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Efficient Reversible Operation and Stability of Novel Solid Oxide Cells

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Overview

Timeline

- Project Start Date: 10/01/18
- Project End Date: 09/31/21

Budget

- Total Project Budget: $1,218,500
  - Total Recipient Share: $243,800
  - Total Federal Share: $974,700
  - Total DOE Funds Spent*: $273,254

* As of 3/31/20

Barriers

A. Durability
   - Durability of reversibly-operated solid oxide cells remains a key question

B. Performance
   - Improved cell performance is needed to meet cost and efficiency targets

Funded Partners

- Northwestern University
- Colorado School of Mines

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Relevance

- Objectives:
  - Develop Reversible Solid Oxide Cells (ReSOCs) for electrical energy storage with high (60-90%) round-trip efficiency at ~ 1 Acm^{-2}
  - Assess long-term stability versus operating conditions
  - Determine effects of pressurized operation
  - Scale up from button cell to > 50 cm^2 cells
  - Develop systems concepts for high efficiency
  - Use techno-economic modeling to validate technology viability
- Impact in the last year:
  - Durability: Life testing protocols and cell quality have been refined resulting in improved stability, ≤ 5%/kh at 0.5 – 0.75 Acm^{-2}
  - Performance:
    - Cell resistance < 0.15 Ωcm^2 at 700^oC achieved
    - Down-select to one cell type (from three) completed
    - Oxygen-electrode pressurized testing completed
  - System level: Identification of a viable system concept for RTE > 65% at 0.6 A/cm^2

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Approach

- Unique aspects:
  - Develop/screen high temperature cells with potential for high current density, long-term stability, and high round-trip efficiency
  - Experiments coupled with system modeling and TEA to provide early feasibility evaluation
- Addressing Program technical barriers
  - Development of improved solid oxide cells allowing high efficiency
    - Go/no-go: cell ASR < 0.15 Ωcm^2 achieved (FY19/20)
    - Milestone: downselected best cell design from 3 options (FY19/20)
    - Mileston: pressurized testing data obtained (FY19/20)
  - Life testing of reversible operation with electrochemical and microstructural evaluation to establish long-term stability
    - Go/no-go: degradation rate ≤10%/kh at 0.5 Acm^{-2} (FY19) and ≤6%/kh at 0.75 Acm^{-2} (FY20) achieved
  - Modeling to establish realistic efficiency and cost estimates
    - Go/no-go: Downselected 3 best system concepts; one with RTE~65% (FY19)
    - Viable RFC system with system LCOS of <30¢/kWh (FY20, ongoing)

Accomplishments: Cell Development & Testing

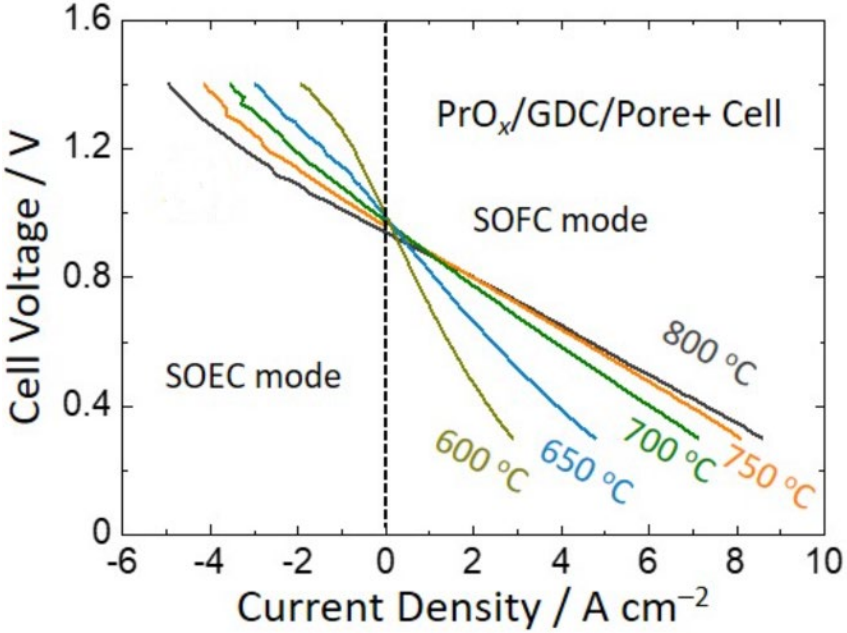
Three different cell designs prepared and tested

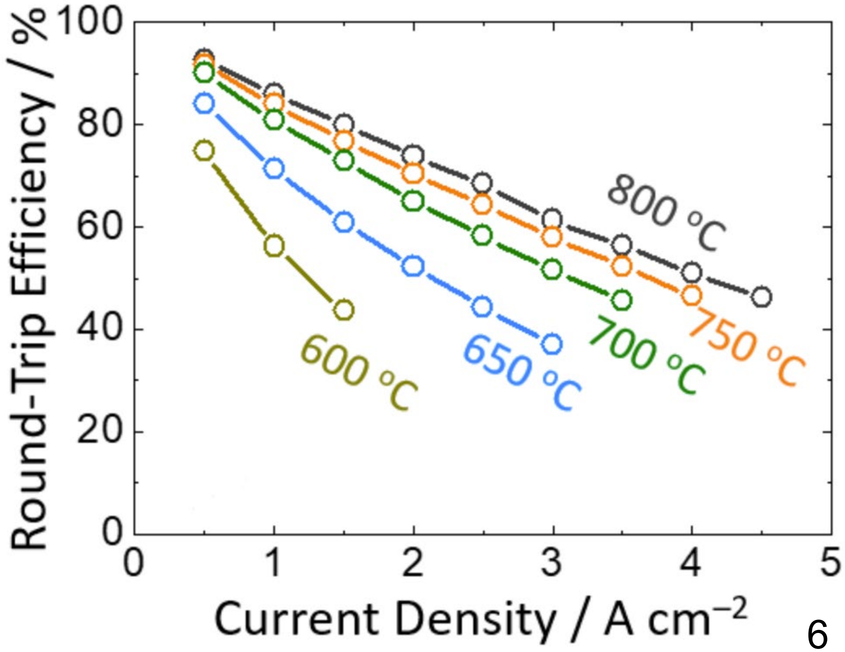
- Fuel-electrode supported cells (*FY19 Milestone 1.1.1*)
  - Common design for solid oxide cells
  - Both our fabricated cells and modified commercial cells
  - Only design achieving target ASR
- Oxygen-electrode supported cells (*FY19 Milestone 1.1.2*)
  - Design aims to reduce fuel concentration polarization
  - Performance exceed best reported values for this cell design, but still did not reach project targets
- 3D printed fuel-electrode supported cells (*FY19 Milestone 1.1.3*)
  - Novel approach aiming to reduce fuel concentration polarization
  - Promising results but insufficiently developed to allow selection for further development at this time

Accomplishments: Improved Cells

- ASR < 0.1 Ωcm^2 @ >750 ^{o}C
  - *Surpasses Milestone 2.1.1 (FY20): ASR < 0.15 Ωcm^2*
- Achieves high round-trip voltage efficiency

Fuel-electrode supported cell with modified structure and electrodes improved via infiltration



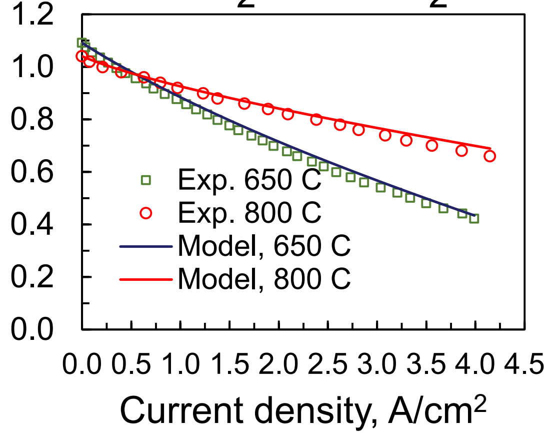


Accomplishments: Electrochemical model validation

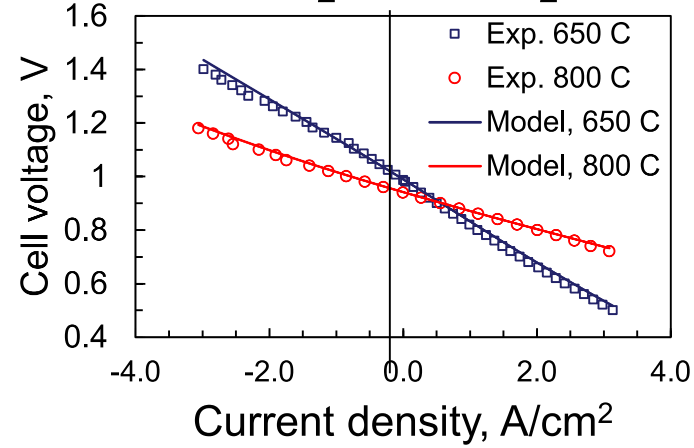
- The button cell model of the ReSOC is calibrated by considering experimental voltage-current data at different temperatures for the inlet compositions of 50% H_2-50% H_2O and 97%H_2-3%H_2O
- *Milestone 1.5.2 FY19: fits data within small error*

AAD= 1.7%

97% H_2 - 3% H_2O

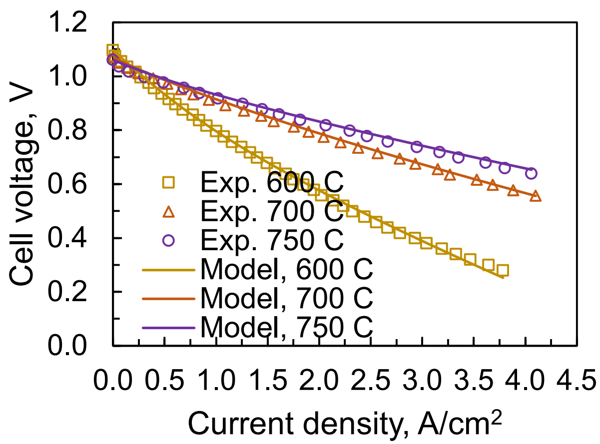


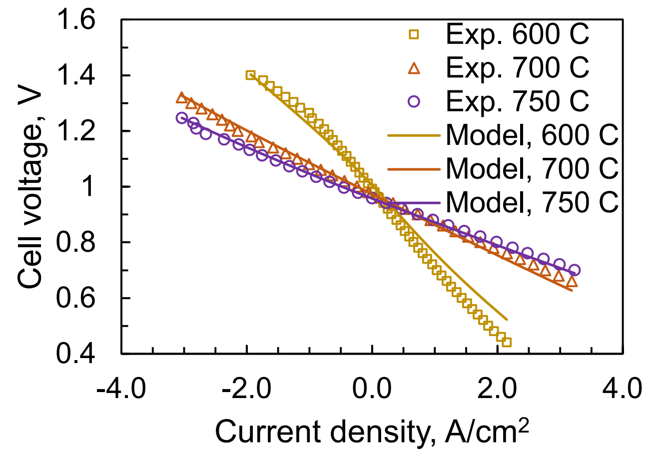
50% H_2 - 50% H_2O



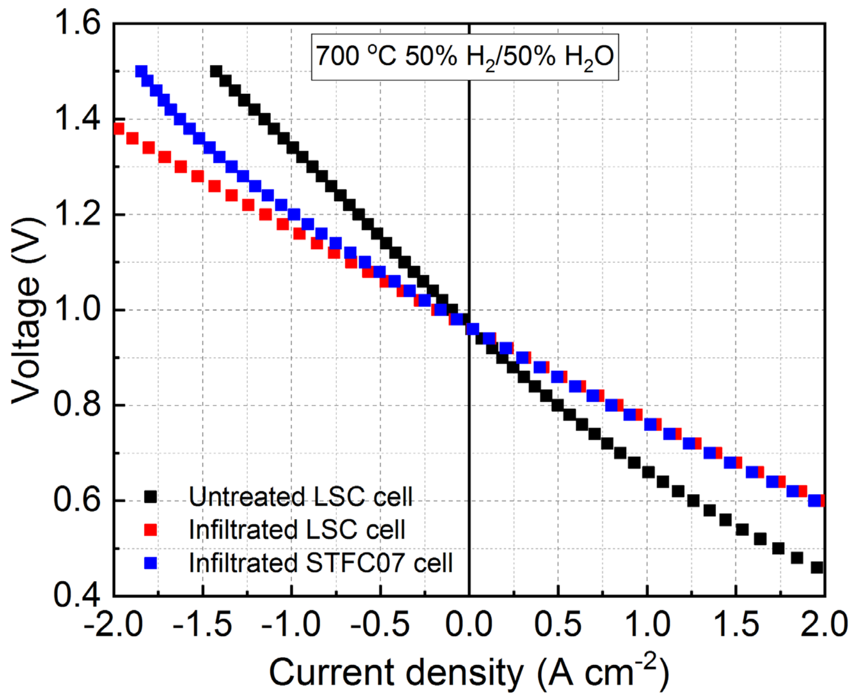
Absolute average deviation

$$\text{AAD} = 100\frac{\sum\left|\frac{V^{exp}-V^{model}}{V^{exp}}\right|}{number\ of\ data\ points}$$





Accomplishments: Modified Commercial Cells



- Commercial cells (Nexceris) have fuel-electrode supported design similar to Northwestern-developed cells
- However, modification is needed to reduce ASR
  - Ceria infiltration into Ni-YSZ fuel electrode
  - Alternative oxygen electrode based on $Sr(Ti,Fe,Co)O_3$ and infiltrated with PrO_x
  - ASR value of 0.2 Ωcm^2 achieved at 700 ^oC; close to project target
- *Milestone 1.1.1 (FY19): fuel-electrode supported cell demonstration*

Accomplishments: Pressurized Testing

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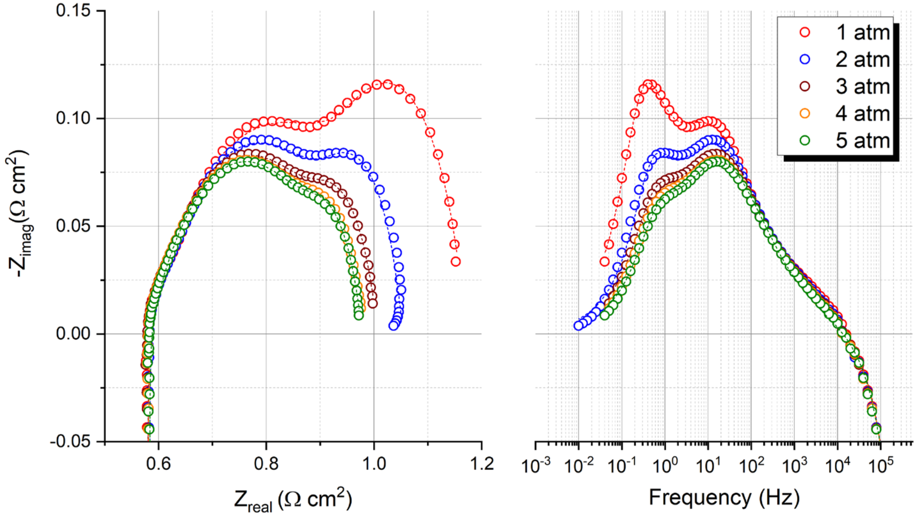
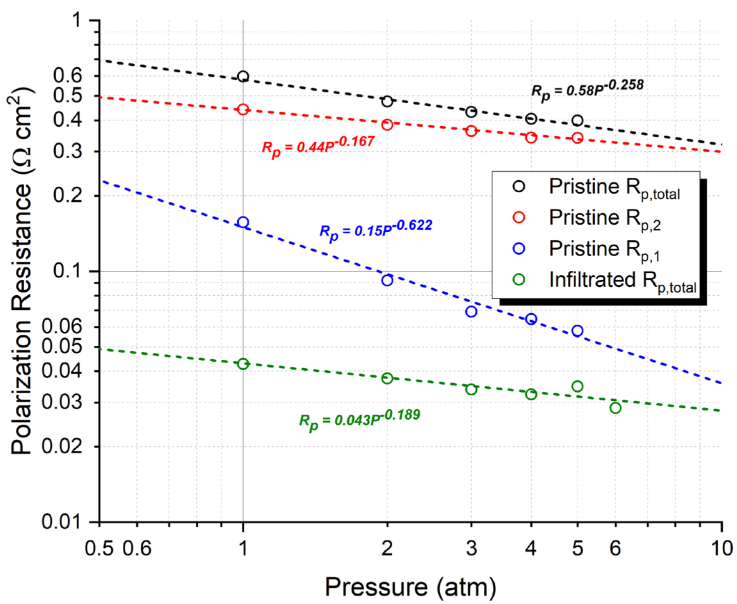
Pristine STFC Symmetric Cell in Pressurized Air, 650℃





- Symmetric cells with $Sr(Ti,Fe,Co)O_3$ (STFC) electrodes, with or without PrO_x infiltration
  - Pressurized air at 650˚C
  - EIS spectra show two main electrode responses
- STFC: total polarization resistance reduced from 0.15 to 0.05 Ωcm² by increasing from 1 - 6 atm
- STFC-PrO_x: polarization resistance significantly reduced by infiltration
  - Reduced from 0.042 to 0.029 Ωcm² by increasing from 1 - 6 atm
- *Milestone 1.2.1 (FY19): pressurized testing*

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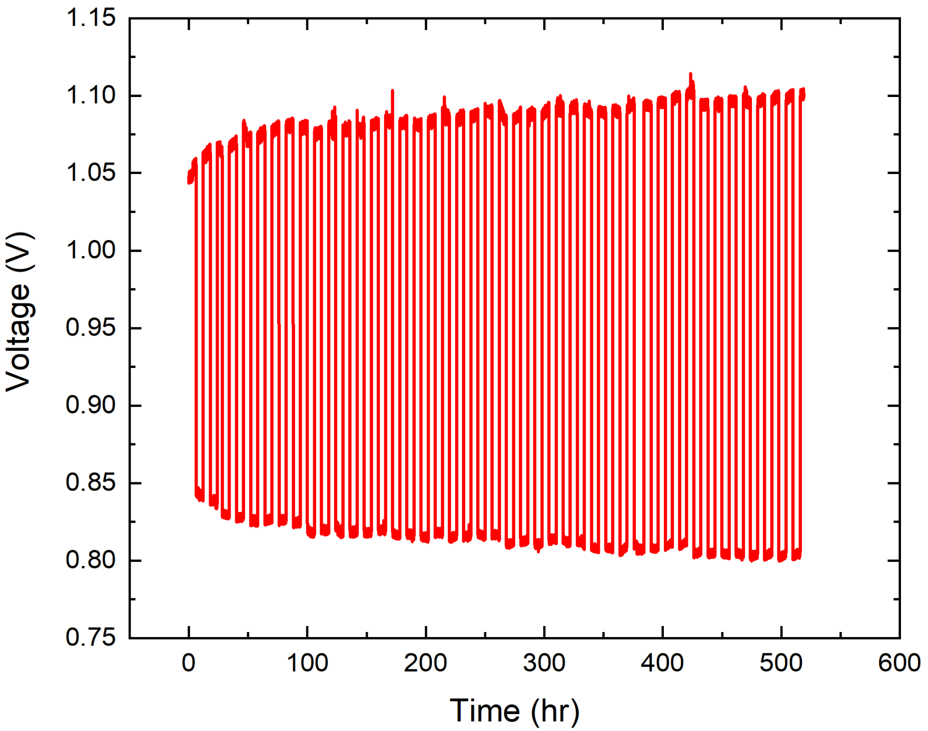
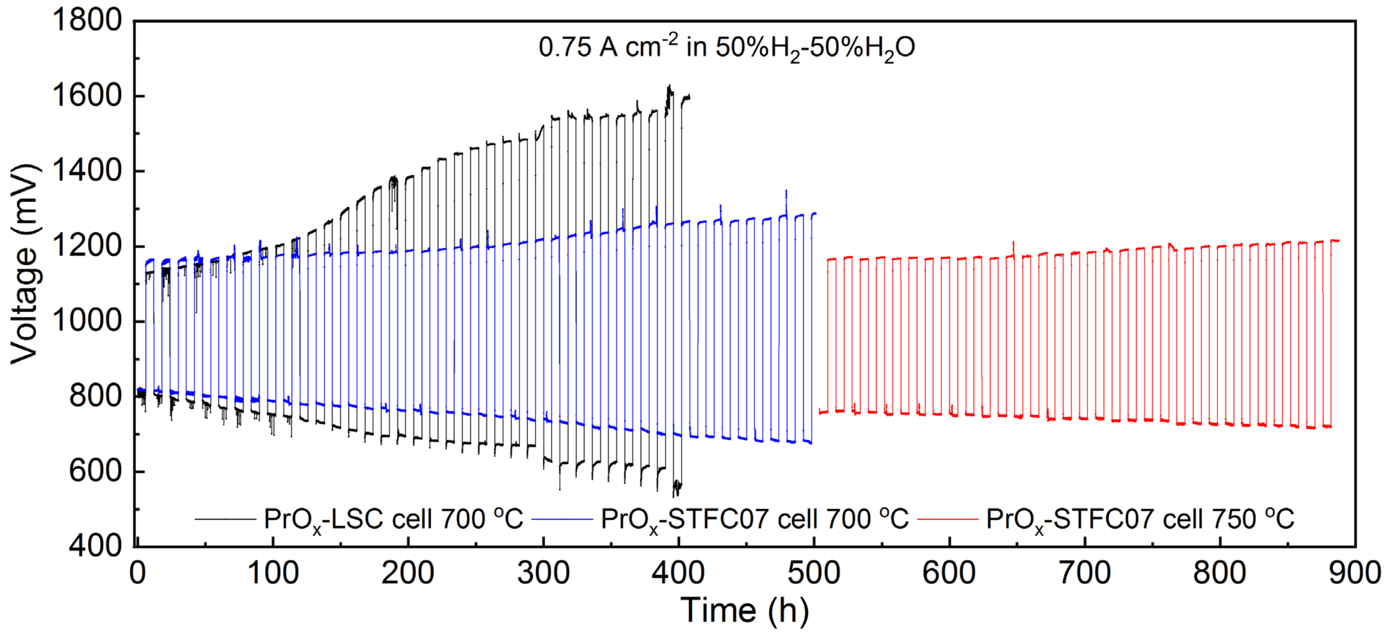
Accomplishments: Life Testing

- Reversible test: 6 h in each direction; 800˚C; 50% H_2 - 50% H_2O; 0.5 A cm^{-2}
- Cell: Northwestern made with Ceria-infiltrated Ni-YSZ fuel electrode, $Sr(Ti,Fe)O_3$ oxygen electrode
- Voltage degradation rate (after first 100 h): 5.1%/kh
- Test interrupted at 500 h due to COVID
- *Go/no-go:*
  - *FY19 - <10%/kh @ 0.5Acm^{-2}*
  - *FY20 - <6%/kh @ 0.75Acm^{-2}*



Accomplishments: Life Testing



- Reversible test: 6 h in each direction; 700 - 750˚C; 50% H_2 - 50% H_2O; 0.75 A cm^{-2}
- Cells: Commercial (Nexceris – electrolyte: 3 μm YSZ; 3 μm GDC)
  - Type 1: Ox. electrode PrO_x-$(La,Sr)CoO_3$; Fuel electrode Ceria-inf. Ni-YSZ
  - Type 2: Ox. electrode - PrO_x-$Sr(Ti,Fe,Co)O_3$; Fuel electrode Ceria-inf. Ni-YSZ
- Initilal stage at 700 ºC: PrOx-STFC cell more stable than PrOx-LSC.
- Second stage with temperature increased to 750 ºC: PrO_x-STFC performance recovered
  - Voltage degradation rates: 8.2%/kh (FC mode) and 8.8%/kh (EC mode)
- *Go/no-go: FY19 - <10%/kh @ 0.5Acm^{-2}; FY20 - <6%/kh @ 0.75Acm^{-2}*

Accomplishments
Design 1: No Thermal Energy Storage

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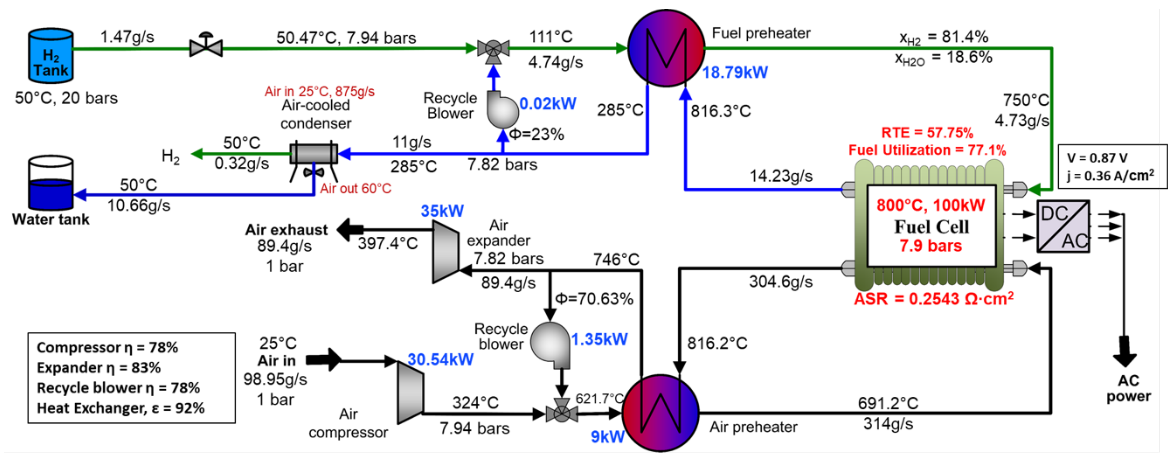
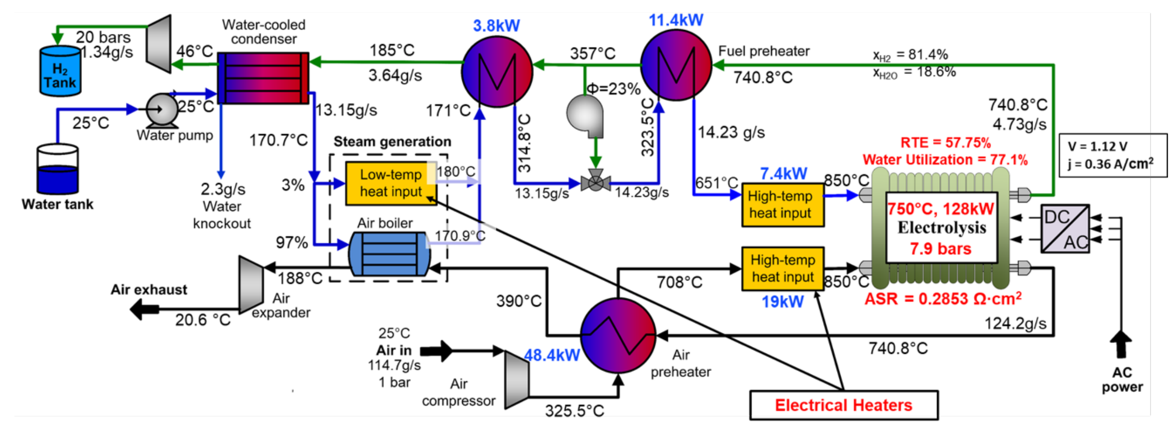
- External heat input instead of thermal energy storage (TES) in SOEC mode
- The system offers simple layout but lower efficiency 58% after optimization
- 100 kW stack power is derived considering 77.1% fuel utilization at ASR of 0.25 Ωcm^2 for SOFC mode and 0.28 Ωcm^2 for SOEC mode



Fuel cell mode



Electrolysis mode

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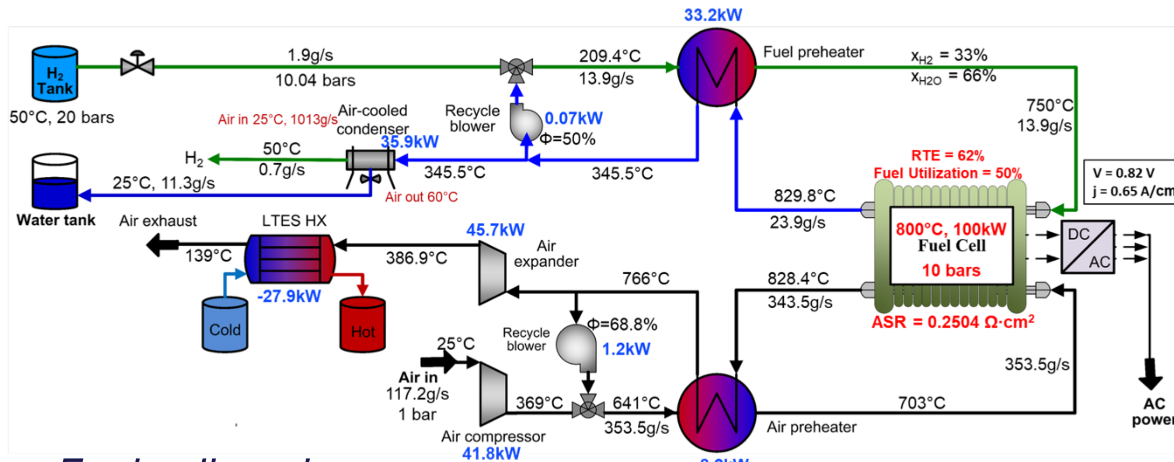
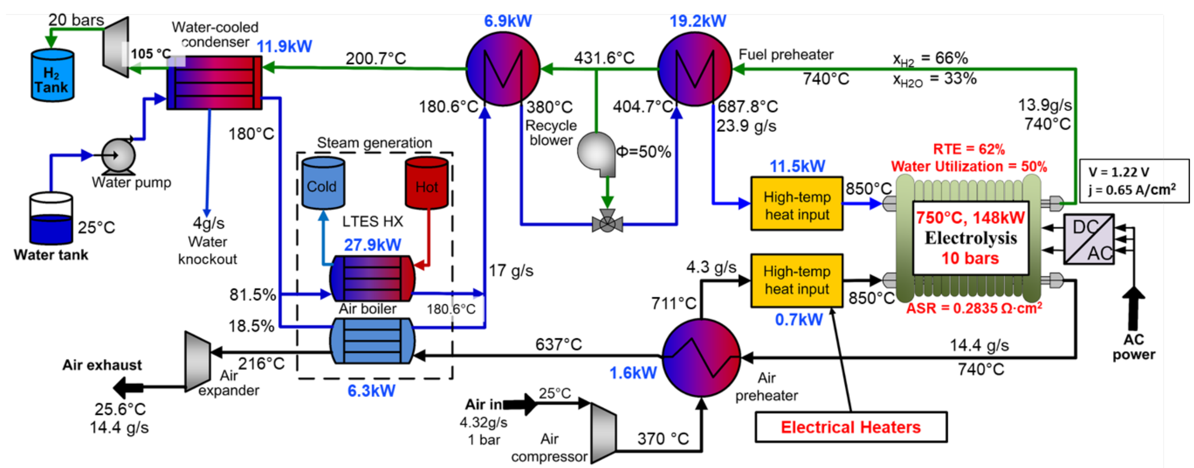
Accomplishments
Design 2: Low-Temperature TES

- LTES (350-400 °C) is utilized to generate steam
- 62% RTE is attained at 0.65 A/cm^2 current density and 10 bar after optimization
- 5% increase in RTE compared to the 1st configuration, due to reduced external heat load
- A two-tank energy storage system is adopted first due to its simplicity and potential as a low-cost solution
- Dowtherm-A is explored as a heat transfer fluid option
- Other alternatives are explored as LTES, which is yet to be completed



Fuel cell mode



Electrolysis mode

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Other Accomplishments: ReSOC Downselect

- The fuel-electrode supported cell design downselected based on ASR & degradation rates meeting targets
  - *Milestones 1.4.1 (FY19) and 2.4.1 (FY20)*
- Developed new high performance PrO_x-infiltrated $(La,Sr)MnO_3$ electrode
- Demonstrated reduced oxygen-electrode degradation in reversible operation compared to electrolysis operation
- Demonstrated improved performance and reduced degradation of Ceria-infiltrated Ni-YSZ fuel electrode
- A third system configuration, combining both low- and high-temperature thermal energy storage, was modeled
  - Round-trip efficiency of 65% at 0.63 A/cm^2
  - *Go/no-go FY19*

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Responses to Previous Year Reviewers' Comments

Project weaknesses and Recommendations:

- "…degradation studies of a technology still in development…. may not be relevant to future systems."
- Response: Cell design being studied is the arguably the main one being developed for ReSOC, with only one other design under serious consideration world-wide. Main results should remain relevant if not all the details.
- "What makes the team's SOFC technology different… not clear what is novel…"
- Response: It is important that our cells are not totally unique, so our results are relevant to the broader community, but there are unique infiltrated electrodes that will be discussed here.
- "…there is not enough focus on scale-up of cell size and stack technology…"
- Response: there are still many key questions that can be answered with button cells. Also, we do not want to reproduce development already done in industry.
- "The project should have…industrial engagement, even in a fairly informal way."
- Response: New focus on Nexceris cells brings them in as an informal partner, and potentially as a full partner in future projects.
- What are the issues are with making cell stacks, and how these risks will be reduced in this project
- Response: Stacks incorporating the Nexceris cells are already available. However, we would have to work with them to incorporate modified electrodes.

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Collaboration & Coordination

- Northwestern University (NU)
  - Prime
  - Cell development, fabrication and scaleup, electrochemical and microstructural characterization
- Colorado School of Mines (CSM)
  - Subcontractor
  - Stack and system modeling, techno-economic analysis
- Collaborative relationships
  - NU provides experimentally-measured cell characteristics as input to CSM stack and system models, allowing accurate prediction of expected system characteristics
  - CSM provides input to NU regarding desired cell characteristics and operating parameters, ensuring that test results are relevant

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Remaining Challenges and Barriers

- Further reduction of ReSOC degradation rates
  - Identification and modeling of degradation mechanisms, and their mitigation
  - Validation that ReSOC degradation rates can be reduced to practically useful levels
- Further improvement of commercial cell performance to reach ASR target
  - Achieve uniform electrode infiltration of large-area cells
- Large-area cell reversible testing
- Techno-economic analysis combined with system efficiency calculations to provide overall assessment
  - Utilizing finalized system definition & component requirements
  - For various system scales

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Proposed Future Work

- Further reduction of ReSOC degradation rates
  - Identify main degradation mechanisms and develop preliminary models
  - Use this information to modify cells and test conditions
  - Aimed at achieving "*End of Project Goal" of <3%/kh at 1 A/cm*^{2}
- Reduce commercial cell ASR to < 0.15 Ωcm^2 (*FY19 & FY20 go/no-go)*
- Develop procedures for electrode infiltration of large-area cells yielding uniformly low ASR (*FY21 Milestone 3.1.1)*
- Develop large-area cell test setup to accommodate special requirements of reversible SOC testing *(FY20 Milestone 2.2.1)*
- Model calibration will be carried out based on the experimental V-j data at high pressure and for ~50 cm^2 cell *(FY20 Milestone 2.5.1)*
- LTES and HTES/LTES system configurations will be updated with the latest calibrated parameters *(FY20 Milestone 2.5.2)*
- FY20 system design efforts will focus on hardware sizing and simulation of ReSOC concepts in both modes of operation at a practical scale (~100 kW/800 kWh) *(FY20 Milestone 2.5.2)*

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Technology Transfer Activities

- Reversible fuel cell storage concept needs validation from the button cell to large cell level (this project)
  - Beyond this, we plan to further validate at the stack/system level
  - After this, we believe it will be possible to obtain private funding for further development
- Our universities aggressively market inventions
- Both NU and CSM hold patents on reversible solid oxide cell energy storage
  - NU (Barnett) recently had a relevant patent issued titled: "Three Dimensional Extrusion Printed Electrochemical Devices," US patent # 10,236,528

Summary

- Project combines reversible solid oxide cell (ReSOC) development, testing, and stability studies with system modeling and techno-economic analysis
  - Assess overall potential of the technology regarding cost/efficiency
- Assessment/downselect of three cell types completed
  - Winner is fuel-electrode supported cell
- Cell ASR and degradation rate targets met
  - Performance data fit well using developed electrochemical model
- Included modified commercial cells in project
  - Facilitates scaleup to large-area cell testing & industrial connection
- Three system configurations with varying thermal storage methods modeled
  - Thermal storage allow up to 65% system round-trip efficiency