X

Approach - Milestones

- Phase 1 Milestones

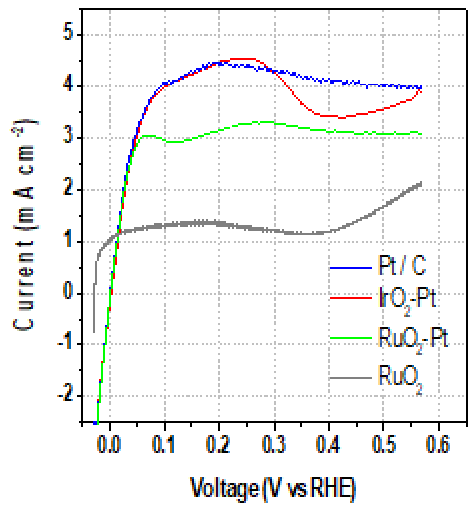
Progress measures	Type	Deliverable	Status
Q1-3/31/2018	Progress measure	Definition of technical targets, and parameters for techno-economic tracking	Complete
Q2-6/31/2018	Progress measure	Flow battery station modified to operate between fuel cell and electrolysis modes using LabView software	On track
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	On track
Q4-12/30/2018	Mileston e	Pt, Ir and Pt-Ir alloy catalysts baselined under RDE and MEA experimental conditions in discrete fuel cell (HOR) and electrolysis (OER) modes	On track
	Go/No-Go	Pt-IrO_2 on high-surface-area carbide or nitride support exhibits OER and HOR overpotentials at 10 mA/cm^2 within 100 mV of state-of-the-art unsupported IrO_2 and Pt/C OER and HOR electrocatalysts and <50 mV increase in overpotential after 5,000 cycles between OER and HOR modes.	On track

Task 1 – HOR/OER Catalyst Development

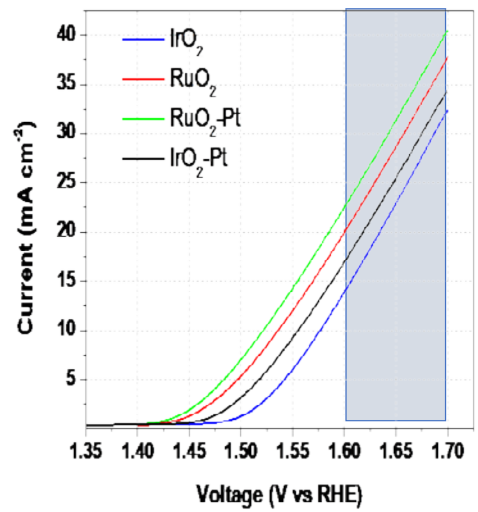
Approach:

- Bifunctional HOR and OER catalyst needs to withstand cycles between 0.1 and 1.7 V while it undergoes HOR and OER, respectively
- Lower limit of loading in MEA will be limited by activity and distribution of unsupported catalysts, need:
  - Stable electrocatalyst supports
  - Low loading, active and stable Pt and IrO_2 catalyst

Hydrogen



Oxygen evolution

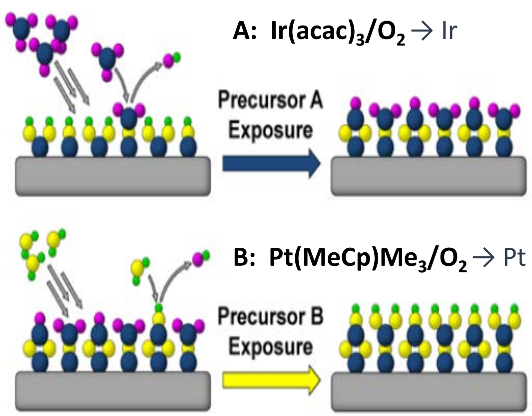


Pre-project result: RDE testing of physical mixtures of Pt and IrO_2 or RuO_2

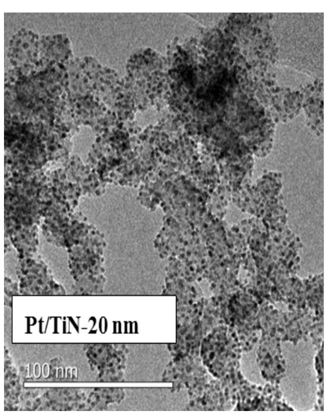
Task 1-HOR/OER Catalyst Development

Approach:

- ANL collaborators Debbie Myers and Jeff Elam will engineer a supported bifunctional electrocatalyst using ALD
- Proposed catalysts: Thin Films of Pt-IrO_x on corrosion resistant high-surface-area support
  - Supports are transition metal carbides and/or nitrides chosen to have high electronic conductivity, corrosion resistance, and strong and favorable interactions with Pt and Ir and stability in the catalytic environment
  - Preferred method for forming thin film of catalytic metals is atomic layer deposition (ALD) which can result in thin conformal films and strong interactions with support
  - ALD system at Argonne can coat powders at kilogram scale



ABAB… → Pt/Ir alloy
A/(A+B) controls composition



Pre-project result: Pt on TiN fabricated with ALD

Accomplishment

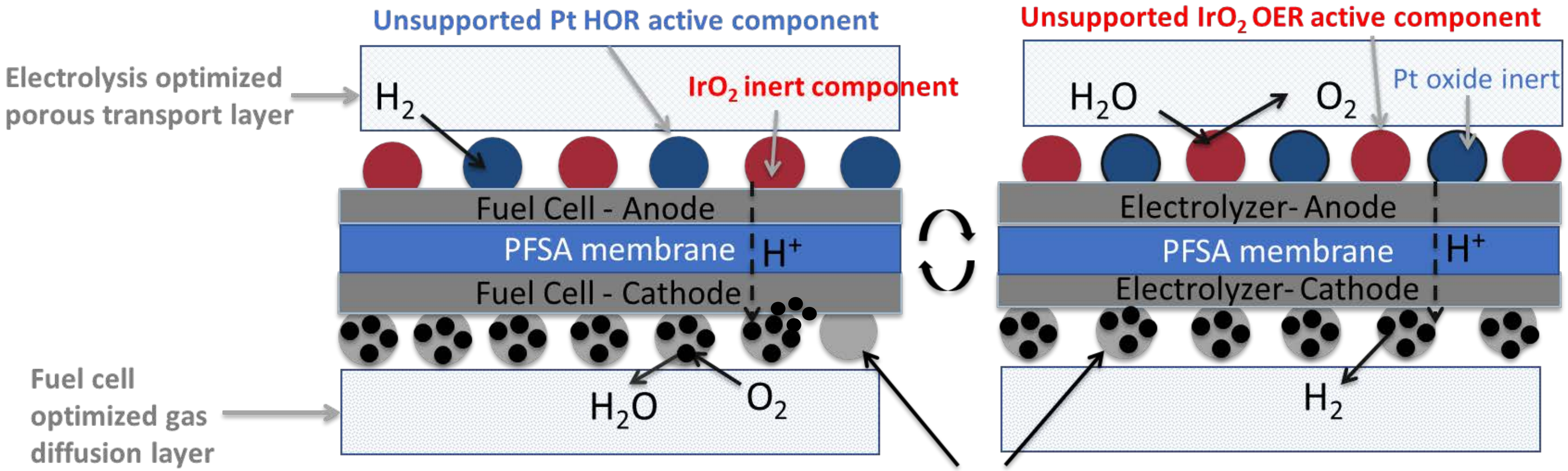
Test matrix for baseline catalysts

Material	Fuel Cell	Electrolyzer	URFC
ORR catalyst	Pt46wt% /C	n/a	Pt46wt%/C
HOR catalyst	Pt46wt% /C	n/a	Pt black
OER catalyst	n/a	Ir black, IrO_2/TiO_2	Ir black, IrO_2/TiO_2
HER catalyst	n/a	Pt46wt%/C	Pt46wt%/C

Task 2 – MEA development and testing

Approach:

- URFC membrane electrode assembly (MEA) and gas diffusion layers (GDLs) needs to allow for efficient feed of reactants and removal of products within discrete modes and cyclic operation
- Fixed polarity electrodes optimize for gas and water management on ORR electrode
- Proposed URFC cell shown with baseline bifunctional catalysts:



Task 2: MEA development and testing

Approach:

- In cell water management as important as catalyst selection
- Determine target cell catalyst and diffusion layers
- Cell optimization to start with baseline materials and flowfields in discrete modes of operation, before cycling operation

Accomplishment

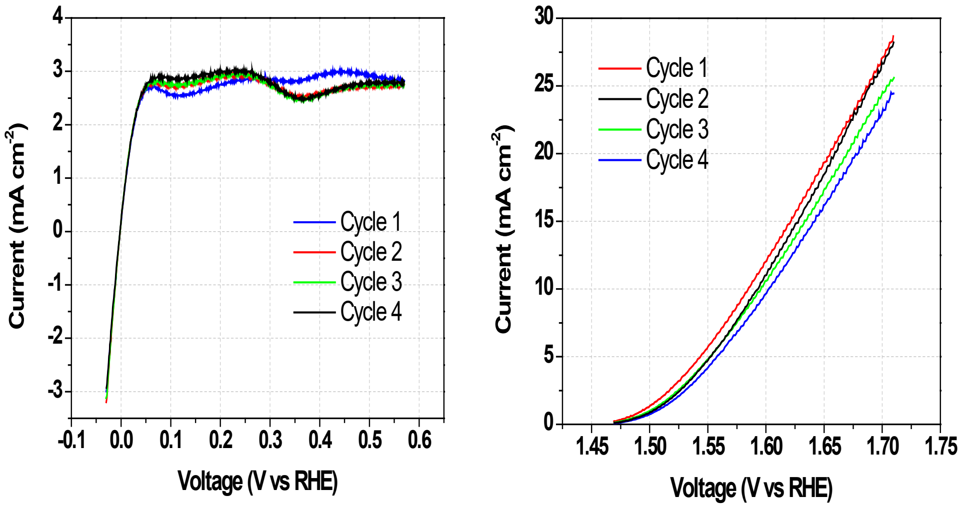
Identified baseline MEA and cell components

Electrode	Fuel Cell Mode	Electrolyzer mode	Catalyst and support	Target catalyst loading	Diffusion layer
Anode	HOR: $H_2 \rightarrow 2H^+ + 2e^-$	OER: $H_2O \rightarrow 2H^+ + ½ O_2 + 2e^-$	Baseline: Pt-IrO_2 blacks BP2: ANL catalyst	0.4 mg/cm^2 Pt 1 mg/cm^2 Ir	Sintered titanium porous transport layer
Cathode	ORR: $½ O_2 + 2H^+ + 2e^- \rightarrow H_2O$	HER: $2H^+ + 2e^- \rightarrow H_2$	Pt 46wt% @ C	0.4 mg/cm^2 Pt	Carbon paper with microporous layer

Task 3 (BP2) – Cyclability and Durability

Approach

- Preliminary data on physical mixtures of Pt-IrO_2 shows good stability between HOR/OER cycles



Pre-project result: RDE cycling of Pt-IrO2 between HOR and OER

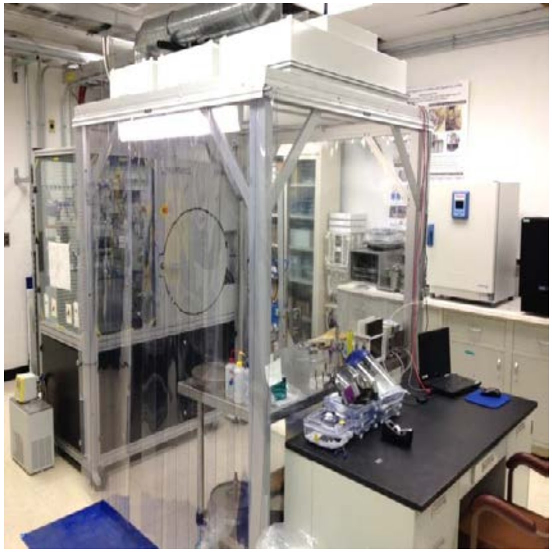
- Cycling and durability ASTs to be defined by operating use case and TEA analysis

Task 4 (BP2) – Cost Analysis

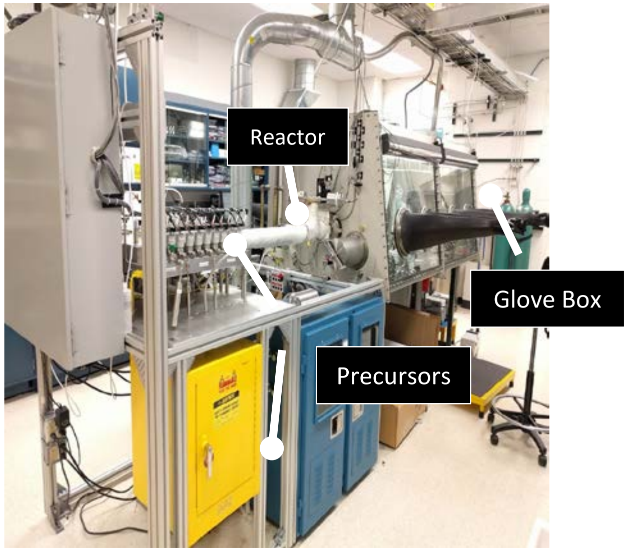
Approach:

- Opex and Capex of URFC will be defined and tracked
- To help define the competitive market and storage time/current density required
- Cell materials costs to be tracked based on catalyst loading GDLs and membrane

ALD Systems at Argonne



Beneq TFS500 – up to 20” 3D chamber, larger substrates, scale-up



Technical Accomplishments – URFC test stand

- A Fuel Cell Technologies fuel cell stand was retrofitted for use with this project and integrated with a DC power supply, water bath and pump
- A work planning and control document was written and a successful safety review held for the test stand

URFC Test Stand at LBNL

Technical Accomplishments – TEA Cost Analysis Protocol Definitions

- Framework for technoeconomic analysis established
- Comparison of discrete system component costs with URFC to be tracked over length of project

Component	FC†	ELEC	URFC§
System ($/kW)	50	900‡	tbd
Stack Cost ($/kW)	22	423‡	
Catalyst+Application (%)*	41	43¶	
Membrane (%)*	12	11¶	
MEA Frame/Gasket (%)*	6	4¶	
Porous transport layer/Gas diffusion layer (%)*	9	19¶	
Bipolar Plates (%)*	25	23¶	
Balance of stack (%)*	11	21¶	

* *Percent of stack cost*

† *Based on DOE projections from 2017 Hydrogen and Fuel Cells Program Record.*

‡ *Based on TEA from Strategic Analysis presented at Electrolyte Hydrogen Production Workshop 2014.*

¶*Based on TEA from Strategic Analysis of H2 Production Pathways, 2013.*

Collaboration & Coordination

Entities	Role	Type	Relationship with FCTO	Extent of collaboration
LBNL	Prime	Federal Lab	Within	
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

- Cost of of Pt and Ir catalysts
  - With optimization of the electrode structure we expect a net decrease in PM use (cost) over discrete systems
  - Key is a supported catalyst, using inexpensive support
  - Use of core-shell structures on cathode side will also reduce PM loading
- Stability of Pt and Ir under cycling between operating modes
  - Preliminary testing has shown stability equivalent to current fuel cell/electrolyzer components
- Water management
  - Challenges of water management may remain even with more optimal GDL/PTL layout in proposed design
  - May necessitate other strategies to manage water in cell
- Safety of H_2 storage and operation with O_2 presence
  - Pressurized storage of hydrogen has a strong industrial track record
  - URFC can be designed to output pressurized H_2 (compressor is unnecessary, saving compression energy)
  - Industrial collaborator has assured us that there are no technical or safety obstacles to proposed URFC

Proposed Future Work

- Screen HOR/OER activity and stability in RDE
- Deposit ALD Pt_xIr_{1-x} alloys on TiN and screen in RDE
- Baseline MEA and cell operation
  - Vary anode catalysts and test in discrete operation
  - Vary flowfields with discrete MEAs
  - Evaluate cycling of URFC MEA in down-selected cell hardware
  - Evaluate performance/durability of traditional vs proposed URFC concept
- Evaluate different HOR/OER activity catalysts in URFC MEA and cell
- Track performance and cell costs for TEA

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

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 TiN supports with ALD
- Technical Accomplishments
  - Test stand: Modified and safety review completed, testing protocols established
  - TEA: Defined materials and performance metrics
- Collaborations
  - ANL: sub on project will screen materials and produce novel supported catalysts for MEA integration
  - Established collabarations with two industrial partners
    - Proton OnSite (NEL): Provided catalysts for preliminary testing and for MEA screening
    - 3M: Discussions around utilizing NSTF based MEAs
- Proposed Future Work
  - ANL: Catalysts screening w/ RDE and supported catalyst development
  - LBNL: MEA testing, cell optimization and URFC cycling

Acknowledgments

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