



2020 DOE H₂ and Fuel Cell Annual Merit Review Meeting

High-Temperature Alkaline Water Electrolysis

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Project
P143

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Project Overview

GINER

Timeline

- Project Start Date: Jan. 1, 2017
- Project End Date: June 30, 2020

Budget

- Overall \$ 1,722,885
 - DOE share \$ 1,375,123
 - Contractors share \$ 347,762
 - Spent \$ 1.73 million (cost sharing ~ **25%**)

Giner Researchers

Judith Lattimer, Kailash Patil, Steve McCatty, and Yamini Mohan

Collaborator

- University of Connecticut (Sub.)
- Giner ELX (Sub.)
- Chao-yi Yuh (Consultant)

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-cm² at 300 to 550 °C using a membrane thickness of 200 μm.
- Stack electrical efficiency > 90% LHV H₂ with current density at 1.2 A/cm²

Overall Project Objectives

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

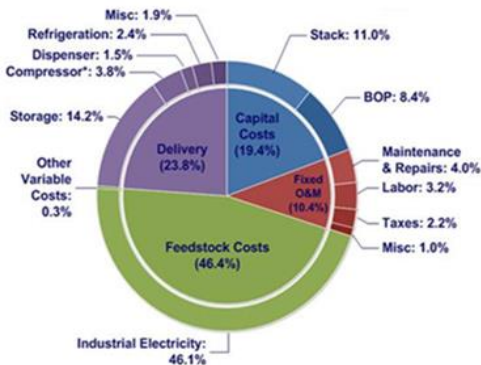
Technical Objectives

- Develop electrolyte support metal oxide matrix
- Evaluate the matrix materials solubility in hydroxide electrolyte at 400-550 °C.
- Demonstrate single cell performance <1.5 V at 1,000 mA/cm² at temperature <550 °C.
- Reduce the electrolyzer cell temperature of 550 °C to 450 °C.

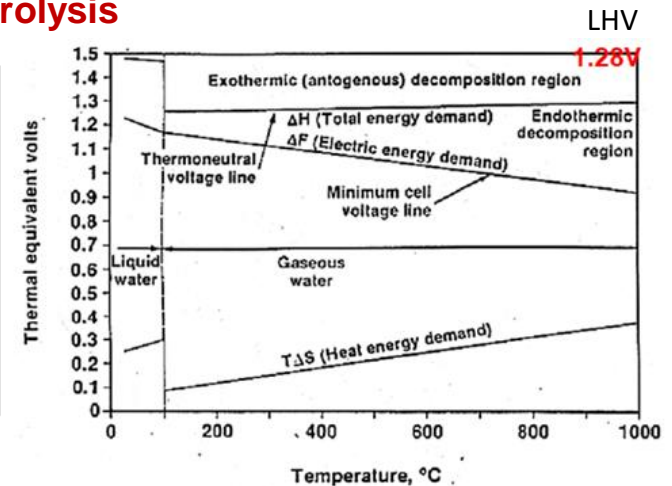
Impact

- 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



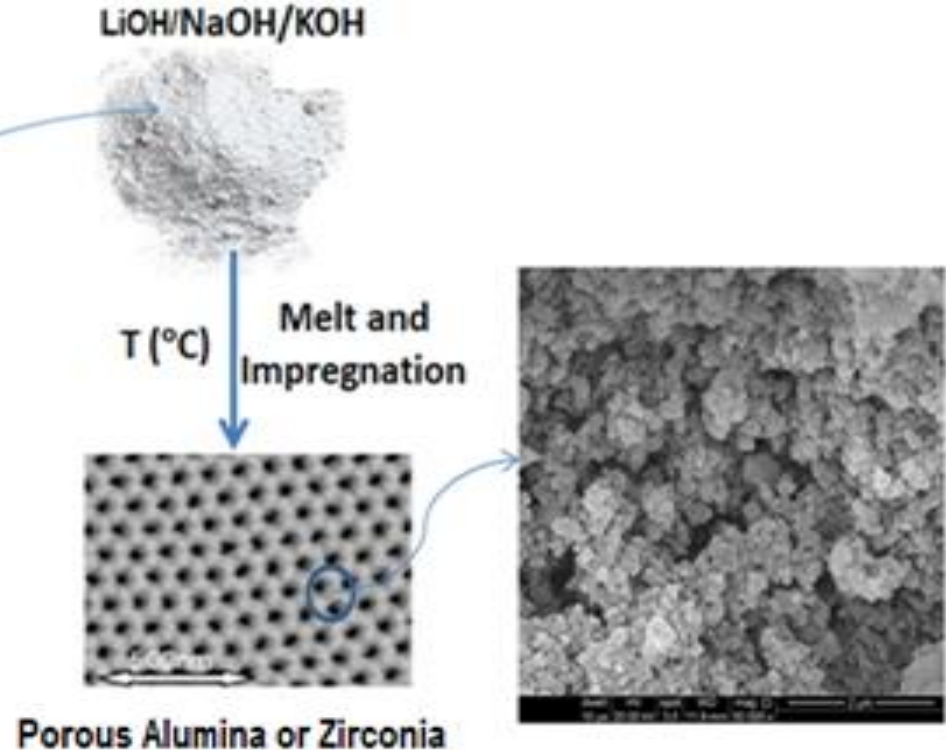
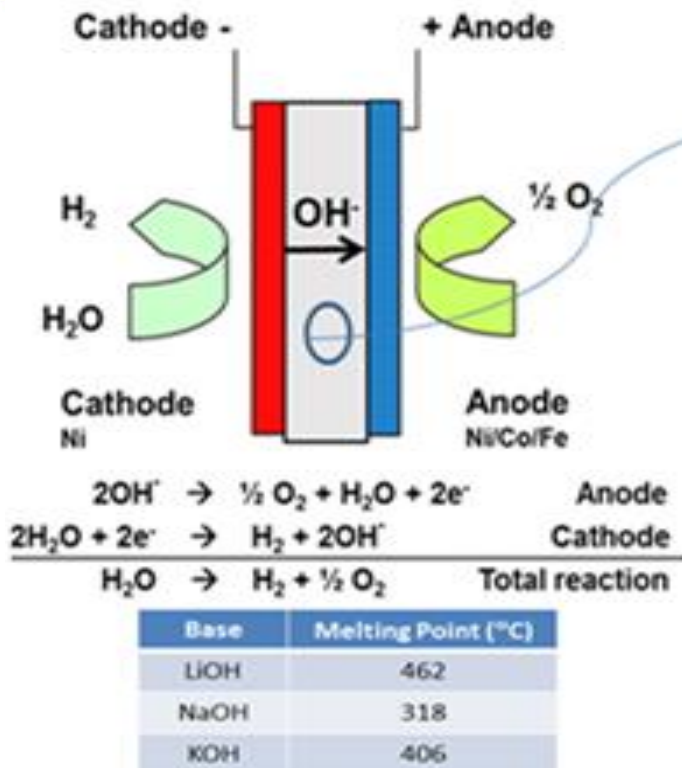
Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost ^d (Production Only)	\$/kg	4.20 ^d	3.90 ^d	2.30 ^d
Electrolyzer System Capital Cost	\$/kg \$/kW	0.70 430 ^{e,f}	0.50 300 ^f	0.50 300 ^f
System Energy Efficiency ^g	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency ^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 Approach

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Major Advantages

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

Key to Success

- ❑ Porous metal oxide matrices stable in molten hydroxides
- ❑ Microstructure of the porous oxide matrices determines whether it can successfully retain molten hydroxides
 - thickness, porosity and pore structure



Approach: Tasks and Milestone Progress

Task No.	Task Title	Milestone Description	Progress Notes	Status
1	Stability of Metal Oxide Materials	<ul style="list-style-type: none">Select stable metal oxide in molten hydroxide electrolyte	<ul style="list-style-type: none">Identified stable metal oxide in molten LiNa and NaCs electrolytes	100 %
2	Corrosion Mechanism of Non-active Components	<ul style="list-style-type: none">Optimize corrosion of current collector in molten hydroxide electrolyte	<ul style="list-style-type: none">Performed hot corrosion/oxidation of various metal materials (SS-316 and Ni-metal) in molten hydroxide	100 %
3	Assemble and Test single cells	<ul style="list-style-type: none">Complete testing at least 5, 25 cm² cells with composite electrolytesPerformance and durability test	<ul style="list-style-type: none">Designed and construct HT-electrolyzer test stationDesigned button cell area of 13 cm²	100 %
4	Perform Energy Balance	<ul style="list-style-type: none">Perform compression costEnergy balance for 1MW mass and energy balance	<ul style="list-style-type: none">Conducted compression cost based on 1 A/cm², active area and operating current densityPerformed energy balance at 450 °C, 1.50V/cell and 550 °C, 1.40V/cell	100 %

- **Electrolyte loss from matrix**
 - Non-optimal matrix microstructure
 - Electrolyte pumping out onto external surface of cell housing via migration
- **Hot corrosion of electrode leads, cell housing, and current collectors**
 - Nickel unstable under oxidizing molten hydroxide environment
- **Hot corrosion of sintered porous Ti and Ni GDL (gas diffusion layer), leading to high electrolyte loss**
- **Gas leaking both through the matrix (cross-over) and seal area**
 - Insufficiently mechanically strong matrix, leading to cracking
 - Organic binder burnout temperature higher than electrolyte melt temperature, disrupting de-binder process causing poor pore structure
 - Incomplete burnout
 - Formation of molten carbonates due to CO₂ generation (higher melting point, increased resistance)
 - Insufficient crack resistance

Accomplishment 1 – New Cell Design

- **Cell Housing:** Now made of stainless steel aluminized on exterior and wet seal area
 - Aluminization forms intermetallic surface protective layer: During operation, a thin protective Al_2O_3 layer forms, reducing hot corrosion and electrolyte pumping
- **Current Collectors:** Made of SS on anode side, and Ni on cathode side
 - Using perforated plates now
 - Increased thickness for enhanced electrode and matrix mechanical support
 - Additional support material between PP and housing prevents matrix deformation
- **Gas Diffusion Layers:** Made of SS on anode side, and Ni on cathode side
 - SS mesh cloth as anode GDL
 - Densified Ni foam supported on Ni screen as cathode GDL
 - Both GDLs are coated with catalyst ink, using low-burn out temp binders
- **Electrolyte Matrix – Reformulated completely**
 - Tape-cast matrix recipe modified to improve strength and microstructure
 - Standardized matrix slurry tape casting process
 - Added Al_2O_3 boulders as crack arrestor and Al powder to increase strength
 - Used lower temp burn-out binders to reduce conditioning time/temperature and ensure complete binder removal
 - Complete conditioning before adding electrolyte
 - Prevents molten hydroxide from reacting with organics in cell and damaging components
 - Allows electrolyte addition during cell operation as needed

Matrix Fabrication Reformulation

- Initial tests with reinforced matrix showed good performance/low resistance for a short time, with rapid performance degradation and increased cell resistance
- Post-test analysis confirmed matrix expansion and deformation
- Using new cell components with improved matrix support and optimized cell compression has largely resolved the matrix expansion problem, leading to cells with $ASR < 0.2 \Omega \cdot \text{cm}^2$



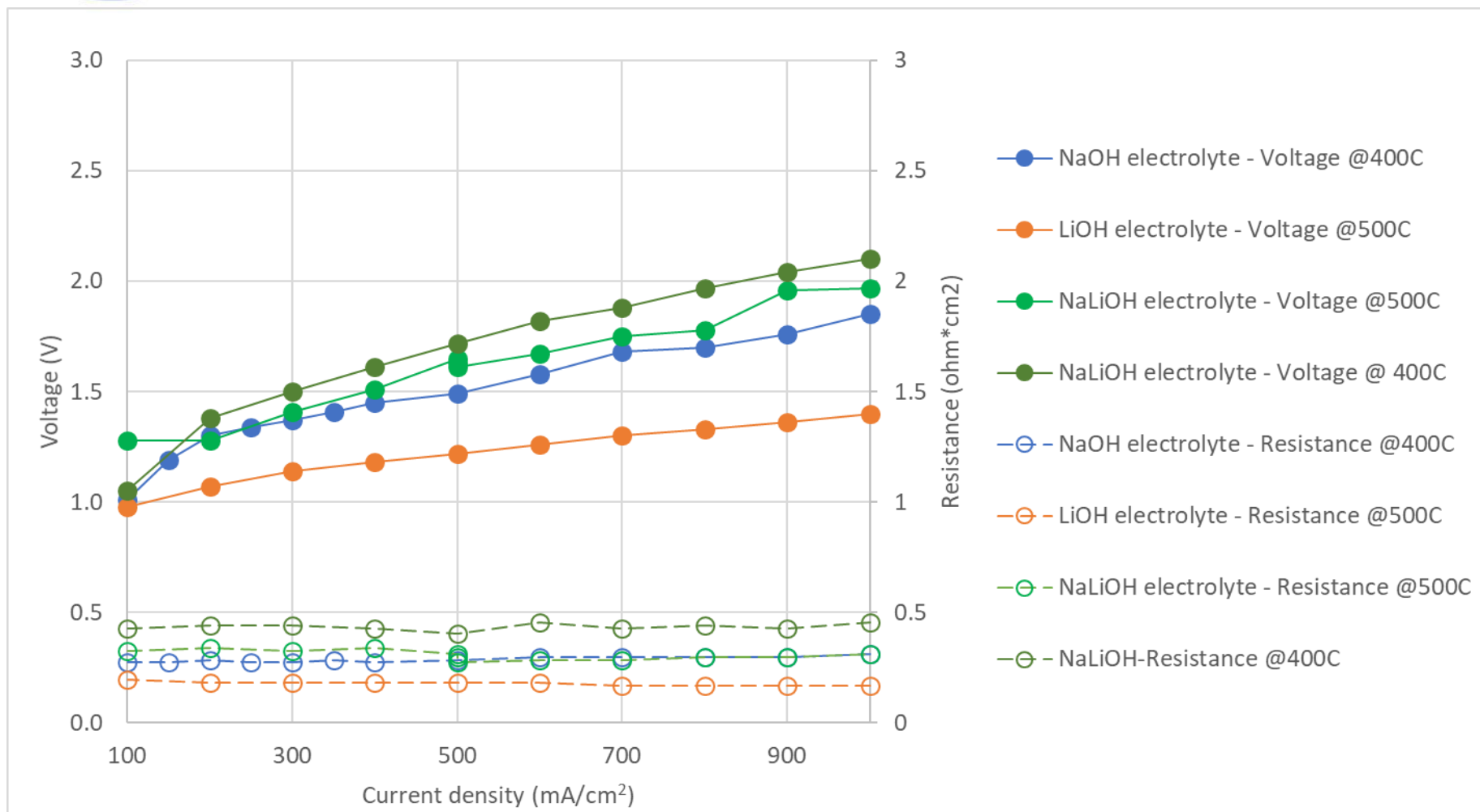
Matrix deformation and expansion was an issue in the initial cells



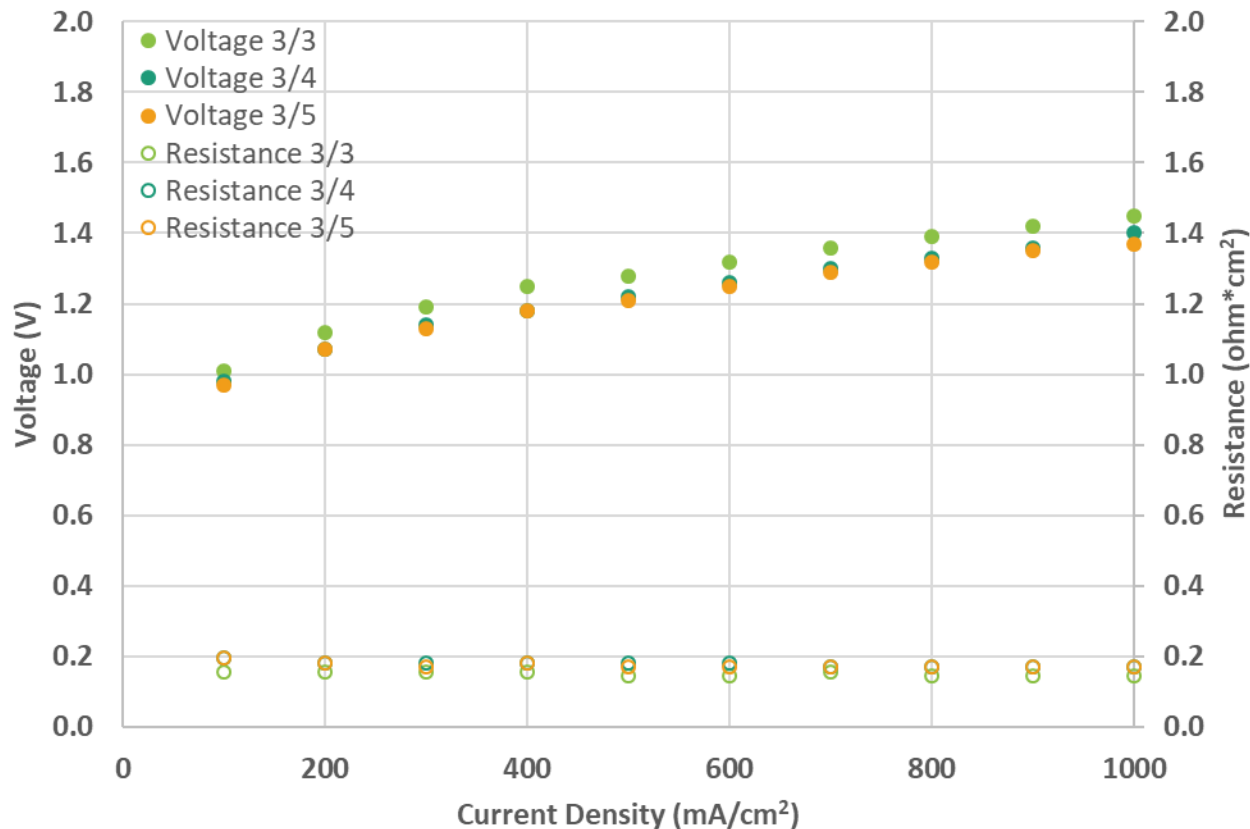
After instituting new components, matrix deformation and expansion was largely resolved.

- However, results from UConn indicate that the LiOH reacts with YSZ and alumina
- Currently pursuing Strontium Zirconate based matrix formulation after UConn showed promising stability under molten hydroxide – results shown later
- Have used the new formulation in the latest cell build. However, data is unavailable due to statewide shutdown

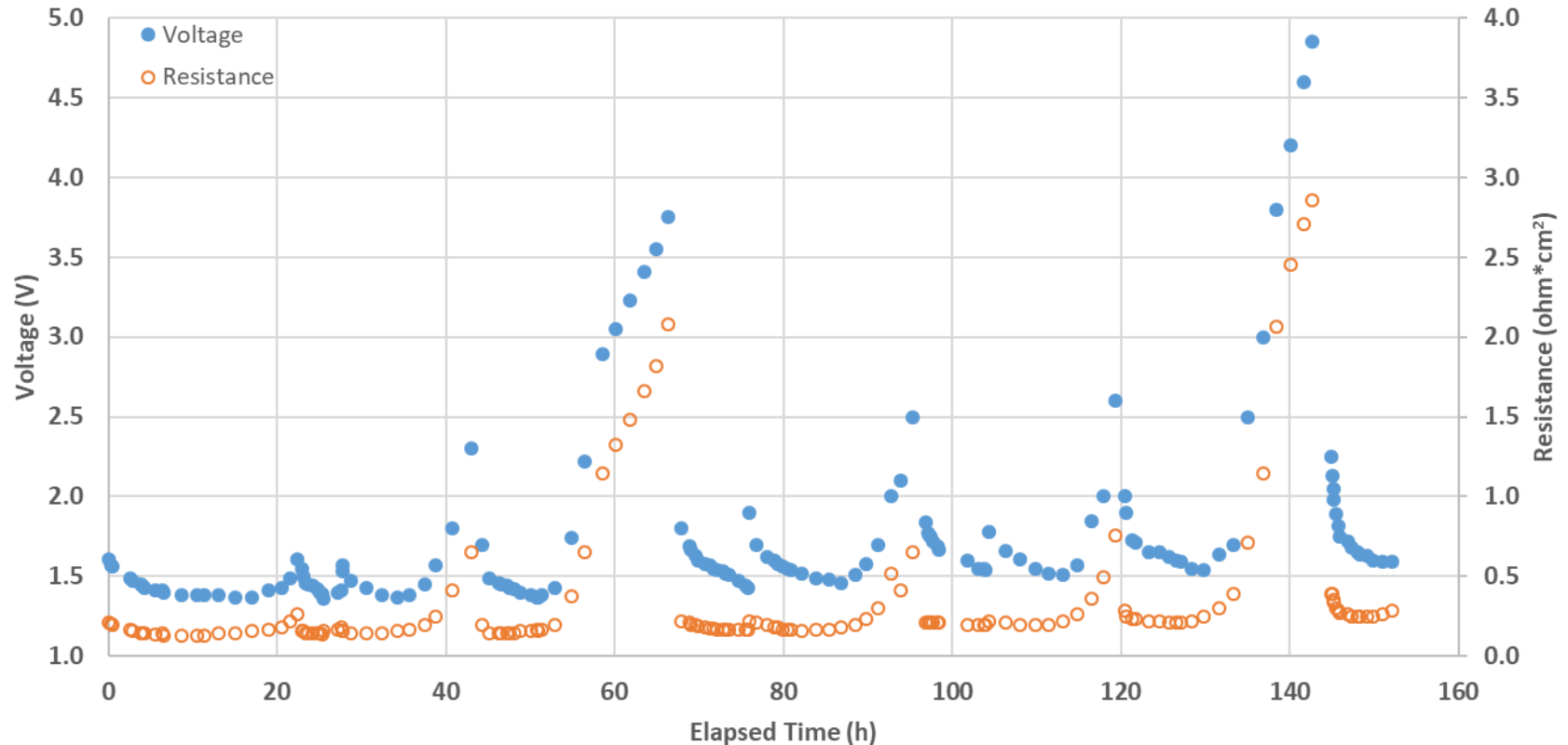
Accomplishment 2: Impact of Electrolyte Composition



- Polarization curves of all three cells
- Overall, the cell with LiOH as electrolyte had lower voltage and resistance at all current densities, with performance of 1.4 V at 1000 mA/cm² at 500 °C



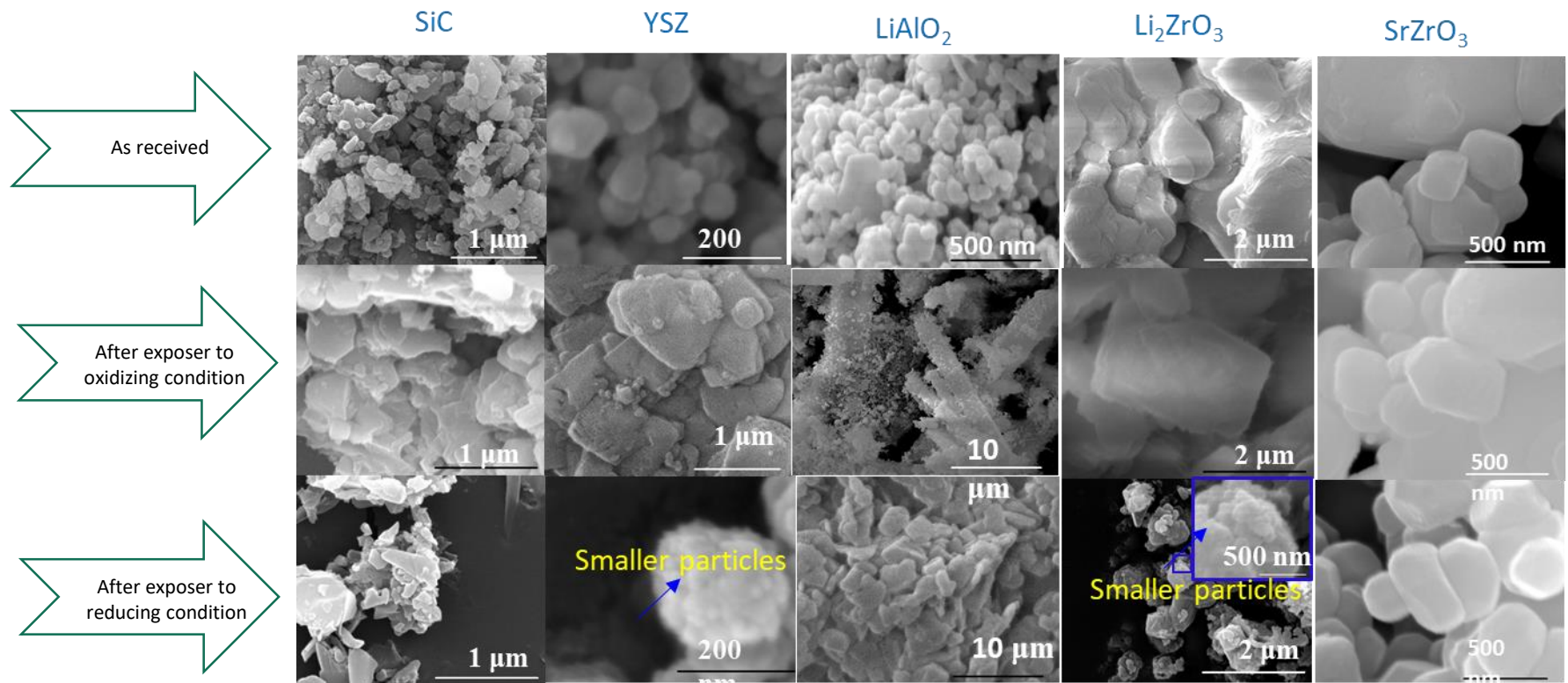
- Polarization curves at 500 °C
- Overall the cell showed good and stable performance
- Voltage at 1000 mA/cm² was consistently below 1.5 V after the cell stabilized
- Voltage stable at 1.4 V or below for a continuous duration of 8-12 hours



- Long term testing of cell with LiOH electrolyte at 500 °C and 1000 mA/cm² condition
- The cell showed recoverable performance every day after electrolyte addition
- Cell was run for a total of 150 hours with voltage around 1.5 V

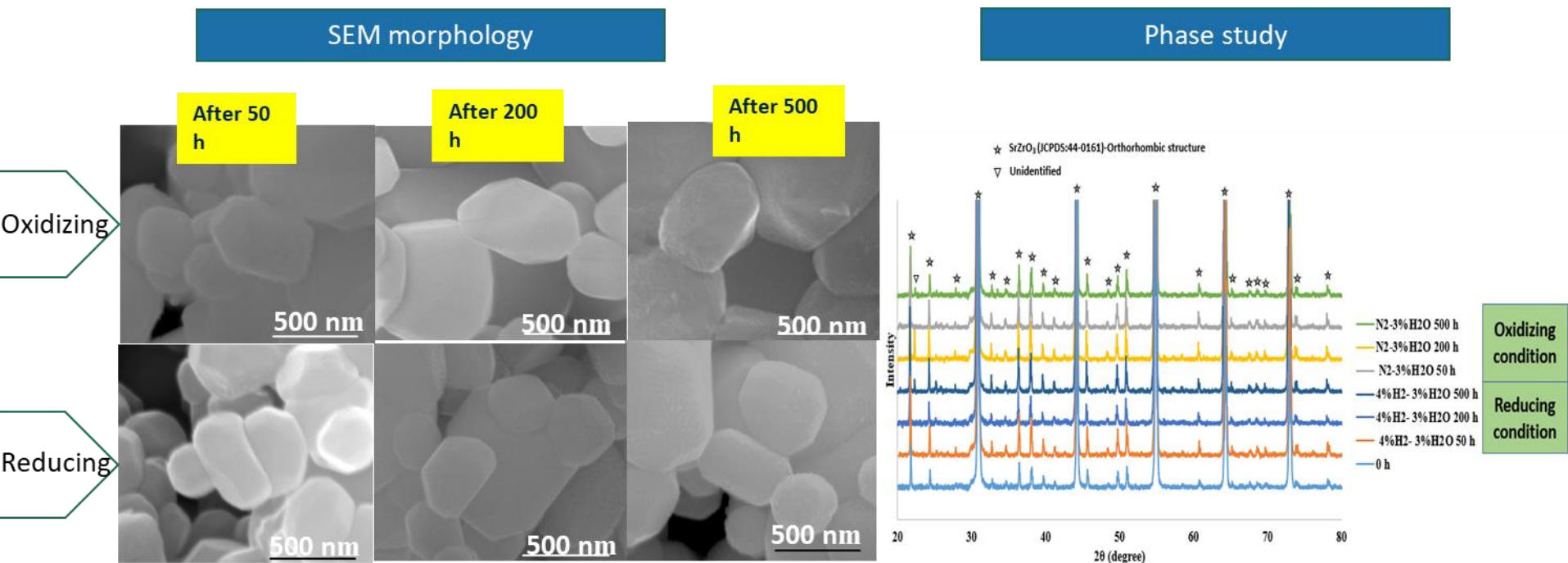
Accomplishment 3: New Matrix Development

Stability of Matrix in hydroxide melt at 550 C during 50 h test



Compared to SiC, YSZ, LiAlO₂, Li₂ZrO₃ matrix materials, SrZrO₃ shows improved structural stability

SrZrO₃ stability in hydroxide melt under oxidizing and reducing condition at 550 C

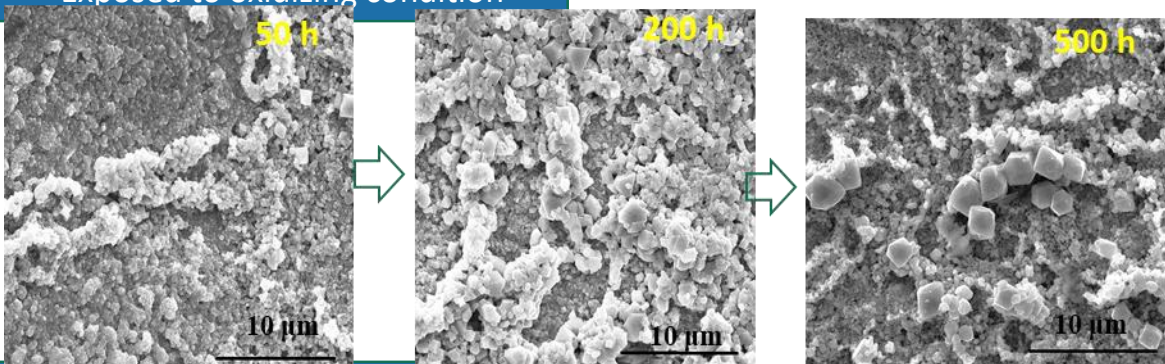


- Particle size and morphology of SrZrO₃ powder remain unchanged during 500 h exposure in hydroxide melt
- No chemical change in SrZrO₃ was observed under both the oxidizing and reducing condition during 500 h test

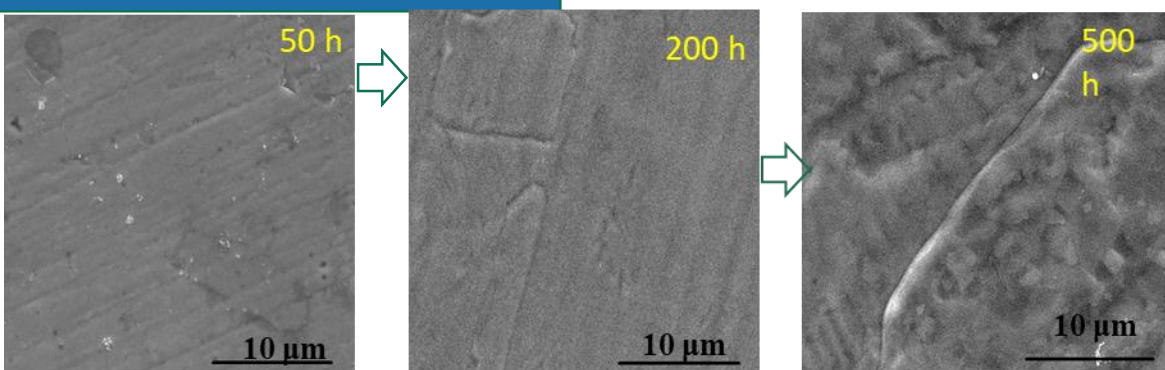
Accomplishment 4: Component Stability

Surface morphology and chemistry of Ni in hydroxide under oxidizing and reducing conditions at 600 C

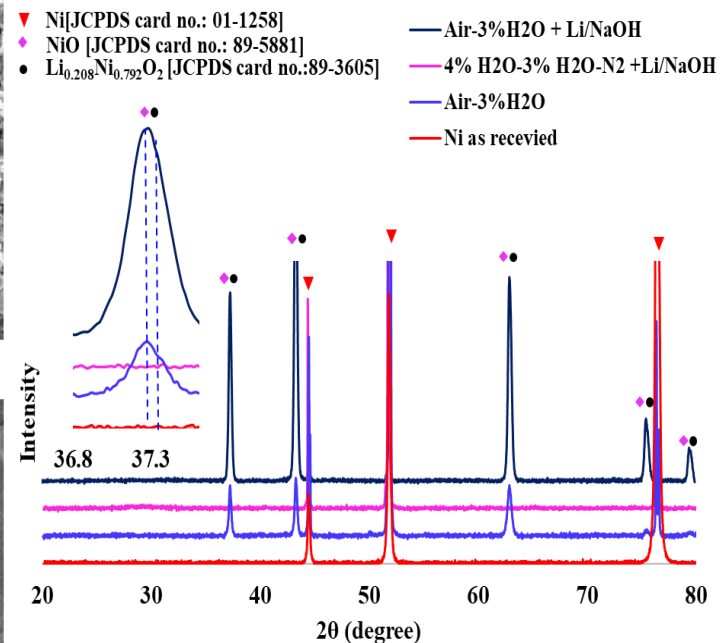
Exposed to oxidizing condition



Exposed to reducing condition



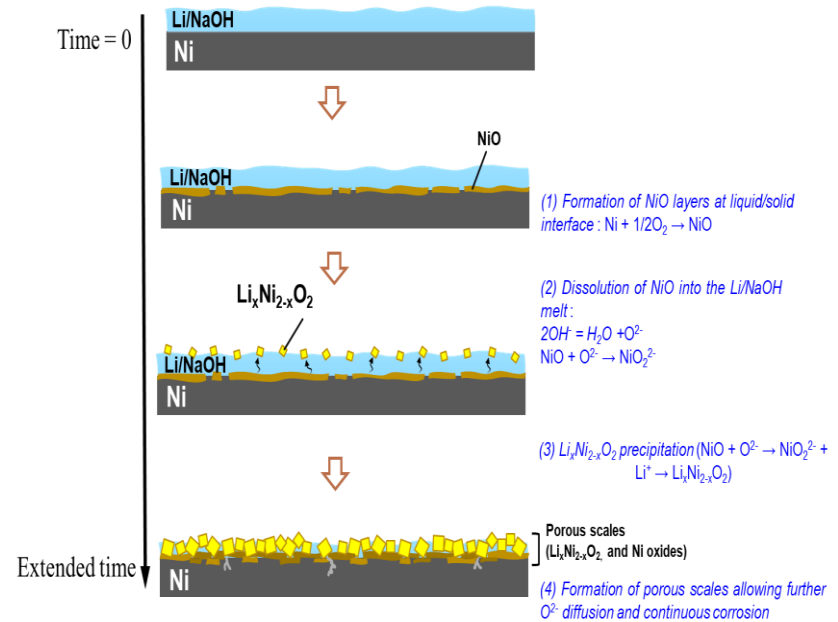
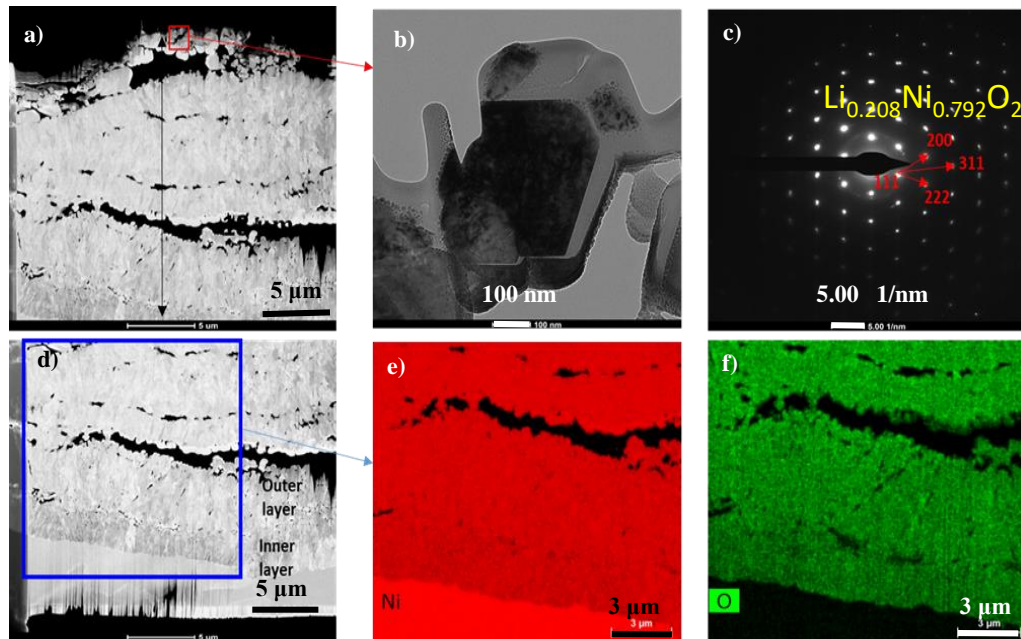
XRD analysis after 50 h test



- Porous lithium nickel oxide scale forms on Ni under the oxidizing condition
- Ni remains metallic under reducing condition

Component stability under water electrolysis conditions

Corrosion of Ni in presence of hydroxide under oxidizing condition during 50 h test at 600 C



- An extremely porous scale formation is observed in the presence of hydroxide.
- Thick oxide scale between 10 μm to 18 μm appears within 50 hrs.
- The oxide scale growth on the Ni does not maintain diffusion-controlled growth in hydroxide melt

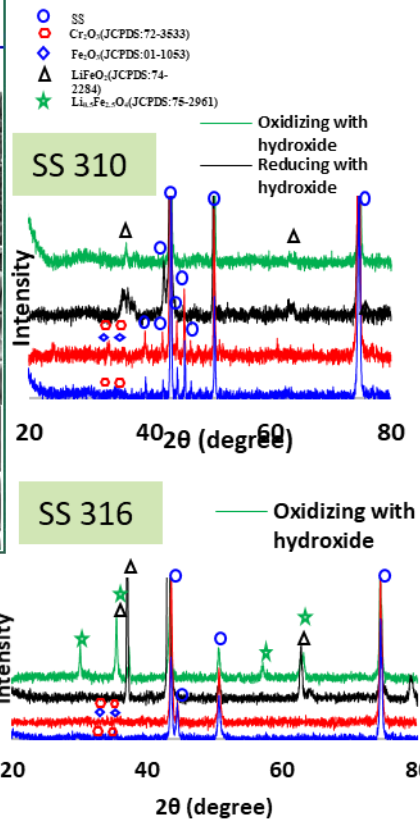
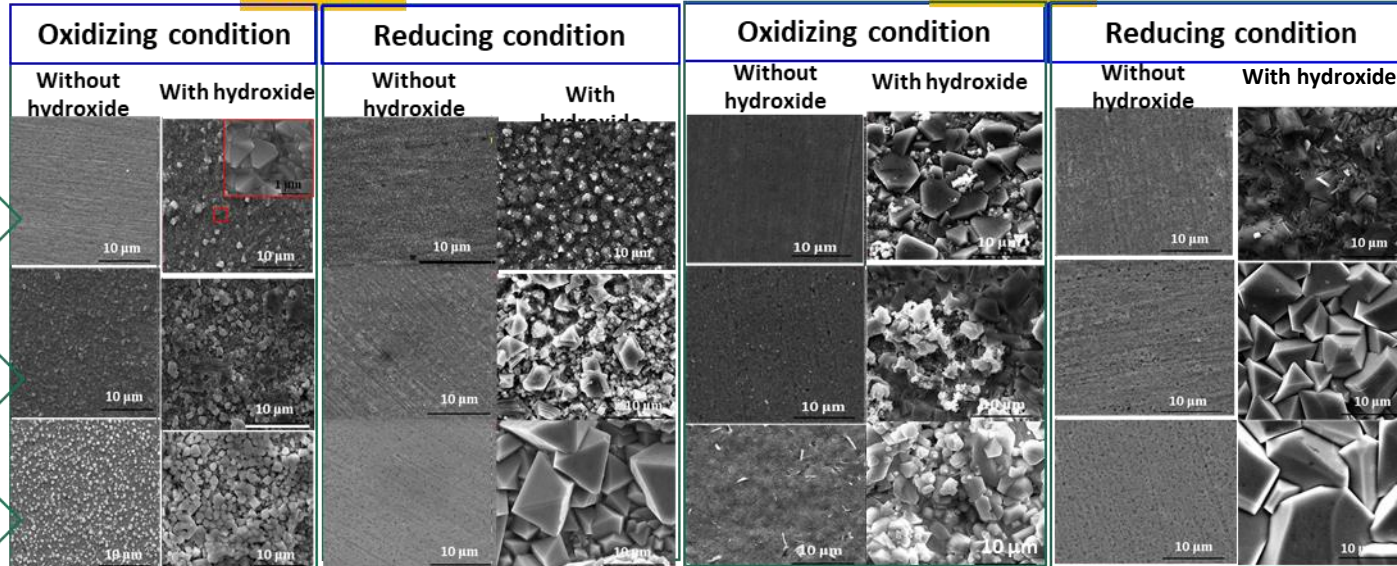
Component stability under water electrolysis conditions

Corrosion of stainless steels in hydroxide under oxidizing and reducing conditions at 600 C

AISI 310

AISI 316

XRD analysis after 50 h

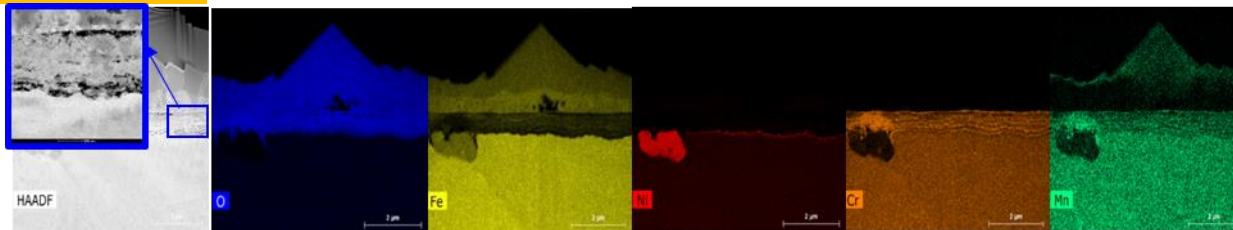


- Oxidation of SS 310 and 316 without Li/NaOH shows formation of dense oxide scale.
- Corrosion of SS in presence of Li/NaOH at 600 °C under both the oxidizing and reducing condition forms porous lithium iron oxide scale

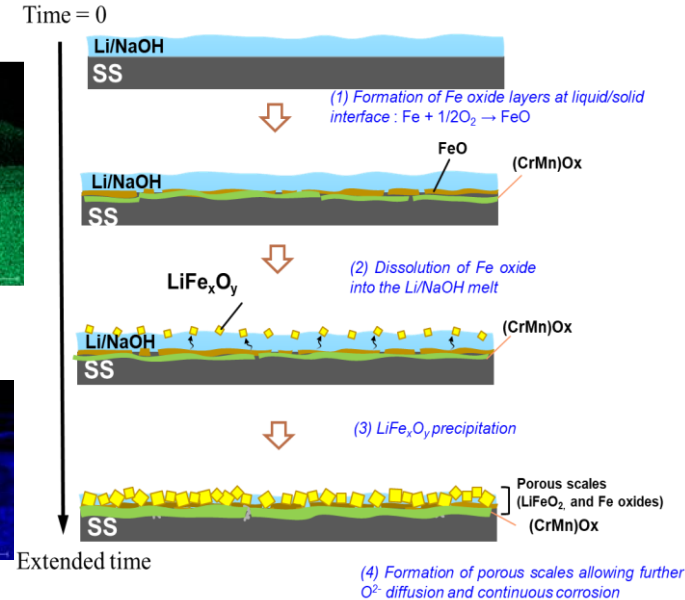
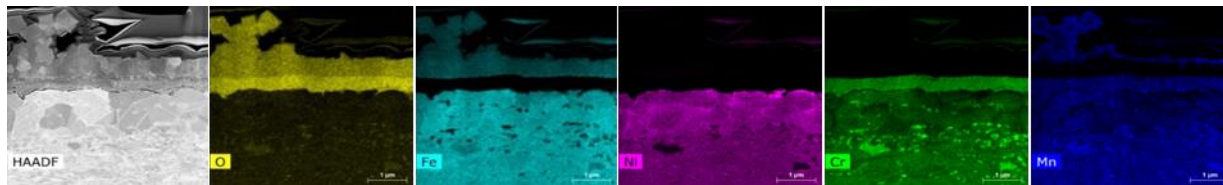
Component stability under water electrolysis conditions

Corrosion of stainless steels in hydroxide under oxidizing condition during 50 h test at 600 C

AISI 316



AISI 310



- Growth of multilayer oxide scale appears after 50 hrs in Li/NaOH.
- Outward diffusion of Fe and Mn takes place
- (Cr,Mn)Ox scale remains near the metal/oxide interface.
- Cr rich scale does not appear to be protective.



Responses to Previous Year Reviewers' Comments

Reviewer's Comments	Response
"More focus on corrosion issues and cell performance degradation is recommended."	Significant work analyzing the corrosion mechanisms of the matrix and hardware materials were performed this year by Giner and UConn in order to better understand how corrosion leads to performance degradation during cell operation.
"Focus on long-term durability and corrosion mitigation should be increased."	Redesign of the cell, including reformulation of the matrix and replacement of many of the cell components to reduce corrosion and improve long-term durability was successfully implemented in the past year.
"Future work [should be] aimed at evaluating the newly discovered matrix material and optimizing performance at lower temperatures."	Development of both new matrix materials and formulations to improve matrix strength and durability during testing have been done in the past year. Performance optimization at lower temperatures by varying the electrolyte composition has been investigated, and preliminary data is promising.

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	Fundamental research and understanding of the matrix coarsening and corrosion of the components in the molten hydroxide medium.

- ❑ Successfully conceptualized, designed, fabricated and validated HTAWE, demonstrating significant advantage of HTAWE
- ❑ HTAWE cell was redesigned to address many of the structural and performance issues
 - Cell components were replaced to improve stability/durability under operating conditions
 - Matrix was reformulated to improve strength and electrolyte retention
 - Current collectors were redesigned to use the cell housing as direct voltage/current leads
- ❑ HTAWE cell assembly procedure was reconfigured to improve reproducibility and stability
 - All components were precision machined to ensure optimal protrusion and good contact between all components, catalysts, and matrix
 - Extensive posttest analysis performed to improve cell performance with successive cell builds
- ❑ **Cell performance of <1.4 V at 1000 mA/cm² was achieved at 500 °C**
 - Cell resistance was decreased to <10 m Ω across cell (0.13 Ω ·cm²) with great repeatability
 - Performance was stable for >120 h, and was recoverable upon addition of electrolyte to reduce resistance/voltage back to optimal levels
- ❑ Matrix material stability under molten hydroxide conditions investigated
 - SiC, YSZ, α -LiAlO₂ and Li₂ZrO₃ show chemical and structural changes
 - No chemical and structural change in SrZrO₃ were observed under both the oxidizing and reducing condition during 500 h test
- ❑ Corrosion of Nickel under oxidizing and reducing conditions was investigated
 - Ni was stable under reducing conditions
 - Ni forms porous scale under oxidizing conditions and in molten electrolyte
- ❑ Corrosion of SS-316 and SS-310 under oxidizing and reducing conditions was investigated
 - Porous scale formed on unprotected surfaces under both oxidizing and reducing conditions

Future Plans

- ❑ Matrix and composite electrolyte optimization
 - ❑ **Integrate new SrZrO₃ material into matrix formula**
 - ❑ Assess performance using more binary and tertiary electrolyte compositions to decrease operating temperature
 - ❑ Optimize matrix-electrolyte interaction for long-term durability at lower temperature
 - ❑ Improve electrolyte retention to increase operating durability
- ❑ HER and OER catalyst/electrode optimization
 - ❑ Integrate new electrode materials into cell design to improve mass transport, reduce corrosion
 - ❑ Optimize catalyst ink formulation to increase stability
- ❑ **Reduce electrolyzer cell temperature to 450 °C or less**
 - ❑ Utilize improved components/electrolytes to reduce operation temperature
 - ❑ Run long-term durability testing for >150 h

Future Challenges

- ❑ Maintaining the electrolyte in the single/stack cells for long term durability
- ❑ Maintaining the seals of single/stack cells
- ❑ Reducing operating temperature to below 450 °C



Acknowledgments

- ❑ Financial support from DOE H₂ and Fuel Cell Technologies Office under award # DE-EE0007644
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- Corky Mittelsteadt
- ❑ Dr. Chao-yi Yuh