COMPOSITE SOFC DESIGNS FOR SMALL SCALE COGENERATION

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ABSTRACT

The main problem of SOFC development now is making high quality ceramic components, sub-assemblies and stacks by economic methods. Demonstrations by Westinghouse and others have shown that the zirconia electrolyte, nickel cermet, perovskite cathode and lanthanum chromite interconnect materials have all performed satisfactorily in tests up to 50,000 hours. But, the cost of manufacturing cells and stacks in current designs is too great to compete in the present small-scale cogeneration market, based on reciprocating engines. This paper shows that new composite designs can now be envisaged with lower costs than existing devices. In particular, composite planar and tubular components are described with enhanced ceramic forming and assembly potential.

1. INTRODUCTION

A Solid Oxide Fuel Cell (SOFC) stack may be viewed as a composite ceramic, akin to a piezoelectric actuator, a multi-layer electronic circuit, or a honeycomb automobile catalyst. This paper suggests that SOFC stacks may be built most economically using composite ceramic methods.

The stacks considered here comprise five materials: the electrolyte of yttria stabilised zirconia; the anode of nickel/zirconia cermet; the cathode of strontium doped lanthanum manganite, the interconnect of calcium doped lanthanum chromite and the support or separator structural material. These five materials must be assembled economically during the manufacturing process, to produce a stack whose final performance depends on a range of design parameters, such as electrolyte thickness, electrode path length, etc. This performance is geared to the final application; in this case, small-scale cogeneration, in which natural gas powers a 5 to 30 kWe unit, with waste heat driving a boiler or chiller. For the UK, this application appears to offer the clearest target in the near term (1-3). However, only a few hundred $/kWe are available for production of stacks in these devices, so it is necessary to pay close attention to the design and manufacturing of the ceramic pieces.
The main problem of SOFCs has been creating designs which give good performance, while allowing economic use of materials together with cost effective manufacturing. Existing materials appear to be adequate on technical and cost grounds, so there is little incentive to search for new electrolytes or interconnects. The overwhelming questions are how to make larger ceramic foils of the desired thickness without leaks or cracks, and how to assemble the large number of cells effectively to obtain the desired power output.

The purpose of this paper is to show progress towards these goals. Existing materials are selected. Powder processing methods are adopted for economy. Improving the powder disagglomeration is shown to give enhanced processability and properties of the ceramic foils. Larger foils have been demonstrated. The assembly problem has been addressed by co-processing electrolyte and interconnect together to form composite structures with many cells on a single ceramic sheet. These developments are put in the context of existing designs. First sequential designs are considered. Then existing composite designs are discussed. Finally new composite designs are proposed.

2. SEQUENTIAL DESIGNS

Sequential designs are those in which the components are added together one by one to build up the final structure.

For example, a single cell may be constructed by taking a porous support plate, laying down a layer of lanthanum manganite, firing it, depositing a layer of electrolyte, firing, laying on nickel cermet and firing again (Figure 1a). These single cells have been shown to give satisfactory performance up to 50,000 hours in several laboratories (4-6). Such cells are then laid together and interconnected to provide the final stack, typically series connected as in Figure 1b.
In the earliest demonstrations of SOFC stacks, the functions of electrolyte and support were combined. Yttria stabilised zirconia tubes were pressed from powder and machined to around 0.5 mm wall thickness, to give a sound mechanical structure. However, the ionic resistance of such thick tubes was prohibitive. Electrode layers were plasma sprayed inside and out. Then the tubes were stacked end to end (Figure 2), glued together with a layer of interconnect to give the series connection schematically shown in Figure 1.

![Diagram of SOFC stack](image)

Figure 2 ABB (left) and Westinghouse tubular designs

Unfortunately, in this arrangement the current flowed largely in the plane of the electrodes, leading to a high electrode resistance if the cells were more than 20 mm long. Each cell consequently delivered only 1 W which meant that several thousands of such pieces had to be put together to build a 10 kWe generator, giving an expensive assembly operation. Clearly, larger cells were needed to ease the assembly problem, and thinner zirconia was required to drop the cell resistance.

These problems were solved in part by Westinghouse, who made the cells much larger by laying the interconnect along the tube, rather than across it (Figure 2). This design allowed cells up to one metre in length to be manufactured, giving about 50 W from each cell, and easing the assembly of stacks. Better and thinner zirconia electrolyte was made by a vapour deposition route, allowing low ionic resistance. Against these benefits were several drawbacks: the necessity for a thick support tube to facilitate vapour deposition, the expense of the deposition process and the substantial in-plane resistance around the large diameter air electrode. Thick lanthanum manganite layers were needed to lower this resistance, leading to high material costs.

Since the demonstration of the Westinghouse design, several novel ideas have been introduced. Westinghouse began to use lanthanum manganite tubes as both cathode and support tube. Plasma spraying of the layers onto the support tube was demonstrated by Mitsubishi Heavy Industries (7). Planar designs have been developed. ABB sought to make square section support tubes onto which flat layers could be screen printed or plasma sprayed. They failed to obtain dense electrolyte and
interconnect by these methods. Nickel cermet anodes have been made thicker and used as support structures by Fuji Electric (8). More often, the lanthanum chromite was thickened, gas channels were moulded or machined in place, and this interconnect was used both as separator and support (Figure 3).

Figure 3 Planar design with interconnect as support (left) and Argonne composite design (right)

A radical departure was to use metal alloy as the interconnect material, which could then also act as support and separator while being cheap to fabricate, thin in section and good for heat transfer. Siemens, Tonen and NKK have been developing metals for this purpose. Problems of oxidation, contact resistance and differential expansion remain to be solved.

3. EXISTING COMPOSITE DESIGNS

Composite designs of SOFC are those which combine the components during the manufacturing process, thereby reducing the number of ceramic processing steps, while cutting the component assembly operations.

A straightforward example of this composite approach is the co-firing of the electrolyte plate together with its electrodes. Whereas ECN (9), for example use 3 firings, one for the electrolyte, one with anode, then another with cathode, Mitsubishi Heavy Industries (7) and Risoe have demonstrated co-firing of all three layers together. Typically, the electrolyte is tape-cast and dried. Then electrode inks are deposited on the plastic electrolyte tape. The whole structure is then fired in one shot. The materials must be carefully selected and matched to allow this, because all components must shrink the same amount, but the electrolyte has to densify, whereas the electrodes must remain porous. There are additional problems of sintering temperature, because the lanthanum manganite should be kept below 1400°C to inhibit sintering and reaction with the zirconia, whereas zirconia sinters best above 1400°C, except for high surface area powders which are more difficult to handle.
In the most ambitious demonstration yet of the composite design, Argonne (10) and Allied Signal (11) have developed structures which were formed and assembled into a monolith while in a plastic carrier, then fired together to create the final ceramic stack. Plastic tapes were calendered from zirconia powder and also from anode and cathode powders. These three tapes were rolled together to form a flat PEN plate. Electrode tapes were also calendered separately to form gas channel spacers. An interconnect tape was also made by calendering lanthanum chromite tape together with anode and cathode tapes to make a triple layer tape which could be corrugated to form gas and air channels. Then the flat electrolyte PEN tape was laminated with the corrugated interconnect tape in sequence to form the monolithic structure which was fired at about 1350°C to give a ceramic stack shown schematically in Figure 3.

The problem with such monolithic stacks is the differential shrinkage that can occur between the separate components, causing cracking or debonding. It is difficult to match the burn-out and sintering of four components. However, if this is a problem, for example, because the interconnect has to be fired at higher temperature, then the separate components can be fired separately, and stacked later.

Murata (12) have developed a different composite design, using flat PEN and interconnect discs, with porous anode and cathode distributors, all co-fired around 1350°C with shrinkage of 21%. Only small stacks have been made so far. Chubu Electric Power Company and Mitsubishi Heavy Industries have also investigated a composite design called MOLB which appears to give certain advantages (13).

4. NEW COMPOSITE DESIGNS

Although the Argonne composite design has been difficult to implement on a kW scale, there is no doubt that the composite idea leads to economic manufacturing benefit over sequential designs which are slow and costly to make. Therefore, we have been exploring designs which incorporate the composite idea, but which do not require the difficult co-firing of four materials.

Our approach was to consider the most important elements of the structure. The critical components are the electrolyte and the interconnect which must both be gas tight. An additional benefit can be gained if these materials are mechanically strong, because the support structure can then be removed, to make the cells self-supporting.

To this end, we have developed the extrusion and tape-rolling method for making high quality zirconia and lanthanum chromite elements. Disagglomerated powders were mixed with polymer, then extruded and calendered to produce stronger ceramic with higher reliability (14). These materials had several benefits over tape-cast...
foils. First they were stronger in the plastic state. Secondly, they had higher solids content and consequent lower shrinkage on firing, typically 14%. This allowed larger foils to be fired without cracking. 200 mm square foils have been produced. Finally the ceramic had higher strength and reliability. Typical improvements are shown in Weibull plots in Figure 4.

![Figure 4 Improvement in strength and reliability of electrolyte. Left curve was for agglomerated powder; right curve was for disagglomerated material.](image)

The main virtue of the plastic processing method was that plastic mixes of zirconia and lanthanum chromite could be calendered or extruded together, then co-fired to produce a single ceramic structure incorporating both electrolyte and interconnect elements. This could not easily be achieved by powder pressing, tape casting or screen printing.

Several methods were investigated to produce such composite structures using 8 mole % yttria stabilised zirconia, and 15 mole % calcium doped lanthanum chromite containing a sintering aid, typically yttria. The ceramic powders were first prepared by calcining and grinding in organic solvent to near 1 μm mean particle size, measured using the Malvern Mastersizer. After drying, each powder was mixed with polymer and solvent to give a plastic mix with a ceramic volume fraction around 0.55. Such mixes could be calendered or extruded, then dried and fired at 1500°C for one hour, after burn-out of organics at 1°C/min to 500°C. Shrinkage was 13.5% linear, from dried tape to fired foil. The particle size of each mix was adjusted to match the dilatometer traces, so that both electrolyte and interconnect shrank equally when co-fired. Otherwise warping and cracking of composite pieces was observed.

In the first composite plate experiments, strips of plastic sheet 1 mm thick were laid side by side (Figure 5a), then pressed to join the materials together, and finally calendered to give 200μm thick foils (15).
After firing, it was discovered that a plane of weakness existed at the interface between the zirconia and the interconnect. The 3-point bending strength measured across the interface was ten times less than the bend strength of 400 MPa measured across the zirconia. To avoid this problem, the interconnect strips were split up, to form separate patches interspersed in the 8Y-zirconia plate (Figure 5b). This increased the strength of the composite plate several fold and also allowed the number of cells on the plate to be increased substantially (Figure 5c). The advantage of increasing the number of cells was that a larger voltage could be obtained from each plate. Sub-dividing the interconnect regions also made the composite less likely to warp and crack during the firing steps.

Electrodes were positioned on the composite plates by screen printing. Inks of nickel cermet and strontium doped lanthanum manganite were made by mixing ball-milled powder with polymer vehicles based on terpineol. These inks were deposited in layers 50 μm thick, dried at 90°C for 10 minutes, then fired at temperatures between 1150 and 1300°C. By choosing suitable electrode powders, both anode and cathode could be fired in one step around 1250°C. Thus the whole process required only two firings, one at 1500 and the other at 1250°C.

A second method for making composite electrolyte/interconnect structures was extrusion. This was most convenient for producing tubes, or arrays of tubes. In a typical experiment, a ram extruder was used with a tube die made using the ICI honeycomb die method (16). This die was made from a single piece of steel by drilling feed holes halfway from one side, and cutting an extrusion slot from the other side. To extrude a composite tube, the feed material was composed of 8Y-zirconia and interconnect, arranged in the barrel as shown in Figure 6.

This was rammed through the die, to produce a zirconia tube with an interconnect strip along its length. The tube was dried and fired at 1550°C for one hour after burn-out at 1°C/min to 500°C. Typically the tube wall thickness was 200 μm. Using this principle, it was quite...
straightforward to conceive of more complex dies which could be used to extrude composite SOFC stacks in a one-shot process. In essence, the assembly of zirconia and lanthanum chromite was achieved by extrusion. Then the assembly of electrodes was effected later by dipping, thereby simplifying the overall process considerably.

5. CONCLUSIONS

Existing methods for producing ceramic SOFC stacks are either too slow and costly in the sequential designs, or difficult to co-fire and scale-up in the Argonne composite design. New designs which concentrate on making composites of electrolyte and interconnect, fired once to densify these materials, then again to deposit electrodes, offer potential for avoiding these problems. Of particular interest is the calendered composite plate design, in which small patches of interconnect are spaced through a zirconia sheet, to form a composite ceramic foil onto which electrodes can be screen printed. This design is being studied under a Joule contract in the CEC fuel cell programme with British Gas and Tioxide as main contractors. Alternatively, composite tubes can be extruded, giving an interconnect strip along the length of a zirconia tube. Such tubes can be joined to form composite arrays.

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