HIGH PERFORMANCE CELL DEVELOPMENT AT CFCL

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ABSTRACT

Improvement in the power density of solid oxide fuel cells (SOFC's) is important to develop cost effective, compact size fuel cell systems with increased efficiencies. After evaluating a number of options involving high conductivity electrolyte materials, and thinner electrolyte structures, CFCL focused on laminated 8YSZ, anode supported cell technology with internal reforming capability and mixed oxygen ion – electron conductivity cathodes. The technology developed by CFCL has achieved high power densities at 750. These technologies will be developed further to lower the material and processing risks for integration of the cell into CFCL's future products.

INTRODUCTION

CFCL has been developing SOFC technologies for improved performance since 1993. From initial work, at 1000 °C, CFCL has now reached the stage in its development program of having generated and evaluated a large number of concepts in materials selection, structure and processes.

A multi layered cathode system based on lanthanum strontium cobalt iron oxide (LSCF) has been developed. The cathode consists of a barrier layer, an active cathode layer and a porous layer for uniform gas diffusion and current collection. CFCL has put significant effort into development of anodes for high power density because of the stringent demands imposed on them by multiple functional requirements, such as high electronic conductivity, ability to reform methane, prevention of carbon formation, stability in anode environment, stability in start-up and shutdown environments, electrochemical oxidation of fuel and a stable support structure in the anode supported cells. These multiple functional requirements of the SOFC anode are only achievable in a multi-layer structure.

This paper provides a general account of CFCL's development efforts in evaluating concepts for high performance SOFC for 750 °C operation and an indication of future direction.

CELL COMPONENT DEVELOPMENT
Cathode

CFCL has investigated a number of cathode concepts aimed towards increasing the reaction zone of the oxygen reduction reaction. Two main approaches have been taken. Pure electronic conductors such as strontium substituted lanthanum manganite (LSM) (1) and strontium substituted praseodymium manganite (PSM) (2) function through the reduction and charge transfer of oxygen at the three phase boundary (tpb) between cathode, electrolyte and air. Their performance has been enhanced through a process including acid etching of surface passivating layers (3) and addition of secondary phases. Composite materials of LSM and yttria stabilised zirconia (YSZ) or scandia stabilised zirconia have been evaluated. Robust processes have been developed and verified for the preparation of, LSM powders, LSM inks and LSM screen printed coatings. Additional investigative work is progressing on evaluating LSM cathodes with extended tpb by increasing the roughness of the electrolyte surface (4).

The second approach is the use of mixed oxygen ion – electron conductors (MIEC) with fast surface exchange rates. Improved performance is expected from the extended reaction zone due to the ability for the material to conduct oxygen ions rapidly through its bulk, and the faster surface exchange kinetics (5). Material compositions investigated include the LSFC (6) lanthanum strontium manganese cobalt oxide LSMC (7) and lanthanum strontium manganese iron oxide LSMF (8). Due to the increased reactivity of these materials with the zirconia electrolyte to form insulating SrZrO$_3$ and/or La$_2$ZrO$_7$ phases (9) a doped ceria layer has been developed as a reaction buffer layer (6). Both porous MIEC layers and combined active MIEC layer – porous MIEC layer cathodes have been developed and shown to have significant improvement in performance at 750 °C compared to LSM based cathodes (figure 1). Cathodes of this type have also been shown to be superior in stability than LSM in the presence of chromia containing alloys (6,10). The development of robust larger scale fabrication capability for this type of cathode is presently underway.

Anode

The SOFC anode has some of the most stringent requirements amongst the fuel cell components. These are: i) good activity for electrochemical oxidation of hydrogen, ii) good electronic conductivity >10$^2$ S/cm at anode operating conditions, iii) good catalytic performance for 100% methane reforming, iv) stability in anode environment, at operation and during heat up and cool down v) compatibility with electrolyte, vi) good adherence/bonding to the electrolyte surface, vii) ease of economical fabrication with minimal processing problems.

There are two approaches to meeting these requirements. The simplest approach is to combine all the functionality of the anode in a single layer supported on a substrate, which may be an electrolyte, or it may be a porous anode substrate. The anode substrate has the additional requirements of mechanical integrity, gas permeability, and thermal expansion matching with the other cell layers. However, it may be difficult to achieve a multi-functional single electrode layer. The other approach is to distribute the different
functions of the anode into separate layers. An example is an anode with an electrochemical functional layer with a reforming and conductive overlayer.

![Initial Performance of Anode supported Cells with different Cathode Concepts.](image)

Temperature = 750 °C
Utilisations < 10 %

Fig. 1, The initial performance of anode supported laminated 8YSZ electrolyte cells with various cathode concepts; PSM (diamonds), LSM (squares), LSFC porous layer (triangles), LSFC active layer – porous layer combination (circles). The cells were 50mmx50mm operated at 750 °C at low utilisation in 3%H2O-H2 fuel.

For the single layer anode and for the electrochemical layer, almost all SOFC groups have accepted Ni/ZrO2 cermet, as the anode material, because nickel is inexpensive, a good electronic conductor and exhibits high catalytic activity for hydrogen oxidation and for steam reforming of methane. Nickel is however prone to carbon formation during methane reforming and to sintering on prolonged operation at high temperatures, particularly at high steam partial pressures that exist at high fuel utilisation. Performance of the Ni/ZrO2 cermet anode is very dependent upon the associated microstructure and the performance-microstructure relationship is very complicated and not well understood.

There are different approaches to manufacturing the Ni/ZrO2 cermet anode. The method used by Westinghouse involves the initial preparation of a Ni skeleton anode followed by an ECVD process, which produces an intergrowth of zirconia within the porous Ni framework. The rate of degradation appears relatively small for the Westinghouse Ni/ZrO2 structure. The morphology of the zirconia intergrowth appears to restrict grain growth of the Ni particles and also provides an effective pathway for oxygen ions from the electrolyte to the adjacent Ni particle. This method appears to give a reproducible microstructure.
Amongst the groups that use NiO and YSZ powders as the starting material for the anode, some seem to prefer fine NiO dispersed within a framework of non-shrinkable larger YSZ in order to achieve nickel percolation for electronic conduction as well as high triple phase boundary (TPB). Another approach is to mix the NiO with both fine and coarse YSZ, where the fine YSZ promotes adhesion to the electrolyte and prevents Ni agglomeration to some extent. Typical values are NiO: 1-2μm, YSZ: 0.2 -15μm (this can be bimodal or uni-modal with a broad distribution). Surface area of NiO is another important factor. Larger NiO, giving low surface area gives low TPB, whereas smaller NiO (large surface area) are prone to agglomeration.

Steele et al (1) reported that particles larger than 3μm retain a core of NiO after reduction. They suggest that the conducting pathway occur around the outside of the larger particles. The pathway may be blocked under fuel cell operating conditions if the voltage falls sufficiently for the electrochemical formation of nickel oxide to occur. It is thought that the performance problem can be overcome in part by controlling the NiO particle size prior to making the ink. Other groups (2, 3) have noted that only YSZ particles contribute to the shrinkage on firing of the anode. These authors have noted that considering YSZ particles sinter to 98% density at 1400°C, spacing around NiO and YSZ particles will not change further during the anode firing process if the cermet powder is coarsened at that temperature before printing on to the electrolyte. If the coarsening temperature is lower, YSZ powders are allowed to shrink further in the firing step and it causes a relatively loose microstructure around the nickel oxide particles, since the dimensions of a sintered electrolyte substrate do not change on firing.

Work at CFCL and by other groups have shown that anode microstructure can be changed by: 1) varying the Ni/YSZ volume ratio, 2) changing the particle size ratio of the starting powders 3) changing the type and level of pore-former and 4) changing the firing temperature.

These considerations have been taken into account in our anode development work. For development of the overlayer, desirable properties of conventional steam reforming catalysts are combined with high electronic conductivity for the current path along with the requirement of reducing electrochemical losses in the anode.

The internal reforming function of the anode and the reduction of overpotential losses due to concentration polarization require sufficient permeability in the anode structure. This was achieved by using pore-formers of appropriate particle size and at some optimum level determined through development work (4). Our current electrochemical layer is between 5 and 10 microns thick and has a much finer porosity than the reforming and conductive layer. For development of the internal reforming function of the anode various additives were added to the anode composition. These additives are based on materials, which have the potential to reduce carbon formation during reforming by enhancing the gasification of carbonaceous deposits on active sites of the anode. The results of an internal reforming test on a standard anode supported cell are shown in Figure 2. During open-circuit operation of this anode with a CH4-H2O mixture at a...
steam/carbon ratio of 2.0, the methane reforming activity of the anode dropped from 98% to 88% in 20 hours. Such a loss is generally attributed to carbon formation on the active nickel sites of the anode, as under open-circuit conditions the cell has no other degradation mechanisms in action. Increasing the steam/carbon ratio to 2.5 reduced the rate of degradation of the reforming activity as the methane conversion dropped further from 88% to 83% in 25 hours with indications of further slowing down of the rate of decline.

Two further test results are shown in Figures 3 and 4 where the anode substrate layer was used as a composite substrate-reforming-conductive layer by the addition of internal reforming additives 1 and 2 respectively in their formulations. It is clear from Figure 3 that the rate of decline of methane reforming activity was arrested by the addition of additive No.1. Although there was a substantial decline in the level of methane conversion from 87% to 73% in the first 20 hours, the conversion was constant during the next 20 hours. The incorporation of this additive seems to have an effect on the initial conversion level, which is lower for this anode compared to the standard unmodified anode. The area specific flow rate of the fuel in these experiments corresponds to very low fuel utilisation levels. Therefore, at flow rates representing higher fuel utilisation, complete conversion of methane is expected to be achieved within the anode. This will have the benefit of distributing the reforming activity of the anode over a larger area of the anode instead of achieving very high conversion in a small area near the inlet. The best result was achieved with additive No.2. Figure 4 shows no decline in methane conversion activity during a 50-hour test. Initially the conversion increased slightly over a 10-hour period after which it was stable at around 75%. With this additive, the rate of decline in methane conversion activity is completely arrested and the reforming rate is somewhat reduced to distribute the reforming as mentioned above.
We have developed an anode supported internal reforming SOFC cell, where the reforming activity is distributed over the active area of the anode to gain the benefits of cell cooling during the endothermic steam reforming of methane on the anode surface by using a suitable reforming additive. This additive also served to prevent degradation of the anode due to loss of reforming activity by carbon formation.

**Electrolyte**
CFCL has investigated the conductivity of a number of oxygen ion conductors (15) and has taken two approaches in the development of fuel cells. The higher conductivity of 9mol%Sc₂O₃-ZrO₂ compared to 3mol%Y₂O₃-ZrO₂ (16) has been investigated as a self supported cell. Improved performance was observed at 750 °C due to a significant decrease in ohmic resistance loss. The second approach has been to fabricate thin electrolyte layers of 8mol%Y₂O₃-ZrO₂ (8YSZ) supported on a porous anode. These types of cells have much lower ohmic resistances and improved power densities (Figure 5). Two process methods have been developed to fabricate thin layers of 8YSZ. RF and DC magnetron sputtering (17) and tape casting (18) have been used to make electrolytes with thickness of the order of 5 and 20 μm respectively. CFCL has focussed on the latter approach and laminating tape cast layers of electrolyte, anode and anode support and cofiring them (18). CFCL presently is developing 10mol%Y₂O₃-ZrO₂ as the electrolyte material due to its superior properties in moist atmosphere during heat up and cool down and its phase and conductivity stability during operation (19).

Fig. 5, The initial power density curves for two electrolyte concepts. Tape cast 20 micron 8YSZ anode supported laminate cell (circles) and 9ScZr self supported cell (squares). The cathode was the same in both cases, the cells were 50mmx50mm and the tests were operated at 750 °C at low utilisation in 3%H₂O-H₂ fuel.

STACK TEST EVALUATION

Contact to Electrodes

Good electrical connection on both anode and cathode side is very important to achieve high power density and long term stability in stacks. A screen-printed Ni contact layer on the anode with Ni expanded mesh pressure layer showed the best result. A pressure layer has been developed which consists of a corrugated Ni expanded mesh sandwiched
between two flat Ni expanded mesh. The Ni expanded meshes were spot welded to the corrugated mesh to avoid any lateral movement in the stack. Post mortem analysis reveals that this anode side current collector was not only stable over a long period of stack operation, but formed chemical bonds between both the anode/Ni mesh interface and the interconnect contact layer/Ni mesh interface. Initial studies on this anode side current collector revealed that the chemical bond was stable after a thermal cycle. Further work is being carried out to investigate the stability and rigidity of this pressure layer under multiple thermal cycling.

Among various cathode side current collectors investigated a screen-printed Ag contact layer on cathode with Ag expanded mesh showed the lowest cell ohmic resistance. During stack postmortem analysis, it was observed that the bond between LSM cathode and the screen-printed Ag contact layer was not as strong compared to the anode side bond between the Ni expanded mesh and anode. This was mainly due to the significant CTE mismatch between the Ag and LSM cathode material. Although this particular cathode side current collector showed a good contact and thus resulted in the lowest cell ohmic resistance its integrity during multiple thermal cycling is still doubtful. An investigation is being carried out to develop a cermet material, with better CTE match with cathode material, which can be screen printed onto the cathode as a current collector contact layer. Further cell and stack testing are being carried out to verify the effectiveness of these contact layers after several thermal cycles.

1 kW stack demonstration

A 22 layer, 2x2 array stack was assembled and tested in August 1999 to demonstrate 1 kW electrical power output in an internally manifold co-flow configuration. The cells were laminated 90x110mm anode supported cells with LSM cathodes. The stack was constructed from components that were fabricated fully at Ceramic Fuel Cells Ltd. The stacking technology used in this 1 kW stack demonstration was verified for power output and stability in several single cell and five-cell stack configuration prior to the 1kWe stack demonstration. Figure 6 & 7 shows the performance of the stack at 750°C over the period of 650 hours. All 22 layers sealed well as evident from the open circuit voltage of 1.11V, which is close to the theoretical open circuit voltage for 2%H2O-H2 versus air. Under load the layer performance was stable for initial 250 hours of operation and then a gradual drop in performance was observed. Stability and performance of individual layers was to some extent fuel and air flow dependent. For example lowering of the fuel flow during the initial 250 hours of operation narrowed the performance spread of the layers. This stacking arrangement is characterised by low pressure drops across the cells resulting in uneven flow distributions between layers due to dynamic pressure variations in the manifold.

SUMMARY

CFCL has undergone extensive research and development into materials, processes, fuel cell design and structures aimed towards high performance at 750 °C. These technologies
Figure 6. Power output of the 22 layer, 2x2 array stack

Figure 7. Performance of the 22 layer, 2x2 array stack

have been demonstrated at different levels up to 1 kWe stack. A large number of technologies have been evaluated and a significant number already evaluated and some proven to achieve the requirements of high power density at 750 °C. Improved understanding of customer requirements is leading CFCL towards developing some of the proven technologies further. The future development work is aimed towards lowering the materials and processing risks for potential integration into CFCL’s future products. The focus of the development effort is on decreasing the materials risk of anode supported thin electrolyte structures through increased fundamental understanding of material, structure, mechanical and electrical performance relationships.
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