SPP Agreement Number FP00010434

Metal-Supported Solid Oxide Fuel Cells for Natural Gas

Final Report
January 2022

Märtha M. Welander, Michael C. Tucker (PI)
Lawrence Berkeley National Laboratory

Table of Contents

Project Summary

Solid oxide fuel cells (SOFCs) are high temperature energy conversion devices that produce electricity efficiently and sustainably. High operating temperatures required for SOFC function endow these devices with many advantages including fuel flexibility and high conversion efficiencies. Fuel flexibility, in particular, distinguishes SOFCs from other types of fuel cells that operate with clean H_2 only, and enables operation with natural gas (NG). LBNL has developed metal supported SOFCs (MS-SOFCs) with unique symmetrical architecture that offer several advantages over state of the art (SoA) ceramic SOFC models including inexpensive materials, rapid start up capability, increased mechanical strength and high tolerance to thermal cycling, Fig 1. These advantages make LBNL MS-SOFCs uniquely suited for fast start-up, portable, and mobile backup generator applications. Specifically motivating this work was a scenario of backup generators fueled by pipeline natural gas delivered from SoCalGas in the event of an electric grid shut down. This project investigates the feasibility of using MS-SOFCs with pre-reformed natural gas as well as direct on-cell reforming of simulated natural gas both with and without sulfur.

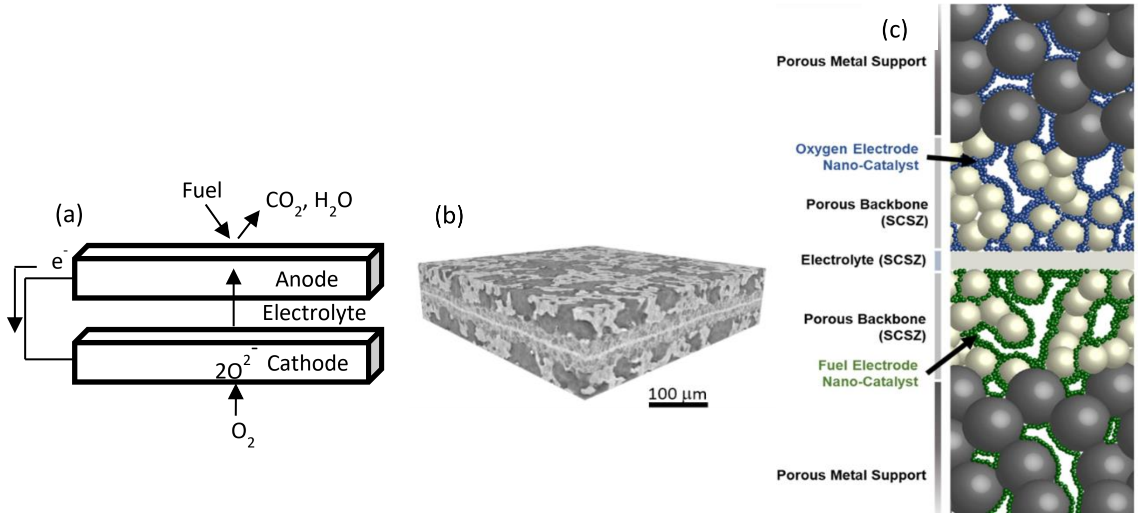

Figure 1. SOFC operation and LBNL MS-SOFC design. (a) Basic operation and components of SOFC. (b) Image and scale of LBL's MS-SOFC used in this work as well as (c) layer and component description.

This project demonstrated the use of LBNL MS-SOFCs for natural gas applications requiring rapid start and stop cycles and assessed the tolerance of the fuel cell to carbon and sulfur species present under all conditions. Electrochemical methods were used to track cell performance under all testing conditions. In general, cells were operated at 700 °C and 0.75 V, chosen as a nominal operating point for efficient and durable performance. Main project achievements and key outcomes are summarized in Figure 2 below and include the following:

- Selection of simulated NG composition, and thermodynamic calculation of reformate gases produced by reforming NG with steam or partial oxidation with air (POX)
- Continuous operation for 1000 h with steam and partial oxidation reformate fuels with sulfur
- Extensive rapid thermal cycling (up to 40 cycles) with reformate fuels, and sulfur levels exceeding SoCalGas pipeline concentration, with minimal degradation
- Quantifying the effects of sulfur on cell performance and durability with reformates
- Screening and identification of a high-performance catalyst for internal reforming
- Internal reforming of methane and simulated natural gas with and without sulfur
- A number of "firsts" for LBNL MS-SOFCs, including long-term operation with carbon- and sulfur-containing fuels

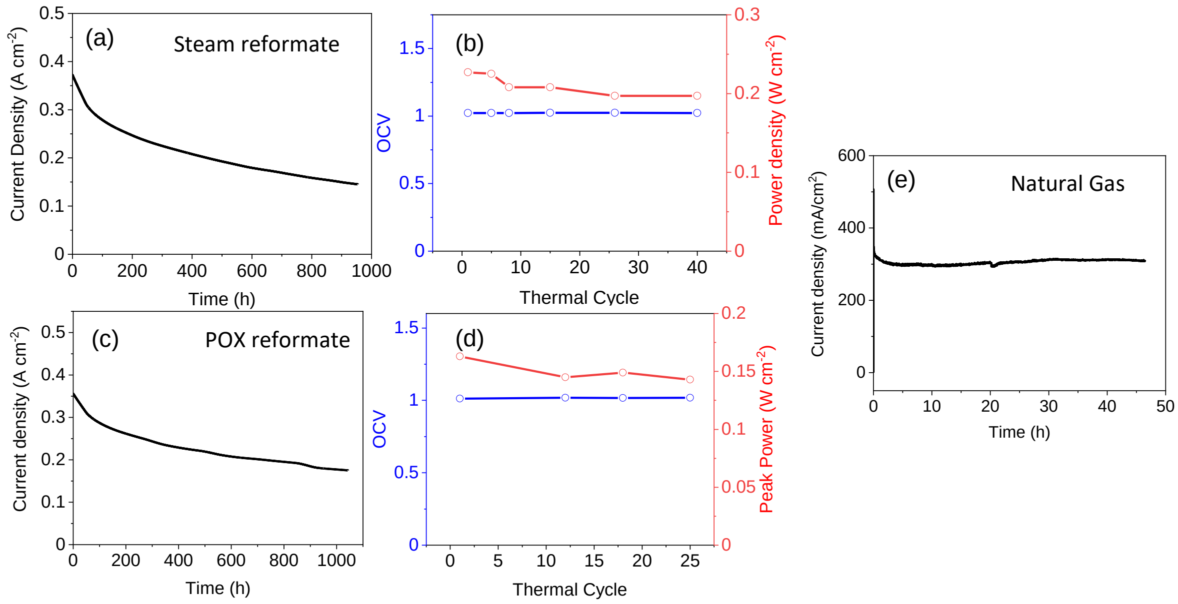

Figure 2. Summary of project results and key outcomes. (a) 1000 hr operation with steam reformate and sulfur at 0.75 V. (b) Thermal cycling with steam reformate and high sulfur levels. (c) 1000 hr operation with POX reformate at 0.75 V. (d) Rapid thermal cycling with POX reformate and high sulfur levels; OCV is open circuit voltage, and indication of the absence of leaks in the seal and cell. (e) Initial testing of direct internal reforming catalyst under simulated natural gas.

Table 1 shows technical targets and end-of-project status for the use of MS-SOFCs in backup generators. Targets were derived from literature review and assumptions about residential backup generators. Goals for this project were to meet targets related to single cell performance, start-up times, and heat-up rates for all types of fuels. These goals were achieved. Stack and system targets are beyond the scope of this project, but projections were made based on single cell data. While single cell results can be used to inform and advise the commercial production of natural gas based backup generators, future research should include scale-up to commercial-size cells and evaluation of stack performance, lifetime and durability.

Table 1. Key technical targets and current status for natural gas fueled SOFC backup generator

Metric	Units	Target	Status	Note
Cell Performance	W/cm^2	0.3	0.38	Steam reformate with 1ppm S. Other fuels provide >0.2 W/cm^2
Operating voltage	V	0.75	0.75	All experiments set at this voltage
Operating current	A/cm2	0.4	0.5	Steam reformate with 1ppm S at 0.75 V
Heatup rate	°C/min	47	40	>40 cycles, heating rate limited by furnace, cells can heat faster
Startup time	min	<15	17	Limited by furnace, cells can heat faster
Lifetime	hours	1680	1000	Operated for 1000 h, can be extrapolated to few thousand hours
Capacity at EOL	%	80	46	At 1000h operation with POx with 1ppm S. Needs to be improved.
Degradation rate	%/kh	12	36	POx with 1ppm S, for hours 500 to 1000. Needs to be improved.
Stack Performance	W/kg	75	200	(Projected) Cells are lighter and performance is higher than SoA
Stack Performance	W/L	200	1000	(Projected) Cells are thinner and performance is higher than SoA
System Efficiency	%	50	45-55%	(Projected) Cell operation is 68% thermodynamic efficiency

Dissemination of Project Results

Publications

1. Welander, M. M.; Hu, B.; Tucker, M. C. Metal-supported solid oxide fuel cells operating with reformed natural gas and sulfur. *Submitted to Int. J. Hydrogen Energy.* **2021**.

2. Welander, M. and M.C. Tucker, Metal-supported solid oxide fuel cells operating with internal reforming of gaseous fuels, planned for submission in **2022**.

Presentations

1. “Assessing the Performance and Degradation of Metal Supported SOFCs Operating with Natural Gas” presented at ECS SOFC-XVII, Stockholm, Sweden (Virtual), July 2021.

2. “Metal-Supported Solid Oxide Cells for Chemical Conversion, Electrolysis, and Power Production” to be presented at European Fuel Cell Forum, Lucerne, Switzerland, July 2022.

3. “Infiltrated Electrodes for High Temperature Energy Conversion, Electrolysis, and Chemical Synthesis”, to be presented at 241st Electrochemical Society Meeting, Vancouver, Canada (Virtual), May 2022.

Plan for Follow-On Funding

Likely sources for follow-on funding include DOE-FE, DOE-EERE-HFTO, DOE Technology Commercialization fund, CEC, and natural gas trade organizations. LBNL will pursue funding opportunities as they are announced, and disseminate the results of this project to decision makers at DOE.

Funding from these sources will likely require cost matching from SoCalGas or a 3rd party. Use of SoCalGas demonstration sites would be a welcome source of cost matching.

The topics for follow-on projects would include cell-level R&D to further improve performance and durability, scale-up to large single cells (~100cm2), assembly into kW-scale stacks, system design and integration, and demonstration of stacks and systems operating on pipeline natural gas.

Summary of Technical Results

Simulated natural gas reformate results:

This projected focused on performance and durability of cells operating with simulated natural gas reformates. Reformate fuels include: steam reformate made up of H_2 (74.6%), CO (16.2%), CO_2 (6.7%), CH_4 (1.9%) and N_2 (0.6%) passed through a heated bubbler to add 16% H_2O; and, POX reformate made up of H_2 (30.2%), CO (13.8%), CO_2 (6.6%), CH_4 (0.3%), and N_2 (49.1%) passed through a heated bubbler to add 9% H_2O.

Figure 3 shows initial cell performance and 200 h durability for cells operating with H_2 in 3% H_2O (baseline), simulated natural gas steam reformate, and simulated natural gas POX reformate. Compared to baseline performance with H_2 fuel, initial performance with reformate fuels was lower. This lower performance is a result of hydrogen dilution and increased partial pressure of oxygen accompanying oxidized species (CO_2, H_2O) in the reformates. Peak power density was ~0.1 Wcm^{-2} lower for POX reformate than steam reformate because POX produces less H_2 per mole of fuel than steam reforming. Despite differences in initial performance, degradation rates were similar. In all cases, initial degradation is fastest due to cell conditioning and catalyst particle coarsening, after which the cell stabilizes. H_2 cell degradation was 35% total, of which 12% occurred in the last 100 hours. The cell operating with steam reformate degraded 46% total and 11% in the last 100 hours, and the cell operating with POX reformate degraded 40% total and 10% in the last 100 hours. No change in OCV was seen after cell operation for 200 hours, suggesting that cells operating with reformate did not suffer from severe coking or oxidation under the chosen experimental conditions.

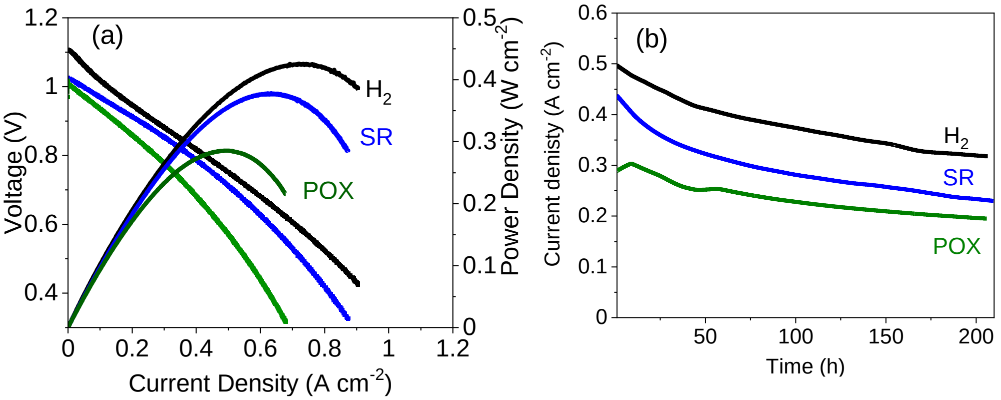

Figure 3. (a) Initial operating performance curves and (b) initial durability of cells operating with 100 sccm H_2, steam refromate (SR), or POX reformate at 0.75 V and 700 °C.

Concerns of catalyst poisoning by sulfur in natural gas was studied by exposing cells to a fuel mixture of natural gas reformates and H_2S to produce 1 ppm and 5 ppm sulfur in the fuel output, equivalent to 5 ppm and 18 ppm of sulfur in the natural gas pipeline. The latter concentration was chosen to exceed the SoCalGas maximum of ~12 ppm in the natural gas pipeline and is significantly higher than the threshold for sulfur poisoning in traditional ceramic SOFC anodes.

Figure 4 shows the difference in initial performance of cells exposed to reformates without H_2S, reformates with 1 ppm sulfur, and reformates with 5 ppm sulfur. The initial performance upon cell exposure to pure reformate fuels and reformate fuels with 1 ppm S are nearly equivalent, demonstrating tolerance to sulfur. With the addition of 5 ppm sulfur to reformates the initial performance is ~0.05 W/cm^2 lower. Note that such a high level of sulfur can be catastrophic for conventional SOFCs, but the MS-SOFC tolerates it because the anode contains minimal Ni and ceria is in intimate contact with the Ni particles.

Steam reformate with no or 1 ppm sulfur meets the project target of >0.3 W/cm^2 (0.4 A/cm^2 at 0.75 V). All other fuels provide initial performance above 0.2 W/cm^2.

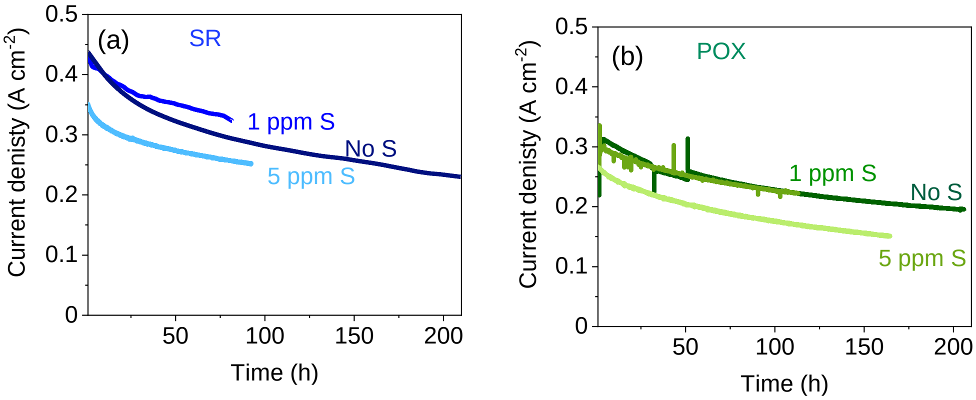

Figure 4. (a) Cells operating with steam reformate and varying levels of sulfur and (b) POX reformate with varying levels of sulfur at 0.75 V and 700 °C.

Following 200 h testing, cell testing time was been increased to 1000 hours with 1 ppm sulfur added to fuel streams. Figure 5 shows change in current over the full 1000 h as well as extracted data from benchmark linear sweep voltammetry (LSV) and EIS measurements. The bulk of the performance drop is observed in the initial 300 of hours of testing for both types of fuel. For steam reformate cell degradation was 60% over 1000 hours, with a degradation rate of 44%/kh for the last 500 h. For POX reformate total cell degradation was 54% after 1000 hours with a degradation rate of 36%/kh for the last 500 h. Ex-situ analysis confirmed that the majority of degradation was the result of significant Ni particle coarsening. This corroborates the growth in cell resistance and loss in performance as the particle sintering results in a loss of electrochemically active sites. Note that this phenomenon occurs with pure hydrogen fuel also, and is not directly a result of the use of NG or the presence of sulfur. Other parallel projects at LBNL have dramatically improved the degradation rate for hydrogen fuel in recent months.

Thermal cycling was performed with reformate fuels both with and without sulfur to assess durability to rapidly changing temperatures as well as potential carbon and sulfur build up at lower temperatures. Figure 6 shows changes to cell OCV and peak power as a result of thermal cycling under reformates with 5 ppm sulfur to mimic worst-case scenarios where sulfur levels exceed those of SoCalGas pipeline maximum. Cells were cooled from operating temperature to < 100 °C in 3-4 hours and quickly re-heated to 700 °C at 40 °C/min to meet project targets. The heating rate was limited by the furnace power, and we presume that the cells can handle much faster heating rate. Under both types of fuel, high tolerance toward thermal cycling stress is observed. OCV remains stable throughout testing while peak power drops slightly. It is estimated that ~50% of the observed degradation is a result of time spent at operating temperature and not due to thermal cycling itself. Carbon and sulfur buildup during cooling was found to be of minimal concern.

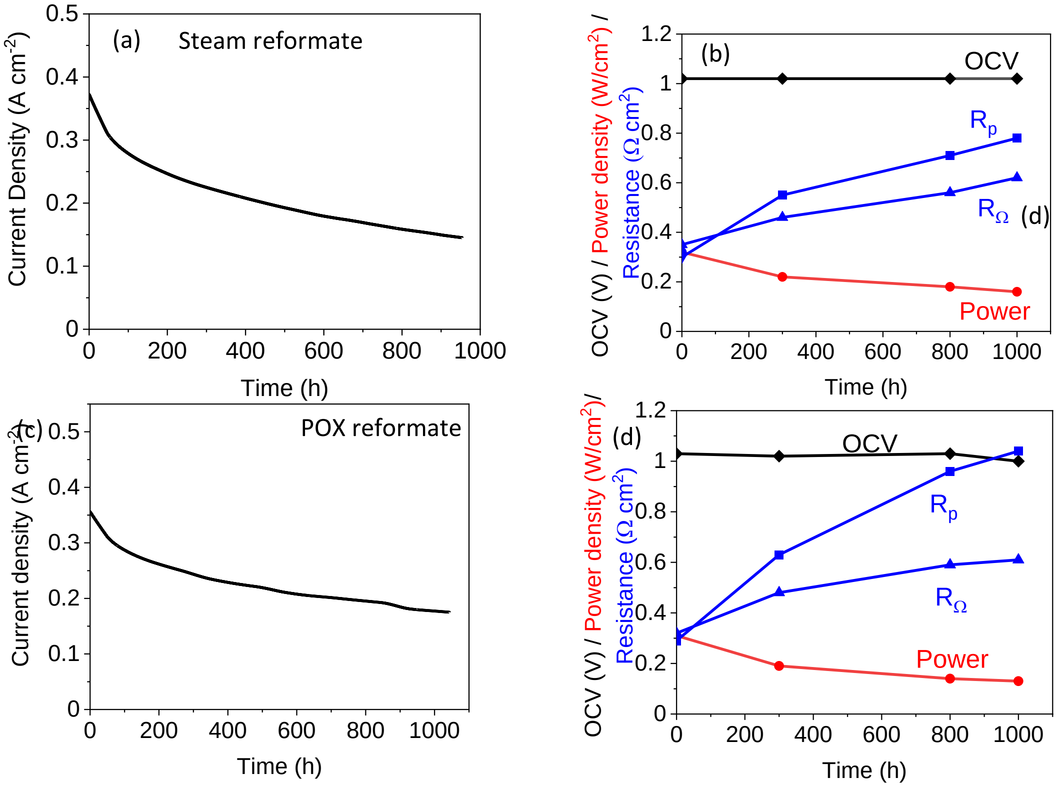

Figure 5. (a,c) Continuous 1000 h performance and (b,d) changes in OCV, power, and ohmic and polarization resistance with (a,b) steam reformate and 1 ppm sulfur and (c,d) POX reformate and 1 ppm sulfur.

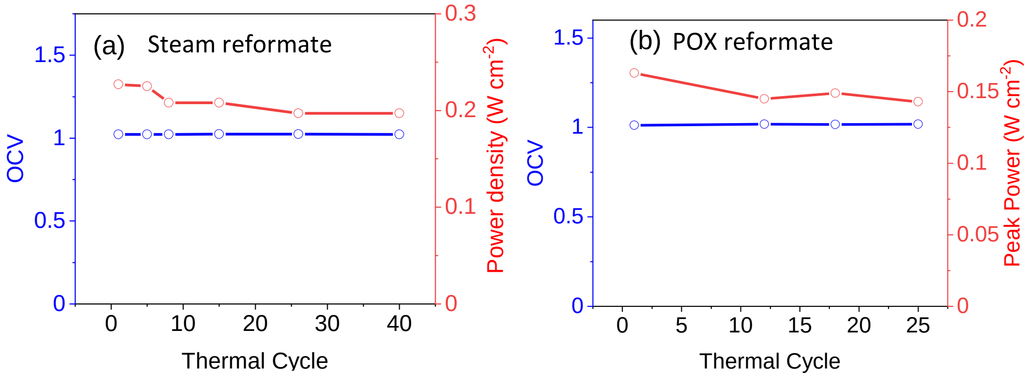

Figure 6. Changes in OCV and power density during thermal cycling under (a) steam reformate with 5 ppm sulfur and (b) POX reformate with 5 ppm sulfur.

To differentiate the effects of reformate fuel and baseline H_2 operation on thermal cycling, experiments with altering fuel exposure were performed. Figure 7 quantifies the difference in degradation between thermal cycling under H_2 and POX reformate. The initial 25 thermal cycles under H_2 were performed after 150 hours of constant operation at 0.75 V. Cell performance does not decrease under these initial thermal cycles, but rather a slight increase in performance is observed. Cycles 26 to 50 were performed under POX reformate. Initial performance is lower due to decreased H_2 concentration. While it's recognized that the cell degrades faster in the POX reformate this degradation difference is minimal, ~ 10 mW/cm^2. The final 25 cycles were again performed under H_2. Initial performance is again increased under H_2 and the total performance drop after cycling is ~15 mW/cm^2. In summary, there is a minimal difference in degradation after direct comparison of thermal cycles under H_2 and POX reformate conditions suggesting that carbon species present in reformates do not risk reducing cell longevity under cyclic operation.

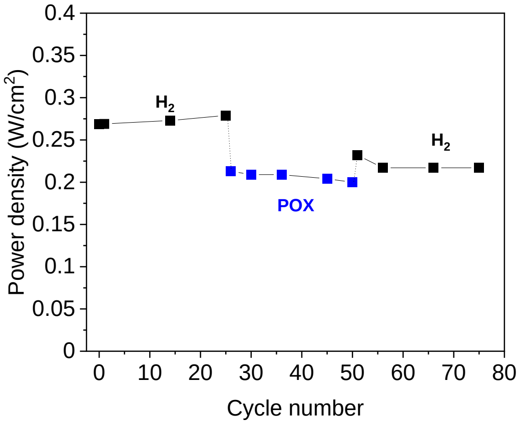

Figure 7. Changes in power density of thermally cycled cell operating under H_2 conditions for 25 cycles, followed by POX reformate for 25 cycles and another 25 cycles of H_2.

Conclusion:

This project demonstrated that LBNL MS-SOFC technology is compatible with natural gas under backup generator scenarios. Initial performance with reformate fuels met technical targets both without sulfur and with sulfur at levels relevant to SoCalGas pipelines. Additionally, initial performance with steam reformate and 5 ppm sulfur, equivalent to 18 ppm in the pipeline and exceeding SoCalGas levels, was close to technical targets. Cells were able to operate for 1000 hours with both types of reformate fuels and 1 ppm sulfur, equivalent to 5 ppm in the pipeline. Project targets were also met for thermal cycling with reformate fuels. Cells withstood extensive thermal cycles, up to 40 cycles tested, with rapid heating and cooling. Little degradation was observed under thermal cycling and sulfur and carbon deposition were not evident.