



2018 DOE H<sub>2</sub> and Fuel Cell Annual Merit Review Meeting

# High-Temperature Alkaline Water Electrolysis

Hui Xu and Kailash Patil

Giner, Inc.

89 Rumford Ave,

Newton, MA

June 14, 2018

Project #  
PD 143

This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Project Overview

## Timeline

- Project Start Date: Jan. 1, 2017
- Project End Date: Dec. 31, 2019

## Budget

- Overall \$ 1,722,885
  - DOE share \$ 1,375,123
  - Contractors share \$ 347,762
  - Spent \$ 592, 422 (by April 2018)

## Giner Researchers

Kailash Patil, Andrew Sweet, and Winfield Greene

## Collaborator

- University of Connecticut (Sub.)
- Giner ELX (Sub.)
- Zircar Zirconia, Inc. (Vendor)

## Barriers Addressed for HTWE

- Operating cost: prohibitive electricity consumption for water electrolysis
- Capital cost: associated with PGM or expensive high temperature materials

## Technical Targets

- Composite electrolyte OH<sup>-</sup> conductivity > 0.1 S/cm in temperature of 300 to 550 °C
- Per-cell area-specific resistance (ASR) of ≤ 0.2 Ohm-cm<sup>2</sup> at 300 to 550 °C using a membrane thickness of 200 μm.
- Stack electrical efficiency > 90% LHV H<sub>2</sub> with current density at 1.2 A/cm<sup>2</sup>

# Relevance

## Overall Project Objectives

To develop high-temperature alkaline electrolysis using molten hydroxides in porous metal oxide matrix

## FY 2017-18 Objectives

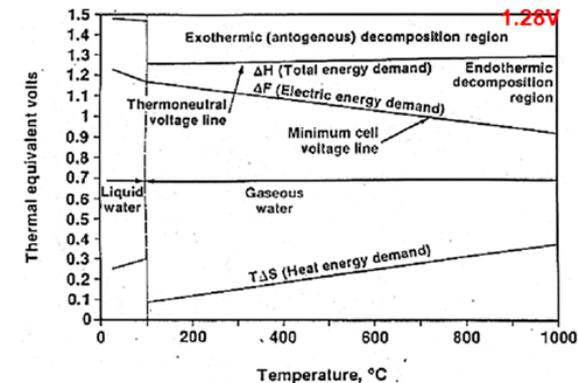
- ❑ Develop electrolyte support metal oxide matrix
- ❑ Impregnate selected hydroxides into porous matrices to make composite electrolytes
- ❑ Select anode and cathode catalysts with enhanced HER and OER activity
- ❑ Assemble single electrolyzer cells and test **their** performance and durability in the temperature range of 300-550 °C.

## Impact

- ❑ Reduce the capital and operating costs of water electrolysis to meet DOE goals and to make water electrolysis more viable and competitive against other technologies

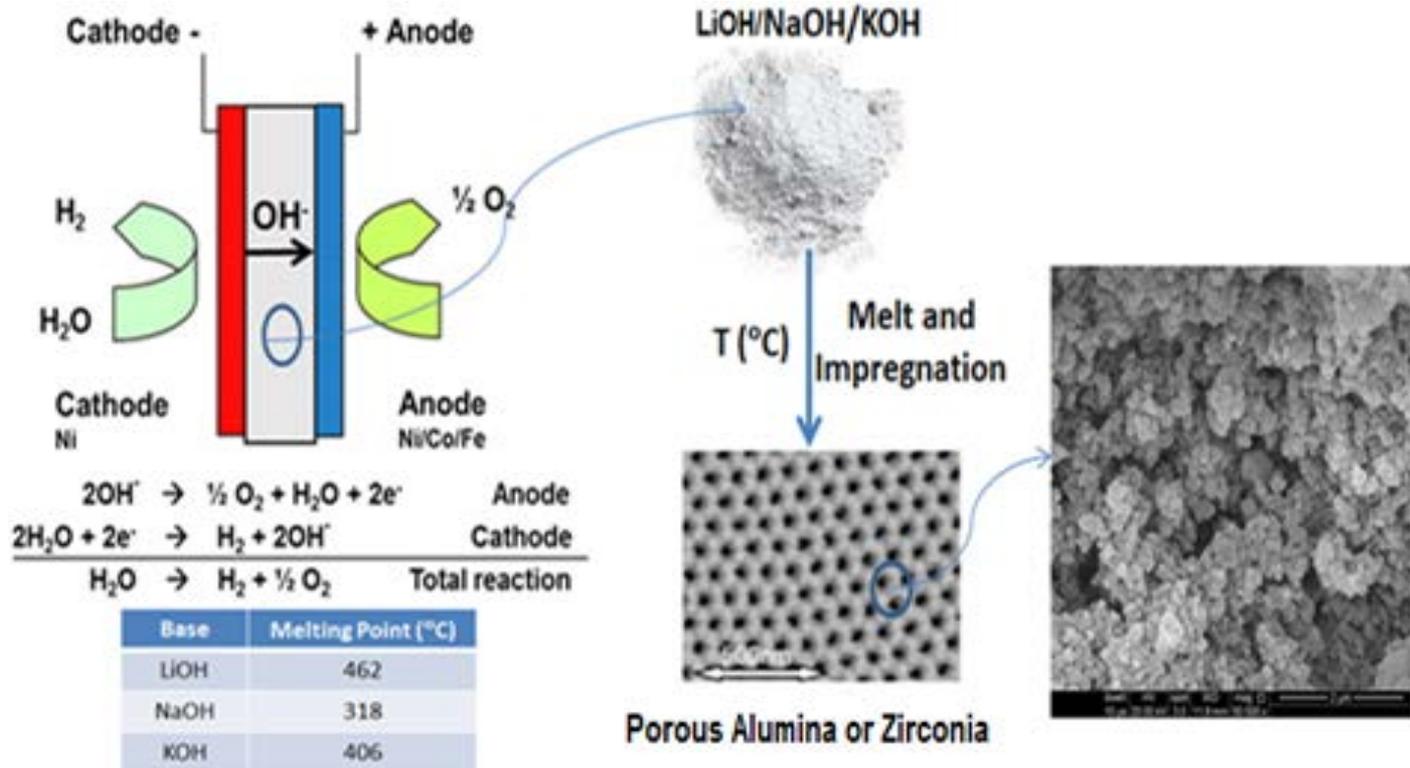
## DOE: Distributed Forecourt Water Electrolysis

Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost <sup>d</sup> (Production Only)	\$/kg	4.20 <sup>d</sup>	3.90 <sup>d</sup>	2.30 <sup>d</sup>
Electrolyzer System Capital Cost	\$/kg \$/kW	0.70 430 <sup>e,f</sup>	0.50 300 <sup>f</sup>	0.50 300 <sup>f</sup>
System Energy Efficiency <sup>g</sup>	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency <sup>h</sup>	% (LHV)	74	76	77
	kWh/kg	45	44	43
Electricity Price	\$/kWh	From AEO 2009 <sup>i</sup>	From AEO 2009 <sup>i</sup>	0.037 <sup>j</sup>



- ❑ Feedstock costs (electricity) consists of 50% of total cost
- ❑ High-temperature electrolysis offers the advantage of lower energy requirements due to both faster kinetics and greatly reduced equilibrium voltages

# Technical Approaches



## Major Advantages

- ❑ Flexible temperatures- intermediate T compared to PEM and SO system)
- ❑ Less expensive materials

## Key to Success

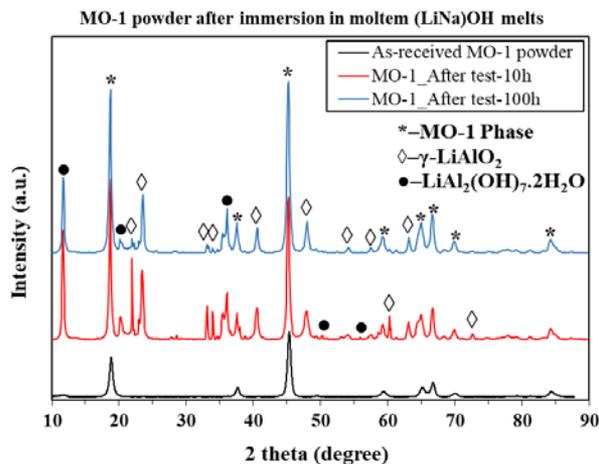
- ❑ Porous metal oxide matrices resistant to molten hydroxides
- ❑ Microstructures of the porous oxide matrices determine whether they can successfully retain molten hydroxides
  - thickness, porosity and pore structures

# Approach: 2017-18 Tasks and Milestone Progress

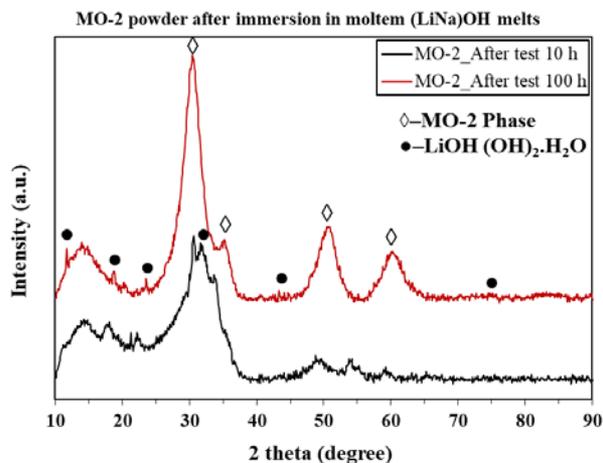
Task No.	Task Title	Milestone Description	Progress Notes	Status
1	<b>Develop Alumina and Zirconia Matrices</b>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Produce five LiAlO<sub>2</sub> matrices with various porosity (50-80%) and thickness (200-300 μm)</li> <li><input type="checkbox"/> Produce six ZrO<sub>2</sub> and YSZ matrices with various porosity (50-80%) and thickness (200-300 μm)</li> </ul>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Developed and fabricated LiAlO<sub>2</sub>, ZrO<sub>2</sub> and YSZ matrices</li> <li><input type="checkbox"/> Developed various porosity (50-80%) and thickness (200-300 μm) of porous matrices</li> </ul>	100%
2	<b>Impregnated Hydroxide into Porous matrices</b>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Down select at least six composite electrolytes with OH<sup>-</sup> σ &gt; 0.1 S/cm</li> <li><input type="checkbox"/> Down select at least four composite electrolyte membranes with ASR &lt;0.2 Ohm-cm<sup>2</sup></li> </ul>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Developed composite electrolyte matrix</li> <li><input type="checkbox"/> Achieved the OH<sup>-</sup> ion conductivity σ &gt; 0.5 S/cm</li> <li><input type="checkbox"/> Achieved ASR &lt;0.1 Ohm-cm<sup>2</sup></li> </ul>	100%
3	<b>Select Anode and Cathode catalysts</b>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Synthesized four OER catalysts with particle size &lt; 20 nm, activity comparable to Ir-black</li> <li><input type="checkbox"/> Select cathode catalyst</li> </ul>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Developed and fabricated anode catalyst</li> <li><input type="checkbox"/> Developed and fabricated cathode catalyst</li> </ul>	100%
4	<b>Assemble and Test single cells</b>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Complete testing at least 5, 25 cm<sup>2</sup> cells with composite electrolytes</li> <li><input type="checkbox"/> Performance test</li> </ul>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Designed and construct HT-electrolyzer test station</li> <li><input type="checkbox"/> Designed button cell area of 13 cm<sup>2</sup></li> </ul>	100%
<b>Go/No-go Decision: FY2018 (06/30/2018)</b>		<ul style="list-style-type: none"> <li><input type="checkbox"/> <b>Achieve single cell performance V &lt; 1.50 V at 1.0 A/cm<sup>2</sup> or 1.4 V at 0.5 A/cm<sup>2</sup></b></li> </ul>	<ul style="list-style-type: none"> <li><input type="checkbox"/> Testing with different cell component configuration</li> <li><input type="checkbox"/> Developed gas sealing materials</li> <li><input type="checkbox"/> Suppressing corrosion of bipolar plates</li> </ul>	<b>90%</b>

# Accomplishment 1: Stability of Metal Oxides in Molten Hydroxides

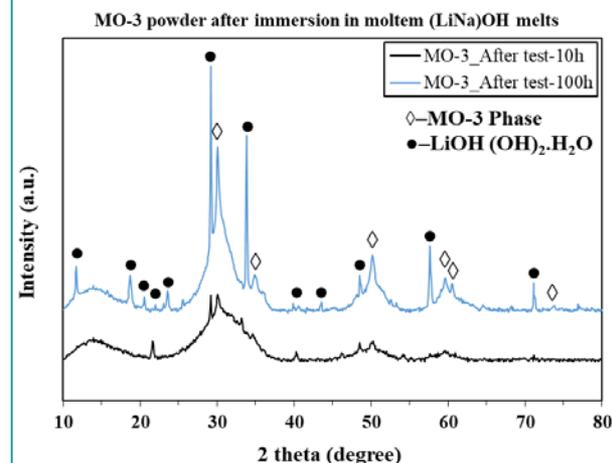
Immersing metal oxide powder in molten (LiNa)OH at 550°C for 100 h



- Major phase: MO-1 phase
- Minor phases: LiAlO<sub>2</sub> and LiAl<sub>2</sub>(OH)<sub>7</sub>·2H<sub>2</sub>O
- Phase transformation occurred in MO-1 powder ( $\alpha$  to  $\gamma$  of LiAlO<sub>2</sub> phase) after 10 h



- Major phase: MO-2 phase
- Minor phase: LiOH(OH)<sub>2</sub>·2H<sub>2</sub>O
- MO-2 phase did not change after 10 and 100 h test



- Major phase: MO-3 phase
- Minor phase: LiOH(OH)<sub>2</sub>·2H<sub>2</sub>O
- MO-3 phase stable after 10 and 100 h test

Phase transformation occurred in MO-1 ( $\alpha$  to  $\gamma$  of LiAlO<sub>2</sub> phase) after 100 h test

# Stability of Metal Oxides in Hydroxides

Immersing metal oxide matrix in molten (LiNa)OH at 550°C for 100 h

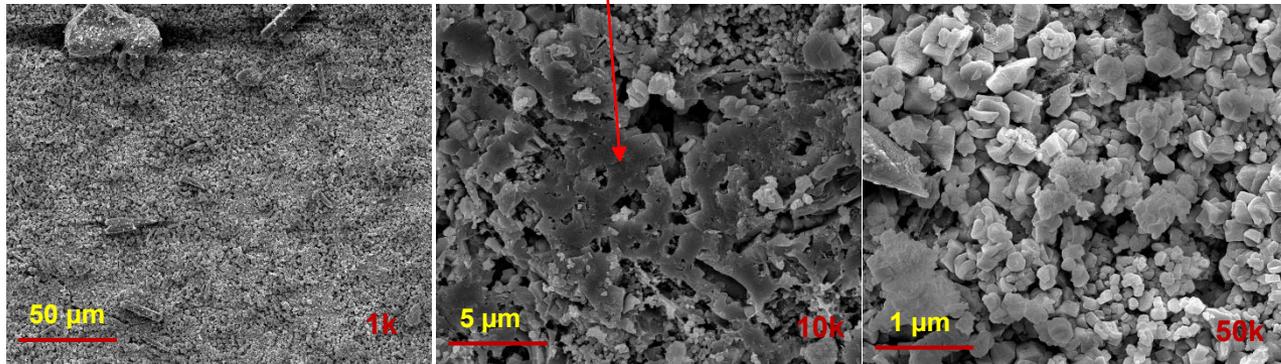
MO-1



Covered Molten hydroxide

Large agglomeration MO particles

MO-3

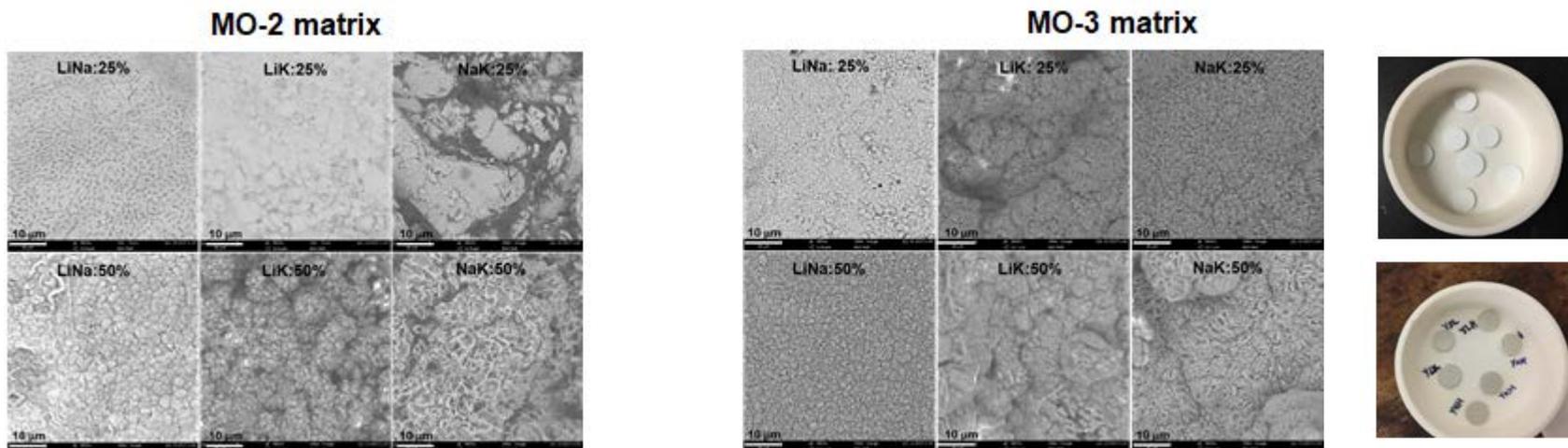


- The MO particles covered with molten hydroxide
- Well defined large agglomerated particles in MO-1 matrix
- Uniform particle size of MO-3 was observed after 100 h of test

# Accomplishment 2: Impregnated Electrolyte into Matrix

Metal oxides Matrices	Hydroxides system	Single/Binary composition (mol. %)	Melting Temperature (°C)	Electrolyte impregnated (wt. %)	Loss of hydroxides (wt. %)
MO-1 MO-2 MO-3	LiOH	100	462	50	20
	NaOH	100	318	50	15
	KOH	100	406	50	17
	LiOH-NaOH	52-48	~300	25 & 50	12 & 28
	LiOH-KOH	62-38	~325	25 & 50	10 & 29
	NaOH-KOH	52-48	~225	25 & 50	14 & 36

## Surface morphology of binary hydroxide impregnated into the MO matrix



□ Slight change of MO surface morphology after impregnating hydroxides into the matrix

# Measurement of OH<sup>-</sup> Conductivity

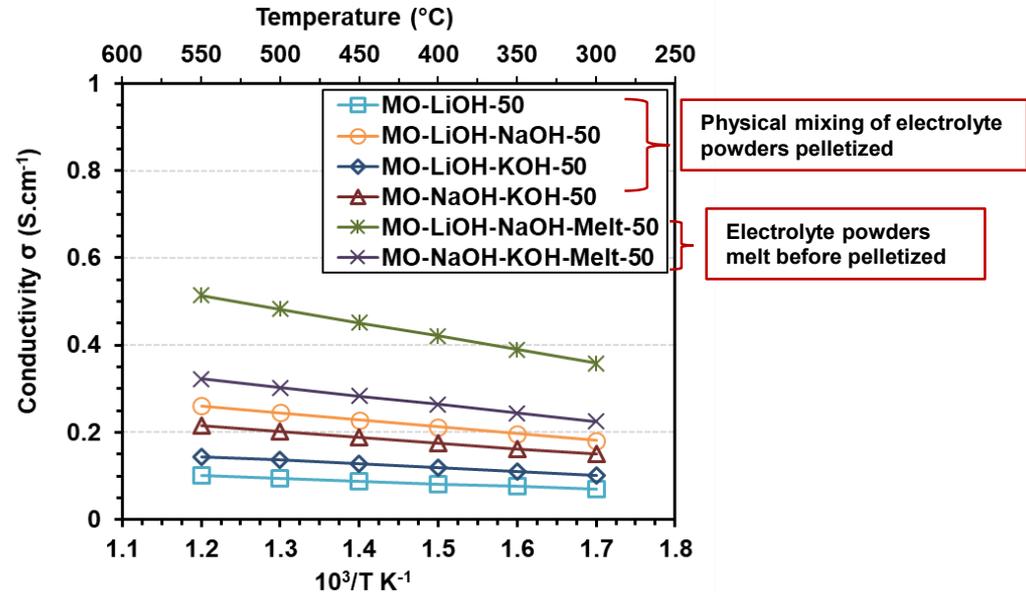
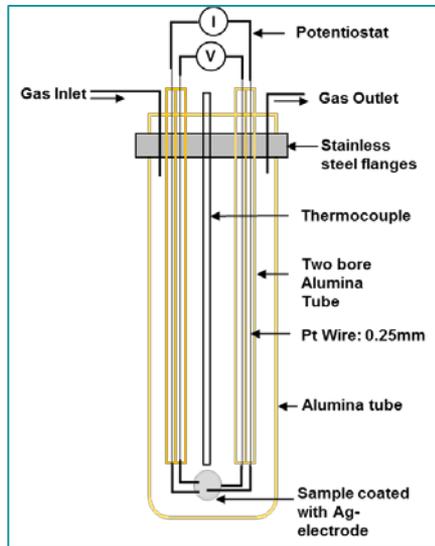
Metal oxide and molten Hydroxides

Mixing and pressing pellet

Sintered @ 650°C for 2 h

Ag-coated and Sintered at 650 °C for 2 h

Characterizations: EIS and ASR

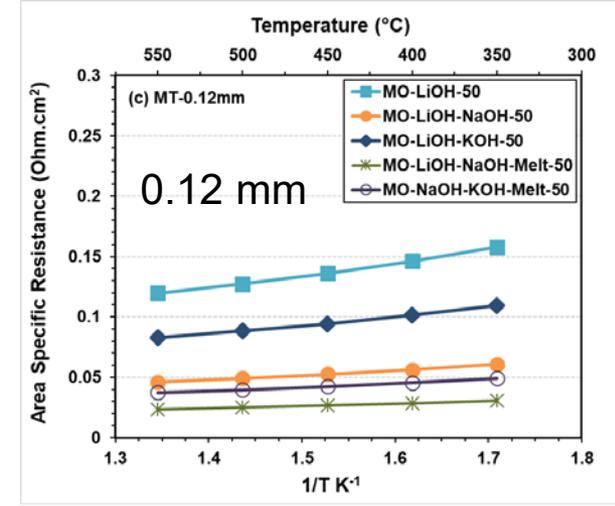
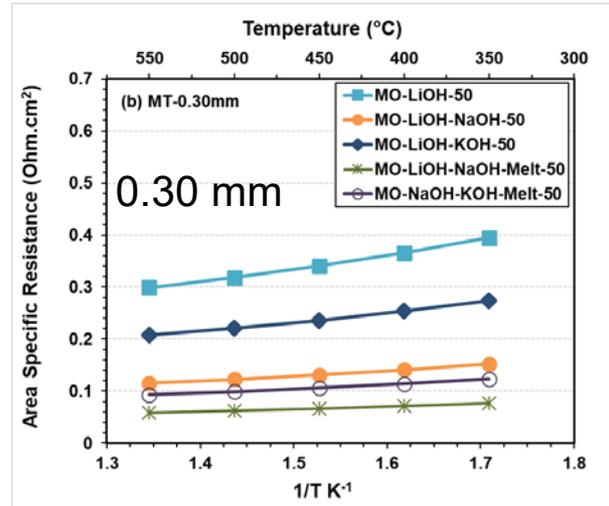
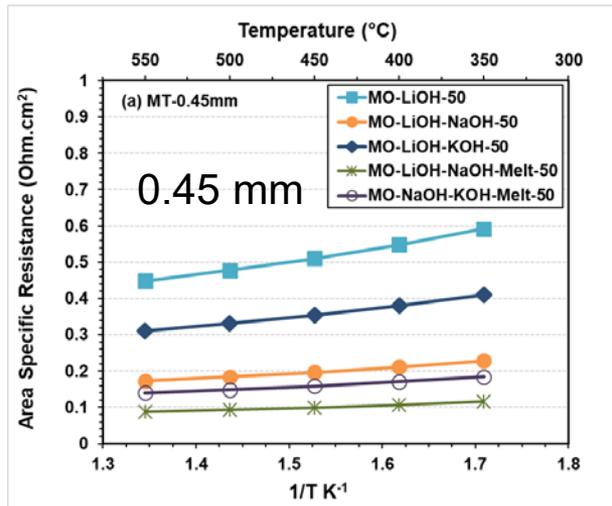


- ❑ The average composite electrolyte powder consists of ~50 wt. % of hydroxide and ~50 wt. % of metal oxide.
- ❑ The binary LiOH/NaOH hydroxide melt showed the highest OH<sup>-</sup> ion conductivity, **0.52 S/cm at 550 °C**.
- ❑ The conductivity of the single/binary hydroxide electrolyte improved with increasing temperature.

Met Q3 Millstone “Down-select at least six electrolytes with conductivity > 0.1 S/cm”

# Area Specific Resistance Measurement

## MO-3



- ❑ The ASR decreased as the temperature lowered from 350 to 550 °C, regardless of the matrix thickness.
- ❑ The matrix with a thickness of 0.12 mm (120 μm) achieved ASR less than 0.02 Ohm-cm<sup>2</sup>.

**Met Q4 milestone “Down-select four composite electrolytes with ASR <0.2 Ohm-cm<sup>2</sup>”**

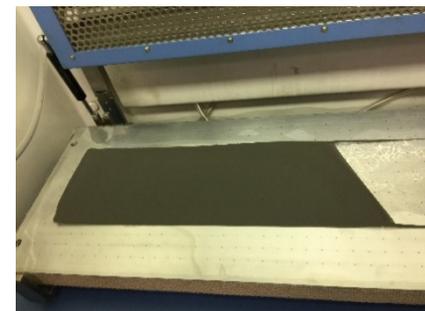
# Accomplishment 3: Tape Cast of Matrix and Electrodes

Developed electrolyte support MO matrix and electrodes (Anode and Cathode)

Matrices	Sr. No.	Matrix and Cathode Thicknesses (mm)	
		Green sheet tape	After sintering
MO-1	1	0.55	0.50
	2	0.33	0.32
	3	0.25	0.23
MO-2	1	0.48	0.43
	2	0.40	0.35
	3	0.35	0.20
MO-3	1	0.37	0.33
	2	0.12	0.11
Cathode	1	0.35	0.33
	2	0.20	0.18
Anode	1	0.33	0.30
	2	0.20	0.17



Thinner MO-3 green sheet matrix

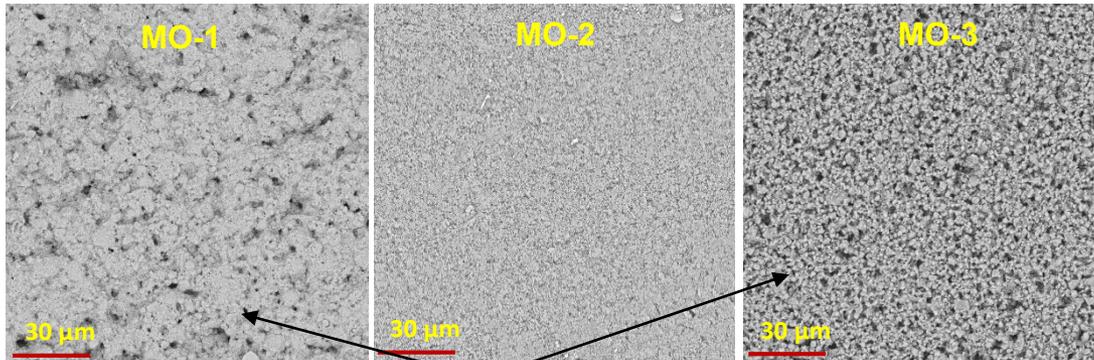


Electrode green sheet matrix

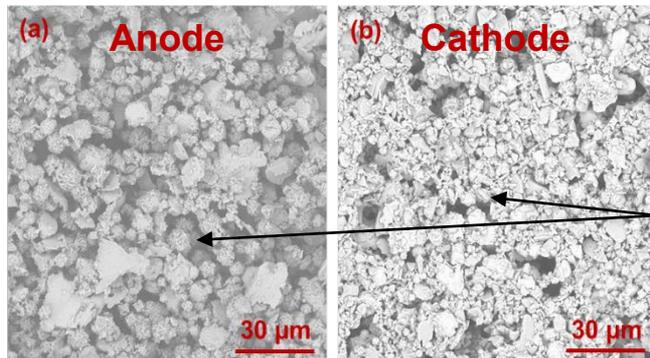
- ❑ Successfully fabricated the electrodes and matrix using tape casting method
- ❑ Optimized green tape of the electrodes and matrix using solvent based slurry process
- ❑ Lab scale 10"x 26" wide, electrode and thinner matrix green tape fabricated

# Characterizations of Electrodes and Electrolyte Matrix

## Surface morphology of sintered MOs matrix and electrodes

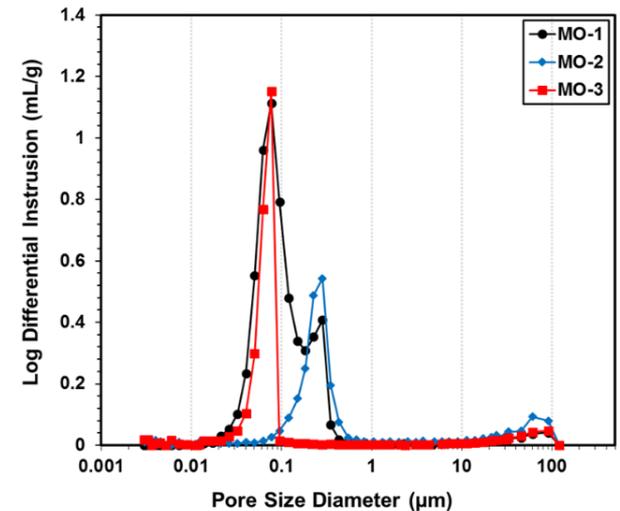


MOs porous matrix structure



porous electrodes structure

## Pore size distributions of sintered MOs matrices



Ideal range between 100 to 200 nm of pore size to retain electrolyte

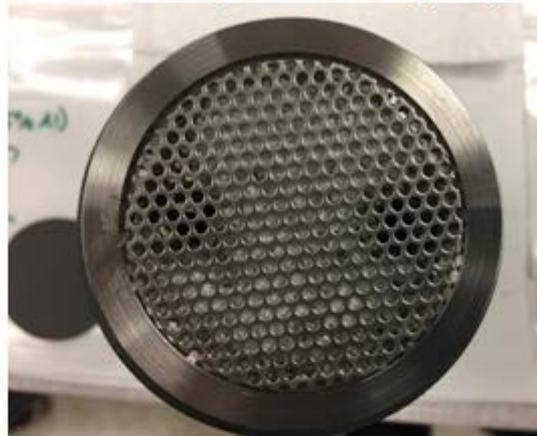
- The median pore size diameter of the prepared MO-1, MO-2 and MO-3 matrices were 0.096, 0.30 and 0.080 μm, respectively
- Sintered MOs matrices and electrodes showed porous structure along with no cracks being observed after sintering at 550 °C in air atmosphere for 2 h

# Accomplishment 4: Single Cell Components

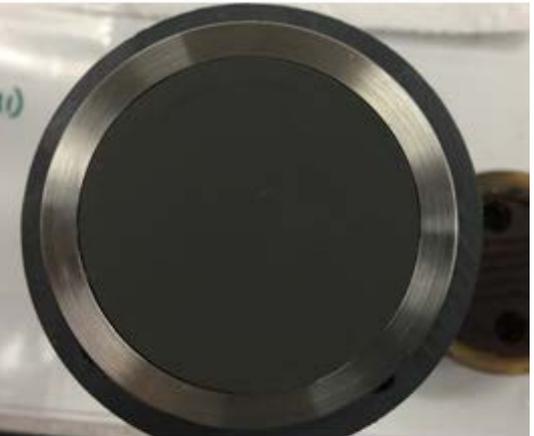
Button Cell Components



Electrolyte stored in cell compartment (CD)



Electrode (CD)



Anode, Cathode and Matrix



- Anode and Cathode: 13 cm<sup>2</sup>
- Matrix: 16 cm<sup>2</sup>

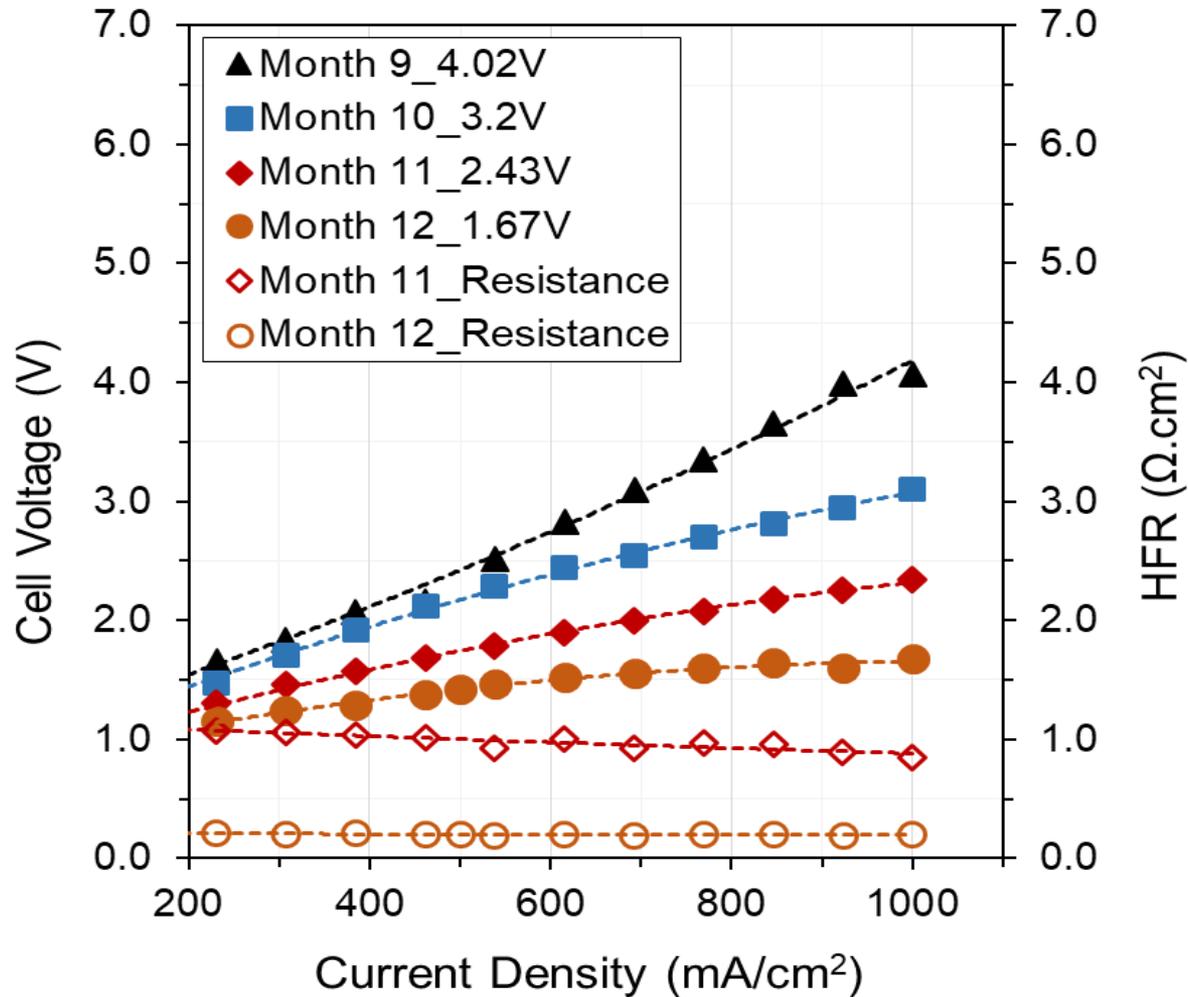
Cell Assembly



Button cell in the Furnace



# Cell Performance Progression



□ Steady progress towards HFR reduction and performance improvement

# Efforts to Improve Cell Performance

Corroded

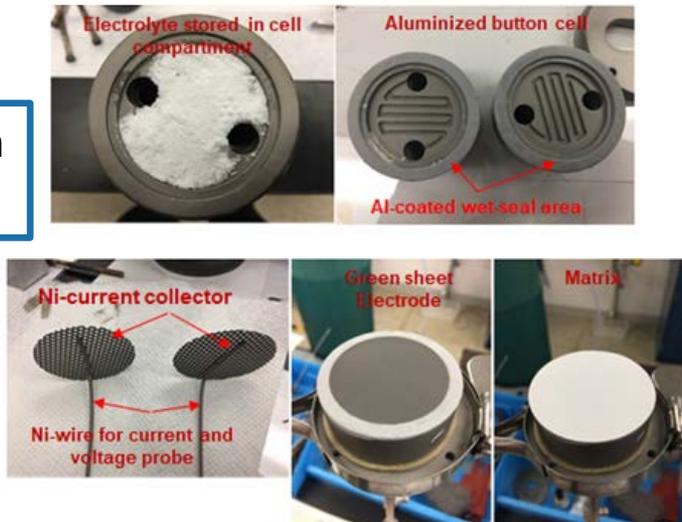


- ❑ Active component improvements
  - HER and OER Catalysts optimization (Ni-or Ni-Co based)
  - Reduced matrix thickness from 0.5 mm to 0.2 mm

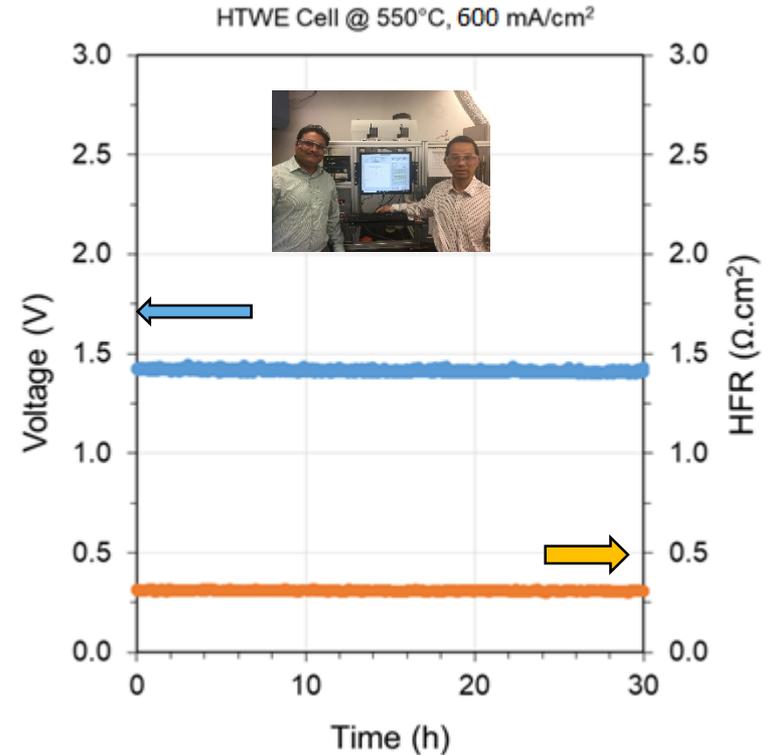
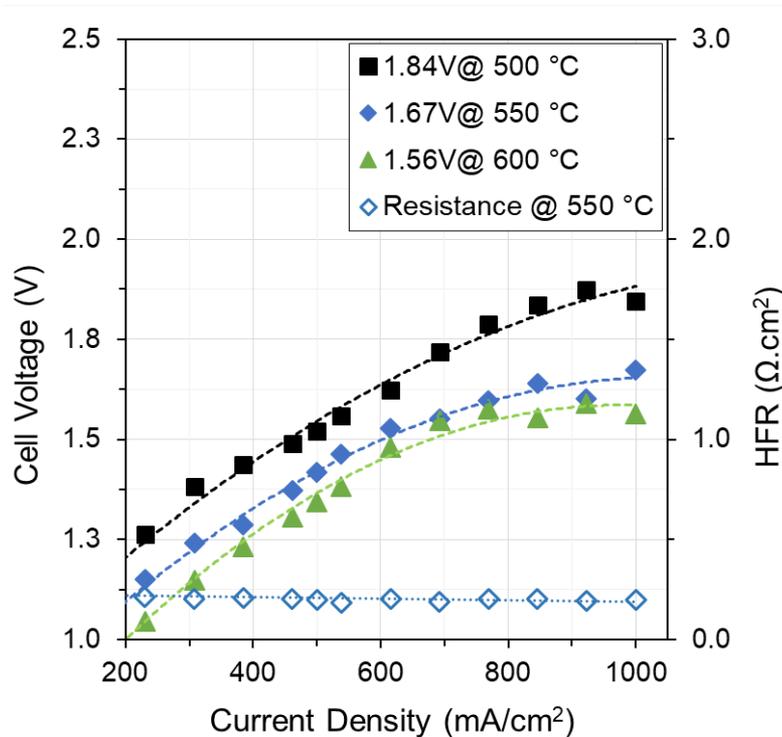
- ❑ Inactive component improvements
  - Ni vs SS current collector for corrosion resistance
  - Aluminized wet-seal area

- ❑ Operating conditions;
  - Increase water flow rate
  - Temperature effect

Corrosion-resistant



# Cell Performance and Durability

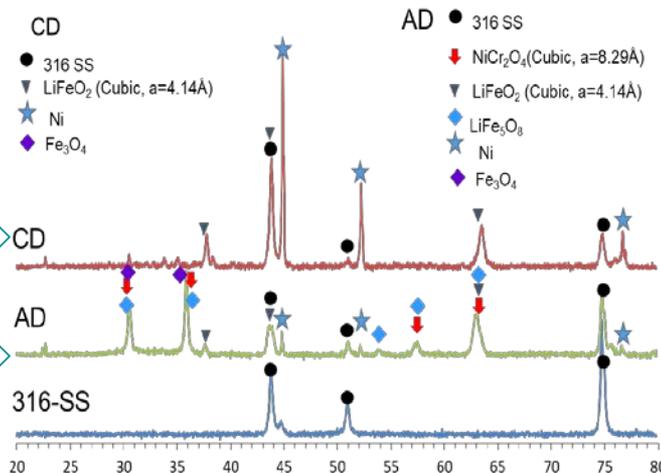
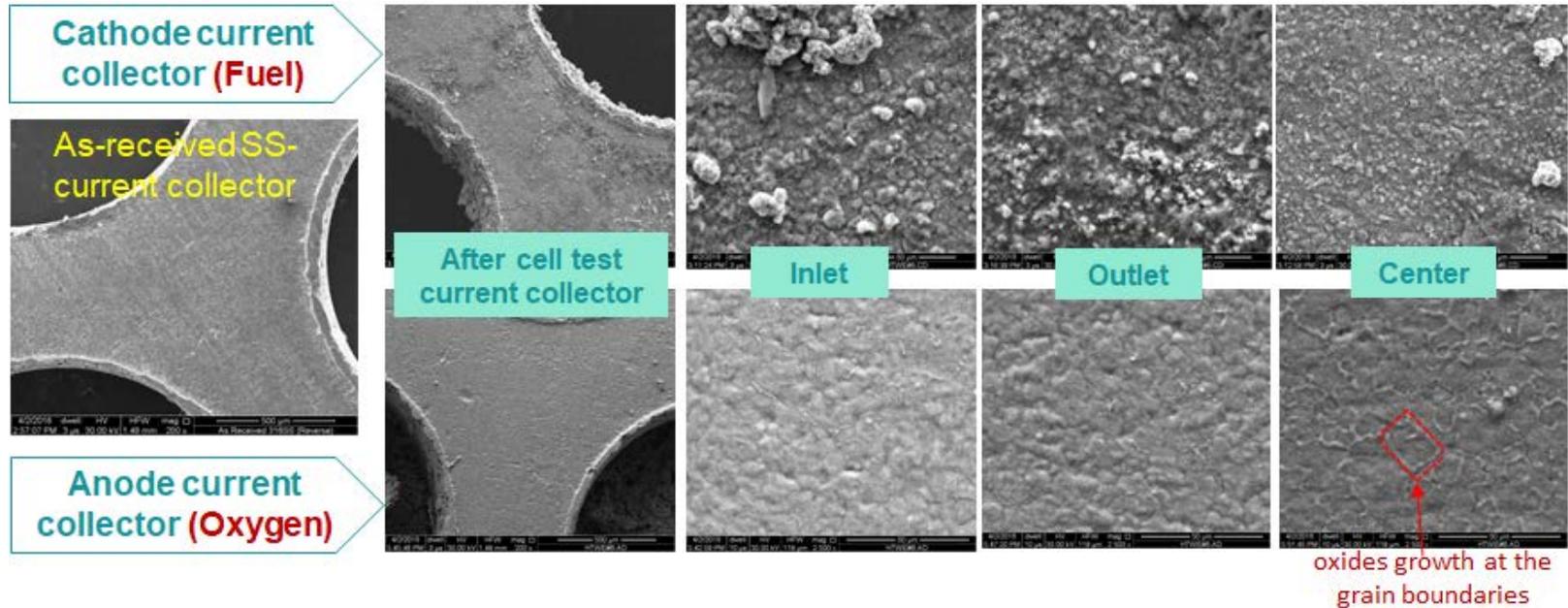


- ❑ Cell performance @ 550 °C: 1.42 V at 0.6  $\text{A}/\text{cm}^2$
- ❑ Achieved cell performance with durability of 30 hours

**Nearly Met Go/No Go Decision Point-** Achieving electrolyzer performance of either  $< 1.50 \text{ V}$  at a current density of  $1.0 \text{ A}/\text{cm}^2$  or  $< 1.40 \text{ V}$  at  $0.6 \text{ A}/\text{cm}^2$ . This performance needs to be maintained for at least 30 min. in the temperature range of 300-550 °C

# Accomplishment 5: Post Analysis

## Effect of "Fuel and Oxygen" production on current collectors



Formation of major  $\text{LiFeO}_2$  phase

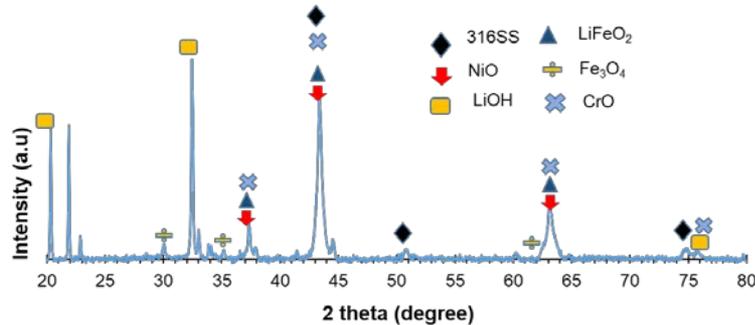
Formation of mixed oxide scales

- Distinct oxide morphologies are observed at the inlet-center-outlet of the SS-cathode current collector
- No apparent surface scale formation appears on the anode current collector from inlet to outlet

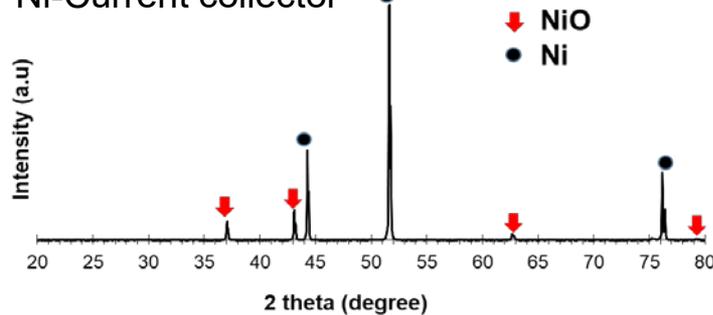
# Matrix Stability and Corrosion Tests

- Metal stability (SS 316 and Ni) in molten (LiNa)OH at 550°C for 50 hrs. in air
- Experimental test set up designed for matrix solubility measurement

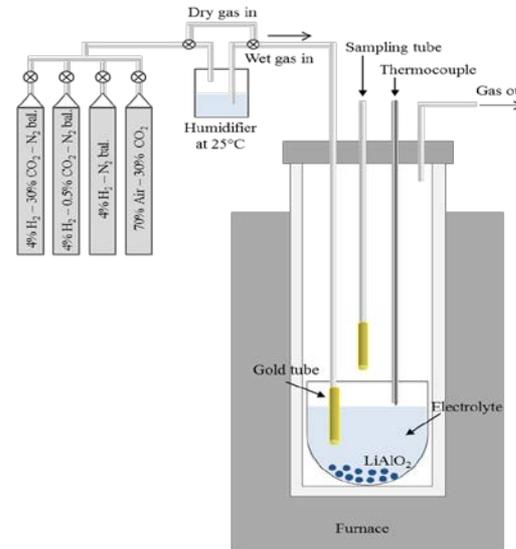
## ➤ SS 316-Current collector



## ➤ Ni-Current collector



## ➤ Matrix solubility measurement set up



### Operation Conditions

Matrix: MO-3; Electrolyte: molten (LiNa)OH

Atmosphere: N<sub>2</sub>-Steam, H<sub>2</sub>-H<sub>2</sub>O, and O<sub>2</sub>-H<sub>2</sub>O

Temperature: 550°C; Immersion time: ~1000 h (equilibrium)

- ❑ Corrosion tests of SS showed surface corrosion products formation
- ❑ Matrix solubility measurement in hydroxide medium have been initiated

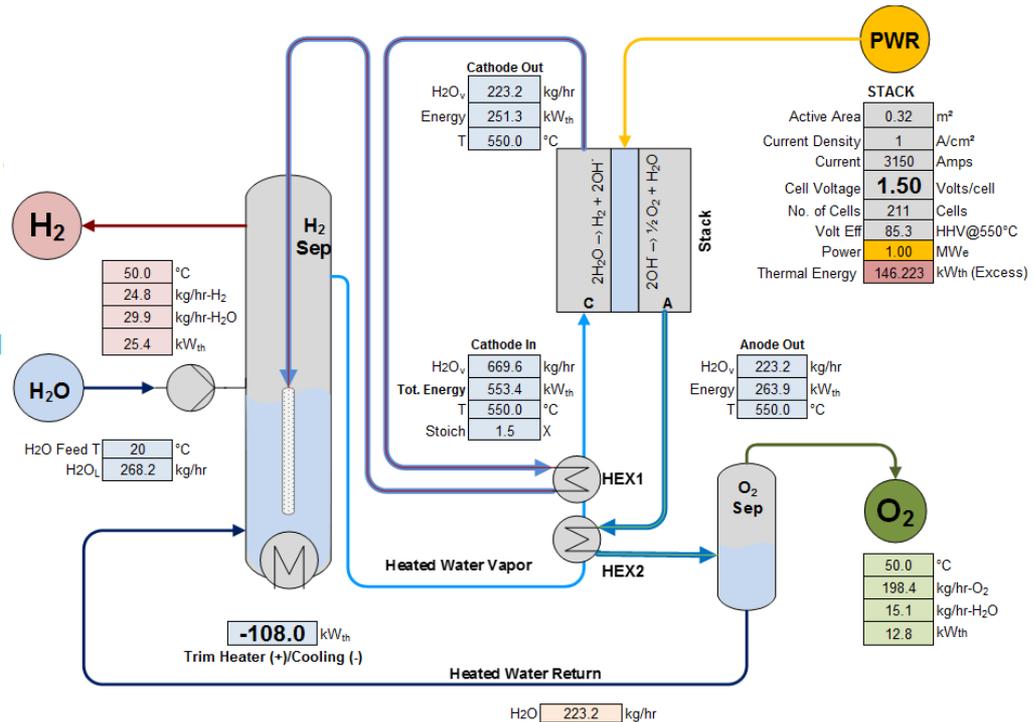
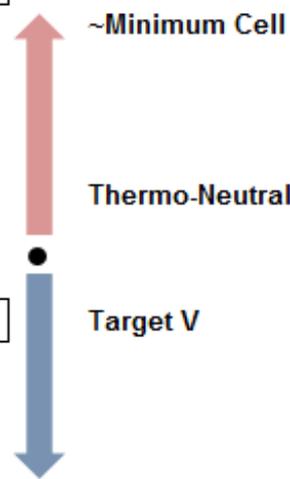
# Accomplishment 6: Energy Balance and Cost

## HT Alkaline Electrolysis, 1MW Mass & Energy Balance, 1.5 V Voltage Target

### Review:

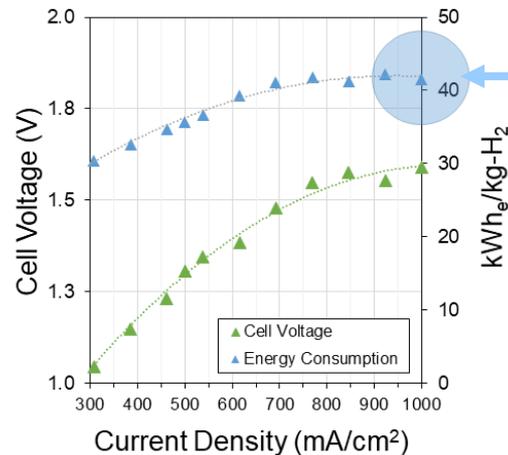
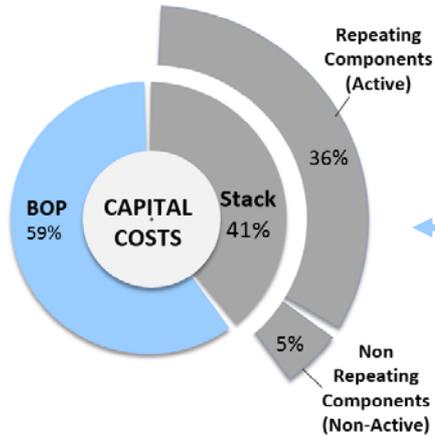
- Mass/Energy Balance assuming 90% Heat recovery from HEX
- Energy equations take into account latent heat  $H_v$ , and water losses from gas exhaust streams (additional water feed required to maintain balance)

Trim Heater/Cooling	
Cell Voltage	Trim Heat
(V)	kW <sub>th</sub> *
0.900	291
1.000	224
1.100	157
1.200	91
1.280	38
1.300	25
1.400	-42
<b>1.500</b>	<b>-108</b>
1.600	-175
1.700	-241
1.800	-307



\* Assumes 90% heat recovery from HEX

# Cost Analysis



CapEx

OpEx

H <sub>2</sub> Production Cost Contribution	HT Alkaline Cost (\$/kg)
Capital Costs <sup>1</sup>	0.38
Feedstock Costs <sup>2</sup>	1.53 (39.3 kWh/kg)
Fixed O&M	0.75
Variable Costs	0.020
<b>Total Hydrogen Production Cost (\$/kg)<sup>3</sup></b>	<b>2.68</b>
Delivery (CSD)	2.46
<b>Total Hydrogen Production Cost (\$/kg)</b>	<b>5.14</b>

CSD Related Cost

1 Bar	\$3.79/kg
20 Bar	\$2.46/kg
40 Bar	\$2.24/kg

PEM Comparison Cost (\$/kg)
1.30
1.96 (50.5 kWh/kg)
0.70
0.020
<b>3.98</b>
2.46
<b>6.44</b>

<sup>1</sup>20 year lifetime, <sup>2</sup>Based on low electrical cost of \$0.039/kWh, <sup>3</sup>Design Capacity: 1500 kg-H<sub>2</sub>/d. Assumes large scale production.

- Economics: determined using H2A cost models
- Based on 1 A/cm<sup>2</sup> Operation. Increasing Active Area & Operating Current Density reduces Capex

# Collaborations

<b>Giner, Inc.</b> -Prime Hui Xu	Industry	Fabrication and optimization of HER and OER catalysts; composite metal oxide development and optimization; cell fabrication, testing & validation.
<b>Giner ELX, Inc.</b> -Subcontractor Monjid Hamdan	Industry	Energy balance, stack and system engineering development.
<b>University of Connecticut</b> -Subcontractor Prabhakar Singh	Academia	Development of the fundamental understandings of the matrix coarsening and corrosion of the components in the molten hydroxide medium.
<b>Zircar Zirconia</b> -Vendor	Industry	Supply of metal oxide powders and matrix

# Summary

- ❑ Successfully developed(?) MO matrix using tape casting process
  - Slurry formulation process optimized to obtain thin green sheet matrix (~100  $\mu\text{m}$ )
- ❑ Stability of sintered matrix soaked in binary hydroxide melts was validated
  - MO powders showed stable phases in molten hydroxide at 550 °C for more than 100 hours
- ❑ OH<sup>-</sup> ion conductivities and calculated area-specific resistance (ASR) were achieved:
  - High OH<sup>-</sup> ion conductivity (0.5 S/cm) of molten binary hydroxide was achieved, which far exceeded the milestone of 0.2 S/cm
  - Low ASR (0.02 Ohm.cm<sup>2</sup>) of the composite electrolyte was achieved with a matrix thickness of 0.12 mm, which is far below the milestone of 0.2 Ohm-cm<sup>2</sup>
- ❑ Electrolyzer cells using HTAE have been validated and performance steadily improved
  - Components (active and inactive) improvements
  - Performance and short-time durability Nearly hit Go/NO Go point
- ❑ Preliminary energy balance of 1MW water electrolysis was conducted:
  - Electrical efficiency can be higher than 90% at 550 °C
  - Tremendous cost savings can be realized using HTAE

# Future Plans and Challenges (FY18-19)

## Future Plans

- ❑ Matrix and composite electrolyte optimizations
  - ❑ Matrix material stability
  - ❑ Optimize the electrolyte evaporation rate with MO-matrix
  - ❑ Optimize electrolyte compositions-e.g. ternary electrolyte inventory
- ❑ HER and OER catalysts optimizations
  - ❑ Fabricate thinner electrodes
  - ❑ Optimize microstructure design
- ❑ Components corrosion mitigations
  - ❑ Optimize Ni-based current collector

## Future Challenges

- ❑ Maintaining the electrolyte in the single/stack cells for long term durability
- ❑ Maintaining the seals of single/stack cells

# Reply to Reviewers' Comments

❑ The seals are not sufficiently developed, and there is no mention of how sealing will be done. The team lacks expertise in developing seals. The project has not done a sufficient thermodynamic analysis to see whether the 90% efficiency target is feasible.

**Reply:** *Two key team members of this project including the PI worked for Fuel Cell Energy, Inc. for many years and learned how to develop wet dealing. We have conducted energy balance on Slide 19 and found that 90% efficiency is feasible (corresponding voltage 1.42 V) assuming thermal neutral voltage to be 1.28 V. We will be able to reach 1.42 basing on our tremendous progress in the 1<sup>st</sup> year.*

❑ The thermal (latent heat of vaporization) energy penalty of using an OH<sup>-</sup> conductor for hydrogen generation is a weakness.

**Reply:** *We performed energy balance on Slide 19. The energy equations take into account latent heat  $H_v$  and water losses from gas exhaust streams (additional water feed required to maintain balance). As long as the voltage is above 1.4V and 90% heat can be recovered, the stack can sustain its operation without needing external heat source.*

❑ There is insufficient consideration of technical challenges in the design of the work plan and the identification of risks and issues is lacking.

**Reply:** *The major risk/challenge is hot corrosion, which may lead to a tremendous increase of cell resistance and component failure. We have developed appropriate strategies to mitigate this problem including using corrosion-resistant materials and lowering operating temperature. The other risk is electrolyte evaporation during long-term operation. This risk will be mitigated via meticulous design matrix pore size and structures.*

❑ The proposed historically low-temperature electrocatalysts seem to be warranted, but their stability at higher temperatures is likely poor. Evaluating electrocatalysts from the solid-oxide conductor field may be a better approach because it is unlikely that their kinetics at these reduced temperatures will be that poor.

**Reply:** *We have added University of Connecticut (UConn) as a subcontractor. The sub-PI at UConn has substantial experience in SOFC development. We will develop catalysts developed from SOFC field.*

❑ Longer-term testing on material stability (only 10 hours to date) is recommended.

**Reply:** *we have tested the matrix stability in molten hydroxides up to 100 hours. We have also developed an accelerated stress test (AST, Slide 18) to test the matrix solubility in molten hydroxides.*

# Acknowledgments

- ❑ Financial support from DOE EERE Fuel Cell Technology Office under award # DE-EE0007644
- ❑ DOE program manager: Dr. David Peterson
- ❑ Giner Personnel
  - Corky Mittelsteadt
- ❑ Fuel Cell Energy: Dr. Chao-yi Yuh

# Back-up Slides

# Stability of Metal Oxides in Hydroxide System

Physical properties of Metal oxides	Hydroxide system	Single/Eutectic Composition	Melting Temperature (°C)
MO-1	LiOH	100	462
MO-2	LiOH-NaOH	52-48	~300
MO-3	LiOH-KOH	62-38	~325

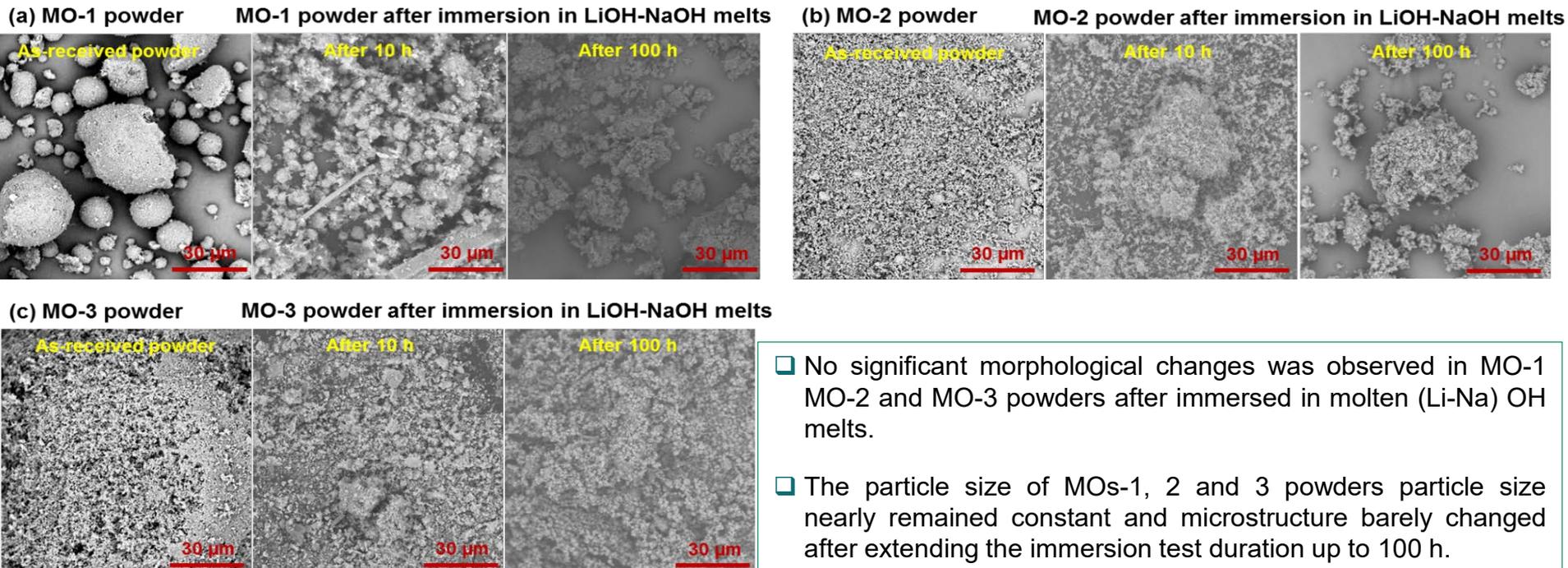
**Approach:** Metal oxide immersed in molten Hydroxides

Heat-treated at 550°C for 10 and 100 h

Washed and Dried

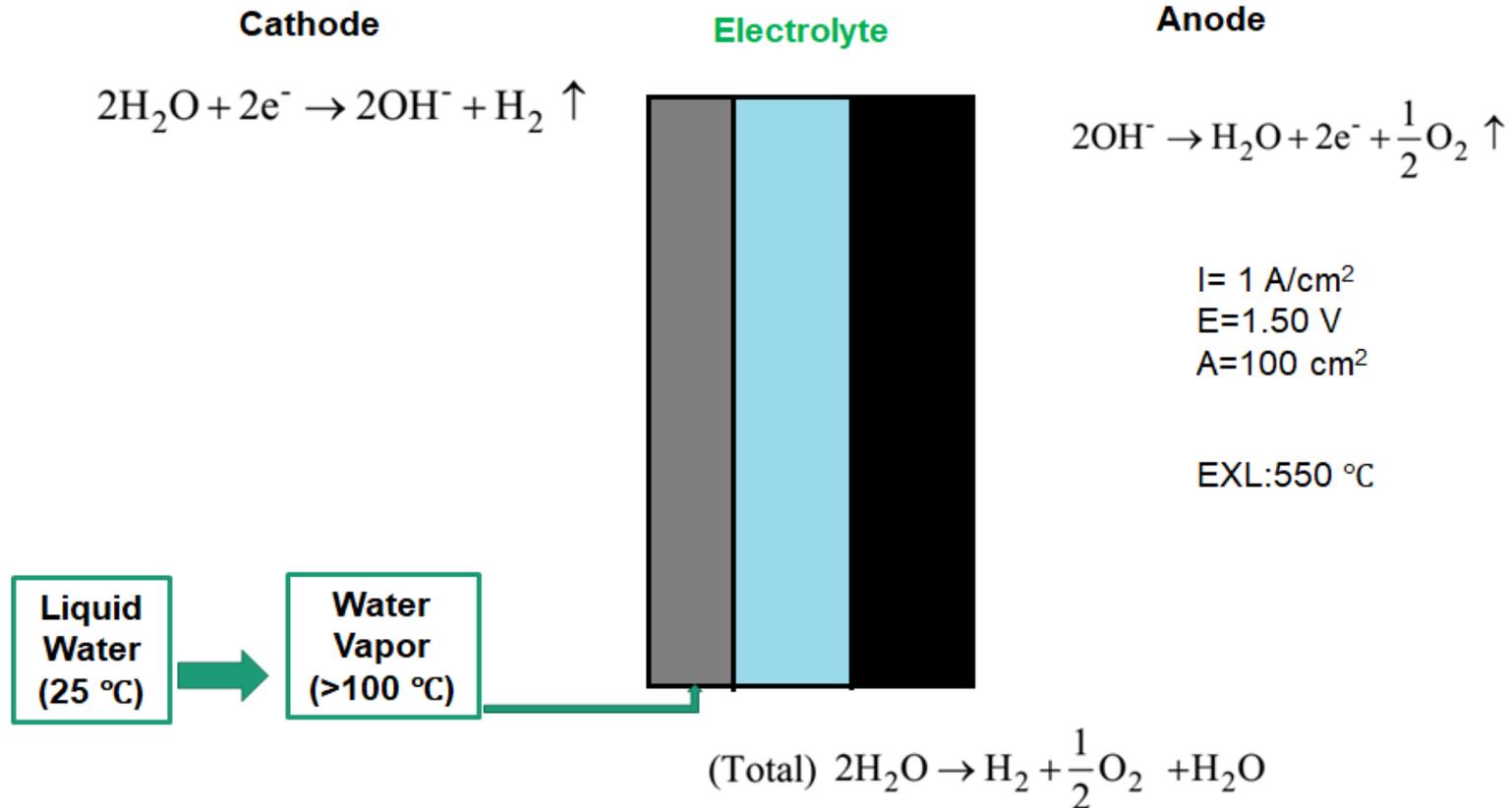
**Characterizations:** XRD and SEM

➤ **Immersion test: Morphology of metal oxides in the molten LiNa)OH melt at 550°C for 10 and 100 hrs.**



# HT Alkaline Electrolysis: Energy Balance

High-temperature alkaline water electrolysis



2 moles  $\text{H}_2\text{O}$  has to be heated for evaporation to get 1 mole of  $\text{H}_2$