MATERIAL DESIGN AND PROCESSING OF CFCL’S CELL ASSEMBLY

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ABSTRACT

CFCL has designed and fabricated cell assembly for its all-ceramic planar stack technology. The cell assembly consists of anode, electrolyte, cathode and gas distribution layers for anode and cathode. After evaluating a number of options CFCL focused on 10YSZ-alumina composite for its electrolyte. Anode, cathode and gas distribution layer, materials have been designed, so that the whole cell assembly is electrochemically and mechanically stable during all SOFC operating modes. The cell assembly has been tested in single and multi layer configurations in hydrogen and natural gas fuel environments. Performance tests continue to show promising results. Further development works are continuing to improve the performance and stability of the cell assembly.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are being developed as a clean and efficient power generating system from a variety of fuels. For efficient and low cost operation, a SOFC system must be designed to have high electrochemical performance. Planar SOFC design has potential advantages over other types of SOFC designs. The advantages include high power density, high efficiency and reduced manufacturing costs. After conducting extensive research and development in planar SOFC since 1992, through experiencing the difficulties associated with the manufacturing and testing of various types of stacks, we decided to focus our attention to a modular all-ceramic planar SOFC design. Whether it is used as a stationary power generating system or auxiliary power unit, thermal cycling of the planar SOFC is a mandatory requirement and without thermal cycling it is impossible to operate the planar SOFC system efficiently. CFCL’s thermally cyclable, high efficiency and compact planar SOFC design is described elsewhere (1). The fundamental component in the CFCL’s all-ceramic stack design is the integrated PEN structure (Positive electrode, Electrolyte, Negative electrode), known as the cell assembly. This paper describes the materials design and their processing for cell assembly of CFCL’s all-ceramic stack.

CELL ASSEMBLY

Cell assembly is the integrated PEN structure, which is fabricated by ceramic processing routes such as tape casting, screen printing or stencil printing. Cell assembly consists of...
fuel electrode, electrolyte, air electrode, fuel gas distribution layer (anode GDL) and air
distribution layer (cathode GDL). The electrochemical and mechanical properties of the
individual layers in the cell assembly will depend on their microstructures and hence on
the way in which they are fabricated. Since at least five individual layers of different
ceramic materials are joined together in the cell assembly, the overall reliability of the
cell assembly will also depend on the interfaces between these layers. The cell assembly
component’s material design, processing and their fabrication are given below.

Electrolyte

CFCL has investigated various materials for its electrolyte. Initially, 3YSZ tetragonal
zirconia was chosen for its mechanical properties, 8YSZ for anode supported cells, but
recent development was based around fully cubic zirconia. Initially, pure 10YSZ was
trialed. Although the electrochemical properties of 10YSZ were satisfactory, the
mechanical integrity was difficult to retain. The mechanical properties of 10YSZ can be
significantly improved by the addition of alumina (2). Alumina also has the potential to
clean grain boundaries by removing vitreous phases such as silica (3). Furthermore,
10YSZ is preferred to 8YSZ because the latter still falls in the two phase region
(tetragonal + cubic) at CFCL’s operating temperatures (850°C ± 20°C) and can hence
undergo a phase transformation from tetragonal to monoclinic in the presence of moisture
(4). It also has been reported that the ionic conductivity of 8YSZ can degrade with time
(5).

All zirconia materials were commercially sourced from MEL Chemicals (MELox 10Y)
and Tosoh (TZ10YS), the alumina is an Alcoa product (A1000SG). The alumina is
initially attrition milled to a required particle size. Zirconia is subsequently added and the
resulting slip is mechanically mixed before being spray dried. Obtained powders and pure
zirconia are processed by slip batching and tape casting. The 170 µm thick green tape is
subsequently cut and pressed to shape, and sintering is carried out in a single fire. The maximum sintering temperature varies from 1450°C to 1600°C, depending on the used powder. The final product is a 150 μm thin circular sheet with appropriate port holes (see Figure 1).

Table 1 shows the properties of various zirconia based electrolyte materials investigated at CFCL. From comparing zirconia materials with various amounts of yttria, a trade off between mechanical and electrochemical properties appears obvious. If the MOR and the fracture toughness are high, the ionic conductivity is poor (tetragonal zirconia), and vice-versa (cubic zirconia). Once a material has been selected (10YSZ cubic zirconia), some properties can be improved by doping it with alumina. The higher the alumina amount, the better the mechanical properties. The limit of 15 wt% was chosen for with higher alumina levels, the material starts to display more alumina like behaviour. SEM micrographs in Figure 2 show the evolution of the grain sizes with increasing alumina addition; alumina pins the grains during sintering, limiting the growth. The location of the alumina particles is nonetheless critical: the pinning is only achieved if the alumina is located at the triple points (connection points of the grain boundaries). If the alumina is intra-granular, no such effect is possible. The small grain size is the main factor in enhancing the mechanical properties. It however also explains the reduction in ionic conductivity: the smaller the grains, the higher the contribution of the grain boundary resistivity. If these grain boundaries contain significant amounts of high resistivity alumina, the conductivity drops.

| Material          | MOR (MPa) | K_{1C} (MPa.m^{1/2}) | $\sigma_\parallel$ (S/cm) |
|-------------------|-----------|-----------------------|---------------------------|
| 3YSZ              | 980 +/- 20| 8 ±0.2                | 0.020                     |
| 8YSZ              | 290 +/- 25| 3 ±0.2                | 0.056                     |
| 10YSZ             | 167 +/- 25| 1.4 to 1.5 ± 0.2      | 0.055                     |
| 10YSZ+5wt% Al$_2$O$_3$ | 200 +/- 25| 1.7 ±0.2            | 0.048                     |
| 10YSZ+15wt% Al$_2$O$_3$ | 258 +/- 35| 2.7 ±0.3            | 0.032                     |

The ionic conductivity, and thus the overall performance of cells prepared with such electrolytes, needs improvement if a commercially viable product is to be manufactured. Present investigations around co-precipitated powders should lead in the right direction. If the alumina is chemically introduced in the powder at the powder processing stage, less of it is required to significantly improve mechanical properties (as it is finer and more evenly distributed across the material). Amounts as low as 1 or 2 wt% alumina could suffice which would considerably reduce the loss in ionic conductivity. Results on this study are to be published at a later stage.
Almost all SOFC groups have accepted Ni/ZrO$_2$ 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/ZrO$_2$ cermet anode is very dependent upon the associated microstructure and the performance-microstructure relationship is not well understood.

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.

A number of researchers (6-9) have proposed that the main contributor to anode degradation and anode failure is the sintering of Ni resulting in a loss of active reaction sites. Therefore, it would be desirable to stem the growth of Ni by sintering through control of the microstructure. An important variable that has effect on sintering is the Ni content. While high nickel contents may provide high electrical conductivity, it does not...
necessarily result in an extension of the TPB zone, as the number of TPB sites is not directly proportional to Ni content. Moreover, higher nickel contents are likely to result in increased sintering and increase the thermal expansion mismatch between the Ni-YSZ electrode and the YSZ electrolyte. It is clear that there exists an optimum level of Ni content for better overall performance of the anode, which may well be related to other factors like particle size distribution of NiO and YSZ, their ratios, and pre-treatment conditions for electrode manufacture. Lee et al (10) found that similar-sized starting powders of NiO and YSZ and a nearly 1:1 volume ratio of Ni and YSZ provide the maximum number of reaction sites with a well-developed channel structure and also a high stability against sintering of Ni. Lower levels of Ni contents e.g. 25 and 35 vol% gave insufficient TPB sites and higher loading of 55 and 65% Ni resulted in increased Ni sintering. CFCL anodes have 45 vol% Ni to ensure sufficient TPB sites while reducing the extent of anode degradation due to nickel sintering.

The effect of the reduction process variables of temperature, flow rate and gas composition on the microstructure and performance of Nickel/Zirconia based solid oxide fuel cell anodes is not well understood. Each fuel cell developer has its own method of anode reduction that is probably strictly applicable to the anode developed or used by them. There is an apprehension that unless the reduction process is followed at the customer’s site, the performance of the anode may be significantly inferior to that verified at the manufacturer’s site. To address these concerns there is need for a deeper understanding of the anode reduction process. While it is unquestionable that such understanding can only be acquired through a systematic study of the effect of reduction parameters on the microstructure and electrochemical performance of the anode, a good starting point is a review of relevant literature for reduction of nickel oxide and nickel oxide based catalysts, particularly of the types used for hydrocarbon reforming which is relevant to the internal reforming aspects of the SOFC anodes.

Since, prior art from the reforming catalyst industry is applicable to a large extent to the nickel-based SOFC anodes, some degree of knowledge already exists with regard to the influence of the reduction parameters. For example, Rostrup-Nielsen (11) has shown that the reduction procedure may influence the size of the resulting nickel particles in a nickel catalyst. The highest nickel area is attained when using dry hydrogen in both heat-up and reduction. Presence of steam in either step has a marked effect. Steam oxidizes the smallest nuclei of nickel or prevents their formation. Consequently, the number of nuclei is decreased. This would result in a smaller number of nickel crystals and hence a smaller area of the catalyst. Relatively large steam production can result from the abrupt addition of hydrogen (e.g. when heated up in nitrogen and then switched to hydrogen at high temperature) that would lead to lower surface area. These effects apply to a Ni-based anode as well.

Small nickel particles with high surface area-to-volume ratio will have a strong thermodynamic driving force to decrease free energy i.e. to minimize surface area. Since the sintering of metals occurs at temperatures exceeding the Tamman temperature, which is 691°C for Ni, it is expected that there will be a considerable driving force for coarsening of nickel particles at current SOFC operating temperatures, particularly for the small nickel particles. As Ni particles coalesce, the reaction points (triple phase boundary) and current passage diminish, since with increasing particle size the number of contact points is reduced with a direct influence on conductivity. On the other hand, low
surface area Ni powders of larger particle sizes will have lesser tendency to agglomerate providing better Ni coverage and contact and resulting in higher conductivity.

While the understanding of performance-microstructure relationship of Ni-YSZ anodes has increased greatly in the last decade, there are still some gaps in the knowledge. The development of stable optimized microstructure therefore remains a challenge. Our own work has shown that the initial microstructure is dependent on reduction parameters namely, temperature, humidity level, flow rate, presence of diluent and presence of additives/promoters in the anode catalyst composition. There are several issues, which contribute to the difficulty of attaining a stable microstructure. Firstly, nickel will invariably undergo some degree of sintering during and after the reduction process. As expected, the primary variable for reduction is temperature.

In addition to its positive effect on the reduction kinetics, temperature has a strong influence on the physical characteristics of the resulting Ni structure. Sintering depends on many factors – initial nickel oxide distribution, porosity of the reduced structure, pore size distribution, temperature and atmosphere (in particular, partial pressure of steam). This is even further complicated by the possibility of repeated reduction/oxidation cycles with thermal cycling. The anode should be maintained in its reduced form during fuel cell operation. Reoxidation of the anode from seal failure either during operation or during thermal cycling is unacceptable. Reoxidation damages the microstructure of the anode, as there is a net increase in volume associated with the reoxidation of the nickel (12). Further work is required for a better understanding of the redistribution of nickel during reduction and during fuel-cell operation. It would be useful to develop an understanding of the relationship between nickel coarsening with initial particle size distribution, pore size distribution, reduction parameters and fuel-cell operating parameters. Such knowledge will assist the development of anodes with minimum degradation during operation, which is one of the greater challenges of SOFC technology.

**Cathode**

CFCL has investigated a number of cathode concepts aimed towards increasing the reaction zone of the oxygen reduction reaction. The cathode that has been scaled up to volume production levels is the strontium substituted lanthanum manganite (LSM) enhanced through a process including acid etching of surface passivating layers (13) and addition of a samaria-ceria phase. Robust processes for LSM powders, inks and screen-printed coatings have been developed and verified for the preparation of the cathode. The understanding of the dependency of critical process parameters with cathode performance has led to a robust manufacturing process. The process gives an LSM structure and 10YSZ-LSM interface structure that is reproducibly formed during production outputs of 1000 parts per week that meet key performance aspects.

CFCL's LSM based cathode technology is aimed at its market entry product operating around 850°C. CFCL has an on-going development program for improved LSM-GDC composites and mixed conducting materials based on LSFC for lower temperature operation. Significant performance gains have been demonstrated and the next objective is to establish a robust manufacturing process for these cathodes.

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Gas Distribution Layer

The purpose of the Gas Distribution Layer (GDL) is threefold. They are: distributing the gas across the electrode uniformly, carrying the electronic current from the electrode to the current collecting plate and bearing the load of the stack.

The design of the GDL has been based on the CFD modeling work on gas flow and consists of a set of pillars fabricated on top of the electrode. The key factors that have been considered during the design are uniformity of gas distribution and ohmic loss for current collection. The pillar pattern on the anode side and the cathode side has been made identical to avoid any stresses on the electrolyte, during the application of mechanical load on the cell assembly.

GDL on the anode has been fabricated with Ni/YSZ/ CeO₂ cermet and applied on to the already fired electrode, with stencil printing process. CFCL has developed a binder system to make ink out of Ni/YSZ/CeO₂ cermet, which is suitable for stencil printing. The dried GDL was fired in the temperature range of 1250-1350°C to sinter on to the anode surface. The composition of the anode GDL cermet was chosen to have sufficient electrical conductivity and strength. The size of the YSZ particles was chosen in a manner to minimize the shrinkage during the sintering process. The particle size ratio of NiO:YSZ in the GDL cermet is ~1:5. Larger YSZ particles contribute to a stronger skeleton for GDL and at the same time reduce the shrinkage during the sintering process & subsequent operation of the fuel cell under fuel environment. The work is in progress in CFCL to co-fire both anode and anode GDL.

Cathode GDL was developed with same materials as with CFCL cathode (LSM). As in the case of anode GDL, the particle size of LSM has been controlled to give optimum shrinkage for the cathode GDL. Cathode and the cathode GDL are fired at the same temperature to give enough adhesion between the cathode and GDL, and to get high enough strength for mechanical load bearing.

Proper selection of particle size distribution, binder systems and firing profiles are very important in the fabrication of GDL. At present, CFCL is in progress in further refining the design and process of fabrication.

PERFORMANCE OF CELL ASSEMBLY

The performance of cell assembly has been evaluated in single and multi layer stacks. As described elsewhere (14), IOYSZ-I5Al₂O₃ separator plates with feed through electrical connections have been used in the stack assembly. Screen-printed Ni and Ag containing layers have been used as current collectors for anode and cathode sides respectively. The cell assembly has been assembled onto an alumina housing and tested in hydrogen and natural gas. Figure 3 shows V-I characteristics of a cell assembly tested in desulphurised pre-reformed natural gas at steam to carbon ratio of 2.25. In-situ GCI tests revealed that the ASR for cell assembly was 0.74 Ohm cm². A five-layer stack was assembled using the same stacking technology as the single layer stack above and tested in hydrogen and natural gas. Figure 4 shows the performance of the stack at 850°C. The stack sealed well and all 5 layers reached the theoretical OCV. Under load, except layer 4, rest has shown...
similar performance. Stability and performance of individual layers were, to some extent air and fuel flow dependent. Uneven flow distributions between layers would have caused this flow rate dependent behavior of the stack.

![diagram](image)

**Figure 3.** V-I characteristics of single cell assembly.

![diagram](image)

**Figure 4.** Performance of a 5 layer stack.
CONCLUSIONS

CFCL has conducted extensive research and development into materials, processes, cell assembly design and structures aimed to achieve a high performance, thermal cyclable, all ceramic stacking technology. Cell assembly has been designed and fabricated for CFCL’s all ceramic planar stack development. Stacks up to 28 cell assemblies have been assembled onto alumina housing and tested in hydrogen and natural gas. The future development work is aimed towards improving the cell assembly performance and lowering the materials and processing risks for integration into CFCL’s products.

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