Development of Planar SOFC Technology: Progress and Problems

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Development of solid oxide fuel cells with planar configuration has received increased attention in recent years primarily due to high power and energy density and rapid commercialization prospects that it offers. However, the high operating temperature of the cell poses challenges related to materials, performance stability as well as engineering issues. High single cell performance was obtained using tape cast stabilized zirconia electrolyte and screen printed electrodes. Several multi-cell stacks were also tested. This paper summarizes the progress made at Ceramatec on planar SOFC device technology development. Issues related to materials stability and cell performance with respect to various cell fabrication techniques are discussed.

1 INTRODUCTION

Fuel cells allow direct conversion of fuels such as hydrogen and natural gas into electricity at very high efficiency. Zirconia based high temperature solid oxide fuel cells (SOFCs) offer several additional benefits over other types of fuel cells; they generate high grade heat and operate at higher efficiency and power density. Various designs of SOFCs are currently under development namely tubular, monolithic and planar. Of these the planar design appears to be the focus owing to its inherent technical advantages such as high power and energy density and fuel recycle capability with separate manifolds. These features coupled with the inexpensive, mature, and scaleable manufacturing techniques used for cell/stack fabrication lead to rapid commercialization prospects. This paper summarizes the recent progress at Ceramatec in the development of planar solid oxide fuel cells. Some aspects of electrode application and cell performance are highlighted.

2 OVERVIEW OF PLANAR SOFC DEVELOPMENT

2.1 Fabrication

The standard materials used for electrolyte, anode and cathode are Yttria stabilized zirconia, Ni-ZrO₂ cermet, and La(Sr)MnO₃ respectively. The major advantage in planar technology is that the cell components of the SOFC can be separately fabricated to achieve the desired characteristics and then assembled. Ceramatec utilizes standard electrode materials and Y₂O₃ (4 mol%) and Yb₂O₃ (4 mol%) stabilized zirconia as the electrolyte. This electrolyte composition exhibits higher conductivity ($\sim 3 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$) as compared to 8 mol% Y₂O₃ stabilized zirconia ($\sim 1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$) at 1000°C. Sr doped LaCrO₃ is used as the bipolar plate for series connection of the cells. The fabrication techniques employed are aimed at fabricating thin electrolyte and interconnection layers in order to minimize ohmic losses. Electrolytes are tape cast and sintered independently to obtain gas tight layers.

Various methods were used to apply electrodes to pre-sintered electrolyte membranes including plasma spraying, screen printing and slurry coating. The latter two processes are cost effective as well as give better control of the electrode morphology. The influence of the

electrode application process on the morphology and electrode performance characteristics is discussed later.

Typically, screen printed electrodes are fired at about 1250°C to achieve good interfacial characteristics and stable morphology. Higher firing temperatures, although beneficial to stronger adhesion between the electrode/electrolyte, can often lead to formation of insulating phases due to interface reactions resulting in lower performance. At the cathode/electrolyte interface, La and Sr zirconates may form. High overpotential losses at the cathode/electrolyte interface have been attributed to formation of such insulating compounds¹⁾. Further, Mn diffusion along grain boundaries is also detected²⁾. Especially in the case of thin electrolytes this can cause undesirable electronic conduction along grain boundaries. Due to poor wetting of Ni metal on zirconia as well as thermal expansion coefficient mismatch, weak physical bonding is often exhibited at the anode/electrolyte interface. As a result, anode debonding during fabrication and/or cell operation has been observed^{3,4)}. This is an important source of overpotential that has been observed by other developers of planar SOFCs. This problem can be solved by proper choice of the Ni and ZrO₂ powders and electrode firing process parameters. Tradeoffs must be made when using high surface area powders; they exhibit better adhesion but the higher shrinkage results in dimensional instability and poor contact in multi-cell stacks.

The most challenging step in the fabrication of planar cells is the sintering of the interconnect material. Doped LaCrO₃, currently the interconnect material of choice, presents special difficulties in meeting the simultaneous functional requirements of high density, controlled stoichiometry, and phase stability during fabrication and fuel cell operating conditions. The primary difficulty in air sintering of LaCrO₃ based materials arises from the volatility of Cr from the structure at temperatures higher than 1400°C, causing surface porosity to develop. This can be minimized by sintering in reducing

atmospheres, with oxygen activities of 10⁻¹²-10⁻¹⁰, in the temperature range 1500 - 1700°C⁵⁾. Sintering aids such as SrCO₃⁶⁾, low melting oxide eutectics, and La, Y and Mg fluorides of up to 8-10 weight %⁷⁾ have been used to increase density of sintered compacts. However formation of insulating spinel phases and chemical reactions at the interfaces between electrodes and interconnections cause performance degradation. Hot pressing has also been investigated as a method of densification of the interconnect.

In an alternate approach, Ca doping of up to 0.05 atom fraction per LaCrO₃⁸⁾ and various other dopants⁹⁾, on both A and B sites of the perovskite structure, have been incorporated to enhance the sinterability in air. These dopants form a transient liquid phase (identified using EPMA, dilatometry and TGA) which increases sinterability in air at temperatures below 1500°C. The details of the different fabrication processes have been given elsewhere^{4,9)}. During fabrication of thin interconnects, the transient liquid phase (Ca, Cr and Co rich composition) can lead to variations in sintered density of thin structures as well as to deleterious surface reactions with other materials in direct contact during the sintering process. By careful control of the stoichiometry however, the onset temperature of the liquid phase as well as the densification regimes can be controlled. Preliminary results with heavily doped LaCrO₃ indicate somewhat lower thermodynamic stability of the perovskite interconnection materials. Ongoing work at Ceramtec is aimed at identifying the origin and nature of this liquid phase as well as determination of the stability limits of such materials via in-cell tests.

The Ceramtec cell design uses a LaCrO₃ bipolar plate with integral ribs. This design has a high ohmic loss due to the thicker interconnect cross-section and consequent longer electron flow path. Alternate designs using a thin planar interconnection with ribs made of the electrode materials are feasible provided that during the fabrication process for such a composite interconnect, deleterious interdiffusion reactions (with concomitant loss in performance) do not

occur. The extent of these reactions and their influence on performance is obviously dependent on the component geometry and can be calculated from Mn/Cr interdiffusion constant, $D_{Cr,Mn}$ estimated to be $\approx 0.36 \exp.(-45450/T) \text{ cm}^2/\text{s}^4$. This suggests that processes involving co-firing between cathode/interconnect and cathode/zirconia interfaces are likely to result in lower cell performance due to interface reactions, unless co-firing temperatures lower than 1400°C can be used.

2.2 Single cell performance

The cell performance of single cells is dominated by anodic overpotential losses. This overpotential loss is attributed mainly to two factors: low porosity resulting in a "Nernst loss" at low current density and weak, non-uniform bonding resulting in greater anode/electrolyte interface resistance. The magnitude of this overpotential loss is determined by the choice of electrode application method employed, mainly screen printing and firing. The cathode/electrolyte interface has good bonding because of the strong chemical interaction between the electrode material and zirconia. At the anode however, due to reasons mentioned earlier, better adhesion is achieved primarily due to improved sintering of the zirconia in the cermet with the zirconia of the electrolyte. This ideally provides a strong rigid framework within which the Ni particles reside. Typical results using two of the anode application techniques evaluated, plasma spraying and screen printing are discussed below.

Figure 1 is a performance curve of a single cell with screen printed electrodes. The starting anode cermet material consisted of very coarse zirconia (5 μm mean particle size) powder, and, consequently resulted in poor anode adhesion to the electrolyte. As can be seen from Figure 2, the major overpotential loss occurs at the anode/electrolyte interface. The anodes of such cells typically were found to completely delaminate from the electrolyte after testing for about 48 h at 1000°C. However, by controlling the particle size distribution of the zirconia in the anode cermet, the adhesion to the electrolyte was greatly en-

Fig. 1 Performance of a single cell with screen printed electrodes.

Fig. 2 Elements of polarization.

hanced. The improved anode/electrolyte interface resulted in better cell performance. The I - V characteristics of various cells with improved anode cermet are plotted in Figure 3. In all cases, the fuel was H_2 saturated with H_2O at 298 K and the oxidant was air. The area specific resistance of the current Ceramtec single cells varies between 0.3 to 0.1 $\Omega\text{-cm}^2$ at 900-1000°C, for electrolyte thicknesses of 150 μm . Typical single cell performance is as high as 800 mA/cm^2 at 0.7 V. The performance loss is dominated by the ohmic loss in the electrolyte and long term tests conducted independently at ABB¹⁰ indicate no degradation in performance in a continuous load test over 600 h. at 1000°C demonstrating stable electrode/electrolyte interface characteristics. Thus far, no efforts have been made to control or measure fuel utilization.

Anodes applied by the plasma spray method were found to have excellent adhesion. Examina-

Fig. 3 I-V Characteristics of various single cells as function of temperature.

tion of polished cross-sections shows evidence of zirconia fracturing at the surface. This is attributed to the poor thermal shock resistance of fully stabilized zirconia. Figure 4 shows the change in anode overpotential at low current densities (< 20 mA/cm²) with time at 1000°C for pure Ni as well as Ni-ZrO₂ cermet anodes. As compared to screen printed anodes (data plotted in Figure 4), the overpotential of plasma sprayed anodes is lower. The performance of plasma sprayed anode cells with time was found to be more stable in general. Comparing plasma sprayed Ni-ZrO₂ cermet anodes with plasma sprayed Ni anodes, the cermet anodes showed an initial change in performance. This is attributed to a slower de-wetting of Ni in the cermet, due to steric hindrance from the zirconia component of the cermet, as compared to pure Ni on the electrolyte substrate surface. The greater stability of the plasma sprayed anodes is attributed to the higher tem-

Fig. 4 Anode overpotential at 1000°C.

peratures of the plasma spray deposition process making further morphological changes at cell operating temperature negligible. The stronger bonding of plasma sprayed anodes to the electrolyte substrate as compared to screen printed anodes results in lower anode overpotentials. Surface stresses from the deposition process may be reduced and further performance improvement may be possible by optimizing the plasma spraying parameters. With subsequent screen printed anode development however, high performance cells can be fabricated as shown in Figure 3. From a process economics point of view screen printing is considered to be a better option, and hence will be developed further.

2.3 Stack performance

Planar SOFC stacks are fabricated by alternating electrolyte layers with electrodes and interconnects in sequence. In the case of a planar, cross-flow design, the challenge is to obtain effective edge seals capable of withstanding the high operating temperatures as well as the reactant environment, especially of the fuel gas. Ideally, the seal material should exhibit some compliance so as to allow good electrical contact between the interconnect and the electrode and prevent gas leakage along the edge. After evaluation of ceramic seals, glass seals and glass/ceramic composite seals, a glass/ceramic composite seal was developed with a composition that withstands the reducing fuel gas atmosphere and has compatible physical characteristics such as glass transition temperature, thermal expansion coefficient etc. Over 7000 hours of cumulative test time have demonstrated the good sealing characteristics against and compatibility with the cell components and materials. The ohmic contribution to area specific resistance of the repeat unit in a multi cell stack is estimated to be $\sim 0.75 \Omega\text{-cm}^2$. The specific geometry is a 150 μm thick electrolyte, 3 mm thick interconnect. The measured contact resistance between the interconnect and the electrode is typically $1 \Omega\text{-cm}^2$ with a low value of $0.32 \Omega\text{-cm}^2$. This is primarily attributed to poor contact between the flow channel rib and the electrode and results in more than an order of magni-

tude lower performance as compared to single cell performance. In a practical SOFC stack, reduction of this large contact loss is essential. This can be achieved by the use of flow fields made from electrode materials. Using this concept, the ohmic drop in the interconnect can be significantly reduced due to the higher conductivity of these materials. Problems with thermal cycling due to mismatch in thermal expansion coefficients between the interconnection material and the Ni-ZrO₂ cermet may be anticipated. Furthermore, manufacturing costs of such "composite" interconnects are expected to be higher. With a suitable design which minimizes the electron flow path in the interconnection and a bonding process which reduces the contact resistance loss to even lower values, planar stack performance can be increased to greater than 300 m W/cm².

In a multi-cell stack, even if the ohmic resistances are minimized and contact resistances are negligible, a reactant flow mal-distribution will result in poor overall stack performance due to an increase in the equivalent series resistance of the stack. A detailed discussion of these topics is beyond the scope of this paper. Manifold designs are critical with respect to assuring uniformity of reactant flow as well as achievement of reliable corner seals. Both of these factors will critically affect the maximum power density achieved in a multi cell stack. Thus, careful attention must be paid to development of reliable manifolds as well as manifold seals.

2.4 Reliability and failure analysis

Several units of 30 cells of $\sim 45 \times 45$ mm have been successfully stacked and tested. Stack tests (> 3000 h.) have shown that the critical aspects of test failure have not been cell hardware related as much as manifold and test hardware related. Planar SOFC stacks with proper edge seal design have been thermally cycled from 298 to 1273 K without degradation in performance or cell component cracking. Edge seal life appears to be adequate. The main problems are in ensuring adequate manifold seal reliability especially with respect to thermal cycleability. Greater emphasis must therefore be placed on seal design

and materials compatibility.

3 SUMMARY AND CONCLUSIONS

The planar SOFC concept is capable of providing high power and energy density using simple, low cost manufacturing technologies. With development of suitable screen printed electrode technology, stable high cell performance can be obtained. Single cell performance of ~ 600 m W/cm² at 0.7 - 0.8 V at 1000°C is obtainable with screen printed electrodes. While studies on the effect of dopants on interconnect sintering have led to increased understanding of densification mechanisms and development of fabrication technology, much work needs to be done to reduce losses as well as increase stability against reduction in the presence of fuel gas atmosphere. Sealing technology as well as manifold technology is being developed to test stacks. Cell degradation mechanisms related to deleterious reactions at interfaces have been studied and can be minimized and/or avoided by the proper choice of component and stack fabrication parameters.

Before commercial development can occur several important technology goals must be met in the area of cell technology alone. Larger active area cells (eg. 10×10 to 15×15 cm size) must be stacked and tested with reliable operation at power densities of ~ 300 m W/cm². Performance testing must also be conducted using natural gas with direct reformation at controlled utilization levels. Along with the development in hardware, modelling work must be carried out to simulate the stack variables under different operating conditions and identify critical failure areas as well as simulate performance in a commercial power plant.

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