Ni-YSZ CERMET SUPPORTED THIN CERIA-BASED ELECTROLYTE SOLID OXIDE FUEL CELL FOR REDUCED TEMPERATURE (500-600°C) OPERATION

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ABSTRACT

A Ni-YSZ cermet supported thin ceria-based electrolyte solid oxide fuel cell based on tape casting, screen-printing and co-firing technologies has been fabricated and characterized. Studies were made of the anode substrate, paste solvent and binder, powder loading, co-firing profiles as well as cathode composition and firing conditions. Interaction between YSZ and SDC was investigated by EDX analysis. Cell performance of different electrolyte thicknesses and cathode firing conditions at low temperatures are also presented.

INTRODUCTION

During the last decade the anode supported thin film-electrolyte configuration has been adopted by many industrial and research groups in the world. Encouraging performance in the medium temperature range (700-800°C) with thin-film YSZ electrolyte has been achieved (1,2). However, stack materials related degradation, in particular, high temperature corrosion of the steel interconnector (3,4) pushes the R&D towards further decreasing cell operation temperature to below 600°C. It is well recognized that the operating temperature of SOFCs is mainly determined by the conductivity and thickness of the electrolyte and cathode polarization.

Doped ceria as electrolyte is a promising option. It shows 2-3 times higher ionic conductivity and higher electrode compatibility than YSZ. Its thermal expansion (12.5x10^-6/K) seems more compatible with the Ni-cermet substrate and commercial ferritic stainless steel interconnects. The maximum power density reached 0.25 W/cm² at 550°C in anode supported thin electrolyte configuration (5,6). The main disadvantage of ceria-based electrolyte is that it becomes a mixed conductor under anode conditions, which causes cell voltage loss and fuel efficiency loss due to internal shorting; chemical and mechanical stability is another concern for long-term service.

Electrolyte thickness is determined by the starting material and thin-film processing technology. A certain electrolyte thickness of several microns may be needed for it to remain free of cracks and pinholes, to decrease the probability of damage during handling and fabrication of stacks, shipping and delivery of the stacks, or during long-term operation of the system where the stacks may be vulnerable to vibration and sudden...
external impact. Likewise, the cells must withstand a significant number of thermal or redox cycles which may lead to easy cracking of the electrolyte due to the build-up of internal stresses if the electrolyte is too thin.

To lower manufacturing costs, efforts have been underway to use proven semiconductor multilayer manufacturing technology to manufacture the SOFCs; such as tape casting, screen printing and co-firing; and interest is growing in applying metal supported cell structures (7,8).

Research at NRC-IFCI Canada is aimed at improving durability and lowering costs by reducing operating temperature and system complexity. The program is focused on developing next generation cells and stacks that permit direct oxidation of practical hydrocarbon fuels containing sulphur and other impurities at reduced temperatures (500-600°C). Our activities involve development of novel materials, including nano-materials, metal-ceramic systems, and catalysts as well as process development, including plasma deposition, tape casting/screen printing and reactive spray deposition. Associated areas include fuel cell characterization, modelling, component integration, and micro fuel cells.

In this study, conventional multilayer technology was used to fabricate Ni-cermet supported ceria based thin electrolyte cells. We have successfully developed Ni-YSZ cermet supported single SDC layer cells for low temperature performance characterization. We characterized the cells mechanical strength, interface elemental mapping, He gas cross-leakage and electrochemical performance.

**EXPERIMENTAL**

**Materials**

Table 1 lists the starting ceramic powders used in this study.

| Component          | Composition   | Properties                | Supplier      |
|--------------------|---------------|---------------------------|---------------|
| Cathode            | Sm₀.₅Sr₀.₅Co₀₃ (SSC) | D₅₀: 0.80 µm  
                        |                   | Surface area: 5.16 m²/g | Praxair      |
| Electrolyte (EL)   | (SmO₁.₅)₀.₂(CeO₂)₀.₈ (SDC) | D₅₀: 0.40 µm  
                        |                   | Surface area: 7.08 m²/g | Praxair      |
| Anode layer (AL)   | (SmO₁.₅)₀.₂(CeO₂)₀.₈ (SDC) | D₅₀: 0.40 µm  
                        |                   | Surface area: 7.08 m²/g | Praxair      |
| NiO type F         | D₅₀: 1.0 µm   
                        | Surface area: 4.0 m²/g | Novamet       |
| Cermet substrate (CS) | NiO-standard   | D₅₀: 16.0 µm  
                        |                   | Surface area: < 1 m²/g | Tosoh        |
|                    | 8YS (YSZ)     | D₅₀: 0.520 µm  
                        |                   | Surface area: 6.2 m²/g | Tosoh        |

Table 2 lists the organic materials used for tape casting and screen printing. Tape casting was conducted after measuring the viscosity of the CS slurry in the range of 8,000-
10,000 cP. The blade gap was controlled to 1.80 mm resulting in a green tape thickness of about 0.72-0.75 mm.

Table 2. Organic chemicals for tape casting and screen printing.

| chemicals                          | function         | supplier                  |
|------------------------------------|------------------|---------------------------|
| Tape casting                       |                  |                           |
| Polyvinyl butyral, B-76            | binder           | Richard E. Mistler, Inc.  |
| Emphos 236                         | dispersant       | Richard E. Mistler, Inc.  |
| Santiciser-160, Ucon-50            | plasticizer      | Richard E. Mistler, Inc.  |
| Toluene, Butyl acetate, MEK, MIBK, Cyclohexane, Ethanol | solvent | Alfa Aesar |

| Screen printing                    |                  |                           |
| B-76                               | binder           | Richard E. Mistler, Inc.  |
| Ethyl cellulose                    |                  | Acros Organics            |
| Menhaden fish Oil (MFO Z-3)        | dispersant       | Richard E. Mistler, Inc.  |
| Sorbitan monooleate(SM)            |                  | GEO specialty chemicals   |
| Butyl acetate, Toluene, isopropanol, Butanol, Terpineol | solvent | Alfa Aesar |

Past Preparation

SDC and NiO-SDC pastes with 3 different powder loadings (54, 57 and 60 wt%) were prepared at fixed 7.5 wt% binder content by ball milling. 42 vol% of Ni in each NiO-SDC paste was designed for the anode functional layer.

Cell Structure and Fabrication

Figure 1 shows the designed cell structure, which consists of the cermet substrate (CS: NiO-YSZ, about 0.6 mm), anode layer (AL: NiO-SDC, about 10-30 μm), electrolyte (EL: SDC: 10-30 μm) and cathode (SSC, about 50-100 μm). We chose Ni-YSZ as anode substrate for its good chemical stability, high mechanical strength and well-matched thermal expansion. The cell fabrication route is tape casting CS, screen-printing AL and EL, high temperature co-firing, printing cathode and firing cathode.

Cell Characterization

1. Density and shrinkage measurement: dimension and weight, Archimedes’s method
2. Helium cross leakage check: 1 psig He at room temperature
3. Mechanical strength test: concentric ring-on-ring flexural loading configuration, refer to (9).
RESULTS AND DISCUSSION

Influence of Co-firing Temperature

Three temperatures were selected for co-firing the cell: 1300, 1350 and 1400°C for 3 hrs. The main results from characterization of the fired cells are listed in Table 3.

Table 3. Results from cell* characterization.

| Co-firing temp, °C | 1300 | 1350 | 1400 |
|-------------------|------|------|------|
| Electrolyte appearance | Semi-transparent | transparent | transparent |
| Shrinkage, % | 13.6 | 14.7 | 15.6 |
| Density, g cm⁻³ | 4.81 | 5.04 | 5.25 |
| Porosity, % | 24.5 | 20.4 | 17.2 |
| He leakage rate, ml.min⁻¹.cm⁻² | Not detectable | Not detectable | Not detectable |
| Flexural strength, MPa | 99.6 | 123.3 | 119.7 |

* 57 wt% powder loading in paste.

As shown in Table 3, the co-fired cells show increased shrinkage, density and flexural strength with increasing co-firing temperature, while the porosity decreases with increasing temperature. All samples prepared at the three temperatures showed He gas tightness, which indicates good continuity of the electrolyte. Generally, the well-sintered electrolyte looks transparent. The EL layer of the samples sintered at 1300°C appeared slightly semi-transparent. Further lowering of sintering temperature was not tried due to a decrease in cell mechanical flexural strength and potential gas leakage.

Influence of Powder Loading in Paste

SEM micrographs of printed layers of pastes with different solids loading after firing at 1400°C are shown in Figure 2; the thicknesses as a function of powder loading are shown in Table 4. It is clear that increasing powder loading in the paste leads to an increase in the printed layer thickness. Meanwhile, high powder loading in the paste results in a thick paste, which may affect the printing quality.

Table 4. Thicknesses as a function of powder loading.

| Powder loading in paste | 60 wt% | 57 wt% | 54 wt% |
|------------------------|--------|--------|--------|
| SDC thickness, μm | 25 | 21 | 16 |
| NiO-SDC thickness, μm | 25 | 18 | 11 |

Interface Elemental Analysis

One of the concerns in fabrication of the designed cell structure (see Figure 1) is the diffusion of elements at the interface during high temperature co-firing. Tsoga et al (10) reported a solid state reaction and interdiffusion phenomena occurring between YSZ and...
doped-ceria. The conductivity decreases by over one-order of magnitude of conductivity after firing at 1500°C. Figure 3 shows the EDX analysis results of a cell fired at 1400°C for 3 hrs. There is no clear evidence that the interface elemental interdiffusion happens. Because of the overlapping yttrium peak with Zr Lα, Y-mapping was not applied in this analysis. It seems that there is Sm diffusion from the Ni-SDC anode functional layer to the Ni-YSZ substrate from the Sm-mapping. However, we are not confident because the base Sm-signal is too low (see Figure 4).

**Figure 3.** SEM images and elemental mapping at the cross-section of functional layers

**Cell Electrochemical Performance**

**OCV and I-V curves.** Figure 5 shows OCV vs. temperature, and Figure 6 I-V and power curves for SDC cells with thicknesses of 25 μm and 16 μm co-fired at 1400°C. Sm₀.₅Sr₀.₅CoO₃ cathode paste was applied and sintered in situ at 800°C before the cell reduction and test.
Figure 4. EDX elemental analysis and elemental mapping line selection (red range).

Figure 5. OCV vs. temperature of SDC cells co-fired at 1400°C.

Figure 6. I-V and power curves at 600°C.
The 25 μm SDC cell shows slightly higher OCV value and lower cell performance than the 16 μm SDC cell. It is reported that OCV value of an SDC cell is related to the SDC thickness. The thinner the SDC electrolyte is, the lower the OCV value due to the internal shorting resistance variation. Blocking the electronic path of SDC by applying bi-layer electrolyte could lead to an increase in OCV (11,12). However, to date, performance improvement is quite limited.

**Cathode sintering temperature.** The cathode has a large impact on the cell performance. After the 800°C sintered cathode test, the cell was cooled down and the cathode was removed easily. After complete cleaning, the 25 μm SDC cell was coated at room temperature on the cathode side with a new SSC paste, and heated up to 900°C at a 300°C/h rate and dwelled for 2 h to investigate the influence of the cathode in-situ sintering temperature. The main results are shown in Figure 7. The OCV slightly decreased in comparison to the 800°C sintering cathode (Figure 5). However, the performance was greatly improved. The maximum power density reached 480 mW/cm² at 646°C and 235 mW/cm² at 535°C, which is in line with the reported results (6,8). Even at 500°C the power output exceeded 100 mW/cm². The microstructure after the cell test is shown in Figure 8. The cathode does not seem not well bonded to the electrolyte after cool-down and fracture. Further studies on co-firing bilayer electrolyte, cathode optimization and starting materials' influence are presently continuing.

![Figure 7. I-V and power curves of 1400°C co-fired 25 μm SDC cell with 900°C sintered SSC cathode, tested at different operating temperatures.](image)

**CONCLUSIONS**

Ni-YSZ cermet supported SDC thin electrolyte cells based on conventional multilayer technology were fabricated and characterized. SDC thickness in 15-25 μm range cells were prepared by varying the solids loading in the pastes from 54 wt% to 60 wt%. Co-firing temperatures could be in the range of 1300-1400°C with a satisfactorily dense electrolyte. Cell OCV value could be influenced by SDC electrolyte thickness and electrode performance. 1400°C co-fired 25 μm SDC cells with 900°C sintered SSC cathode shows promising performance.
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