2019 DOE H_2 and Fuel Cell Annual Merit Review Meeting

High-Temperature Alkaline Water Electrolysis

Hui Xu (PI) and Kailash Patil

Giner Inc.

Prabhakar Singh

University of Connecticut

May 1, 2019

Project # P143

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 $ 970, 105 (by Feb. 2019)

Giner Researchers

Dr. Kailash Patil, Steve McCatty, 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^- conductivity > 0.1 S/cm in temperature of 300 to 550 °C
- Per-cell area-specific resistance (ASR) of ≤ 0.2 Ohm-cm^2 at 300 to 550 °C using a membrane thickness of 200 μm.
- Stack electrical efficiency > 90% LHV H_2 with current density at 1.0 A/cm^2

Relevance

Overall Project Objectives

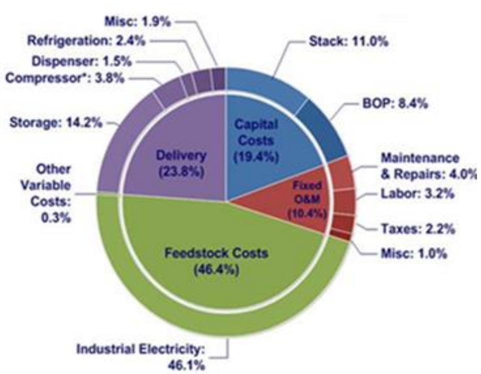
To develop high-temperature alkaline electrolysis using molten hydroxides in porous metal oxide matrix

FY 2018-19 Objectives

- ❑ Develop electrolyte support metal oxide matrix
- ❑ Evaluate the matrix materials stability in hydroxide electrolyte at 400-550 °C.
- ❑ Demonstrate single cell performance <1.5 V at 1,000 mA/cm^2 at temperature <550 °C.
- ❑ Reduced the electrolyzer cell temperature of 550 °C to 450 °C.

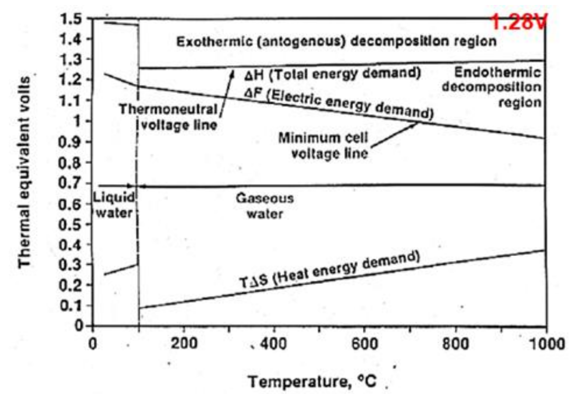
Impact

- ❑ 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



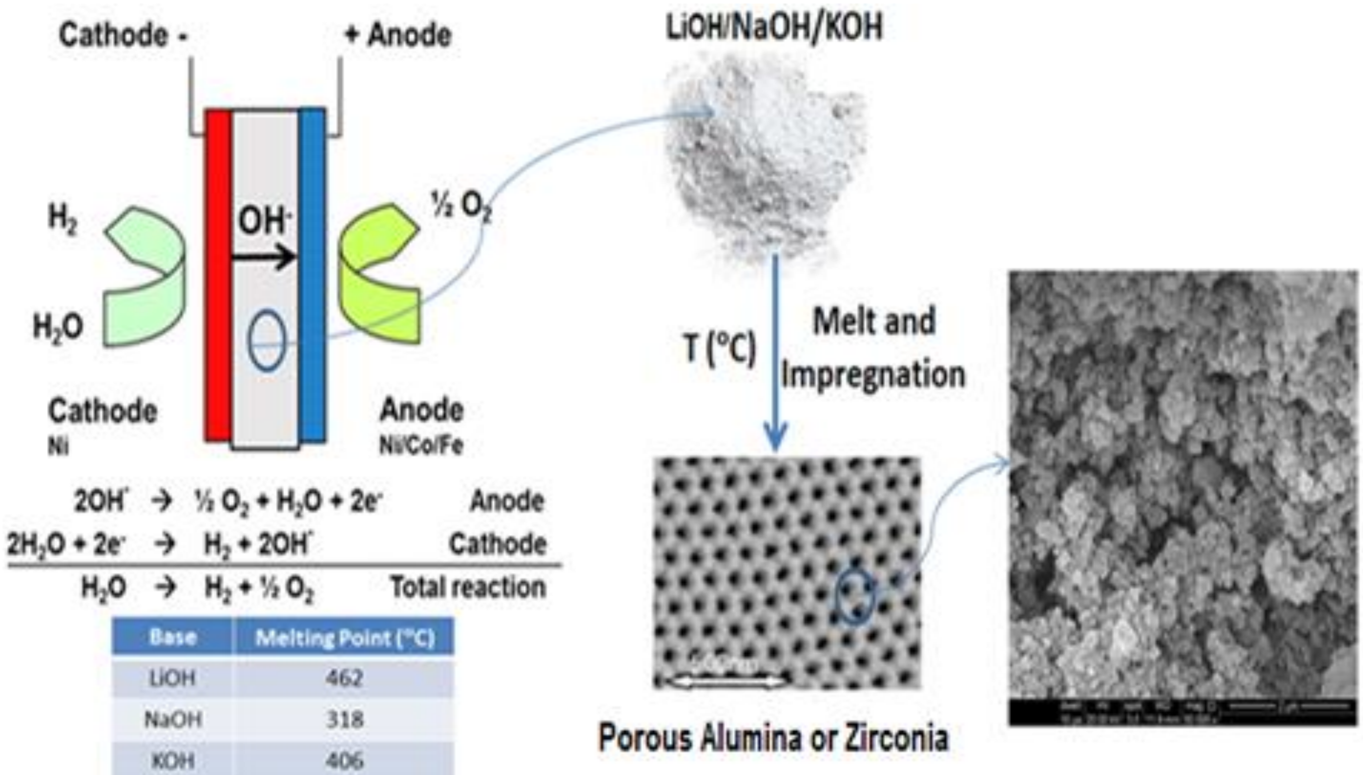
DOE: Distributed Forecourt Water Electrolysis

Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost [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 [i]



- ❑ 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



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

Major Advantages

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

Key to Success

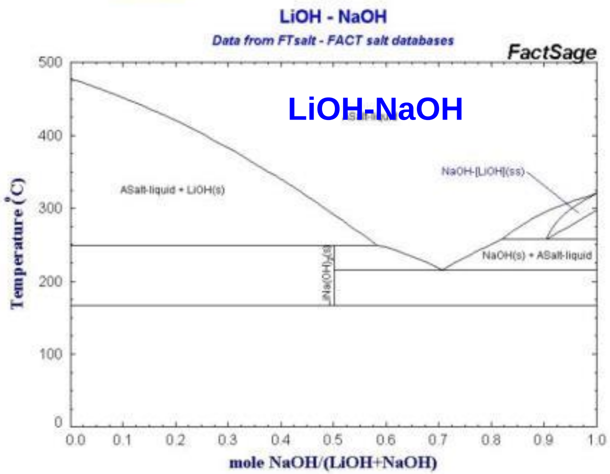
- ❑ Porous metal oxide matrices resistant to molten hydroxides
- ❑ Microstructures of the porous oxide matrices determine whether they can successfully retain molten hydroxides
  - thickness, porosity and pore structures

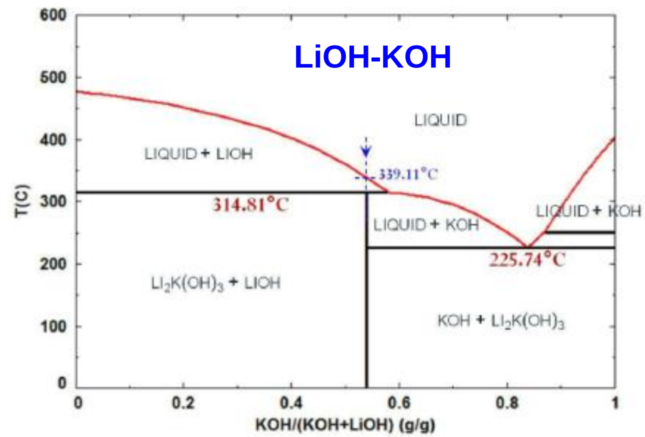
Approach: 2018-19 Tasks and Milestone Progress

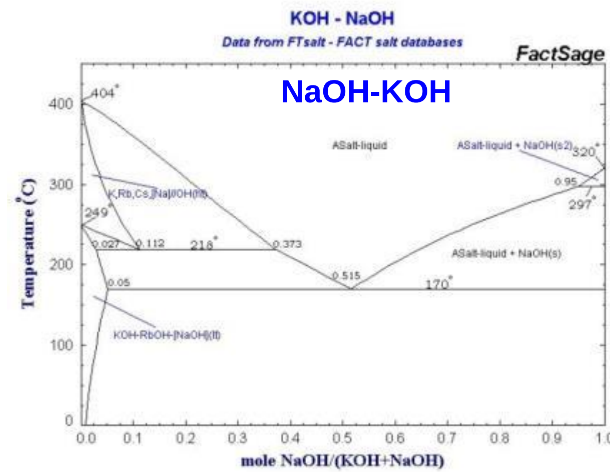
Task No.	Task Title	Milestone Description	Progress Notes	Status
Go/No-go Decision: FY2018 (06/30/2018)		❑ **Achieve single cell performance V < 1.50 V at 1.0 A/cm^2 or 1.4 V at 0.6 A/cm^2**	❑ Testing with different cell component configuration ❑ Developed gas sealing materials ❑ Suppressing corrosion of bipolar plates	**100%**
1	**Stability of Metal Oxide Materials**	❑ Select stable metal oxide in molten hydroxide electrolyte	❑ Identified stable metal oxide in molten LiNa and NaCs electrolytes	100 %
2	**Corrosion Mechanism of Non-active Components**	❑ Optimize corrosion of current collector in molten hydroxide electrolyte	❑ Performed hot corrosion/oxidation of various metal materials (SS-316 and Ni-metal) in molten hydroxide	90 %
3	**Assemble and Test single cells**	❑ Complete testing at least 5, 25 cm^2 cells with composite electrolytes ❑ Performance and durability test	❑ Designed and construct HT-electrolyzer test station ❑ Designed button cell area of 13 cm^2	80 %
4	**Perform Energy Balance**	❑ Perform compression cost ❑ Energy balance for 1MW mass and energy balance	❑ Conducted compression cost based on 1 A/cm^2, active area and operating current density ❑ Performed energy balance at 450 °C, 1.50V/cell and 550 °C, 1.40V/cell	90 %

Task change (upon DOE approval): Instead of building a short satck, more work is on singe cells towards longer durability and lower temperature operations

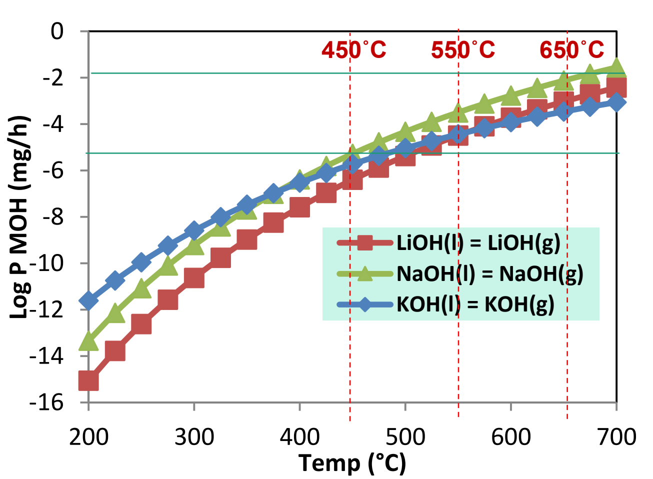
Thermochemical Calculations: Alkali Hydroxide Melt Chemistry







Evaporation of MOH (*l* → *g*) under 100 sccm flow rate



Eutectic composition	LiOH NaOH	LiOH KOH	NaOH KOH
▪ Eutectic composition	30-70	18-82	52-48
▪ Eutectic melting temperature (°C)	220	225	170

Temperature (°C)	LiOH	KOH	NaOH
450	4.0×10^{-7} mg/h	1.9×10^{-6} mg/h	5.6×10^{-6} mg/h
550	3.2×10^{-5} mg/h	3.6×10^{-5} mg/h	3.2×10^{-4} mg/h
650	9.2×10^{-4} mg/h	3.4×10^{-4} mg/h	7.4×10^{-3} mg/h

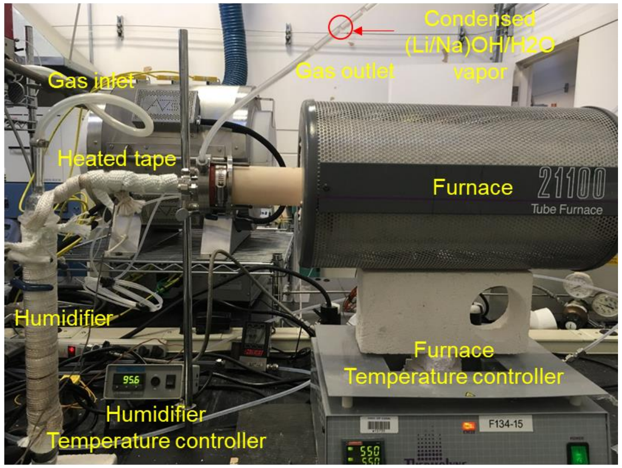
- Reduction in hydroxide vapor pressure can be achieved by 2-3 orders of magnitude in lowering of temperatures from ~600°C to 400°C.

Data from FACT salt databases (FactSage)
Conference: The 13th International Conference on Energy Storage Greenstock 2015

Accomplishment Stability of Metal Oxides in Molten Hydroxides

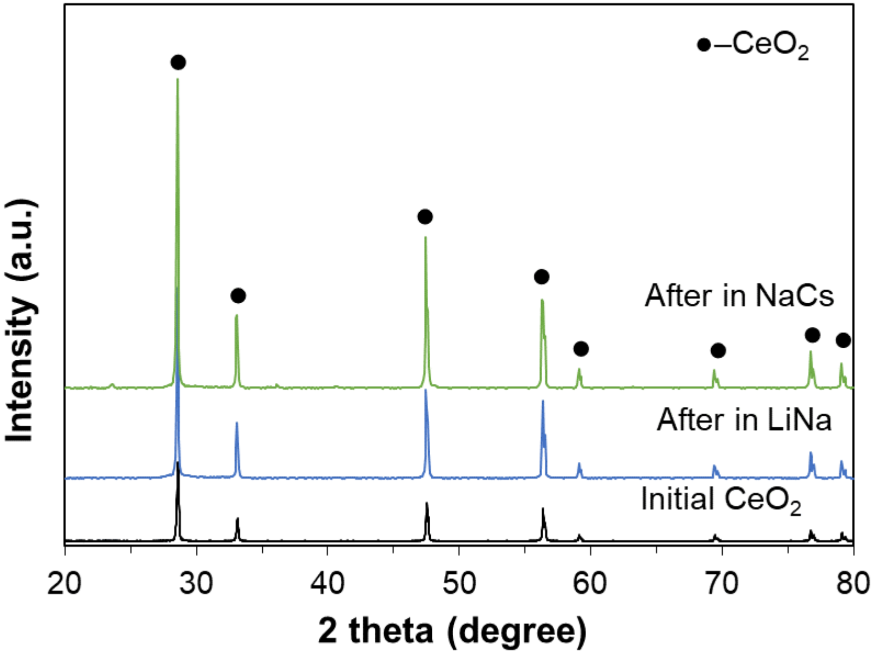
- Experimental test set up designed for **matrix stability** test

➢ Matrix stability test set up at UConn



Experimental Conditions	
Matrix Materials	CeO_2/YSZ/$LiAlO_2$/Li_2ZrO_3 powder
Alkali Hydroxides	Molten LiNaOH and NaCsOH
Atmosphere	3-90%H_2O-N_2
Temperature	550 – 600 °C (3°C/min)
Immersion time	50 - 100 h

Phase stability of CeO_2 in molten LiNa and NaCs hydroxide at 550 °C in air for 50 h

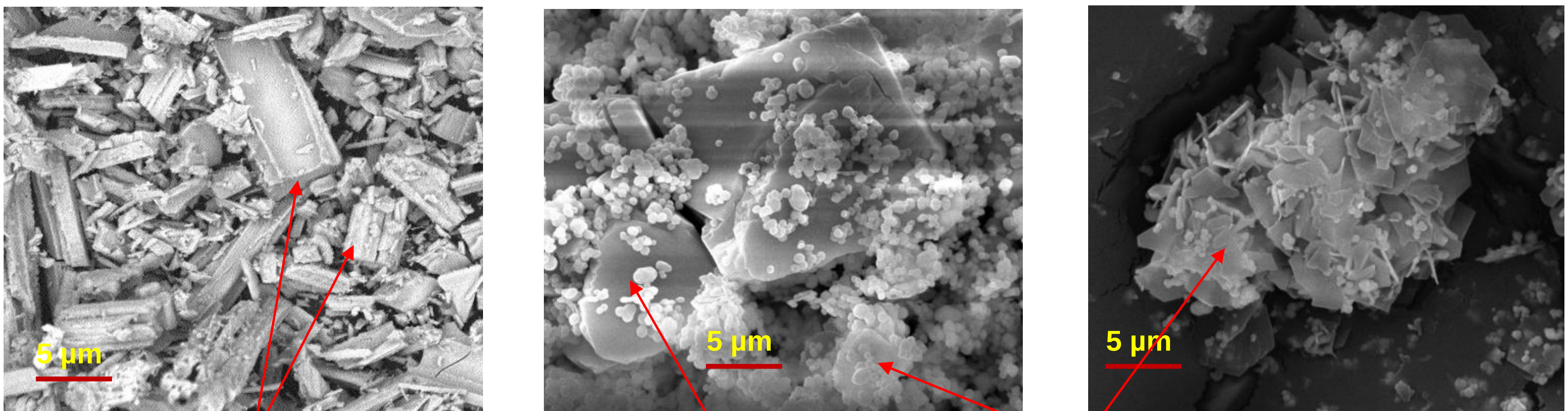


- No phase transformation of CeO_2 was observed in molten LiNa and NaCs hydroxide at 550 °C in air for 50 h.

GINER

Stability of CeO_2 in Molten Hydroxides

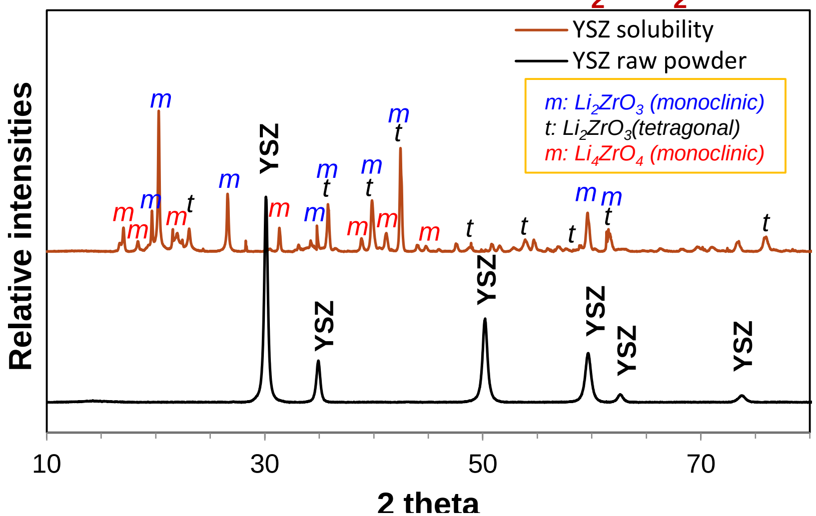
Surface morphology of CeO_2 in molten LiNa and NaCs hydroxide at 550 °C in air for 50 h



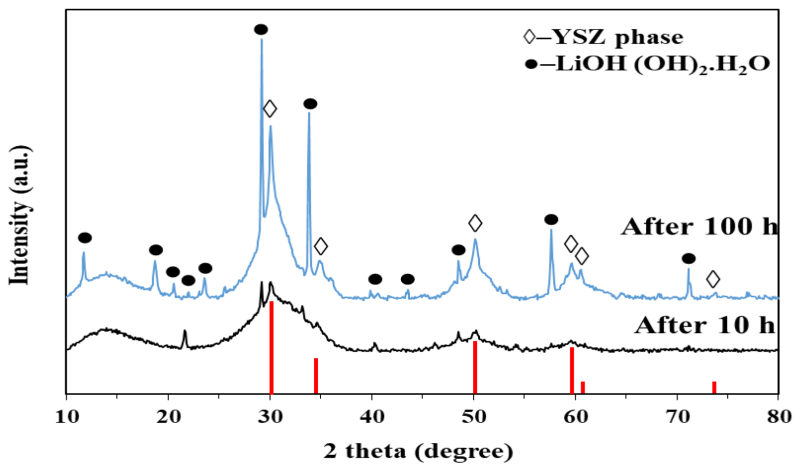
- The CeO_2 bulk fiber morphologies showed rapid agglomeration and particles growth was observed in molten hydroxide medium.
- CeO_2 fiber transformed to the particles during exposure of hydroxide medium

Stability of YSZ in Molten Li/Na Hydroxide

➤ **YSZ in Li/NaOH at 550°C in 3%H_2O-N_2 for 200 h**



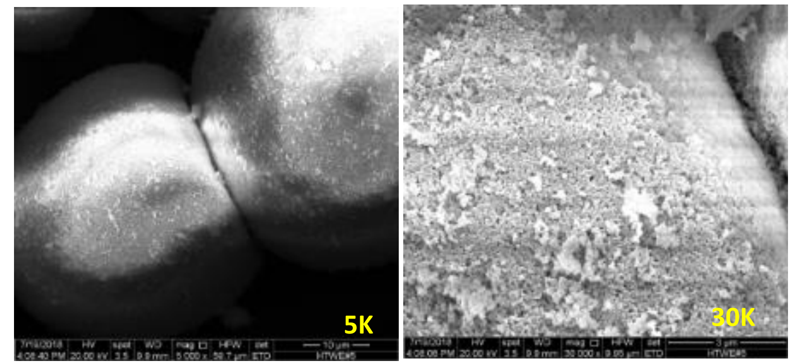
➤ **YSZ in Li/NaOH at 550°C in air for 100 h**



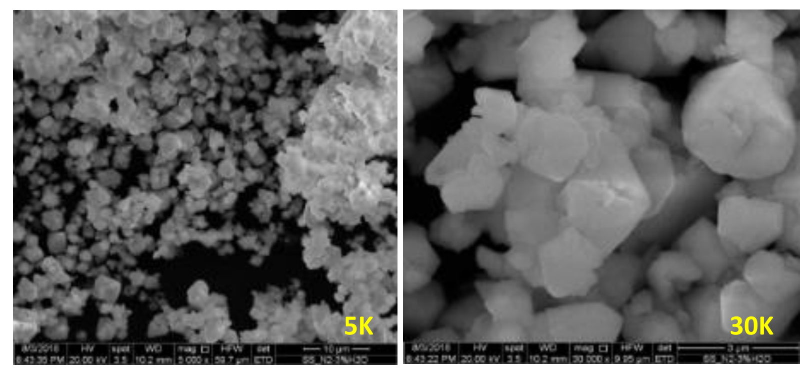
- **Major phase**: YSZ-phase
- **Minor phases**: t-Li_2ZrO_3 and Li_4ZrO_4

Surface morphology: SEM images

Before stability (raw powder, spray dried process)



After stability test of 200 h

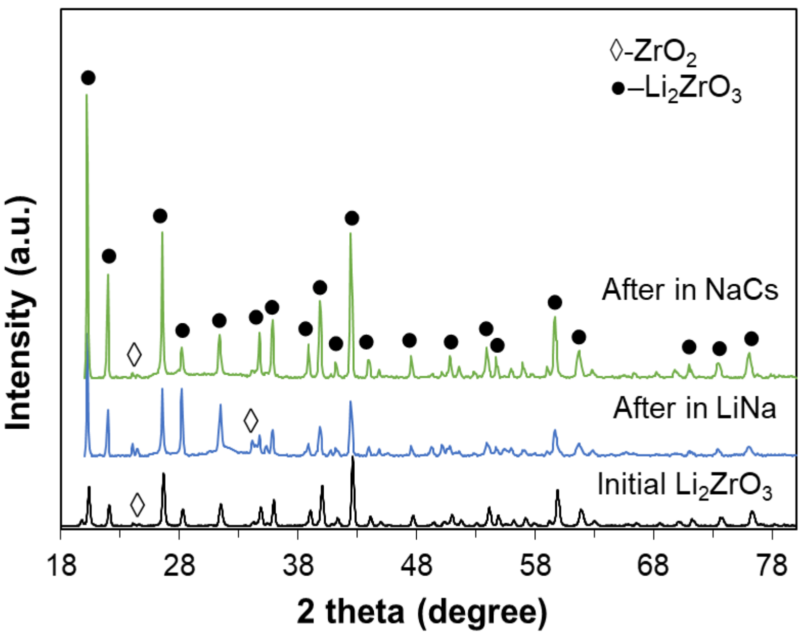


- Agglomeration and particles growth due to molten hydroxides
- New phases formed after exposures to molten hydroxides

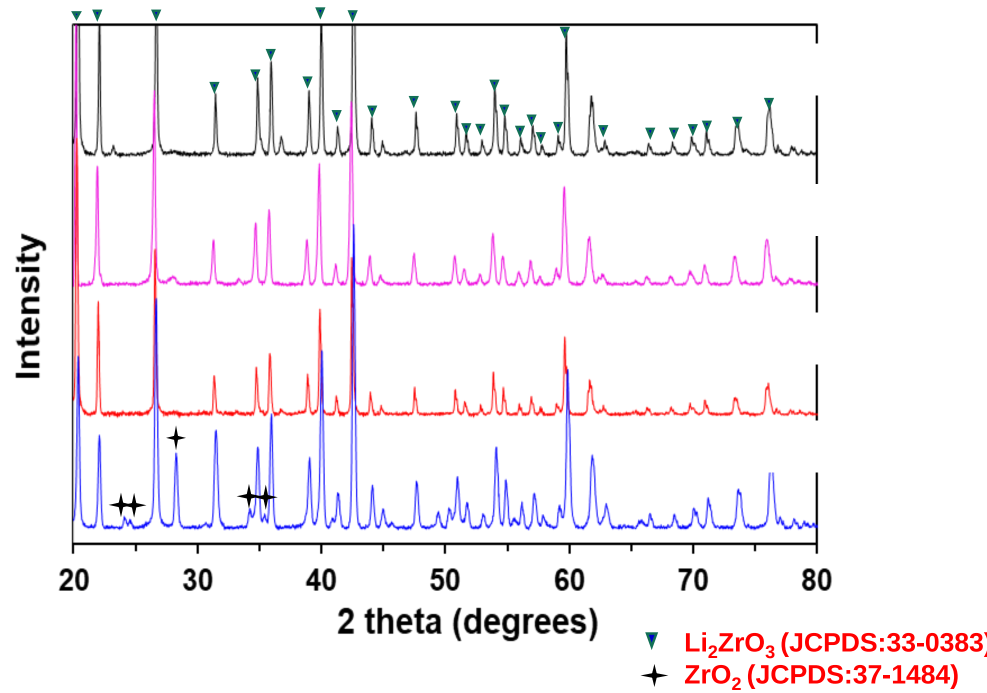
UCONN
UNIVERSITY OF CONNECTICUT

Stability of Li_2ZrO_3 in Molten Hydroxides

Phase stability of Li_2ZrO_3 in molten LiNa and NaCs hydroxide at 550 °C in air for 50 h



Phase stability of Li_2ZrO_3 in molten LiNa hydroxide with different steam ratio



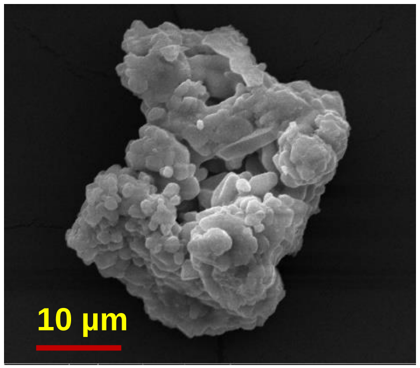
- No phase transformation of Li_2ZrO_3 was observed in molten LiNa and NaCs hydroxide at 550 °C in air for 50 h.
- The Li_2ZrO_3 material is stable phase was observed during the exposure of 50 and 100 h in LiNaOH under different steam ratio (3%-90% H_2O-N_2).

Li_2ZrO_3 will be used as the next generation material to extend the matrix lifetime

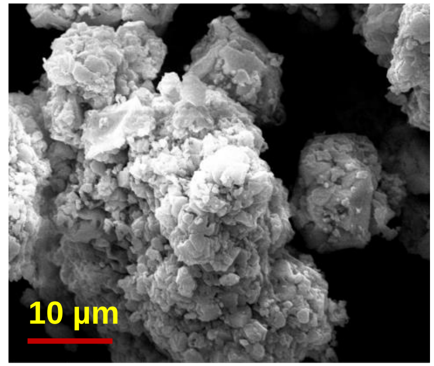
Stability of Li_2ZrO_3 in Molten Hydroxides

Surface morphology of Li_2ZrO_3 after stability test: SEM images

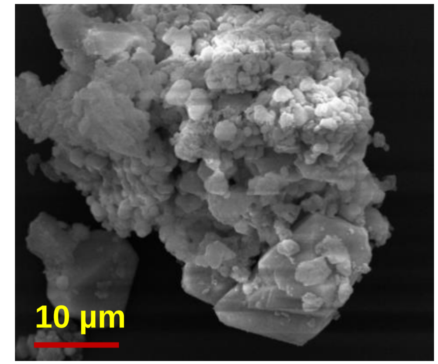
As received powder



(LiNa)OH at 550 °C for 50 h in air

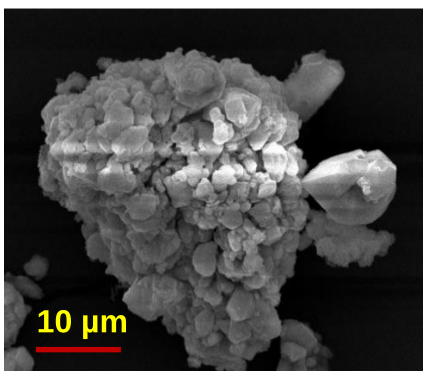


(NaCs)OH at 550°C for 50 h in air

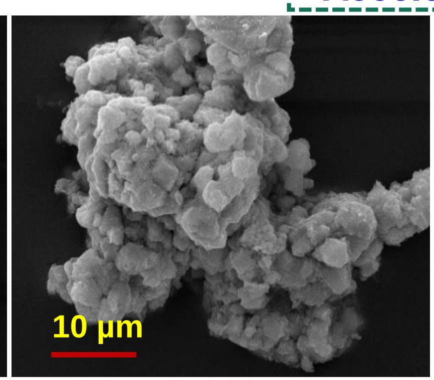


LZO in Molten (Li/Na)OH

at 550 °C for 50h



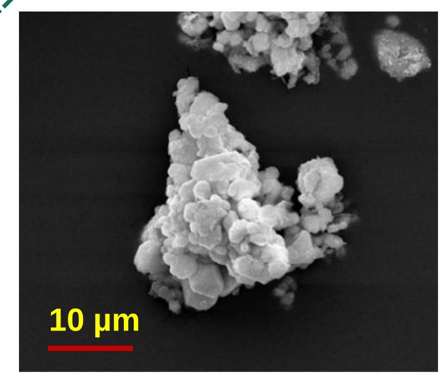
3%H_2O-N_2



90%H_2O-N_2

Accelerated test

at 600 °C for 100h



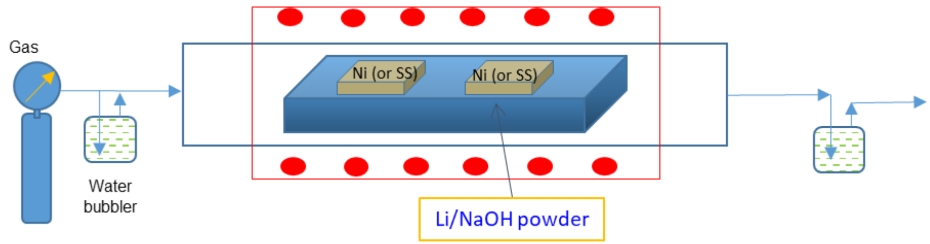
3%H_2O-N_2

- Li_2ZrO_3 powder remains unchanged during exposure to higher steam content and at higher temperatures.
- No significant changes in the particle size and morphology were observed.

Li_2ZrO_3 will be used as the next generation material to extend the matrix lifetime

Accomplishment 2: Corrosion of Components in Molten Hydroxide

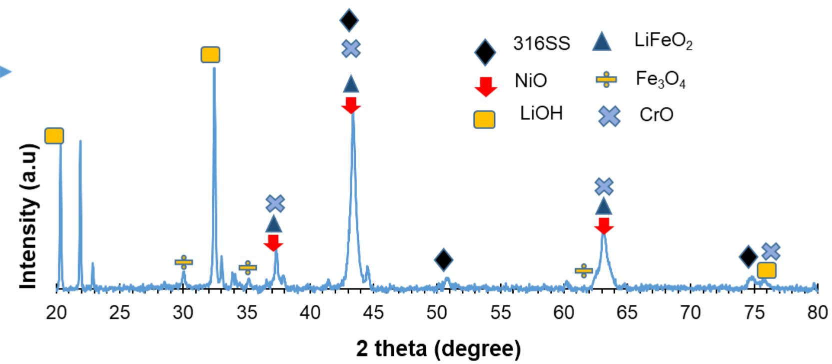
Corrosion test set up



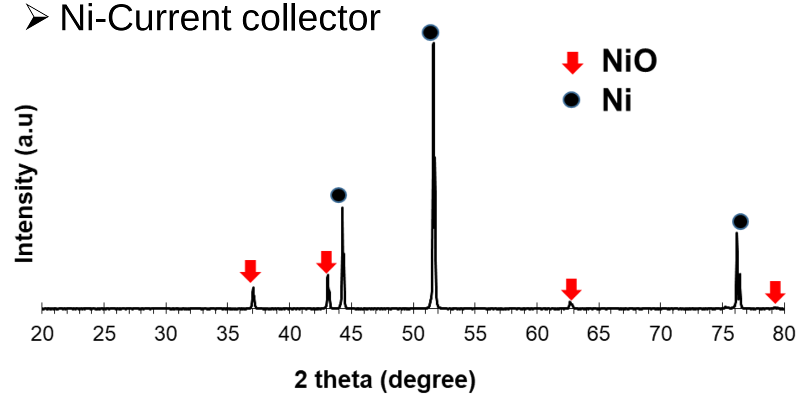
Operation Conditions
Materials: SS and nickel sheet (1''x1'');
Electrolyte: molten (LiNa)OH
Atmosphere: N_2-3% H_2O (100 sccm)
Temperature: 550°C; Immersion time: ~50 h

Structural Analysis: 550°C in air for 50 h

➢ SS 316-Current collector



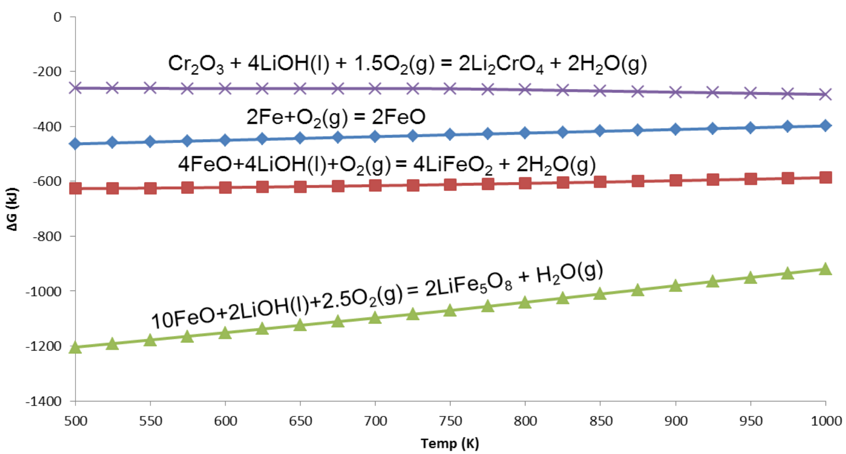
➢ Ni-Current collector

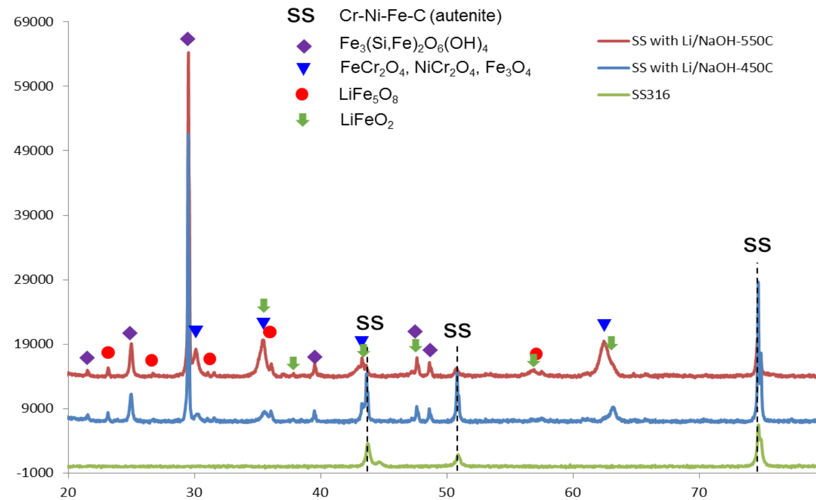


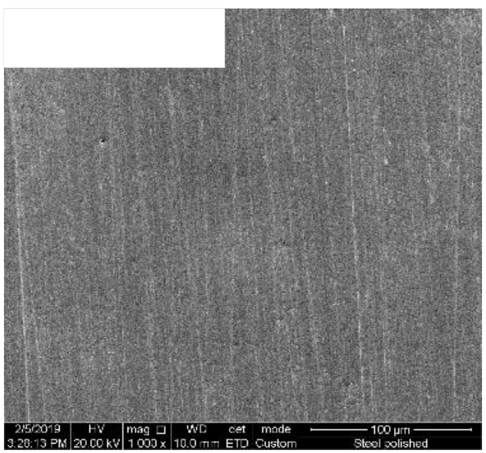
- ❑ Corrosion tests of SS showed surface corrosion products formation.
- ❑ Ni sample showed NiO phase only after corrosion test of 50 h.

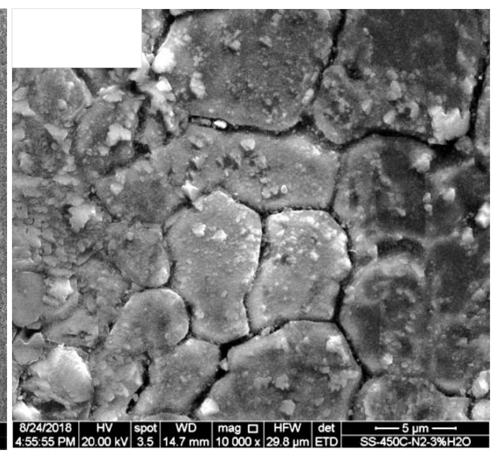
Hot Corrosion Test: 316L SS-in Li/Na Hydroxide

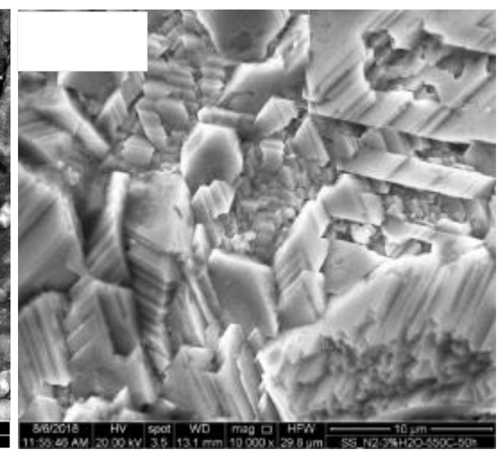
Test Condition: N_2-3%H_2O at 450 and 550°C for 50 h.







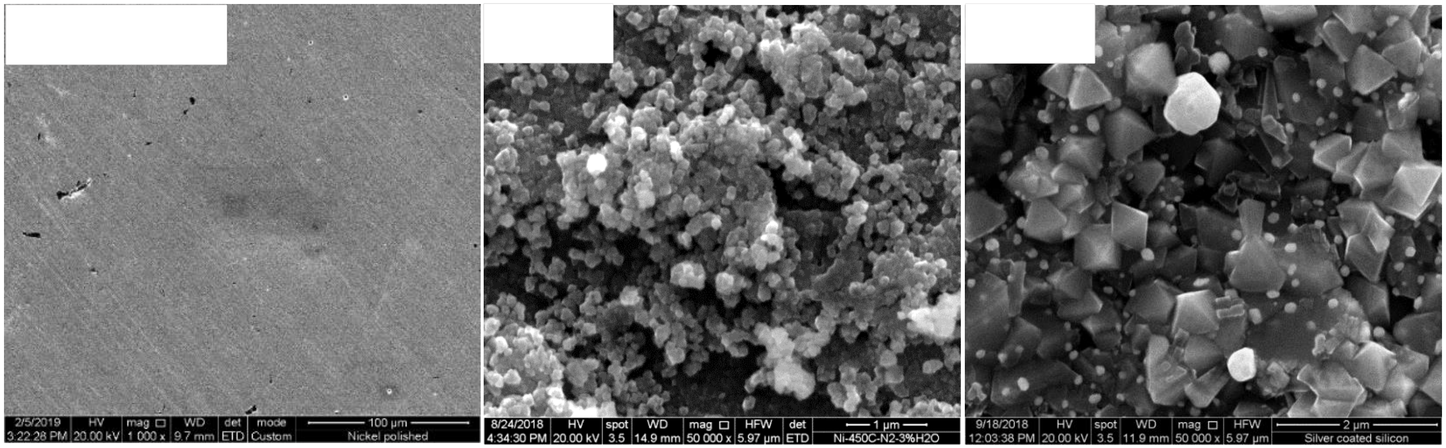


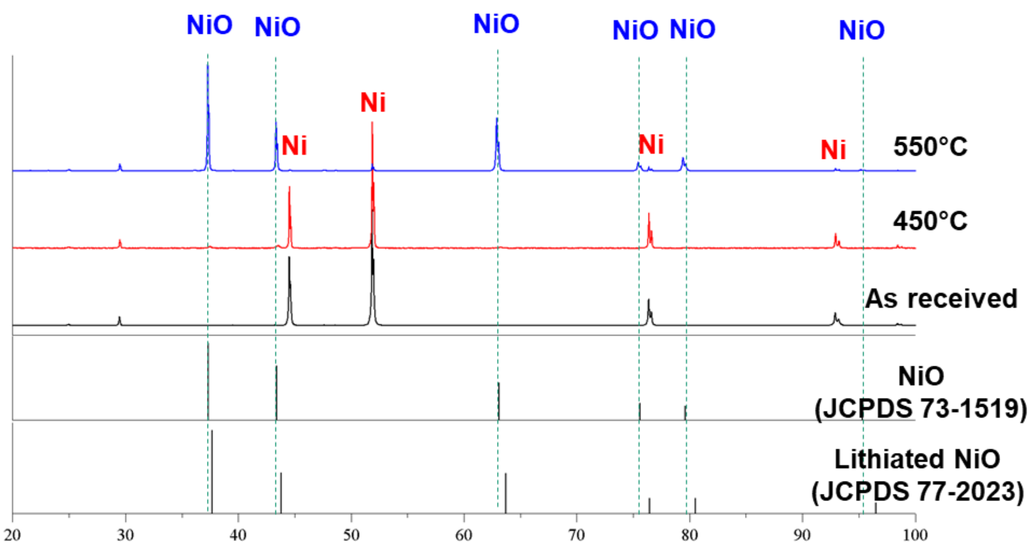


- Formation of mixed oxide scales ($LiFeO_2$, $LiFe_5O_8$) with faceted morphology could be spontaneously produced in Li/NaOH electrolyte due to its negative Gibbs energies.

Hot Corrosion Test: Ni-Metal in Li/Na Hydroxide

Test Condition: N_2-3%H_2O at 450 and 550°C for 50 h.





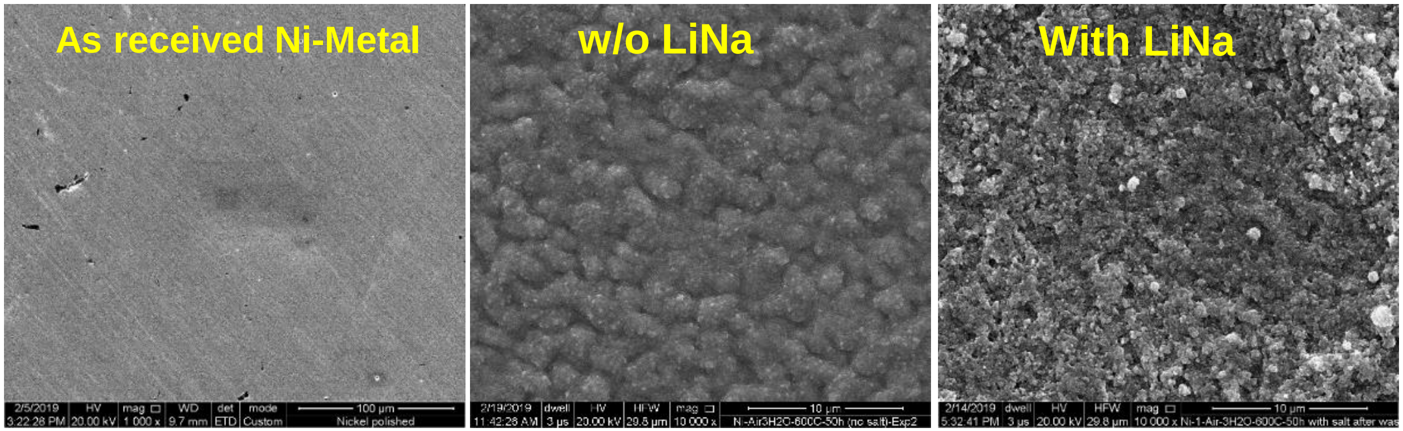
- At 550 ℃, nickel was oxidized to form NiO phase on the surface and the NiO peaks increase in a higher temperature.
- **Lowering temperature to 450 ℃ can mitigate hot corrosion tremendously**
  - No NiO observed from XRD

UCONN
UNIVERSITY OF CONNECTICUT

Hot Corrosion Test: Ni-Metal in Li/Na Hydroxide

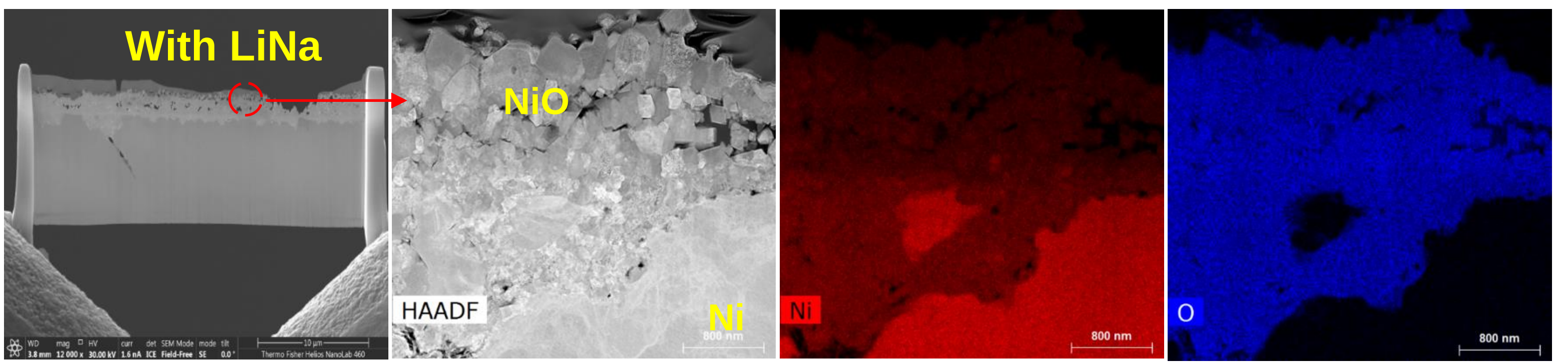
Accelerated Test Condition: 3%H_2O-Air at 600°C for 50 h.

After oxidation in 3%H_2O-Air



Dense oxide scale

Porous oxide scale

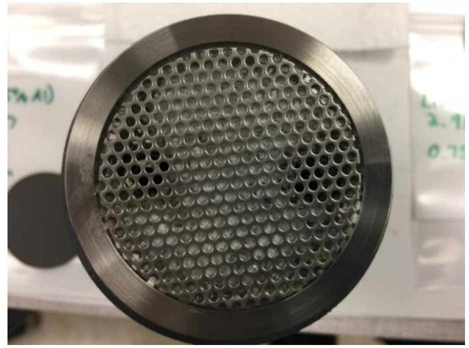


- Extremely porous oxide microstructure appears after 50 hrs in LiNaOH at 600 °C.
- Oxide scale consists of NiO, and appears denser near metal/oxide interface as compared to oxide/air interface.
- **Varying molten hydroxides can also change the degree of hot corrosion**

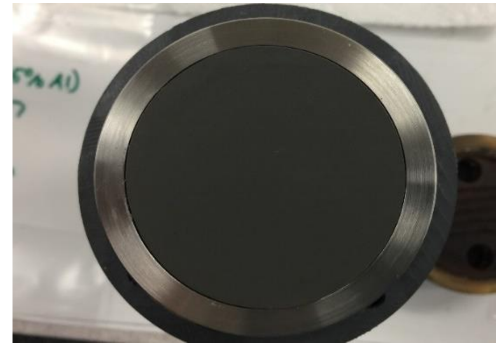
Accomplishment 3: Single Cell Design and Testing

Button Cell Components

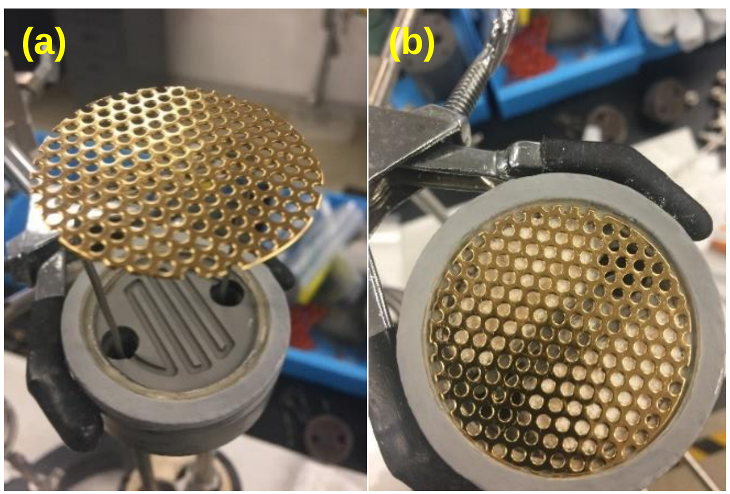
Electrolyte stored in cell compartment (AD)



Electrode (CD)



Advanced Electrolyzer Cell Components



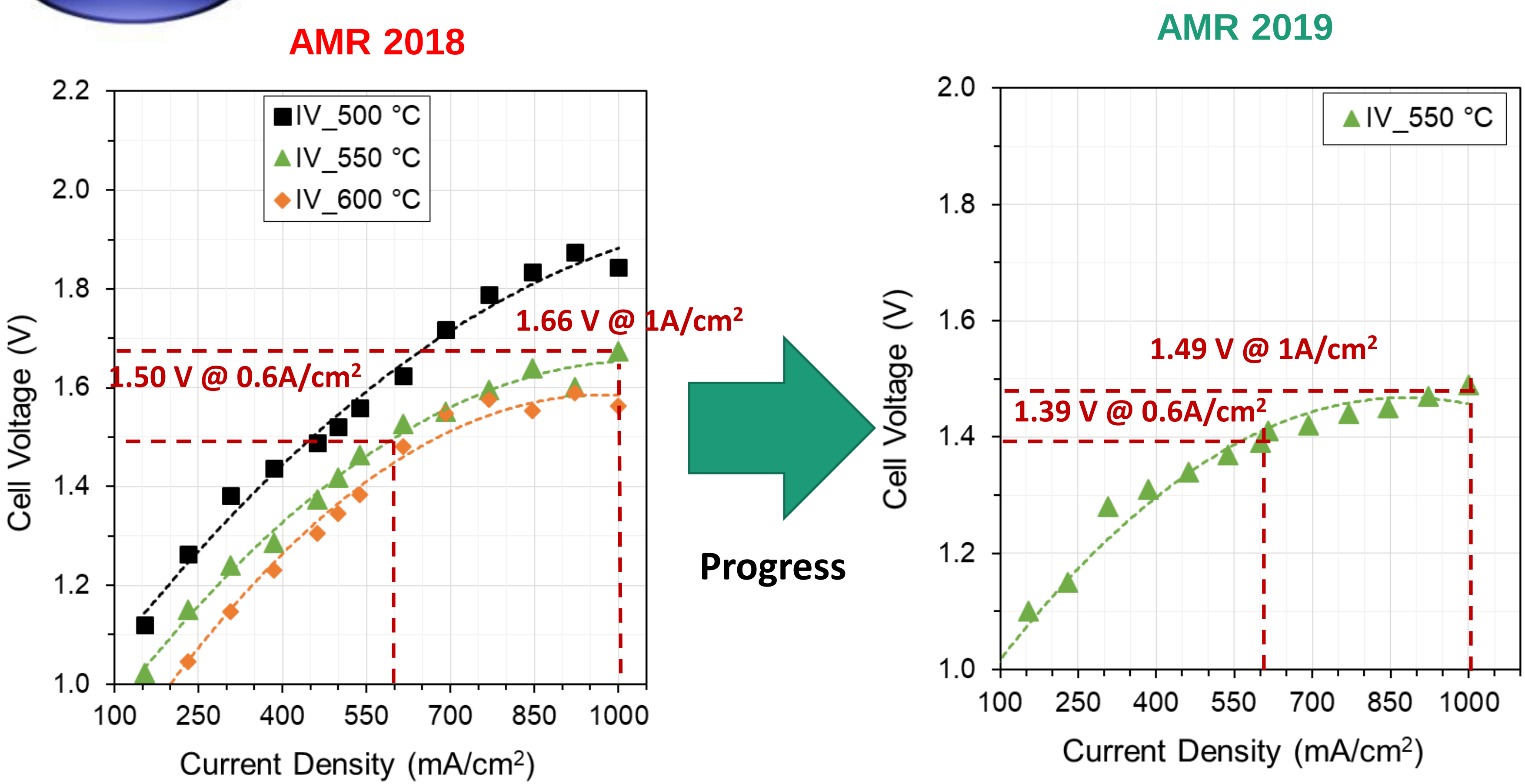
Gold plated-Ni current collector

Advanced Active Cell Components
- Anode: AD-1 (thickness ~200 µm)
- Cathode: CD-1 (thickness ~200 µm)
- Matrix: YSZ (thickness 200-400 µm)
- Electrolyte: molten NaCsOH or variations

Advanced Inactive Cell Components
- Gold plated Ni-current collector
- Aluminized wet-seal area
- Advanced sealing materials

Gold (thin-film)-plated Ni current collector can enhance corrosion resistance

HTAWE Cell Performance at 550°C

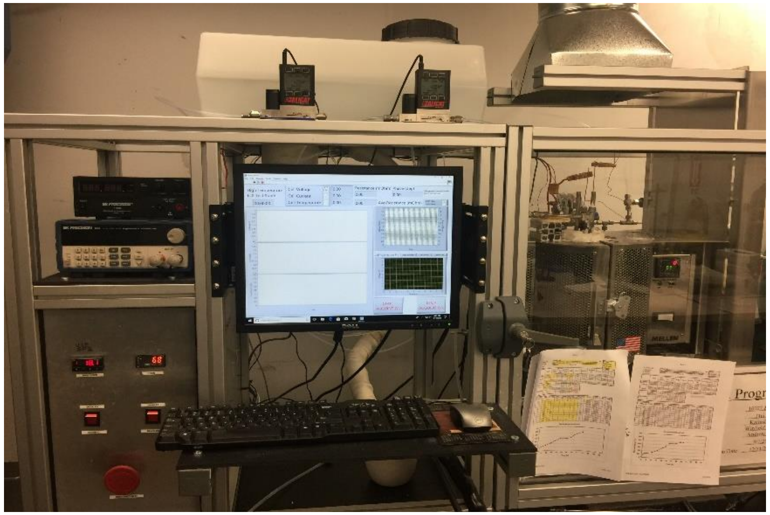


Met Go/No Go Decision (1st performance period) Point

- ❑ Achieve electrolyzer performance of < 1.5 V at a current density of 1.0 A/cm^2 at temperature of 550 ^{o}C;
- ❑ Achieve electrolyzer performance of < 1.4 V at a current density of 0.6 A/cm^2 at temperature of 550 ^{o}C

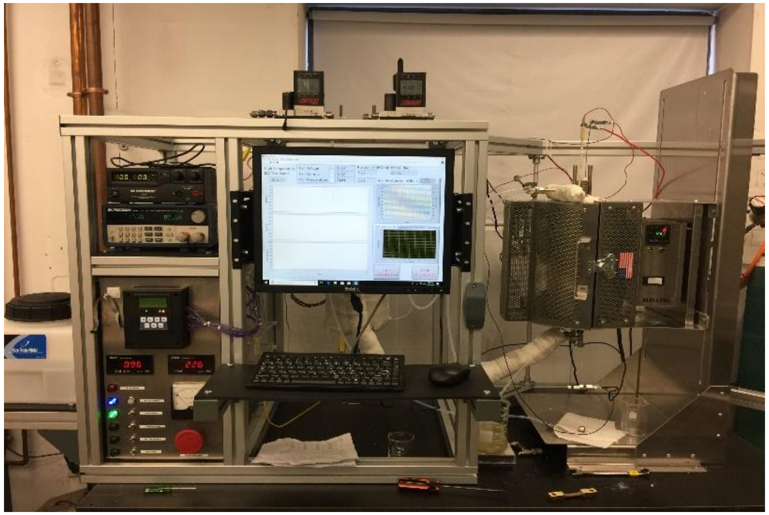
Constructed Automatic Electrolyzer Test Station

Old Test Station



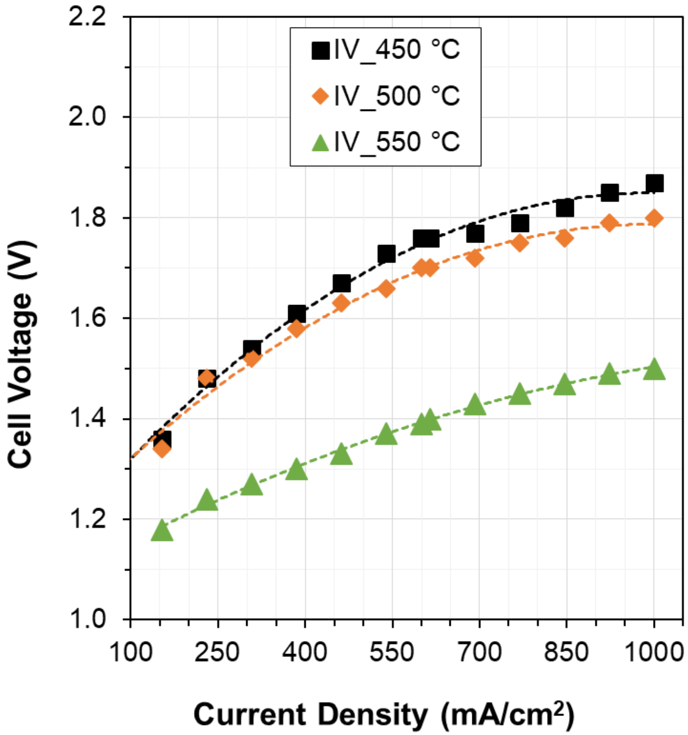
- ❑ Use nitrogen as a carrier gas in order to deliver reactants
- ❑ Manually refill the boiler, and regulate steam flow rates and temperatures

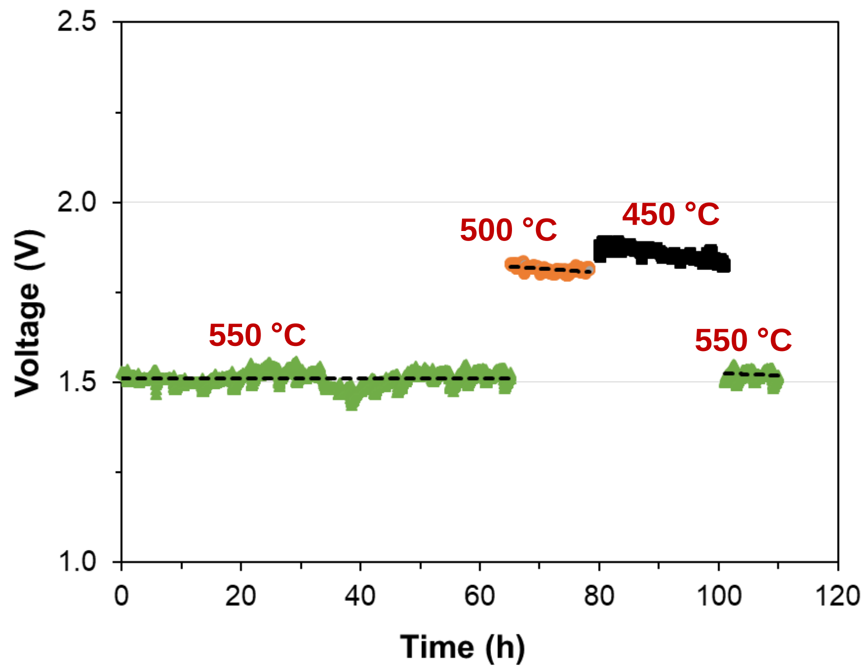
New Test Station



- ❑ No nitrogen as a carrier gas
- ❑ Industrial controller to continuously monitor cell conditions
- ❑ Automatically refill the boiler, and regulate steam flow rates and temperatures
- ❑ Ability to produce up to 1.7kg/h of pure steam at atmospheric pressure

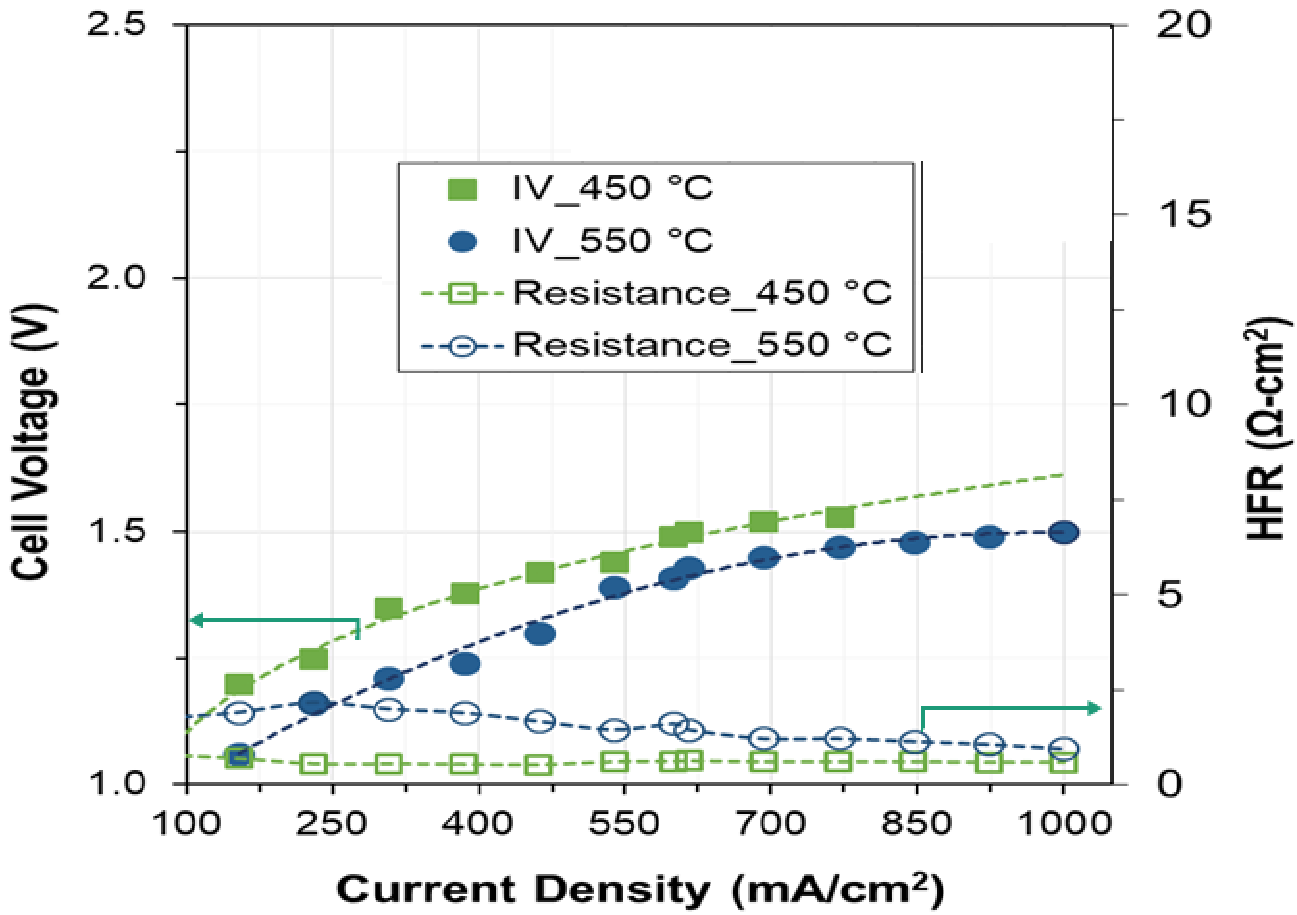
HTAWE Cell Performance and Durability





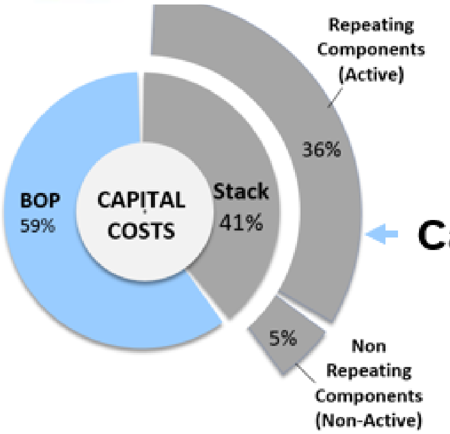
- Successfully achieved a cell performance of 1.5 V at a current density of 1000 mA/cm^2 after 120 h.
- Lowering temperature dramatically deteriorates cell performance, due to suppressed kinetics and increased resistance

Improved Performance at Lowered T (450 °C)



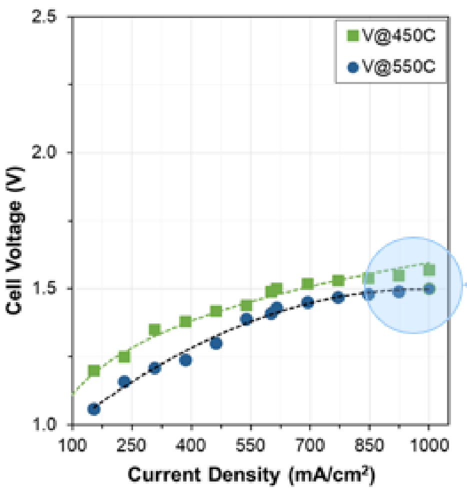
- Cell performance improvement at 450 °C (vs Slide 19) due to
  - Low melting-point electrolyte (conductivity barely increased when T> 450 °C)
  - Reduced corrosion (corrosion-resulted cell resistance decreased at lower T)

Accomplishment 4: Projected HTAWE Cost



CapEx

OpEx



H_2 Production Cost Contribution	HT Alkaline Cost ($/kg)	PEM Comparison Cost ($/kg)
Capital Costs[1]	0.38	1.30
Feedstock Costs[2]	1.44 (39.3 kWh/kg)	1.96 (50.5 kWh/kg)
Fixed O&M	0.75	0.70
Variable Costs	0.020	0.020
Total Hydrogen Production Cost ($/kg)[3]	**2.59**	**3.98**
Delivery (CSD)	2.46	2.46
Total Hydrogen Production Cost ($/kg)	**5.05**	**6.44**

CSD Related Cost

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

[1]20 year lifetime, [2]Based on low electrical cost of $0.039/kWh, cell voltage of 1.4V, [3]Design Capacity: 1500 kg-H_2/d. Assumes large scale production.

- Economics: determined using H2A cost models
- Based on 1 A/cm² Operation. Increasing Active Area & Operating Current Density reduces Capex.

Energy Balance

HT Alkaline Electrolysis, 1MW Mass & Energy Balance

Target: 450°C, 1.50V/cell

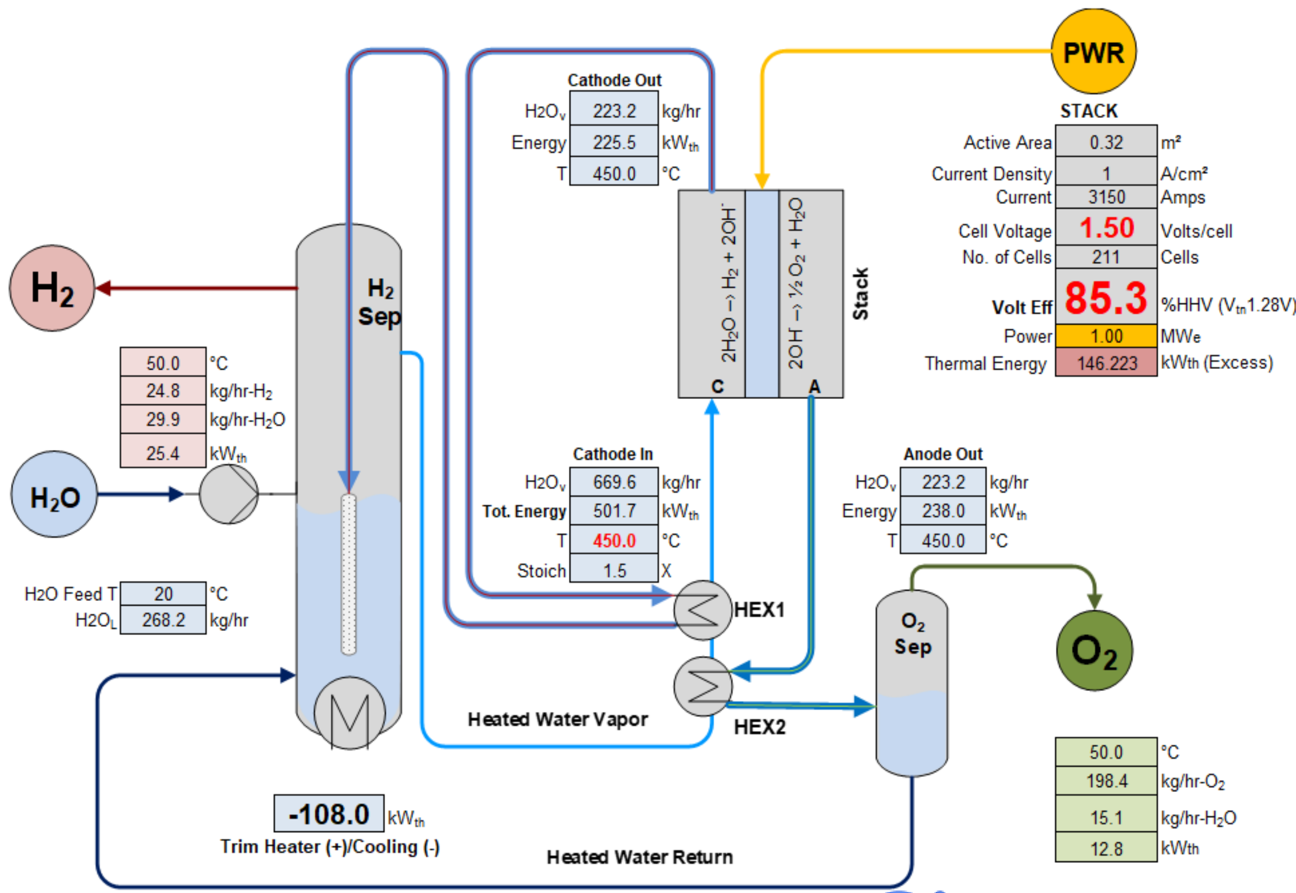
Trim Heater/Cooling

Cell Voltage (V)	Trim Heat kWth*	
0.900	291	~Minimum Cell V
1.000	224	
1.100	157	
1.200	91	
1.280	38	Thermo-Neutral V
1.300	25	
1.400	-42	
1.500	**-108**	Target V
1.600	-175	
1.700	-241	
1.800	-307	

Heat Req'd ↑ / Cooling Req'd ↓

** Assumes **90%** heat recovery*

- Operating cell above Vtn (1.28V) results in excess thermal heat from system (can be used for trim heater)
- Operating below the Vtn can require a significant amount of energy to operate Trim heater



HTAWE Efficiency reached 92% at 550 °C

GINERELX

Collaborations

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

Summary

- **Stability of a variety of metal oxides was investigated under simulated HTAWE temperature and reactant conditions**
  - YSZ underwent a degree of degradation via the formation a new oxide phase
  - CeO_2 was partially dissolved in molten hydroxides and followed up by re-deposition
  - Li_2ZrO_3 powders demonstrated remarkable stability in molten hydroxides and can be used the next generation material to extend matrix lifetime
- **The corrosion of the SS-316 and Ni-materials in molten Li/NaOH melt was conducted under simulated HTAWE conditions**
  - Formation of surface oxide scale was observed for both materials while Ni showed less degree of corrosion
  - Lowering temperature and changing electrolyte composition can help to mitigate the component corrosion
- **HTAWE cell performance continuously improved**
  - Achieved 1.5V at 1000 mA/cm2 at 550 °C, meeting Go/No Go milestone
  - Newly developed components led to stable cell performance up to 120 hours
  - Lower temperature (450 °C) operation was realized
- **Preliminary energy balance of 1MW water electrolysis was conduced**
  - Electrical efficiency can be higher than 90% at 550 °C
  - Tremendous cost savings can be realized using HTAWE

Future Plans and Challenges (FY18-19)

Future Plans

- Matrix and composite electrolyte optimizations
  - Synthesize new matrix material (e.g. Li_2ZrO_3-fine powder)
  - Optimize the Li_2ZrO_3-matrix fabrication process
  - Optimize electrolyte compositions-e.g. ternary electrolyte inventory
- HER and OER catalysts optimizations at 450 °C
  - Fabricate thinner electrodes
  - Optimize microstructure design
- Reduced electrolyzer cell temperature to 450 °C
  - Perform durability test at 450 °C for 300 h
- Components corrosion mitigation
  - Optimize SS-316 or 310 and Ni-based current collector
  - Perform perovskite oxides coating to minimize corrosion at lower T
- Design the stack module
  - Cost analysis and system design (Giner-Elx)

Future Challenges

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

Acknowledgments

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