2017 DOE H_2 and Fuel Cell Annual Merit Review Meeting

High Temperature Alkaline Water Electrolysis

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Newton, MA

June 7, 2017

Project #
PD 143

Project Overview

Timeline
- Project Start Date: January 1, 2017
- Project End Date: December 31, 2020

Budget
- Overall $ 1,722,885
  - DOE share $ 1,375,123
  - Contractors share $ 347,762
  - Spent $ 60,363 (as of April 30, 2017)

Giner Researchers
Kailash Patil and Winfield Greene

Collaborator
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

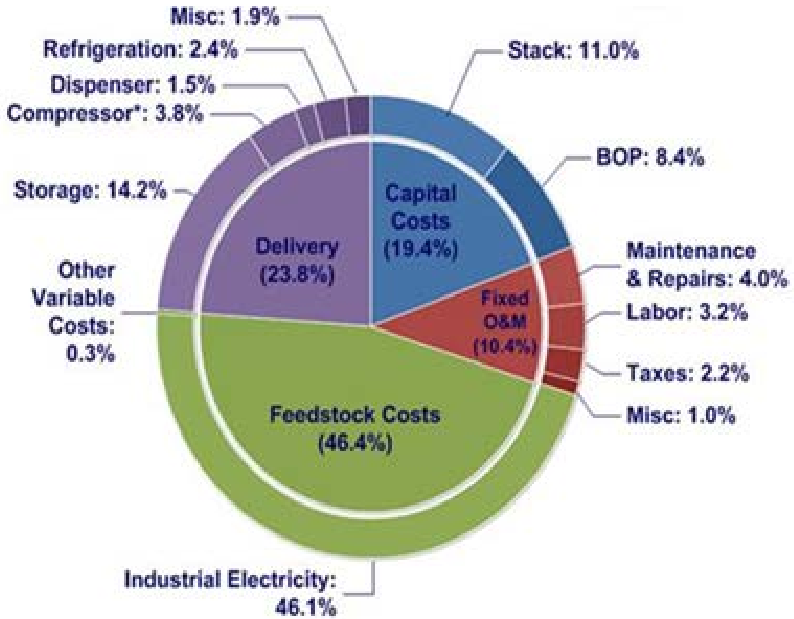
Technical Targets
- Composite electrolyte OH^- conductivity > 0.3 S/cm in temperature of 350 to 550 °C
- Per-cell area-specific resistance (ASR) of ≤ 0.2 Ohm-cm^2 at 350 to 550 °C using a membrane thickness of 200 μm.
- Stack electrical efficiency > 90% LHV H_2 with current density at 1.2 A/cm^2

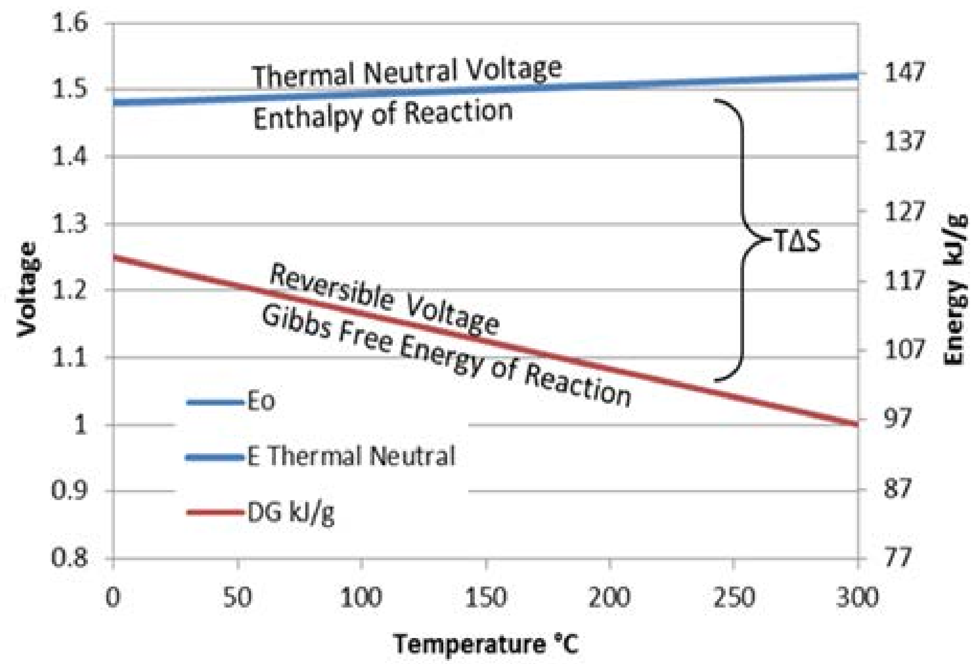
High Temperature Alkaline Water Electrolysis

DOE: Distributed Forecourt Water Electrolysis Hydrogen Production

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

Water Electrolysis Cost

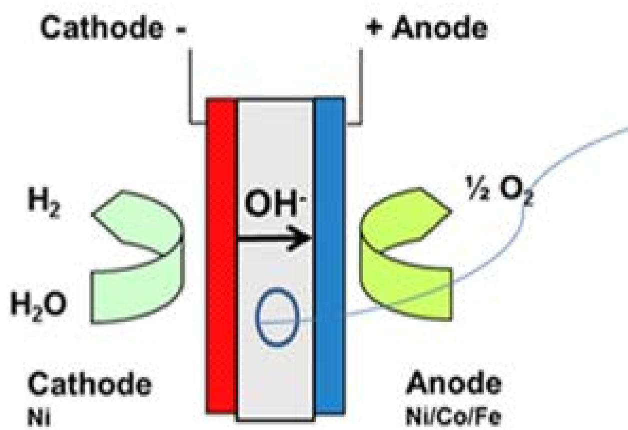




Anthony et al, Hydrogen Energy Challenges and Prospects (RSC Energy Series), **DOI:**10.1039/9781847558022 (2008)

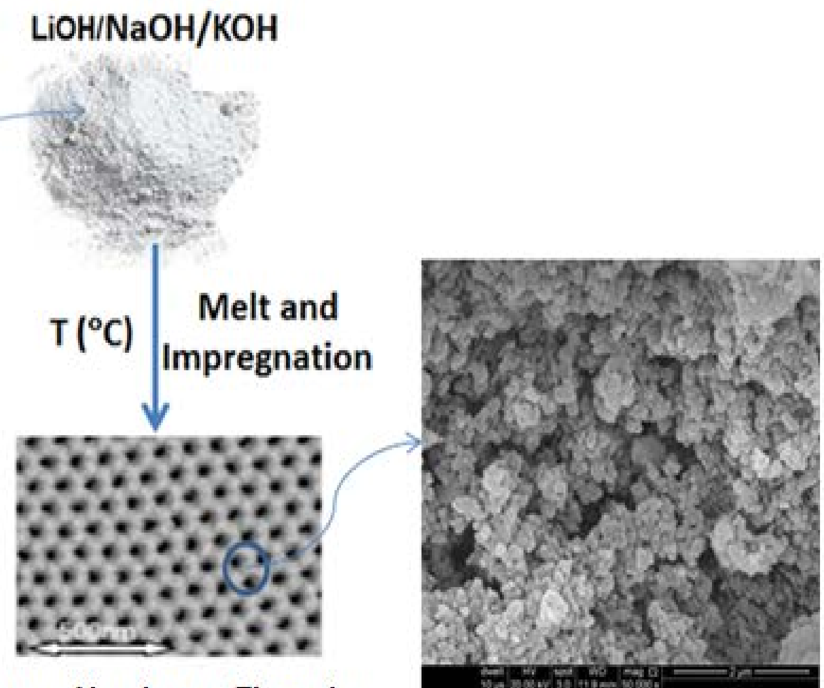
- Feedstock costs (electricity) consists of 50% of total cost: energy costs of \$3.09/kg H_2, 2x higher vs. DOE 2020 total cost target, \$1.60/kg H_2
- High-temperature electrolysis offer the advantage of lower energy requirements due to both higher kinetics and greatly reduced equilibrium voltages

Technical Approaches



$2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^-$		Anode
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$		Cathode
$H_2O \rightarrow H_2 + \frac{1}{2} O_2$		Total reaction

Base	Melting Point (°C)
LiOH	462
NaOH	318
KOH	406



Porous Alumina or Zirconia

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

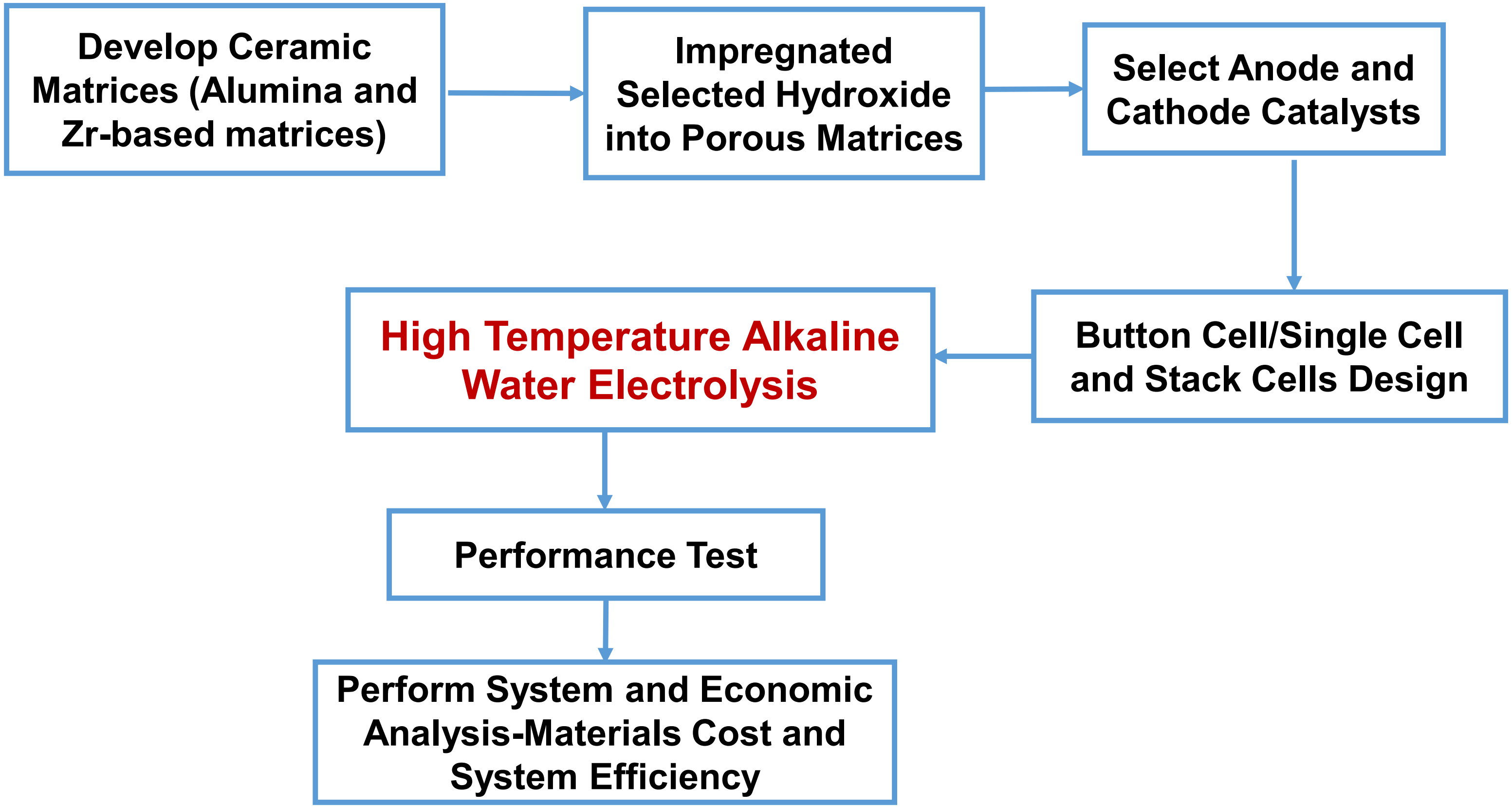
Tasks and Performance of Schedule

		Period 1						Period 2					
ID	Task Name	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
1	**Task 1: Develop alumina and zirconia matrices**												
2	1.1 Develop $LiAlO_2$ Matrix												
3	1.2 Prepare ZrO2 and YSZ Matrix												
4	**Task 2: Impregnate hydroxides into porous matrices**												
5	2.1 Electrolyte impregnating												
6	2.2 OH- conductivity measurement												
7	2.3 Electrolyte structure characterization												
8	2.4 Wettability and Capillary Pressure												
9	**Task 3: Select anode and cathode catalysts**												
10	3.1 Anode catalyst												
11	3.2 Cathode catalyst												
12	**Task 4: Assemble and test 25 cm2 single cells**												
13	4.1 Single cell fabrication												
14	4.2 Crossover Measurement												
15	4.3 Performance test												
16	4.4 Durability test												
17	**Task 5: Construct and test 1.8-KW electrolyzer stack**												
18	5.1 Design parameter												
19	5.2 Component selection												
20	5.3 Stack Fabrication												
21	5.4 Stack Test												
22	**Task 6: Perform systematic and economic analysis**												
23	**Program Management**												

Milestones

Milestone Summary Table							
Recipient Name:	Giner, Inc.						
Project Title:	High Temperature Alkaline Water Electrolysis						
Task No.	Task Title or Subtask Title	Milestone Type	Milestone Number	Milestone Description	Milestone Verification Process	Anticipated Date	Anticipated Quarter
1	Develop alumina and zirconia matrices	Milestone	M1-1	Produce five $LiAlO_2$ matrices with various porosity (50-80%) and thickness (200-300 μm)	Using tape-casting technique, pore size, 20-200 nm pores>50%	M3	Q1
1	Develop alumina and zirconia matrices	Milestone	M1-2	Produce six ZrO_2 and YSZ matrices with various porosity (50-80%) and thickness (200-300 μm)	Using tape-casting technique 20-200 nm pores > 50%	M6	Q2
2	Impregnate hydroxides into porous matrices	Milestone	M2-1	Downselect at least six composite electrolytes with OH^- $\sigma > 0.1$ S/cm	Using AC Impedance at 350 to 550 °C	M8	Q3
2	Impregnate hydroxides into porous matrices	Milestone	M2-2	Downselect at least four composite electrolyte membranes with ASR <0.2 Ohm-cm^2	Using 4-probe resistance measurement, at 350 to 550 °C	M12	Q4
3	Select anode and cathode catalysts	Milestone	M3-1	Synthesized four OER catalysts with particle size < 20 nm, activity comparable to Ir black	Using hydrothermal approach for synthesis and XRD for particle size	M15	Q5
3	Assemble and test 25-cm^2 single cells	Milestone	M4-1	Complete testing at least 5, 25 cm^2 cells with composite electrolytes	Using Giner corrosion-resistant hardware	M15	Q5
4	Assemble and test 25-cm^2 single cells	Go/No-Go decision	M4-2	Achieve single cell performance V < 1.50 V at 1.0 A/cm^2 or 1.4 V at 0.5 A/cm^2	Using polarization curves	M18	Q6
4	Assemble and test 25-cm^2 single cells	Milestone	M4-3	Achieve 300-h durability test at 0.5 A/cm2 for 300 hours with a degradation rate < 0.1 V/1000 hours	Using constant current at 0.5 A/cm^2	M21	Q7
5	Construct and test electrolyzer stack	Milestone	M5-1	Complete design of the stack	Using CAD and solid works	M24	Q8
5	Construct and test electrolyzer stack	Milestone	M5-2	Complete construction of the stack	Using selected components	M27	Q9
5	Construct and test electrolyzer stack	Milestone	M5-3	Achieve stack electrical efficiency > 90% LHV H_2 at 1.0 A/cm^2	Using I-V polarization curves	M30	Q10
5	Construct and test electrolyzer stack	Milestone	M5-4	Demonstrate adegradation rate of < 0.1 V/500 hours at =0.5 A/cm^2	Measuring voltage at constant current	M33	Q11
6	Perform systematic and economic analysis	Milestone	M6-1	Deliver a 5-page cost analysis for developed supports and catalysts	Using small-scale short production	M36	Q12

Project Flow Chart



- Matrix Long-term Stability;
- Electrolyte Matrix and Electrode Fabrication Technology

Accomplishment 1: Stability of Metal Oxides in Hydroxide System

Physical properties of Metal oxides			Hydroxide system	Single/ Eutectic Composition	Melting Temperature (°C)
No.	Metal oxides	Surface Area (m^2/g)			
1	Baseline α-Al_2O_3	7-9	LiOH	100	462
2	MO-1	5-20	LiOH-NaOH	52-48	~300
3	MO-2	10-15	LiOH-KOH	62-38	~325
4	MO-3	13-19			

Approach: Metal oxide immersed in molten Hydroxides

Heat treated at 450-550°C for 10 h

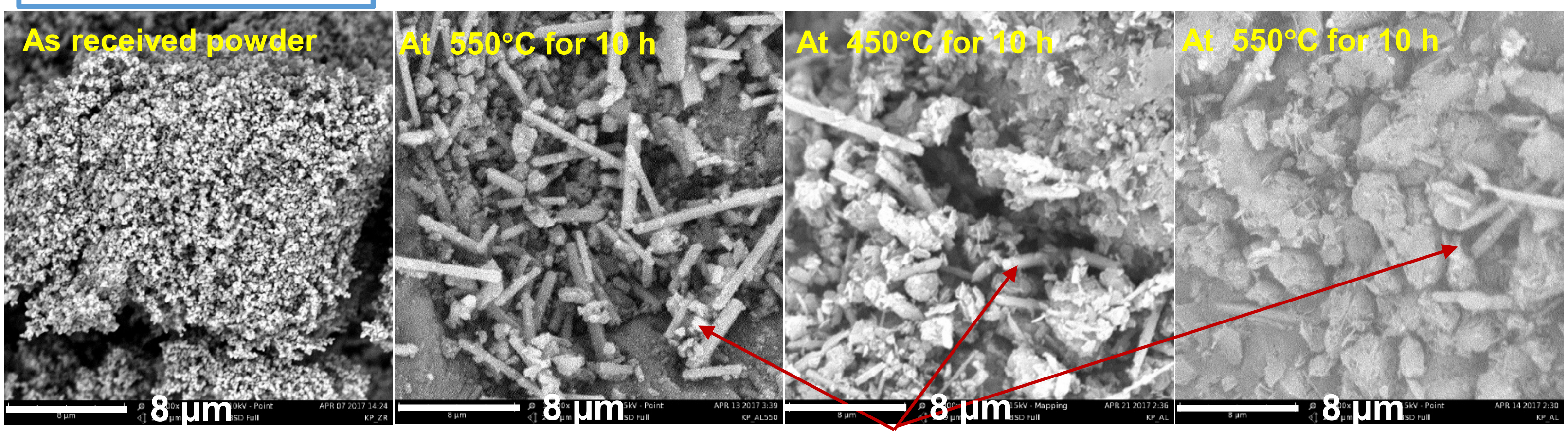
Washed and Dried at overnight

Characterizations

Baseline MO powder

α-Al_2O_3 powder after immersed in LiOH

α-Al_2O_3 powder after immersed in molten LiOH-NaOH

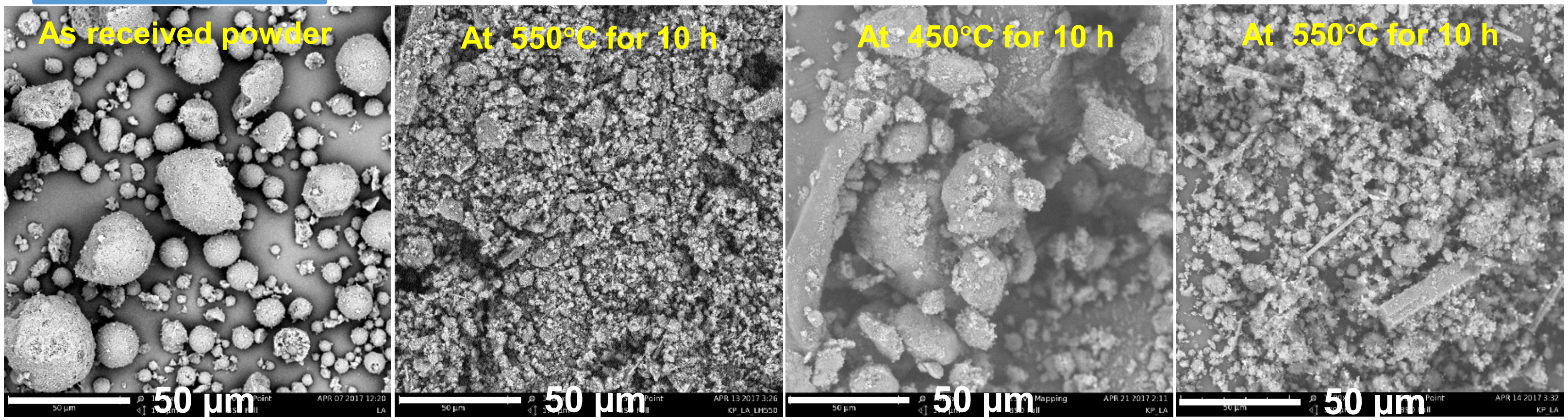


Rod-shape structure

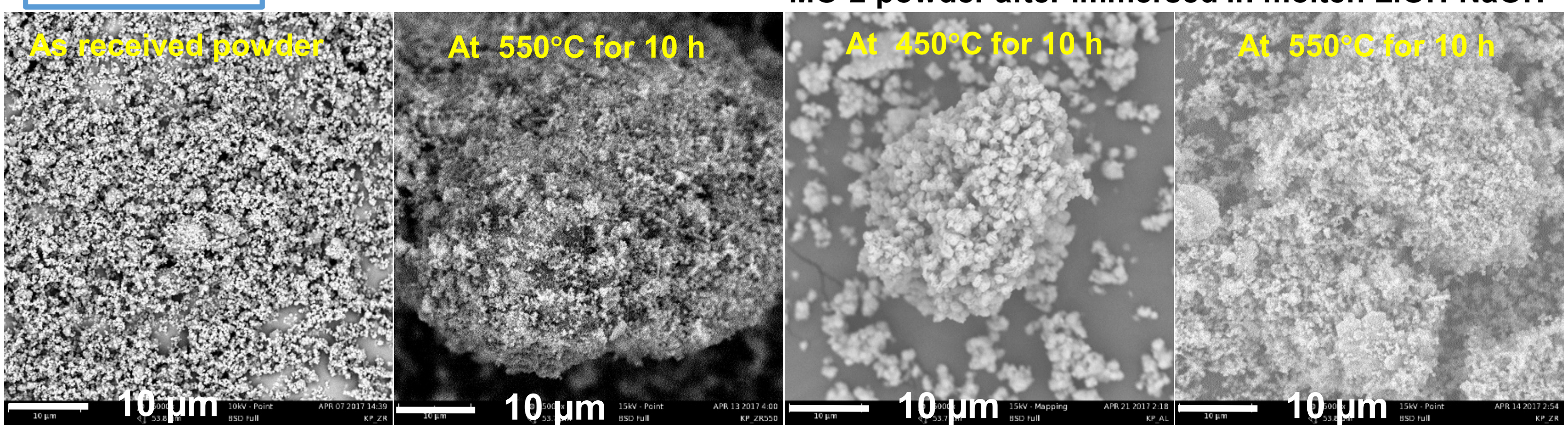
- The baseline metal oxide (α-Al_2O_3) shows significant particle changes after immersion test
- in Rod-shape structure was observed in α-Al_2O_3 powder after immersed in single or binary hydroxide melts

Stability of Metal Oxide in Hydroxide System (II)

MO-1 Powder | **MO-1 powder after immersed in LiOH** | **MO-1 powder after immersed in molten LiOH-NaOH**



MO-2 powder | **MO-2 powder after immersed in LiOH** | **MO-2 powder after immersed in molten LiOH-NaOH**



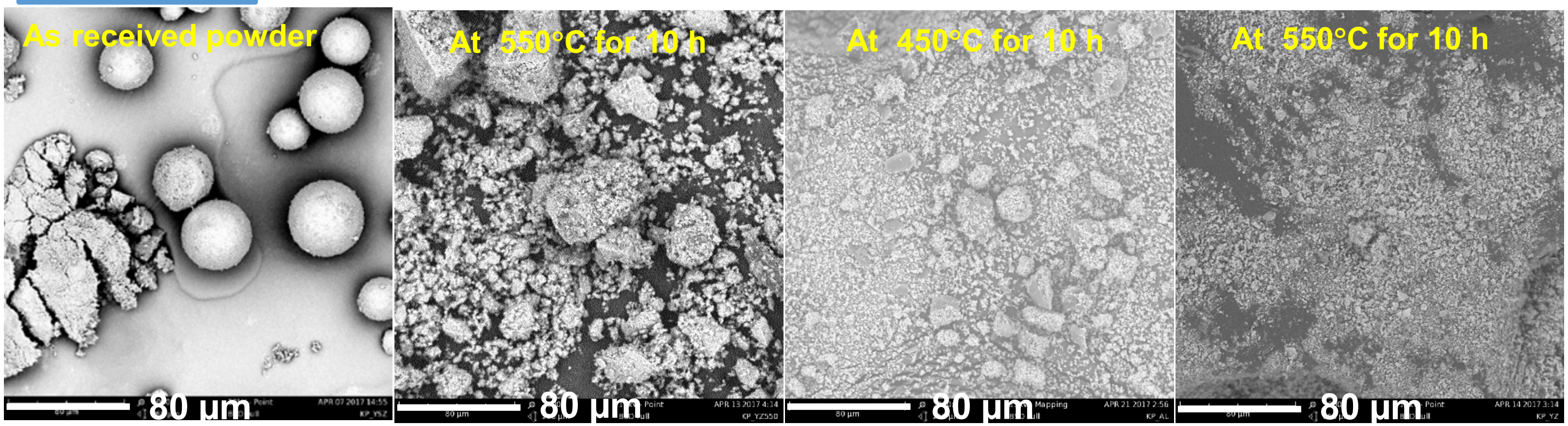
- No significant morphological changes was observed in MO-1 and MO-2 powders after immersed in single or binary hydroxide melts
- MO-1 and MO-2 powders showed stable morphology at 450 or 550 °C during immersed time of 10 h

Stability of Metal Oxide in Hydroxide System (III)

MO-3 powder

MO-3 powder after immersed in LiOH

MO-3 powder after immersed in molten LiOH-NaOH



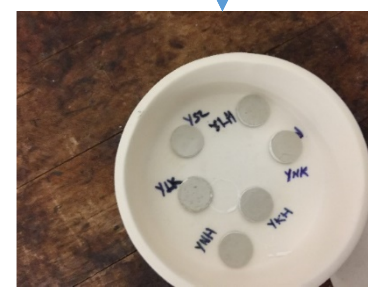
- The MO-3 powder shows stable morphology after immersion in both LiOH or LiNa hydroxide systems

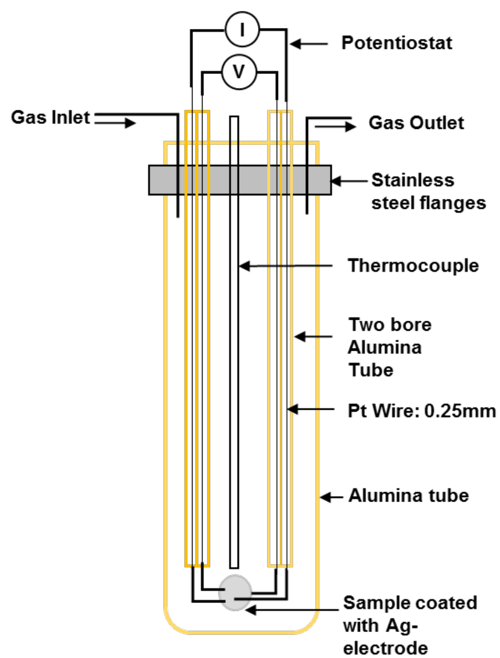
Accomplishment 2: Measurement of OH^{-} Conductivity

Experimental Metrics / Metal Oxide	Hydroxide system	Single/Eutectic composition (mol %)	Melting Temperature (°C)	Electrolyte (Wt %)
Metal oxides (MO-1, MO-2, MO-3) and Baseline MO (Al_2O_3)	0	0	-	0
	LiOH	100	462	25
	NaOH	100	318	25
	KOH	100	406	25
	LiOH-NaOH	**52-48**	**~300**	25
	LiOH-KOH	**62-38**	**~325**	25
	NaOH-KOH	**52-48**	**~225**	25

Metal oxide and Hydroxides
→ **Mixture and agate mortar**
→ **Pressing Pellet @ 5~10 Ton**
→ **Sintered @ 650 °C for 2 h**

→ **Ag paste coated on both side**
→ **Sintered @ 650 °C for 2 h**



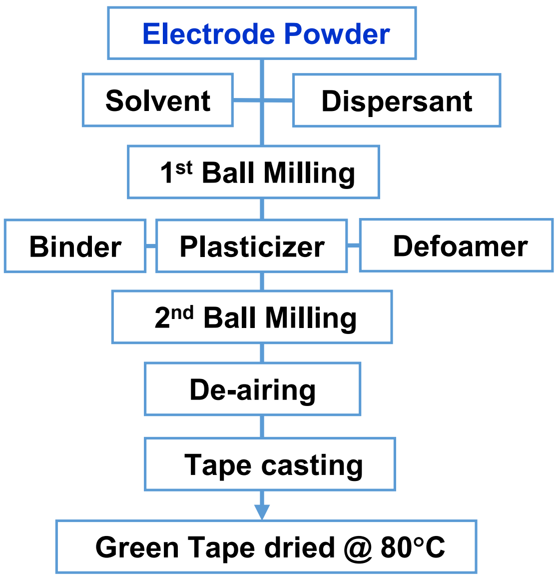


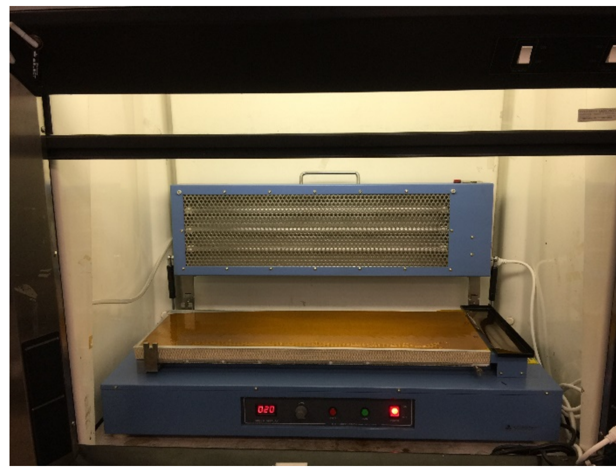
Schematic and Test Assembly for OH^{-} conductivity measurement

Conductivity measurement:
- **Electrochemical Impedance spectroscopy**
- **Area-Specific resistance**

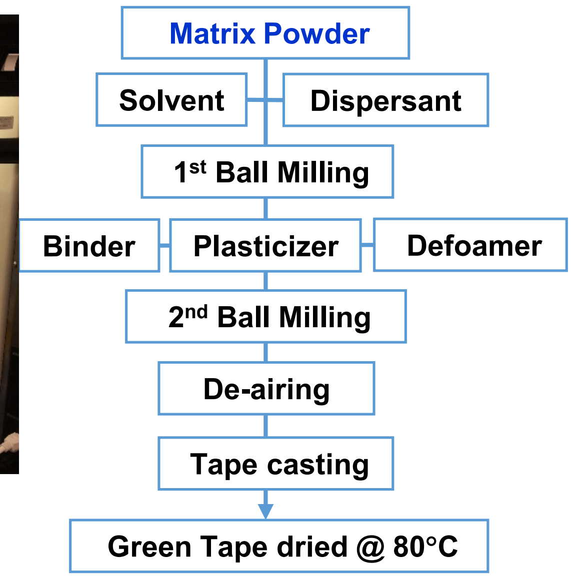
Accomplishment 3: Fabrication of Electrodes and Electrolyte Support Matrix

➢ **Tape casting process for Fabrication of Electrodes and Matrix green tape**



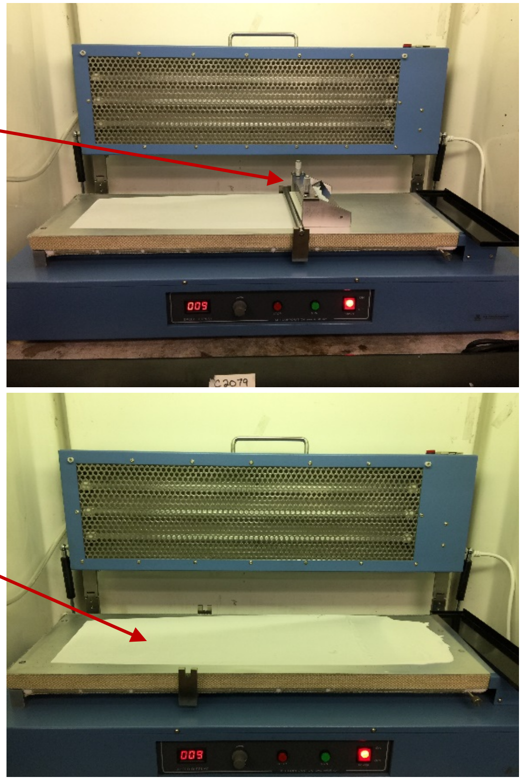


Newly purchased MTI lab-scale tape casting machine with heating system



- Assembled Lab-scale tape casting machine with heating system
- Fabrication of electrodes and matrices will optimized using tape casting process
- Solvent based slurry process will be optimized the green tape of matrices

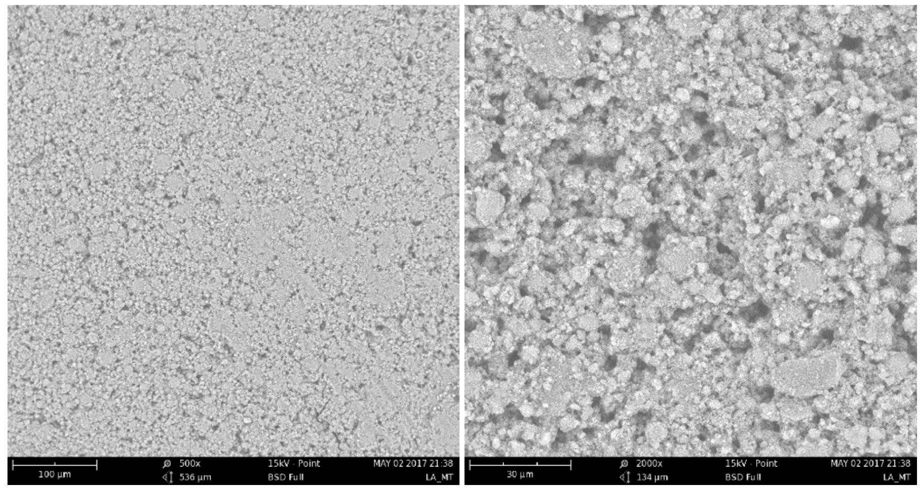
Fabrication of Electrolyte Support Matrix



Fabrication of green tape of matrix using doctor blade

Parameters of before and after sintered green sheet matrix

Matrix	Matrix Thickness (mm)		Solid content (%)	Solid content (%)	Porosity (%)	Pore size (µm)
	Green sheet tape	After sintered	before sintered	after sintered		
MO-1	0.6	0.5	69.78	66.57	In progress	

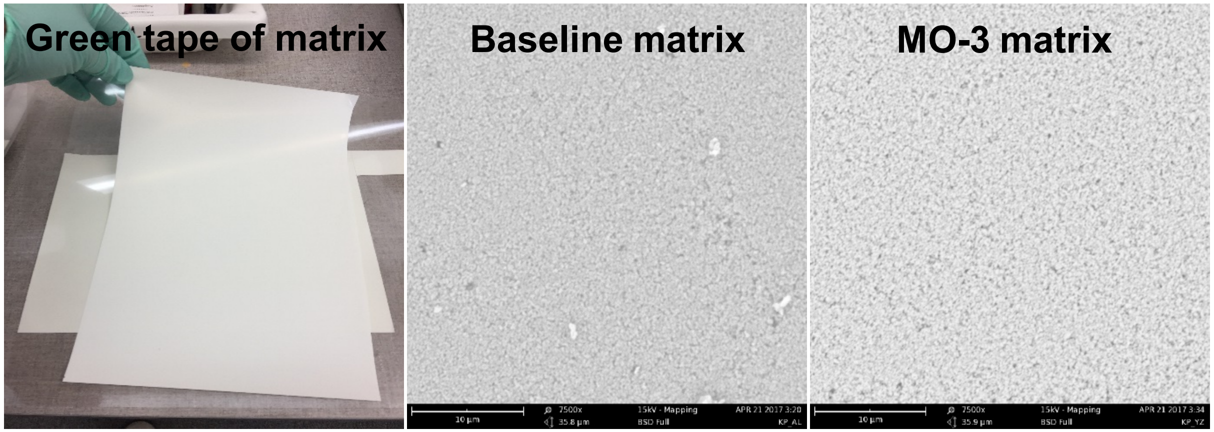


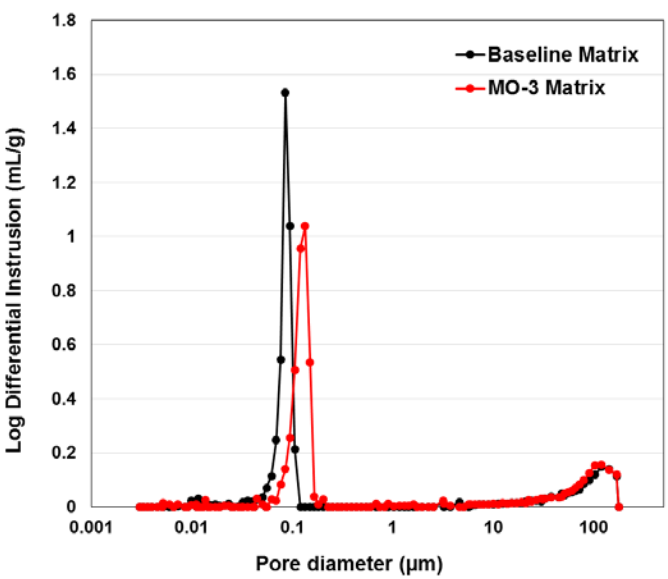
SEM images of MO-1 after sintered at 550 °C for 2 h in air

- Fabrication of MO-1 matrix has been developed and optimized through tape casting process
- The SEM images show porous MO-1 matrix after sintered at 550 °C for 2 h in air atmosphere
- Porosity and pore size of fabricated matrix will be characterize by Hg-porosimetry technique

Pore size distribution of Matrices

SEM images of sintered porous matrices





Matrices	Median Pore Diameter (μm)	Porosity (%)
Baseline Matrix	0.0957	59.1840
MO-3	0.1424	76.1506

Pore size distribution of commercial matrices:

- Pore size distribution of metal oxide matrices sintered at 550°C for 2 h in air
- Pores size distribution of commercial matrices showed very narrow pore size structure
- Both matrices showed narrow pore size distribution in the range of 0.09 to 0.14μm
- MO-3 based matrix showed higher porosity compared to baseline matrix

Stability of Electrolyte Matrix in Molten Hydroxides

➢ **Physical and chemical properties of metal oxide and molten hydroxides**

Physical properties of Metal oxide			Hydroxide system	Single/ Eutectic composition	Melting Temperature (°C)
No.	**MO Matrix**	**Surface Area (m^2/g)**			
1	**Baseline matrix**	7-9	**LiOH**	100	462
2	**MO-1**	15-20	**LiOH-NaOH**	52-48	~300
3	**MO-2**	10-15	**LiOH-KOH**	62-38	~325
4	**MO-3**	13-19			

Experimental plan:

- **Approach**
  - Stability of matrix in hydroxide media
- **Conditions** :
  - Temperatures: 350 to 550 °C
  - Atmospheres : Air and 3%H_2-Ar
- **Characterizations**
  - XRD, SEM, and BET

Electrolyte Matrix Immersed in Hydroxide melt

↓

Heat treated at 350 ~ 550°C for 10 h

↓

Washed with Water

↓

Overnight Dried at 100°C

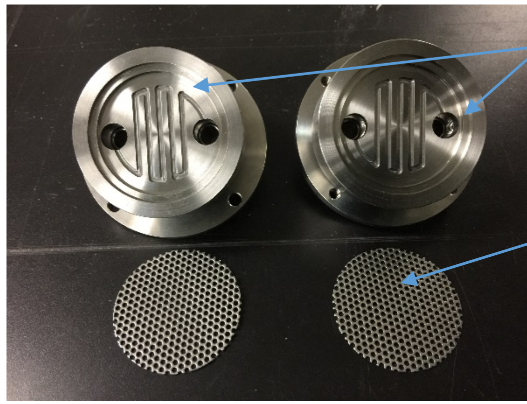
↓

Characterizations

- Experimental approach is to understand the physical and microstructure stability of electrolyte matrix in molten hydroxide melts

Accomplishment 4: Button Cell/Single Cell Electrolyzer Assembly

➢ **Design of Button Cell Electrolyzer Testing:**



Anode and Cathode cell frame

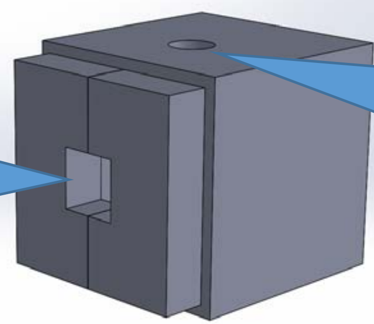
Anode and Cathode current collector

➢ **Button Cell capacity**
- Screening the anode, cathode and electrolyte matrix materials
- 2” diameter cell testing

➢ **Single Cell capacity**
- 5x5 cm or 10x10 cm cell testing

➢ **Single Cell Testing: Box furnace**

4x4” opening in center of doors. Water will be fed to the electrolyzer cell through four 0.25” ⌀ tubes. These tubes will pass through an insulating block.



3” ⌀ loose-fit holes in both the top and bottom of furnace. A pressure bar will apply a clamping force to the electrolyzer cell through these ports.

- The customized box furnace for 5x5 cm or 10x10 cm cell testing has been requested to Mellen Company

Physical Modifications as Shown

Summary

- The short term stability of different metal oxides has been performed in single and binary hydroxide melts:
  - The MO-1, 2, and 3 powders showed stable microstructure in molten LiOH-NaOH system at different temperatures
  - Changes in morphology has been observed in baseline powder in both LiOH and LiOH-NaOH melts

- Testing facilities for OH^- conductivity measurement and matrix stability in molten hydroxide systems have been assembled

- Lab-scale tape casting machine has been in place for fabrication of the electrodes and electrolyte matrix and green tape of matrix (MO-1) using tape casting process developed

- Commercial baseline matrix and MO-3 matrices have been characterized with pore size distribution and porosity.
  - The ideal pore size distribution is instrumental in retaining the electrolyte for long term operation

- Button electrolyzer cell has been obtained and customized box furnace for 5x5 cm^2 or 10x10 cm^2 single cell designed

Collaborations

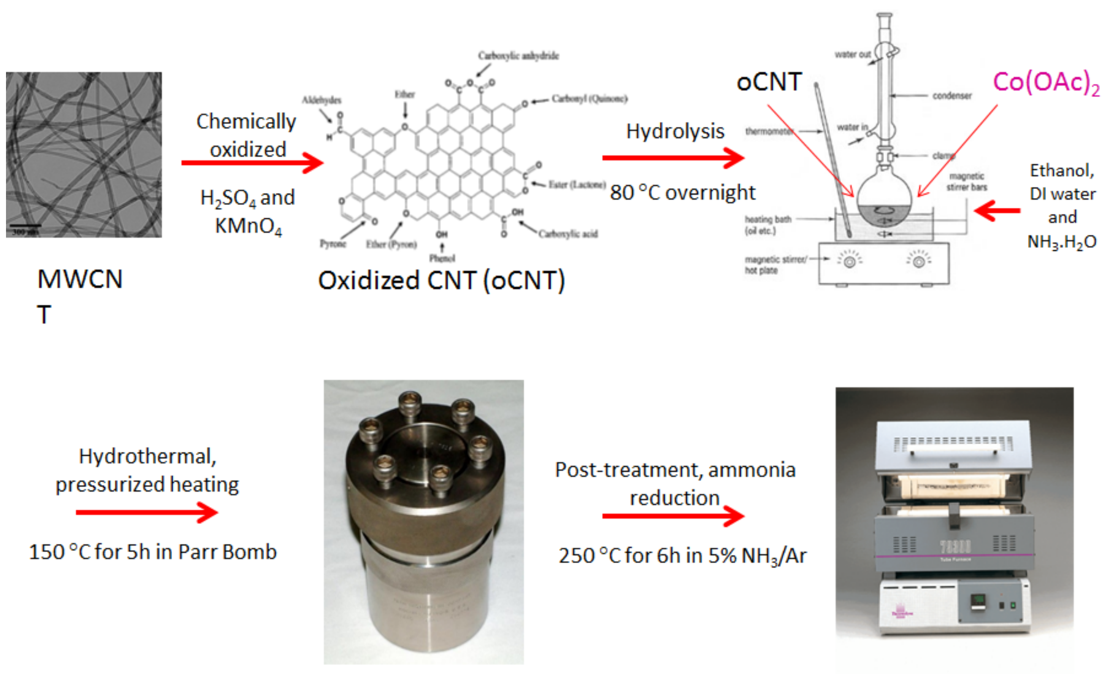
Institutions	Roles
Giner Inc. (Giner) Hui Xu (PI), Kailash Patil, Cortney Mittelsteadt	Oversees the project; composite electrolyte development; catalyst selection, button cell, single cell and stack evaluation; cost analysis
Zircar Zirconia Inc.	Vendor for customized metal oxide matrices
Fuel Cell Energy Dr. Chao-yi Yuh	Will provide advice on stack assembly (w/o financial commitment)

Future Plans

- ❑ Perform OH^- conductivity measurement
- ❑ Optimize in-house fabrication of electrolyte matrix
- ❑ Perform characterizations of prepared green tape matrix
- ❑ Assemble and testing button and single electrolyzer cells with selected HER and OER catalysts

Select Catalysts for Anode (OER) and Cathode (HER)

- **Cathode:** Ni-Al or Ni-Cu alloy catalyst
- **Anode:** Co_3O_4/CNT or $NiCo_2O_4$



- Data validated from low-temperature water electrolysis;
- Elevated temperature enhance electrode kinetics

Acknowledgments

- Financial support from DOE EERE Fuel Cell Technology Office under award # DE-EE0007644
- DOE program manager: Dr. David Peterson
- Giner Personnel
  - Corky Mittelsteadt and Winfield Greene
- Fuel Cell Energy: Dr. Chao-yi Yuh
- University of Connecticut: Prof. Prabhakar Singh