FABRICATION OF SIMPLIFIED ANODE SUPPORTED PLANAR SOFCs – A RECENT ATTEMPT

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ABSTRACT

The present concept of anode supported planar thin film SOFC fabrication at Forschungszentrum Jülich includes several processing and firing steps. Attempt have been made recently to combine some of these processing steps in order to simplify the manufacturing process. The results of these modified SOFCs are compared with the cells produced by standard technique.

INTRODUCTION

The concept of anode supported thin film planar solid oxide fuel cells (SOFCs) by Forschungszentrum Jülich (JULICH) has been well accepted by the SOFC community mainly because of its certain advantages. These advantages include: mechanical stability of the 1.5 - 2.0 mm thick anode support and thus, enhancement of the effective cross-sections (up to 25x25 cm²), low operation temperature because of substantial reduction in electrolyte thickness (down to 5µm) and use of special varieties of low cost steel as interconnect etc. (1-4). A new dimension has recently been added to the ongoing development of the Forschungszentrum’s anode supported structure by eliminating one processing step during manufacturing of the SOFCs. One of the problems associated with the production of the Jülichs thin film SOFC is the relatively high number of sintering steps during production. Both the production time and more important the production cost of the cells depends strongly on the number of sintering steps. It would therefore be highly favorable to eliminate one or more of these sintering steps. With the manufacturing processes used up till now, this is not possible. A study was therefore started to investigate the production of the different thin layers within the concept using alternative methods with the aim to eliminate one or more sintering steps. The first option considered after an analysis of the standard production process was the elimination of the pre-sintering of the anode functional layer (AFL). This would lead to a co-firing step for the AFL and the electrolyte layer (EL). A increase in the number of deposition techniques would lead to a increase in production cost of the SOFC cells. Therefore the deposition technology wet powder spraying (WPS®), as already used in the standard production process for the cathode layer, was tested as an alternative for the deposition of the AFL and the electrolyte layer.
STANDARD APPROACH

The standard approach for manufacturing SOFCs at JÜLICH undergoes several processing steps followed by intermediate pre-firing or sintering-step. Fabrication of different cell components conventionally followed at JÜLICH are listed in Table 1:

Table 1. Different processing / firing steps for manufacturing cells at JÜLICH

| Component | Material | Process | Firing (°C) | Thickness (µm) |
|-----------|----------|---------|-------------|---------------|
| Anode Functional Layer (AFL) | NiO+8YSZ | VSC | 1000 | 5 |
| Electrolyte | 8YSZ | VSC | 1400 | 5 |
| Cathode Functional Layer (CFL) | La0.65Sr0.3MnO3+8YSZ | WPS | 1100 | 15 |
| Cathode | La0.65Sr0.3MnO3 O3 | WPS | 1100 | 40 |

VSC = Vacuum Slip Casting, WPS = Wet Powder Spraying

Normally, the anode functional layer (AFL) (NiO+8YSZ) is deposited on the perfectly flat surface of a pre-sintered porous cermet anode plate (NiO+8YSZ) by means of vacuum slip casting (VSC) followed by calcination at 1000°C. Another thin layer, made of electrolyte (8YSZ), is then applied on the top of AFL, also by VSC. Finally, the pre-fired AFL and green electrolyte film together with porous anode substrate is sintered at 1400°C. At this stage, the gas-tightness of these sintered electrolyte layers are routinely checked using standard He leak test method (4). Two other films, CFL (La0.65Sr0.3MnO3+8YSZ) and cathode film (La0.65Sr0.3MnO3) are then deposited one after another with an intermediate room temperature drying. A complete single cell module is obtained after firing at 1100°C. Detailed microstructural investigations and electrochemical tests are then performed.

PRESENT APPROACH

The present approach is essentially an attempt to simplify the cell fabrication by introducing co-deposition and a single-step firing of thin films of anode functional layer and electrolyte on thick anode supports. The rest of the processing and firing steps remains the same (as described in Table 1). The flow chart for the fabrication of cells by this modified approach is given in Fig. 1. Under this technique, it is most important to develop an entire process for producing a very thin layer (~5µm) of AFL by wet powder spraying (WPS). The WPS is a simple and inexpensive particulate deposition technique and has been widely used for thin film depositions (5-7). WPS has also been exploited, to a large extent, for AFL and electrolyte film fabrications in this investigation. All experiments have been carried out in an enclosed area (fume hood) to prevent the NiO mists to mix with the environment.
Particulate Suspension Preparation

For all particulate deposition processes, the suspension preparation played a vital role because it controls the quality of the final product (thin film) deposited on the porous anode substrate. Brief description of suspension preparation for electrolyte and for anode functional layer (AFL) are given below:

Electrolyte

8YSZ (Tosoh, Japan) powder was ball-milled (for 120 hours) under industrial grade ethanol, PEI binder, along with zirconia grinding media, followed by settling and sedimentation. The details of the process were described elsewhere (4). The particle content of the electrolyte suspension thus prepared is around 100g/l.

Anode Functional Layer

A NiO suspension is prepared with the same concentration (100g/l) as the electrolyte suspension. Required amounts of NiO and 8YSZ suspensions (52.1 vol% NiO and rest 8YSZ) are then thoroughly mixed in a ball mill. At the final stage an additional amount of isopropyl alcohol was added to the ethanol based 100g/l AFL suspension. The AFL suspension is now ready for spraying. The thickness of the AFL can be varied by spraying several layers of the suspension on the porous anode support. Fig. 2 depicts the optical microphotographs of different thicknesses of AFLs on porous anode supports. Normally, it is required to deposit about 7 layers (by WPS) to obtain a 6-7 μm thick AFL (after sintering).

Thin Film Fabrication and Characterizations

Different schemes that are adopted to make thin films of electrolyte and AFL on porous anode substrates are given in Table 2. Both VSC and WPS have been utilized to produce these layers. As has already been mentioned, for the standard approach, first the AFL is deposited on a porous anode substrate by VSC, then after pre-firing the AFL at 1100°C, the electrolyte is laid down on top of the AFL by VSC – sintering at 1400°C yields the desired structure – referred to as standard approach (cell nos. 951-1 and 2 in Table 2). On the other hand, present approach (all other cells, except 951-1 and 2, as described in...
Fig. 2 Control of anode functional layer (NiO+YSZ) thickness during deposition on porous anode substrates by wet powder spraying (WPS) technique. Above specimens are sintered at 1400°C and then optical photo-micrographs are taken from polished cross-sections.

Table 2. Leak rates of the cells prepared following the standard and the present approach. Cell dimensions: 5cm x 5 cm x 1.5mm.

| Cell No. | Thin film depositions and firing steps on flat porous anode substrates | No. of Layers | Approximate AFL Thickness (μm) | Leak Rate (mbar.l/cm².s) |
|----------|------------------------------------------------------------------------|---------------|--------------------------------|--------------------------|
| 951-1    | AFL (VSC) + Pre-firing + Electrolyte (VSC) + Sintering                | 3             | 2                              | 3.25 x10⁻⁶               |
| 969-1    | AFL (VSC) + Electrolyte (VSC) + Sintering                              | 5             | 3                              | 9.47 x10⁻⁶               |
| 958-1    | AFL (WPS) + Electrolyte (WPS) + Sintering                              | 7             | 6                              | 4.51 x10⁻⁵               |
| 967-4    | AFL (WPS) + Electrolyte (VSC) + Sintering                              | 7             | 6                              | 7.22 x10⁻⁴               |

Table 2) refers to those cells where AFL and electrolyte film deposition is combined followed by a single firing step. In this case, the AFL and electrolyte both are deposited either by VSC or by WPS. At the end of the co-deposition a single sintering step (at 1400 °C) yields the desired product. The pre-firing step (1000 °C), which is normally necessary for the conventional fabrication approach can be totally abolish under this process conditions. Once the sintered films are made, series of leak tests are performed. The leak rate values of the samples obtained by this new route and by the standard approach are demonstrated in Fig. 3 the absolute values are listed in Table 2. The lower the value of the leak rate, the higher is the gas-tightness of the electrolyte film. It is evident that one of the present approaches – AFL (by WPS) + Electrolyte (by VSC) + Sintering – produces similar quality of the product as obtained under the standard
Fig. 3 Comparison of leak rates for all specimens prepared both by standard and by present approach.

approach (cell nos. 951-1 and 2 in Table 2 and Fig. 3). A large number of specimens (5x5 cm²) were prepared following this co-deposition and single step firing. The results are reproducible. Samples with larger area cells (10x10 cm²) have also been successfully fabricated. Detailed microstructural characterizations (both optical and SEM) were performed by examining the polished cross-sections of the samples. The specimens prepared by two different approaches are shown in Fig. 4a and b. In both the cases, the microstructures as developed are almost similar in nature. Fig. 4c represents the SEM photograph of the sample prepared using this modified process. A gas-tight zirconia electrolyte film thickness about 5μm has been obtained. The microstructure of the AFL is well adhered to both the electrolyte and porous anode substrate. The approximate thickness is found to be around 7μm. To produce single cells, another firing-step (at 1100 °C) is required (after deposition of cathode films). These single cells are used for electrochemical test. The summary of electrochemical tests are given in Table-3 for some representative samples prepared by both approaches. The current densities for the samples prepared by the present approach – (AFL by WPS) + Electrolyte by VSC + Sintering – shows better performance even compared to the standard approach (cell nos. 951-2). The current densities are measured at four different temperatures (750, 800, 850 and 900°C) and at 0.7V. At 750°C, the measured current density is around 0.63 A/cm² (for sample 967-4), which is much higher than that of the other measured values. This may be due to the fact that during processing, the AFL is laid down first by WPS, then electrolyte deposition took place by VSC. It is believed that this particular combination might have a better impact at the two interfaces - substrate + AFL and AFL+ electrolyte – causing higher current densities.
Fig. 4. Cross-sectional views of the specimens prepared using standard (a) and present approach (b and c).

Table 3. Temperature dependence of measured current densities of representative cells prepared following the standard and the present approach.

| Cell No. | Approach | Current Densities at 0.7V (A/cm²) |
|----------|----------|-----------------------------------|
|          |          | Measurement Temperature (°C)      |
|          |          | 900  | 850  | 800  | 750  |
| 951-2    | Standard | 1.07  | 0.92 | 0.70 | 0.46 |
| 969-1    | Present  | 1.00  | 0.78 | 0.62 | 0.44 |
| 958-1    | Present  | 0.82  | 0.53 | 0.32 | 0.20 |
| 967-4    | Present  | 1.40  | 1.14 | 0.93 | 0.63 |
CONCLUSIONS

It has been possible to omit one pre-firing step during cell fabrication by the modified approach. The present approach is basically two step process (i) co-deposition of AFL and electrolyte on porous substrate and (ii) sintering at 1400°C. One remarkable change which is introduced in the approach is to deposit the AFL by WPS, instead of VSC. The leak rate obtained by this modified route is of the order of $10^{-6}$ mbar.l/(s.cm²) which is in the same range of the specimens prepared by standard approach. Microstructural investigation are also supports this data. Current density (at 0.7V) values for this variety of specimens at 750 and 800°C are 0.63 and 0.93A/cm² respectively. The overall properties of this new cells open up a lot of promise for more efficient SOFCs in future.

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