Efficient Reversible Operation and Stability of Novel Solid Oxide Cells

Scott Barnett (Primary Contact), Tianrang Yang, Jerren Grimes
Northwestern University
2220 Campus Drive
Evanston, IL 60208
Phone: 847-491-2447
Email: s-barnett@northwestern.edu

DOE Manager: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

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Project End Date: December 31, 2021

Overall Objectives

- Develop and test novel reversible solid oxide cells (ReSOCs) specifically designed to achieve the low area-specific resistance (ASR) (<0.15 Ω cm^2) required to achieve high round-trip efficiency in reversible operation at high current density (e.g., 1 A/cm^2).
- Design ReSOCs that can be operated efficiently and durably in both fuel cell and electrolyzer modes.
- Improve long-term ReSOC durability using mechanistic degradation models to predict long-term durability using input data from accelerated testing that combines electrochemical life testing with quantitative microstructural and chemical evaluation.
- Develop designs based on system modeling that can achieve efficiency targets, using experimental cell test data as input to accurately predict system efficiency.

Fiscal Year (FY) 2019 Objectives

- Fabricate, electrochemically test, and microstructurally evaluate three different types of solid oxide cells, and improve the cells based on the results.
- Conduct accelerated life testing on the ReSOCs over a wide range of conditions and assess electrochemical and microstructural changes.
- Use the results to guide development of a theory for cell degradation during reversible operation, including the effects of switching current direction.
- Develop a detailed experimental plan for the following budget period based on the results, including a down-select from three to two ReSOC types.
- Down-select reversible fuel cell system concepts to three most promising ones that minimize life cycle costs of energy/storage (e.g., levelized cost of storage [LCOS] <30¢/kWh) while targeting maximum round-trip efficiency.
- Use an electrochemical model to predict experimental *V-j* polarization data.

Technical Barriers

This project addresses the following technical barriers from the Reversible Fuel/Flow Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Durability
- Performance—Cell Issues.

Technical Targets

This project aims to study the operating characteristics and degradation mechanisms in state-of-the-art ReSOCs using accelerated life tests combined. ReSOCs are of interest because of their potential to achieve relatively high round-trip storage efficiency compared with other reversible fuel cell or flow battery technologies. The goal is to achieve an understanding of how switching between fuel cell and electrolysis modes impacts

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

degradation, with the aim of achieving ReSOCs that operate at high current density, high efficiency, and good long-term stability. The project also incorporates stack and system modeling based on experimental cell performance results in order to provide early predictions of the expected system characteristics, particularly efficiency, and LCOS.

The Multi-Year Research, Development, and Demonstration Plan does not yet provide targets for reversible fuel cells, but targets for this project include:

- Cell ASR ≤0.15 Ω cm^2 providing round trip voltage efficiency of ≥70% at ≥ 1 A/cm^2
- Projected degradation rate ≤3%/kh at 1 A/cm^2
- Minimum LCOS of <30¢/kWh while maintaining a high system efficiency.

FY 2019 Accomplishments

- The three different cell types have been successfully fabricated and electrochemically tested showing good cell performance in each case.
- The fuel-electrode-supported cells have shown outstanding performance with ASR values <0.1 Ω cm^2, well below the target ASR of 0.15 Ω cm^2 for relevant operating conditions. The other cell types traditionally have been far less developed but are being rapidly improved toward the target performance level.
- Reversible life testing results show promising results, with degradation rates close to the first-year target of 10%/kh.
- Three different system designs have been evaluated and one of them is yielding round-trip system efficiency >65%.

INTRODUCTION

ReSOCs have the potential to store electricity via a steam/hydrogen cycle at higher round-trip efficiency than lower-temperature electrochemical cells. However, high efficiency at high current density requires unusually low overpotentials (η) and, thereby, low cell ASR that places a premium on cell materials and design to optimize performance. High current density and reversible operation can also promote cell degradation, such that it is important to prove that ReSOCs can operate stably over useful cycle lives. Despite these challenges, our previous ReSOC studies have shown promise for meeting these requirements. The focus of the experimental work is on operating conditions that yield very low cell ASR, cells that have low degradation at relatively high current density, demonstration of larger-area cells, and cell operation at elevated pressure. Also, achieving high system-level round-trip efficiency poses considerable challenges, particularly in thermal management. Thus, system studies are included that will connect synergistically to the cell development and testing aspects of the project. The modeling and system-level studies will establish cell/system design requirements and identify ReSOC system configurations that enable 70% round-trip efficiency at levelized energy costs that are competitive with leading battery technologies (e.g., LCOS = 10–30 ¢/kWh).

The three proposed ReSOC types have been successfully fabricated and tested. The fuel-electrode-supported cells are the most advanced type, and significant development in the first year has yielded outstanding performance that easily beats the project ASR target. The other cell types—oxygen-electrode-supported cells and 3D-printed supported cells—have significant potential advantages for concentration polarization losses. However, they have been much less developed and hence performance is not as good, but they still have potential to reach project targets. Three different system design strategies have been developed; model calculations utilizing input data from the cell performance characteristics mentioned above show good potential to meet project round-trip efficiency of 70% with reasonable LCOS.

APPROACH

The project approach includes the following: (1) development and short-term testing of three types of ReSOCs, including fuel-electrode-supported cells, oxygen-electrode-supported cells, and novel SOCs with patterned 3D printed supports, with a down-select to one type by Year 3; (2) testing of cell operation under pressurized conditions and pure oxygen; (3) reversible SOC accelerated testing with electrochemical and microstructural characterization aimed at assessing long-term stability (including the impact of cycling between fuel cell and electrolysis modes) and determining methods for decreasing degradation; (4) determination of the operating conditions where degradation is minimized; (5) evaluation of new electrode materials and processing methods

that minimize degradation rate; (6) fabrication and testing of the selected ReSOC type in a larger-area cell format; (7) development of viable ReSOC system concepts to enable thermally self-sustaining, high-round-trip efficiency performance; (8) development of detailed cell and system models to help understand experimental results, optimize balance of plant and stack integration, and guide mode-switching operational strategies; and (9) final assessment of ReSOC technology based on expected system round-trip efficiency, long-term stability, and preliminary techno-economic analysis at scales required for distributed energy storage applications.

RESULTS

Fuel-electrode-supported ReSOCs have been successfully fabricated that yield much-improved electrochemical performance over past cells. The new cell materials and structure push the limits of the ASR values, fuel-cell power densities, and electrolysis current densities that can be achieved. Each of the main cell components are altered to achieve extremely low cell resistance. A key measure is a new approach for achieving high oxygen electrode performance and stability—a $Sr(Ti,Fe,Co)O_3$ (STFC, $Sr(Ti_{0.3}Fe_{0.63}Co_{0.07})O_3$) porous electrode scaffold infiltrated with a PrO_x catalyst. The Ni–YSZ ($(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$) fuel electrode is improved via a low-temperature co-firing process that increases triple phase boundary density, along with GDC ($Gd_{0.1}Ce_{0.9}O_{1.95}$) infiltration. With these much-improved electrodes that also provide reasonable stability at elevated temperature, other cell components limit performance. Thus, a GDC/YSZ bi-layer electrolyte with thickness reduced to ~2.5 μm is utilized, and the Ni–YSZ support porosity is increased to minimize mass transport limitations. Figure 1 shows the j-V results. Electrolysis current densities at 1.3 V reach values of 4.25, 2.9, and 1.25 A/cm^2 at 800°C, 700°C, and 600°C, respectively. Fuel cell maximum power density reaches ~3 W/cm^2 at 750°C and above and exceeds 1 W/cm^2 at 600°C. The ASR values are well below the project target ASR for temperature, ≥700°C, such that round-trip efficiency values (Figure 2) are very promising.

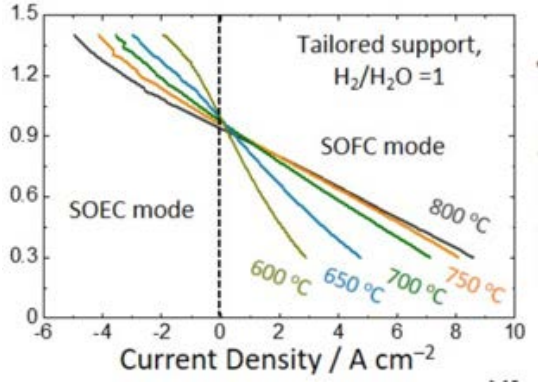

Figure 1. j-V curves for the STFC:PrO_x/Ni–YSZ:GDC fuel-electrode-supported cells measured at 600°–800°C in 50 vol % H_2–50 vol % H_2O and air.

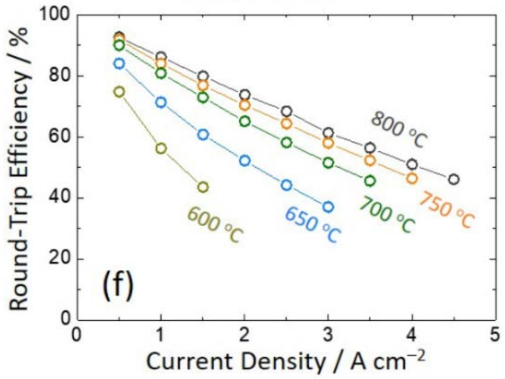

Figure 2. Round-trip voltage efficiency vs. current density at different temperatures, calculated from the cell test data in Figure 1.

Initial reversing-current cell life tests have been carried out but have been limited due to premature cell failure. Figure 3 shows an example; although the cell voltages increased substantially during the first ~50 h, the cell voltages then stabilized. However, the cell failed at ~200 h, apparently due to short circuiting from Ag current collecting wires. Work is underway to eliminate this testing artifact in order to obtain longer life tests.

Oxygen-electrode cells with the desired structure have been successfully produced. Initial performance is not as good as the fuel-electrode-supported cells. The best cells currently operate at voltages of 1.17 V in electrolysis mode and 0.83 V in fuel cell mode, both at 800°C in air and 50% steam, 1 A/cm^2. This corresponds to a round-trip voltage efficiency of 71%; while this meets program targets, clearly system efficiency would be lower.

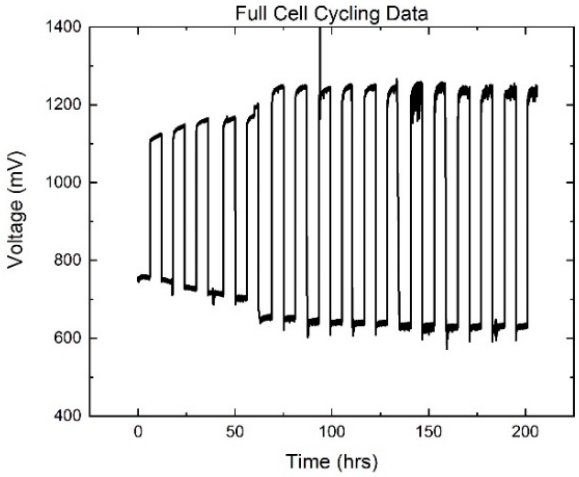

Figure 3. Fuel-electrode-supported ReSOC life test carried out at 800°C and 0.8 A/cm^2 in air and 50% steam; the cycle was 6 h in fuel cell and 6 h in electrolysis mode.

One of the ideas to be tested in the project is the idea that oxygen produced during electrolysis could be stored and then used during the fuel cell portion of the cycle to improve cell performance. This advantage could be most important for oxygen-electrode-supported cells where the thick support could provide substantial gas diffusion limitation in air, but not with oxygen. Figure 4 compares the electrolysis and fuel-cell performance of the oxygen-electrode-supported ReSOC tested in air and oxygen. There is no obvious difference on the solid oxide electrolysis cell (SOEC) performance in oxygen and air. Although there is a clear reduction in cell resistance (i.e., lower slope) with oxygen, this is mitigated by the higher open circuit voltage in oxygen; thus, a voltage crossover occurs at ~1.5 A/cm^2. The lack of apparent concentration polarization in SOEC mode is surprising, given the obvious current limitation at ~1.7 A/cm^2 in solid oxide fuel cell (SOFC) mode resulting from the oxygen diffusion limitation in the electrode support. Instead, the j-V curves show positive curvature at all current densities—this is apparently due to the increasing oxygen concentration in the electrode with increasing current. While the oxygen greatly extends the current density compared to air in SOFC mode, at an expected ReSOC operating current density of ~1 A/cm^2, the advantage is not significant.

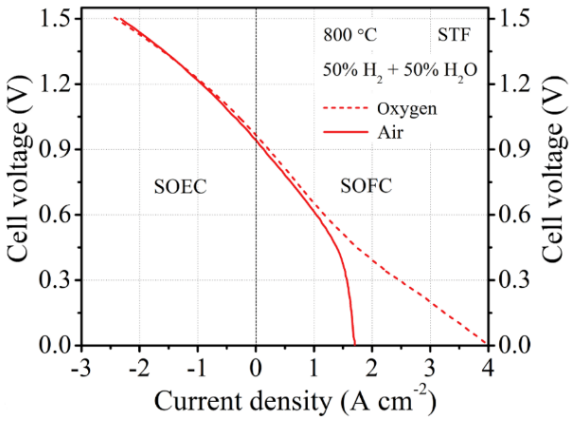

Figure 4. Electrolysis and fuel cell current-voltage curves for oxygen-electrode-supported cells with STF ($Sr(Ti_{0.3}Fe_{0.7})O_3$) fuel electrodes, measured in air and oxygen at 800°C.

Cells with 3D-printed support have been successfully tested electrochemically, yielding good performance, ahead of schedule for that Q4 milestone. Because these cells are based on fuel-electrode-supported cell materials but have not yet been improved as shown in Figure 1, there is good potential for cell performance to be improved. Initial results do show that the 3D-printed support reduces concentration polarization in the thick fuel electrode, providing a factor of three increase in the limiting current density compared to a conventional electrode for a low steam fuel composition.

A baseline system concept for an ReSOC has been developed and preliminary process conditions have been selected that would enable round-trip efficiency of ≥65% using both high- and low-temperature thermal energy storage modules. Three different system configurations have been studied, and a promising example is summarized here. The process flow diagram for fuel cell mode involves hydrogen being supplied from the storage tank and mixed with recycled hydrogen and steam before preheating to 750°C in a fuel preheater by exchanging thermal energy of stack exhaust available at 827°C. Preheated hydrogen is then delivered to the fuel cell stack module. Air is pressurized and mixed with recycled air before preheating to close to 680°C. The SOFC operates at near 800°C to enable fast charge transfer kinetics and conductivity through the electrolyte. The direct current produced as a result of oxidation of hydrogen and reduction of oxygen is inverted to alternating current in the inverter. The unused hydrogen from the anode side and excess air from the cathode side are recycled after charging the high-temperature thermal energy storage. Waste heat from the air expander exhaust is used to charge the low-temperature thermal energy storage.

For electrolysis mode, water is pumped from the storage tank and is used to condense unutilized steam in the fuel stream. The reactant water is boiled using a combination of waste heat from the air stream and low-temperature thermal energy storage, before being further preheated to 780°C in a recuperator and then with the high-temperature thermal energy storage. Air is pressurized and preheated to close to 780°C in the air preheater and high temperature thermal energy storage module. Hydrogen recycle enables high system reactant utilization and improves the performance of the electrolysis stack. Because the stack is operating below the thermoneutral voltage, the H_2/H_2O mixture and air temperatures decrease down the length of the stack. Because the thermal energy storage is charged by the fuel cell in SOFC mode, the stack must operate at a lower temperature during electrolysis mode in order to account for second-law losses across high-temperature thermal energy storage heat exchangers. As a result, the stack will not perform as well in electrolysis mode, so in this study we assume that the stack ASR in electrolysis mode is 0.25 Ω cm^2. Because the stack cannot fully convert all steam to hydrogen, excess water in the product stream exiting the stack is condensed so that a fairly pure stream of hydrogen can be compressed to 20 bar for tank storage. The condensed water would either be cycled back to the water storage tank or directly into the reactant steam stream. Air exiting the stack at 750°C is utilized to preheat the incoming air and boil reactant water.

CONCLUSIONS AND UPCOMING ACTIVITIES

The above results show that fuel-electrode-supported ReSOCs have been developed with outstanding performance that is consistent with high round-trip efficiency. The other cell types developed have also shown good performance, although not as good, and have intriguing advantages. We will choose the two most promising of these cell designs for further development and testing in the second project year. While initial reversing-current life testing looks promising, the second year of the project will emphasize elimination of life test artifacts. Longer accelerated life tests will be carried out in order to achieve project degradation rate targets. Initial system modeling results show promise for achieving program round-trip efficiency targets. The three different system designs will be evaluated and the best selected for further refinement.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Scott A. Barnett, "Electrochemical and Microstructural Studies of Degradation Mechanisms in Solid Oxide Cells," (Invited) 235th Electrochemical Society meeting, Dallas, TX, May 26–30, 2019.
2. Scott A. Barnett, Qinyuan Liu, Qian Zhang, Beom-Kyeong Park, and Peter Voorhees, "Degradation Phenomena in Solid Oxide Electrolysis Cell Fuel Electrodes," 2nd International Conference on Electrolysis, Loen, Norway, June 9–13, 2019.
3. Scott A. Barnett, Beom-Kyeong Park, Qian Zhang, and Peter Voorhees, "Degradation Phenomena in Solid Oxide Electrolysis Cell Oxygen Electrodes," 2nd International Conference on Electrolysis, Loen, Norway, June 9–13, 2019.