ABSTRACT

Ceramic Fuel Cells Limited has developed an all ceramic stack that has an electrolyte assembly consisting of an electrolyte support of 10 mol% $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ mechanically mixed with 15 wt% alumina to increase toughness, an LSM cathode, a Ni cermet dual layer anode, and gas distribution layers of LSM (air side) and Ni cermet (anode side). During the development phase, the power output of the electrolyte assembly was offset to achieve a structurally sound thermal cyclable stack. The electrolyte assembly has been demonstrated to thermal cycle at least 13 times in a stack environment. This paper describes the optimization development of Ceramic Fuel Cells electrolyte assembly aimed to provide more than 5 W per layer and about 300 We/L in stacks of 1-1.5 kWe size whilst retaining greater than 50% electrical efficiency and thermal cycling capability.

INTRODUCTION

Initially the development of CFCL’s electrolyte assembly focused on the mechanical integrity of the all-ceramic stack and demonstration of thermal cycling as a key product requirement (1-5). The design power density target for CFCL’s all-ceramic stack has been reported as 100 mW/cm$^2$ and 0.3 kWe/L (1,2) that is equivalent to 5.4 W per layer in 10% pre-reformed NG at greater than 65% fuel utilisation. In taller stacks, the average power per layer is lower due to the increase in axial and lateral thermal gradients. The electrolyte assembly has been demonstrated to operate on NG with complete internal reforming of methane with fuel utilization greater than 60% (6) and electrical efficiency greater than 50% with these factors dominated by stacking effects rather than the electrolyte assembly technology itself.

When the structural integrity of the stack to thermal cycling was successfully demonstrated, the development focused towards electrolyte assemblies that achieve higher power output per layer in stacks that produce 1 kWe to 1.5 kWe whilst retaining the structural integrity on thermal cycling, high internal reforming of methane and high efficiencies. Higher power outputs result in an increase in thermal gradients during operation and the electrolyte assembly and stack design have been modified to retain the level of mechanical robustness when operated at the higher power outputs. Target attributes are given in Table 1.
Table 1. Target attributes for the electrolyte assembly to increase power per layer whilst retaining mechanical integrity.

| Attributes                              | Target                                                                 |
|-----------------------------------------|------------------------------------------------------------------------|
| Thermal cycles                          | Greater than 10.                                                       |
| Power per layer                         | Greater than 5 W per layer in stacks that produce 1 kWe to 1.5 kWe     |
| Maximum Fuel Utilisation of the electrolyte assembly | >80%                                                                  |
| Internal reforming of methane           | 100%                                                                  |

RESULTS AND DISCUSSION

Detailed Analysis of Losses

A detailed analysis of the voltage losses in the stack was performed. The predominant contributor to power loss within the stack was the electrolyte assembly itself, with less than 0.01 Ω.cm² across each separator assembly and auxiliary end plates in the stack. Estimates of the resistive losses of each component are shown in Figure 1. The “base level” is the lowest $R_{\text{cell}}$ practically achievable for this electrolyte supported design and is equivalent to 8.5 W per layer and 500 W/L volume power density. CFCL’s design target was to achieve greater than 5 W per layer operating within a stack of 1.2-1.5 kWe and inclusive of the expected scale up factor (0.7-0.85) due to the axial thermal gradient.

Figure 1. Analysis of the losses for individual contributions in the cell.

The analysis clearly indicates where most gains were possible:
- Increased ionic conductivity due to lowering alumina content;
- Decreased interfacial resistance at electrodes/electrolyte interfaces by lowering surface alumina concentrations
- Improved cathode (a lower activation energy of the cathode would also help with axial temperature gradient losses).

**Improvements to Electrolyte Plates**

There are significant power gains to be made by lowering alumina concentrations in the electrolyte plate. The alumina has been included to improve the mechanical properties of the 10YSZ to achieve high yields of CFCL's monolithic Level 1 unit and robustness during thermal cycling. The 15wt% mechanically mixed alumina decreases the ionic conductivity of the electrolyte plate from 0.055 S/cm to 0.033 S/cm at 850°C. The alumina present on the top surface of the plate (Figure 2A) reacts with the NiO to form Ni$_2$Al$_2$O$_4$ spinel phase that acts to increase anode overpotentials. Microanalysis performed at the University of Queensland shows the penetration of the NiAl$_2$O$_4$ spinel phase grows about 3 μm into the grain structure of the electrolyte (Figure 2B and 2C).

![Figure 2. (A) Top surface SEM of the electrolyte with alumina showing (dark particles). (B) Cross section elemental mapping across the anode-electrolyte interface. (C) TEM microanalysis of the anode-electrolyte interface.](image)

On the cathode side the alumina blocks the active area and the alumina reacts with LSM to form a rich manganese oxide and alumina containing phase (Figure 3A). The EDAX trace (Figure 3B) is from the dark contrasted particle that has been arrowed in Figure 3A.

![Figure 3. (A) Cross section SEM of the cathode-electrolyte interface. (B) The associated EDAX spot analysis of the highlighted dark contrast particle.](image)
The development program has focused on (a) reduced alumina levels in the electrolyte powder whilst retaining the mechanical toughness of the existing plate (b) sourcing purer alumina and (c) applying thin coatings of pure 10YSZ to function as a pure ionic electrolyte layer that blocks the impact of alumina at the electrolyte-electrode interface. Early versions of 10YSZ coating on this surface (Figure 4A) were prepared through typical ceramic methods and coated and fired on the sintered electrolyte plate. The coatings were 3-5 μm and left a residual porosity allowing vapor transport of nickel oxide to migrate and react with Al₂O₃ during the anode sintering. Advances have been made to the methodology of fabricating this coating that creates a fully dense <3 μm thick 10YSZ coating that covers the alumina and there is no formation of the nickel alumina spinel during anode firing (Figure 4B). This coating is used on both sides of the electrolyte plate.

![Figure 4. (A) Top surface SEM of early version 10YSZ coatings on the 10YSZ-alumina electrolyte. (B) Top surface SEM of recently developed 10YSZ coatings. (C) Cross section SEM of recently developed 10YSZ coatings.](image)

**Cathode Advances**

CFCL has kept its (La₀.₇Sr₀.₃)ₓMnO₃₋ₓ (LSM) cathode for a number of years that provided a stable production base to develop other components. This cathode is modified with a rare earth oxide after the LSM firing step. From the literature there are well known performance gains to be made from improved composite based LSM cathodes and LSFC based cathodes. Developments in CFCL from 1994-2000 led to a new cathode based on a sub-micron 10mol%Gd₂O₃-CeO₂ (GDC) layer and a porous (La₀.₈Sr₀.₂)(Fe₀.₈Co₀.₂)O₂ₓ cathode capable of low overpotentials at temperatures as low as 750 °C (7). The fabrication method during that time was not suitable for larger production outputs and relied on sputtering thin layers. The key development in CFCL recently has been to establish a manufacturing method capable of volume outputs of a thin GDC layer with an extended high surface area structure that extends the contact with the porous LSFC cathode. The performance improvements are typical of the previous LSFC cathodes. The added benefit of LSFC cathode is its lower activation energy that will increase the stack power scaling factor from the higher performance achievable from cells located in cooler regions of the stack.

**Anode Advances**

The dual layer anode performed adequately given the presence of Ni₂Al₂O₄ spinel. It has been determined that high shrinkage of the anode coating during sintering of the anode layers increased the stress at the anode — electrolyte interface and decreased the mechanical strength of the electrolyte assembly by a factor of three compared to the
The uncoated plate as measured in ring-on-ring tests. The reduced mechanical capability of the electrolyte assembly limits operational stresses caused by temperature gradients and thus can limit power outputs to remain below safe stress margins. The anode dual layer structure is therefore being re-developed to sustain the power outputs with low shrinkage anode coatings.

**Gas Distribution Layer Advances**

The gas distribution layer (GDL) pattern has been optimized to achieve optimal gas diffusion under the pillar structure and minimal voltage loss from lateral conduction path in the electrodes. The height of the GDL’s dominate the pressure drop in the stack and the air side GDL’s have been increased in height from 380 μm to 500 μm to reduce the parasitic demand from the air blower that enables a smaller stack for the target system output. The taller cathode GDL’s are fabricated by stencil printing from an optimized bimodal LSM particle morphology. A reduction in process steps has been achieved with co-firing of the airside GDL with the cathode. The stack fuel utilization is dictated by the underlying capability of the electrolyte assembly and the amount of fuel supplied to each layer in the stack. This is governed to a large degree by the manufacturing tolerances on the GDL pillars in conjunction with seal height and the compliancy of the separator assembly. The fuel utilisations in 28 layer stacks have achieved greater than the targeted 65% (Figure 6) with stack performance as measured by its average Rcell value remaining constant to about 80% utilization of NG.

![Figure 6. Plot of the average layer Rcell value as a function of Fuel (NG) utilization for a 28 layer stack.](image)

**Advances in Plate Design**

The plate design was determined through stress and thermal-mechanical modeling to limit power outputs due to thermal stress concentrations in vulnerable zones on the electrolyte plate. The plate has been redesigned through the output of these models to withstand higher thermal gradients generated from the higher power outputs achieved. The primary redesign has been the location, size and number of air and fuel ports. Table 2 shows modeling output data for operating conditions of: coflow, insulated stack (not...
furnace operated), 1000 W, 0.75 SLM air per layer, 850 to 860 maximum stack
temperature. The critical flaw size is calculated using $K_1C = 2.25 \text{ MNm}^{-3/2}$ for 10Y15A.

Table 2. Modelled data output for stress levels in optimized plate design.

|                | Maximum Tension (MPa) | Maximum Comp (MPa) | Critical flaw (micron) |
|----------------|-----------------------|--------------------|------------------------|
| Original Design| 80                    | 76                 | 200                    |
| Optimised Design| 44                   | 41                 | 663                    |

CONCLUSIONS

The electrolyte assembly has been developed to meet the product needs of CFCL’s stacks for its micro-CHP product. Figure 7 shows the output at 840°C of CFCL’s modular ceramic monolith of 28 layers with 150 W (5.4 W/layer) at 0.695 V per layer average and 56% fuel utilization and electrical efficiency of 37.4%. The stack was capable of higher efficiency. This technology is being implemented in production for 1-1.5 kWe stack and system demonstration. Further optimization is continuing aimed at further reduction in stress levels and reliability.

Figure 7. Performance plot for a 28 layer stack. The average $R_{cell}$ value is given on the right hand axis with a x10 multiplier. The average $R_{cell}$ at 0.7 V per layer is 1.5 $\Omega\cdot\text{cm}^2$.

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