SOL-GEL PROCESSED MULTILAYER THIN FILM DESIGN FOR SOLID OXIDE FUEL CELL APPLICATIONS

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ABSTRACT

The high operating temperature of ceramic membrane electrolyzers (800-1000°C) can lead to complex materials problems. In order to reduce the high temperature, the resistive loss in the electrolyte should be minimized. One of the solutions would be to decrease the thickness of the solid electrolyte. Thin dense yttria-stabilized zirconia (YSZ) membranes (about 20 μm) were prepared, characterized and tested in a multilayer device with lanthanum strontium manganite (LSM) electrodes, built on a porous alumina tube. By using a sol-gel process, a molecular bond was produced between the electrode layers and the solid electrolyte. The YSZ can withstand a pressure differential of 3 psi. At lower operating temperature of 700°C, the calculated voltage drop across our thin YSZ film is about 1/3 of the voltage drop using conventional thicker membranes. Experimental data show that our sol-gel processed multilayer thin film device (as oxygen generator) performs better at lower operating temperature.

INTRODUCTION

Solid oxide fuel cell systems and oxygen generator/removal are devices based on oxygen ion conducting technology. Oxygen is transported from one side of a solid ceramic membrane to the other side under a potential gradient, at about 800-1000°C. The high operating temperature can lead to complex materials problems (interfacial diffusion, electrode sintering, mechanical stress, thermal and mechanical fragility, leaks, and electrode debonding) (1). In order to reduce the temperature, the resistive loss in the electrolyte should be minimized. One of the solutions would be to decrease the thickness of the solid electrolyte. The reduction in the thickness of the electrolyte should not reduce the conductivity of the membrane appreciably at a particular temperature.

International Conference on Environmental Systems (ICES) paper 881040 provided references on electrochemical systems to remove CO2 (2). Westinghouse used YSZ membranes in two of these references. One of the references used vapor deposition to produce thin film electrolyte. Reference (3) outlines work on the preparation of thin (<20 μm) zirconia layers on porous substrates by the electrophoretic deposition process.

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An yttria stabilized zirconia (YSZ) film was fabricated by a modified chemical infiltration process at 1000-1200° C on NiO substrate that also served as an oxygen source. ZrCl₄ and YCl₃ were used as metal sources. This is a combination of chemical vapor infiltration (CVI) and electrochemical vapor deposition (EVD) (4). Typically electrochemical/chemical vapor deposition processes are capital intensive and expensive to operate (5). Alternative electrolyte deposition methods that show promise are spray coating and dip coating followed by sintering (6).

NexTech Material’s website (7,8) indicates that they have developed an electrolyte deposition process based on nanoscale YSZ. NexTech claims to have produced fully dense film approximately 15-30 microns in thickness. NexTech claims that the new process is less capital intensive and expensive to operate than the former electrochemical vapor deposition process. There is no discussion on the conductivity of these thin membranes, as to the effect of thickness on the membrane conductivity and how much pressure differential these membranes can withstand.

No reference has been found in the literature showing ability to produce thin dense membranes cost effectively, workable on a large area prototype without defects and electrical shorts, and ability to withstand high pressure differential across thin YSZ.

Today most commonly used cathode material is lanthanum manganite (LaMnO₃). Siemens Westinghouse cell is constructed by extruding a cathode tube and building the rest of the cell around it (5). At NexTech Materials, cathode is designed as the bottom-supporting layer, and fabricated with tape casting techniques using nanoscale particles (8). In both cases, the challenge is to sinter the cathode adequately, often by co-sintering with the other components, while maintaining sufficient interconnected porosity.

OVERALL PROGRAM APPROACH

CHEMIONIC/Rutgers have developed a technology for oxygen separation from air that is capable of yielding considerably higher concentration of oxygen from air. It is envisioned that the oxygen generator can be engineered into a battery-operated, suitcase-sized package for use in medical and other applications where high concentration of oxygen is needed and can be handled easily by a single individual. The goal of this research is to increase the current density (to obtain higher production of O₂ per unit weight in oxygen generator and higher specific energy for SOFCs), and to achieve higher stability and reliability.

Figure 1 shows a schematic of the experimental electrochemical oxygen generator we have used for oxygen generation from air. We chose to use the sol-gel process to fabricate thin electrolyte/electrode layers in the desired shape. Sol-Gel processing is a convenient way of sintering YSZ at low temperatures (9). The unique benefits of our design should be realized due to the chemical bonding of the membrane layers. The key innovations of this technology are (10,11):

- The thin ceramic layers result in lower voltage across the membrane. This allows the system configuration to operate at higher current density and lower electrode area (lower system weight/unit volume of oxygen production or higher specific energy Wh/Kg in SOFC).
• A molecular bond is produced which results in excellent strength and no leakage.

• Use of thin, very stable yttria stabilized zirconia (YSZ) as the solid electrolyte will help to achieve lower operating temperature.

• Easy scale-up.

Figure 1. Experimental Electrochemical Oxygen Generator.

We are extending our multilayer sol-gel processed thin electrolyte and electrodes design testing for solid oxide fuel cell (SOFC) applications and for electrochemical removal of CO₂ applications.

ISSUES IN ALL CERAMIC MEMBRANE ELECTROLYZERS

Interfaces

• Electrode/Current collector
• Electrode/electrolyte
• Electrode/Interconnects

Failures

• Increased contact resistance
• Chemical reactivity
• Delamination.
• Microstructure changes 1) sintering 2) crystallization
• Thermal expansion mismatch

SOL-GEL FABRICATION PROCESS

The key to innovation is in the construction of the membrane and electrodes using sol-gel technique. This process is inexpensive and results in thin membrane and electrodes that improve electrical performance and alleviate many of the material design problems other companies are struggling with, chief among these are sealing and membrane longevity.

The sol-gel process is a chemical synthesis of the oxides from the soluble precursors. Organic and inorganic salts of the metal species are mixed to produce the overall stoichiometry for the required material. The salts are dissolved in a liquid medium,
preferably water, so that thin layers can be applied directly to the supporting materials. Multiple layers can also be used to build up desired thickness. The liquids increase in viscosity upon application to form a solid gel. The gel requires heat treatment to develop the proper crystal phases.

The anodic layer, oxygen conductor layer, and cathodic layer can be applied by placing successive coatings on top of a porous ceramic support tube. Sol-gel process can be performed either by brush-coating or dip-coating depending on the nature of the substrate and thickness and quality of the film required.

**Why are we using sol-gel processing?**

- Multiple components in devices
- Direct application of layers
- Maintain porosity/promote continuous phase
- Reduce need for sealing materials/seals
- Grade interface of mismatched materials
- Selective placement
- Low temperature/pO₂ sensitive phases
- Barrier layers/interlayers

**Electrodes**

In an oxygen generator device, oxygen transport at high temperatures requires materials for electrode that are highly stable chemically and thermally and also have high electrical conductivity and catalytic activity. Considering these conditions, the best electrode material for such devices would be lanthanum cobalt oxide (LaCoO₃). This perovskite has the best electrical conductivity, in addition to the lowest overpotential. Unfortunately, this material is damaged during operations. For this reason, lanthanum strontium manganite or LSM (La₁₋ₓSrₓMnO₃) has been chosen. LSM has reasonable electrical conductivity and high catalytic activity for oxidation of O₂. It also has thermal expansion coefficient very close to that of ZrO₂. The microstructure of this LSM is a compromise between a porous layer, which would allow the gas to diffuse through the cathodic layer and a density high enough to provide good conductivity.

**Electrolyte**

The ceramic electrolyte has to work at high temperatures. At room temperature, their ionic conductivity it too low. Pure zirconia cannot be used because it undergoes lattice changes when heated causing it to crack. The addition of some oxides, such as yttria, decreases these changes. The fully stabilized zirconia (F-YSZ) has no lattice changes from room temperature up to 2500°C. Its crystalline structure is a cubic solid solution. Moreover, pure zirconia is a low ionic conductor. However, due to the addition of aliovalent oxides, oxygen ion vacancies are created through which ionic conduction can occur. Oxygen ions can jump from one unoccupied site to the next.

The sol-gel process involving zirconia begins with zirconium oxychloride solutions or zirconium propoxide solutions. These are readily available from NJ-based Magnesium Electron Corporation. The solution is reacted with ammonia and water to create the fine
distribution of zirconia particles that deposit on the electrodes. Layer thickness can be controlled, along with the density and adhesion.

**Overall Design**

The originality of the preparation lies in the use of the sol-gel route to prepare the multilayer device. The sol-gel method provides the means to deposit thin layers on any kind of substrate shape. The benefit of our unique design is due to the chemical bonding of the membrane layers. The concept is that zirconia can be deposited onto the electrodes to form a mechanical separator that is rigid, free of electronic short circuits, but thin enough to provide efficient ionic conductivity. The unique characteristics of the CHEMIONIC/Rutgers sol-gel processed multilayer thin electrolyte and electrode design are:

- The use of thin lanthanum strontium manganite (LSM) as electrodes.
- The use of thin fluorite type structure oxide ZrO$_2$ as the solid electrolyte.
- The use of sol-gel processing to produce multilayer electrochemical cell technology.
- The use of porous thin platinum coating to better distribute the current to the anode and cathode uniformly.

**YSZ CHARACTERIZATION**

The anodic layer, oxygen-conducting layer, and cathodic layer are applied by placing successive coatings on top of a porous support tube (10,11). Sol-gel process is performed either by brush coating or dip coating depending on the natures of substrate and thickness and quality of the film required. The results so far obtained show that thin electrolyte layers can be obtained and tailored through the sol-gel process. The thin electronically insulating YSZ layer is non-porous, and gas tight. Mercury porosimeter, SEM analysis and pressure testing are used to make sure that YSZ layer is dense and non-porous. The electrolyte thickness is about 20 μm, which is about 10-15 times thinner than the conventional laminated electrolyte thickness and hence leads to good electrochemical properties. Impedance spectroscopy has been used to determine the conductivity of the samples.

**YSZ Layer Thickness**

The results so far obtained show that thin electrolyte layers can be obtained and tailored through the sol-gel process. The number of successive gel coatings that produces a gas tight, electronically insulating layer must be greater than 30. SEM pictures give varied thickness. We think it is because of non-uniform nature of the substrate. The thickness of YSZ varies from 18 micron to 37.5 micron. We believe the average thickness of YSZ is about 20 microns. The thickness of the thin YSZ layer is about 10-15 times thinner than the conventional laminated YSZ electrolyte.

**Porosimetry Data**

Figures 2 and 3 show cumulative pore volume vs. pressure for YSZ+substrate and the substrate alone. The data indicate that YSZ layer is not creating any new pores and in
fact closes some of the smaller pores in the substrate. The cumulative pore volume for YSZ+substrate is lower than the substrate. The data clearly show that the YSZ layer is non-porous.

Figure 2. Porosimeter data – Incremental pore volume vs. pressure for YSZ+Substrate.

Figure 3. Porosimeter data – Incremental pore volume vs. pressure for substrate.

Density Measurements

Table 1. Density measurements for YSZ as a function of sintering temperature.

| Real Density (g/cm³) | 5.66 | 5.72 | 5.85 | 5.9 | 5.9 | 5.92 |
|----------------------|------|------|------|-----|-----|------|
| Sintering Temperature (Deg C) | 600  | 800  | 900  | 1000 | 1100 | 1200 |
| Relative Density     | 0.942| 0.952| 0.974| 0.982| 0.982| 0.986|

As shown in Table 1, the YSZ layer was sintered to form the dense solid electrolyte at temperatures of 1100-1200° C to a density greater than 95% of theoretical.
Pressure drop data

At this time, we are able to fabricate thin film YSZ that can withstand a pressure differential of about 3 psi and mechanically very stable. There is no literature or commercial data for thin YSZ films that can withstand high-pressure differential across zirconia electrolyte. Most of the literature and commercial thin YSZ are more towards solid oxide fuel cell applications and the pressure differential data are not reported. For fuel cell applications, a non-porous YSZ should be sufficient because there is no pressure differential between the anode and the cathode. But ability to withstand high-pressure differential across thin YSZ film is a very important characteristics for the following applications:

**Oxygen Generator:** Oxygen is electrochemically compressed inside the section where oxygen is produced and this helps the oxygen to flow through the supply line. The YSZ layer has to be leak proof to avoid the higher concentrated oxygen flowing through the YSZ and mixing with air. Hence, for oxygen generation system, it is very critical that YSZ layer is not only non-porous; it has to withstand higher pressure differential and be mechanically stable. To our knowledge, our thin film YSZ is the first one reported in the literature that can withstand pressure differential close to 3 psi across a thin YSZ membrane. We are working towards higher pressure differentials.

**Carbon Dioxide Electrolysis to Oxygen:** Oxygen production via direct electrochemical reduction of carbon dioxide (CO₂) has been investigated in the literature (1). This technology has direct applications for ongoing space missions (e.g., the International Space Station (ISS), shuttle) and for Human Exploration and Development of Space (HEDS) missions as a means to remove CO₂ generated from human respiration in space cabins during long-term missions. References (12,13) illustrate the oxygen generation system (OGS) that is currently being worked on by students in the Space Technologies Laboratory (STL) at the University of Arizona. STL is under contract from the NASA Johnson space Center to deliver flight hardware to produce oxygen from compressed Mars atmosphere. Once on Mars, it will use solid oxide electrolysis to produce oxygen. Oxygen and fuel would be used to launch a small rocket from the surface of Mars or to power a drill that would take core samples of the Martian surface.

Our new sol-gel processed thin film YSZ technology will provide better oxygen production via direct electrochemical reduction of carbon dioxide (CO₂) because:

- The thin ceramic layers result in lower voltage across the membrane. This allows the system configuration to operate at higher current density and lower electrode area (lower system weight)/unit volume of oxygen production.
- A molecular bond is produced which results in excellent strength and no leakage.
- Use of thin, very stable yttria stabilized zirconia (YSZ) as the solid electrolyte will help to achieve lower operating temperatures.

This new technology will provide advances in the recovery of oxygen from CO₂ for space applications providing dramatic decrease in energy density (Whr/liter of Oxygen produced) for missions ranging from International Space Stations (ISS) through an initial Mars mission.
**Structure of YSZ**

In order to stabilize the high temperature phase (cubic one), a 10% molar of yttrium was added to the gel. The cooling of the sample was also done very rapidly from 1100°C to room temperature. The cubic phase seems to be the main crystalline structure of the electrolyte layers. The SEM chemical analysis done on the surface zirconia layer reveals that the layers are chemically homogeneous. The small size of signal corresponding to the LSM layer below the YSZ (comparing to this to YSZ) led to think that there is no defect in the coat.

**Impedance Measurements**

Impedance spectroscopy has been used to determine the conductivity of the sample. The measurements have been done on thin layers directly. The ionic conductivity of the solid electrolyte improves when the length of the heat treatment is increased. However, an optimum heat treatment time has been found because of the complexity of many layers interactivity (10,11). Table 2 compares conductivity and voltage for our sol-gel thin YSZ membrane (about 20 micron thick) against literature data for the conventional laminated thicker (about 300 micron thick) YSZ membrane.

| Table 2. Calculated voltage drop across YSZ at 700 and 800° C. |
|---|---|---|---|---|
| | 700 Deg C | 800 Deg C |
| | Conductivity s/cm | Voltage Drop at 100 mA/cm², mV | Conductivity s/cm | Voltage Drop at 100 mA/cm², mV |
| Sol-gel thin film YSZ (20 micron thick) | 0.0008 | 250 | 0.0017 | 120 |
| Conventional laminated thicker YSZ (300 micron thick) | 0.004 | 750 | 0.02 | 150 |

Table 2 shows the following:
1. The conductivity of the membrane is reduced with decreasing YSZ membrane thickness.
2. The decrease in the conductivity of the membrane with temperature is more dramatic with conventional thicker membrane. The conductivity of our thin film YSZ decreases by 50%, while the conventional thicker membranes decrease by about 80%, when the temperature is decreased from 800 to 700° C.
3. Calculated voltage drop across the membrane is lower for our sol-gel thin YSZ at both 800 and 700° C. The most important thing to notice is that, we can reduce the operating temperature to 700° C with our membrane, without paying the penalty for a very high voltage drop. At 700° C, the voltage drop across conventional thicker YSZ membrane is 750 mV compared to only 250 mV for our thin film YSZ membrane.
4. The voltage drop across YSZ membrane needs to be less than 1 V for stable YSZ operation for a long time. With our sol-gel thin film YSZ membrane, Table 2 indicates that we can increase the current density and still maintain the voltage drop within 1 V.

It is important to note that we have achieved use of thin, very stable yttria stabilized zirconia (YSZ) as the solid electrolyte to achieve lower operating temperature; and the thin ceramic layers result in lower voltage across the membrane. This allows the system configuration to operate at higher current density and lower electrode area (lower system weight/unit volume of oxygen production or higher specific energy Wh/Kg in SOFC).

ELECTROCHEMICAL CELL PERFORMANCE

The electrochemical cell consists of a) lanthanum strontium manganite (LSM) as electrodes, b) YSZ as the solid electrolyte, and c) platinum current distributor. The following data are collected for oxygen separation from air (the multilayer thin film device as oxygen generator).

Temperature vs. Voltage at a Current Density of 100 mA/cm² for 1 cm² Patch

The YSZ layer needs to function as an ionic conductor for the oxygen ion transport. If there is a short between top and bottom LSM layers through the YSZ layer, the YSZ layer will function as pure resistive load. In any ion conduction medium, the conductivity will increase with temperature. That means that the current density will increase with increasing temperature at a particular set of voltage (1 V in our case) or the voltage will go down with increasing temperature at pre-determined current density (100 mA/cm² in our case). We have included a figure below to illustrate this. Fig. 4 shows data collected from two 1 cm² independent patches plotted as voltage vs temperature at a current density of 100 mA/cm².

![Figure 4. Temperature vs. voltage at a current density 100 mA/cm² for different patches.](image_url)
Figure 4 indicates that the voltage goes down with increasing temperatures at a current density of 100 mA/cm².

**Current vs. Temperature at Certain Voltage**

Figure 5 shows the normalized current vs. the temperature. The actual current at each temperature (at a pre-determined potential) is normalized by dividing by the maximum current at 850°C for our sol-gel thin film YSZ. Figure 5 also shows similar data for a commercial fuel cell YSZ disk of about 100 micron thick.

![Figure 5. Normalized current (i/I_{max}) vs temperature.](image)

At 700°C, the oxygen generation cell containing our sol-gel thin film YSZ and LSM electrodes conducts about 80% of the current compared to at 800°C. At 700°C, the oxygen generation cell containing commercial YSZ disk conducts only about 65% of the current compared to at 800°C. This is another positive aspect of our sol-gel processed multilayer thin film design - better performance at lower operating temperature.

**CONCLUSIONS**

1. The results obtained show that thin electrolyte layers can be obtained and tailored through the sol-gel process.

2. We can produce a gas tight, electronically insulating layer of 20 μm thickness, which is still very thin and leads to good electrochemical properties.
3. At this time, we are able to fabricate thin film YSZ that can withstand a pressure differential of about 3 psi and mechanically very stable. There is no literature or commercial data for thin YSZ films that can withstand high pressure differential across zirconia electrolyte.

4. The thin ceramic layers results in lower voltage across the membrane. This allows the system configuration to operate at higher current density and lower electrode area (higher specific energy Wh/Kg in SOFC).

5. Use of thin, very stable yttria stabilized zirconia (YSZ) as the solid electrolyte will help to achieve lower operating temperature.

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REFERENCES

1. http://technology.ksc.nasa.gov, Research and Technology 2002.
2. A. Isenberg and R. Cusick, International Conference on Environmental Systems (ICES), Publication number 881040.
3. J. Will, M. K. M. Hruschka, L. Gubler and L. J. Gauckler, J. American Ceramic Society, 84, No.2, (2001).
4. K. Kiikuchi, T. Okaya, W. Hirose, K. Matsun, J. Electrochemical Society, 150 (10), C688-C692 (2003).
5. S. C. Singhal, MRS Bull., 25, No.3, 16-21 (2000).
6. Jiann-Hwa Liou, Po-Jou Liou, Tzer-Shin Sheu, Ceram. Trans., 109, 3-10 (1999).
7. Scott Swartz, William Dawson, Cathode supported thin-film solid oxide cells with low operating temperature, NexTech Materials, Ltd, Worthington, OH. DOE Grant # DE-FG02-99ER82844.
8. http://www.nextechmaterials.com/products.htm
9. Tatsuya Okubo, Hidetoshi Nagamoto, J. Material Science, 30, 749 (1995).
10. R. R. Chandran, S. Mege and L. C. Klein, Multilayer Electrochemical Cell Technology Using Sol-Gel Processing, Patent Pending.
11. S. Mege, L. C. Klein and R. R. Chandran, Multilayer Electrochemical Cell Technology using Sol-gel Processing, Presented at NAMS2000, 11th Annual Conference and Workshop, May 23-27, 2000 at Boulder, Colorado.
12. K. R. Sridhar and B.T. Vaniman, Solid State Ionics, 93, 321-328 (1997).
13. http://stl.arne.arizona.edu/mip-ogs/soec.html