Preparation and Evaluation of Multi-Layer Anodes of Solid Oxide Fuel Cell

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ABSTRACT

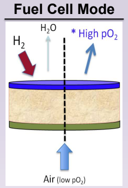
The development of an energy device with abundant energy generation, ultra-high specific power density, high stability and long life is critical for enabling longer missions and for reducing mission costs. Of all different types of fuel cells, the solid oxide fuel cells (SOFC) is a promising high temperature device that can generate electricity as a byproduct of a chemical reaction in a clean way and produce high quality heat that can be used for other purposes. For aerospace applications, a power-to-weight of ≥1.0 kW/kg is required. NASA has a patented fuel cell technology under development, capable of achieving the 1.0 kW/kg figure of merit. The first step toward achieving these goals is increasing anode durability. The catalyst plays an important role in the fuel cells for power generation, stability, efficiency and long life. Not only the anode composition, but its preparation and reduction are key to achieving better cell performance. In this research, multi-layer anodes were prepared varying the chemistry of each layer to optimize the performance of the cells. Microstructure analyses were done to the new anodes before and after fuel cell operation. The cells' durability and performance were evaluated in 200 hrs life tests in hydrogen at 850 ºC. The chemistry of the standard nickel anode was modified successfully reducing the anode degradation from 40% to 8.4% in 1000 hrs and retaining its microstructure.

SOFC: MULTIPLE APPLICATIONS WITH SINGLE TECHNOLOGY

Solid oxide fuel cell is a high temperature (700 – 1000 ºC) ceramic fuel cell that generates energy from an electrochemical reaction.

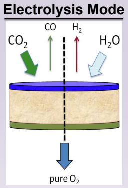
SOFC Advantages:
- High efficiency
- High energy density
- Flexible fuel capability
- Operating on both hydrogen and hydrocarbon-based fuels

Fuel Cell Mode

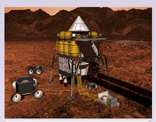


Power generation or High Pressure O_2

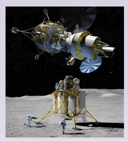
Electrolysis Mode



Space Applications



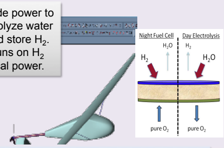
Power Generation Using Methane Generated by In-Situ Resource Utilization



Power Generation for Space Vehicle and Lander With Methane/Oxygen Propulsion System

Long Endurance Flight

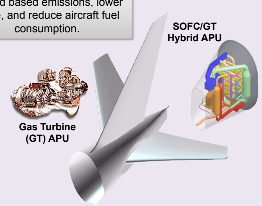
Solar panels provide power to the Stack to electrolyze water during the day and store H_2. At night, Stack runs on H_2 providing electrical power.



Regenerative "Reversible" SOFC Power System

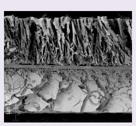
Fuel Cell Auxiliary Power Unit

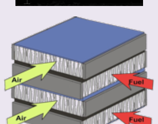
A fuel Cell APU in commercial aircraft will substantially reduce ground based emissions, lower noise, and reduce aircraft fuel consumption.



Bi-Electrode-Supported Cells

Advantages of BSC:
- The cell is structurally symmetrical with both electrodes supporting the thin electrolyte.
- Electrodes containing microchannels for gas diffusion.
- Both low volume and low weight.
- All-ceramic design operates at higher temperatures (750-1000˚C)
- Hermetic ceramic-to-ceramic seals.
- The BSC design has the potential to improve the power density 5x times over state of the art.



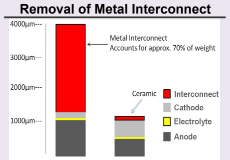


NASA BSC-SOFC enables rapid prototyping of electrode chemistries and microstructures for O_2 pump or other novel applications.

NASA 7-cell stack with seals

Ceramic Interconnects

Removal of Metal Interconnect

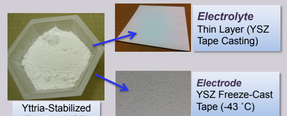


Anode-supported cell (ASC) vs. Bi-electrode-supported cell (BSC)

Standard technology uses metal interconnects, accounting for 70% of the weight, which reduces specific power density to 0.3 kW/kg.

CELL PREPARATION

From Ceramic Powder to Single Fuel Cell



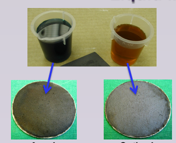
Yttria-Stabilized Zirconia (YSZ) Powder

- Fabrication **processes developed at GRC** take **ceramic powders** and produce the structural body of the Fuel Cell.
- Processes include traditional tape casting, freeze-casting of tapes, slip casting, lamination and co-firing.

Lamination and Sintering

All components sintered together in a single firing creating a inactive structural body.

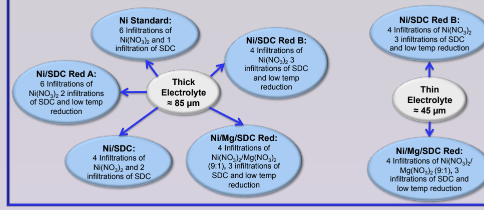
Liquid Infiltration



- Electrode materials are infiltrated after co-firing the structural elements.
- Low temperature infiltration processes greatly expand the types of catalysts which can be used thus providing maximum functional flexibility.

ANODE STUDY

After the development of the structural body of this SOFC, now the effort is focusing on the deposition of catalysts that can show good performance and stability. Our goal is to achieve a percent degradation of less than 2 % per thousand hours. Using one of the advantage of this technology, liquid infiltration, different anode catalysts were deposited varying the layers and the reduction process. Two group of cells were evaluated: One group of cells have an electrolyte of approximately 85 µm and the second group is using a thinner electrolyte (45 µm approximately). All fuel cells were prepared with the same cathode material, 6 infiltrations of LSCF.



FUEL CELL DURABILITY TESTS

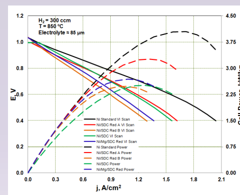


Figure 1. Performances of the cells prepared with the thicker electrolyte. The cells were running at 850 ºC and with a hydrogen flow of 300 ccm.

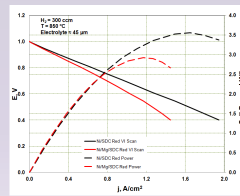


Figure 2. Performances of the cells prepared with the thinner electrolyte. The cells were running at 850 ºC and with a hydrogen flow of 300 ccm.

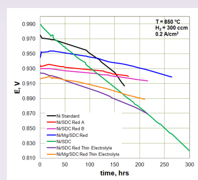


Figure 3. Stability tests of all the fuel cells in a constant current of 0.2 A/cm². The cells were running at 850 ºC and with a hydrogen flow of 300 ccm.

- A VI Scan test was done to all the cells the when the cells were started at Day 1 and at the end of the durability test (approximately day 9 with few exceptions).
- The durability test was done for 200 hrs and the percent of degradation was extrapolated to 1000 hrs.
- Our starting point was the Ni Standard cell that had a great performance showing a specific cell power of 4.0 kW/ (cell) and in the durability study had a 40.7 % of degradation for 1000 hrs.
- The last cells used thinner electrolytes. The electrolyte thickness was decreased from ≈ 85 µm to ≈ 45 µm. The new studies will be done using the thinner electrolyte ≤ 45 µm.

Fuel Cell	Power Day 1 (W/kg)	Power Degradation Day 9 (%)	ASR Day 1 (ohms/cm²)	ASR Degradation Day 9 (%)	Voltage at 0.2 A/cm2 Day 1 (V)	Voltage Degradation 1000 hrs (%)
Thick Electrolyte						
Ni Standard	4.05	67.3*	0.27	196.7*	0.975	40.7
Ni/SDC Red A†	3.27	N/A	0.33	N/A	0.935	8.4
Ni/SDC Red B	2.85	21.6	0.48	31.9	0.914	8.4
Ni/Mg/SDC Red	2.69	31.7	0.44	48.6	0.945	9.6
Ni/SDC	2.52	78.9‡	0.38	405.9‡	0.989	60.8
Thin Electrolyte						
Ni/SDC Red	3.56	51.7	0.31	94.0	0.925	29.8
Ni/Mg/SDC Red	2.93	33.4	0.38	51.0	0.916	10.4

* Degradation calculations were done using data of day 8. † The test was unexpectedly interrupted at day 7.
‡ Degradation calculations were done using data of day 14.

Table 1. Data values and calculations for all the fuel cells. Power from starting day (Day 1), percent of power degradation at day 9, ASR from starting day and its percent of degradation at day 9, voltage at a constant current of 0.2 A/cm², and the percent of voltage degradation extrapolated at 1000 hrs.

SEM ANALYSIS

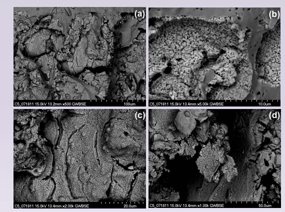


Figure 4. SEM micrographs of the anode electrode of the cell Ni/SDC Red B with the thick electrolyte after the performance and stability test: (a) near the electrolyte, (b) zoom in of an area near the electrolyte, (c) an area between near the electrolyte and the top of the electrode, and (d) near the top of the electrode.

- Micrographs of the cell Ni/SDC Red B after its performance and near the electrolyte (*Fig 4a-b*) reveal areas with and without large nickel particles and a net of SDC, but no exaggerated nickel growth. Big nickel particles growing under the SDC net start to appear in the middle of the electrode (*Fig 4c*), and they are visible and extend beyond the SDC net near the top of the electrode (*Fig 4d*).
- The fuel cell Ni/Mg Red shows a great coating of the layer electrode materials (*Fig 5*) and with less nickel growth particles than the sample Ni/SDC Red B.
- X-ray fluorescence of the cell Ni/Mg Red shows the formation of the cluster with the desirable elements: nickel, manganese, ceria and samarium.

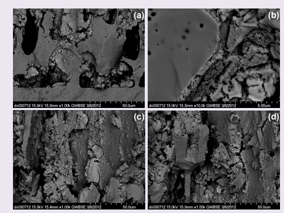


Figure 5. SEM micrographs of the anode electrode of the cell Ni/Mg/SDC Red with the thick electrolyte after the performance and stability test: (a) near the electrolyte, (b) zoom in of an area near the electrolyte, (c) an area between near the electrolyte and the top of the electrode, and (d) near the top of the electrode.

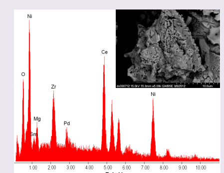


Figure 6. X-ray fluorescence analysis (EDS) of a cluster of particles of the cell Ni/Mg/SDC Red using the thick electrolyte.

CONCLUSIONS

- The performance and stability tests and the SEM analysis confirms the importance of not only the electrode material but also the electrode preparation process on the performance and especially the long term stability of the fuel cells.
- The fuel cells Ni/SDC Red have better stability than the fuel cells of Ni Standard, showing a decrease in the percent of degradation per 1000 hrs from 40.7 % to 8.4 %. The SEM analysis reveals that although the nickel particles appear interconnected and its microstructure near the electrode is maintained after the performance, the nickel near the top of the electrode show particle coarsening and separation affecting their performance and stability.
- Adding magnesium to the anode electrode helped to retain the microstructure after the cell performance and decreased the amount of nickel exaggerated growth on the top of the electrode. The performance was comparable to the Ni/SDC Red cell with a 9.6 % of degradation per 1000 hrs.
- Using a thinner electrolyte provides greater power per cm2 but had only a minor effect on degradation. More studies are needed to have a final conclusion.

CURRENT AND FUTURE WORK

- Ni anodes reduced at higher temperatures, currently being tested, demonstrate better performance and stability.
- New anodes will be created alternating the layers of nickel, magnesium and SDC and increasing the reduction temperature. Better performance and stability is expected with these electrodes.
- Different proportions between nickel and magnesium will be studied for the optimization. The reduction temperature also will be increased for the cells.
- The study of other compositions also is expected.