CHAPTER 8

Fabrication and characterization of single cells

8.1 Introduction

SOFC single cells can be fabricated in various configurations. The two basic configurations that have been widely used are tubular and planar. In each of these configurations, the cell can be anode supported, cathode supported or electrolyte supported. Anode supported planar SOFC has been widely documented in literature [238-241]. Higher power density is normally reported in anode supported planar design mainly due to lower internal resistance of the cell and better current collection. In anode supported planar configuration co-firing has been reported to be an economic route to integrate electrolyte and electrode. The interface formed by this route is reported to have reasonably low polarization resistance [239,241,242]. In general, co-firing approach is not suitable for fabricating cathode supported SOFC. The co-firing temperature is primarily decided by the sintering temperature of the electrolyte material. As reported in Chapter 3, GDC electrolyte prepared using combustion synthesized nano-powders could be sintered to its near theoretical density at 1250 °C. However, at this temperature the
chemical compatibility between cobaltite cathode and GDC electrolyte materials remains very poor [Ref. Chapter 6]. The chemical compatibility of NiO (precursor of Ni) and GDC at the sintering temperature is proven through the innumerable works published in the literature. Therefore, it is more practicable to fabricate a single cell by initially integrating NiO-GDC anode support with electrolyte by co-firing followed by forming the cathode layer by firing at a lower temperature.

Various ceramic processing techniques can be adopted to fabricate anode supported single cell. The anode support has been fabricated by different techniques, such as, doctor blade tape casting, pressing, coat mixing, gel casting and vacuum slip casting [240-247]. As a significant part of internal resistance of a cell comes from the electrolyte resistance, it is desirable to have a thin and impervious electrolyte layer in order to improve the performance of the cell. Fabrication of thin electrolyte film over electrode support can be achieved by various processes, namely, magnetron sputtering, screen printing, wet powder spraying, dip coating, plasma spraying, physical vapor deposition etc. [240,246-248]. Fabrication of both anode support and thin electrolyte layer by doctor blade co-casting has been reported in literature [249-253]. The electrolyte thickness in the half cells formed by this route typically remains in the range of 20 to 50 µm. Although the internal resistance of a cell increases with electrolyte thickness it has been reported that redox stability of the cell increases with increase in electrolyte thickness. Therefore, doctor blade co-casting route can be an attractive and economically viable approach in fabricating planar cell. In the present work anode supported half cells have been fabricated by two different approaches. In the first approach the anode support has been
fabricated by uniaxial pressing and the electrolyte layer has been integrated by brush painting using terpinol based slurry followed by co-firing. In the second approach doctor blade co-casting method has been adopted to fabricate anode supported half cell. The cathode layer has been formed over the dense GDC electrolyte layer by screen printing. Finally, the cells have been tested for their performance.

### 8.2 Experimental

#### 8.2.1. Starting materials

NiO and 12 mol% GDC nano-powders both prepared by gel combustion route have been mixed in 1:1 weight ratio and used for fabrication of anode support. The gel combustion synthesized GDC powder has been used for making the electrolyte layer. Barium doped gadolinium cabaltite (GBC10) powder of composition $\text{Gd}_{0.9}\text{Ba}_{0.1}\text{CoO}_3$ prepared by solution polymerization method has been used as the cathode material.

#### 8.2.2 Fabrication of anode supported half cell by uniaxial pressing

Anode composition was prepared by mixing NiO and GDC powders in weight ratio 1:1 through wet ball milling using stabilised zirconia balls, ethyl alcohol solvent and 1% polyvinyl butyral binder. The powder mixture was dried under an IR-lamp. The dry powder mixture was compacted uniaxially in a hydraulic press at 120 MPa pressure to get
NiO-GDC disc of 25 mm diameter × 2 mm thick (approximately). The density of the green compact was about 55% of theoretical density.

GDC ink was prepared by mixing GDC nano-powders and terpinol (solvent) in a Spex® mill. A thin layer of GDC ink was applied on one side of NiO-GDC substrate by brush painting. After drying of the electrolyte slurry, the bi-layer was co-sintered at 1350 °C.

8.2.3 Fabrication of anode supported half cell by co-casting

8.2.3.1 Preparation of NiO-GDC slurry for tape casting

The tape casting slurry primarily consists of powder, solvent, dispersant, binder and plasticizer. For the preparation of anode slurry for tape casting, NiO and GDC powders were taken in 1:1 weight ratio. The slurry composition was optimised based on preliminary experiments. The formulation used in the preparation of the slurry in the present study is given in Table 8.1. Initially powders, solvent and dispersant were mixed in a ball mill for 12 h. Then the slurry was mixed with binder and plasticizers in the ball mill for 24 h for thorough mixing of all the ingredients.

8.2.3.2 Preparation of GDC slurry for tape casting

For the preparation of tape casting slurry of GDC, the powder was taken and mixed with other ingredients with quantity as given in Table 8.1. The mixing procedure remained same as mentioned above.
Table 8.1: Formulation used for the preparation of tape casting slurries

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity (wt.%) of ingredients for preparation of anode slurry</th>
<th>Quantity (wt.%) of ingredients for preparation of electrolyte slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Powder as mentioned 59 NiO-GDC (1:1)</td>
<td>50.4 GDC</td>
</tr>
<tr>
<td>Dispersant</td>
<td>Oleic acid 3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol 17</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>MEK 17</td>
<td>21</td>
</tr>
<tr>
<td>Plastisizer</td>
<td>PEG 400 0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Binder</td>
<td>PVB 90 3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

8.2.3.3 Co-casting using doctors blade

Doctor blade co-casting approach was adopted in the fabrication of anode-electrolyte half cell in-planar configuration. In this approach, the second layer was cast over the first cast layer without removing it. The doctor blade tape casting machine (EPH, Engineering Associates INC, OREM, UTAH) used in the present study for making green tapes is shown in Fig. 8.1. The blade is moveable on a glass plate by a motor driven machine with controlled speed. A carrier film is generally used for easy removal of the green tape.
Fig. 8.1: Doctors’ Blade tape casting machine

The slurry is poured in front of the doctor blade and the moving blade spreads the slurry over the carrier film. Silicon coated mylar carrier film was used in our experiments. Tape was cast on the side of the film that has lower wet-ability for the slurry i.e. silicon coated surface. The speed of the blade was adjusted to 40 cm/min in all the experiments. Thickness of the green tape was adjusted by suitably adjusting the blade gap through a screw gauge mounted over the casting head. Different blade gaps were used to get tapes of different thickness. It was observed that for good adhesion, the subsequent layer need to be cast in the time period of 1 to 2 minutes. For anode supported planar cell fabrication, tape of electrolyte was first cast on the mylar film. Thereafter, anode slurry was cast over the electrolyte layer. Green tapes were dried for more than 24 h at ambient temperature. Green tapes were punched to make discs of 25 mm dia.
8.2.3.4 Sintering of the tapes

The green bilayer tapes (in the form of circular disc of 25 mm dia.) were placed on a dense alumina plate. A porous alumina weight was placed over the green tapes and sintered at 1350 °C, 6 h. A heating rate of 1 °C / min. and a cooling rate 2 °C / min. were used during sintering. About 20% shrinkage in the lateral direction was observed in most of the cases. The final diameters of the sintered half cells were measured to be within 20 to 21 mm.

8.2.4 Integration of anode supported half cell with cathode

GBC10-GDC composite was used as a cathode functional layer. For this, GBC10 and GDC powders were taken in 1:1 weight ratio and mixed with 5 wt.% carbon black as pore former. A terpineol based slurry of GBC10-GDC composite powder was prepared in a Spex mill®. The slurry was coated over dense GDC electrolyte layer of the sintered NiO-GDC/GDC bilayer by screen printing. Over the GBC10-GDC composite layer a terpineol based slurry of GBC10 + 5 wt.% carbon black was coated by brush painting. The cathode layers were sintered by heating at 1100 °C, 2 h in static air.

8.2.5 Performance testing of single cells

Single button cells of 20 mm dia were taken in the experiment. The active cathode area in these planar cells was about 2 cm². The performance testing of the cells were carried out
using Probostat™ (NorECs, Norway) set up. The sample fixing assembly is shown in Fig. 8.2. The cells were fixed over an alumina tube with ceramic sealant (Aremco CeraBond 885).

![Sample fixing assembly in the Probostat unit](image)

The sealant was baked at desired temperature as mentioned by the supplier. Platinum mesh was used as current collector on the cathode side and nickel mesh on the anode side. About 2 cm² cathode area was used for current collection. On both the anode and cathode side electrical connections were made for current lead wire and voltage lead wire. A vertical tubular resistance heated furnace was used for maintaining the temperatures. Humidified hydrogen gas (composition: about 97% H₂ + 3% H₂O) was passed over anode side (inside alumina tube) and oxygen in the cathode side. The flow rates of the gases were suitably adjusted by rotameter. I-V characterization of the cells was carried out using electronic load and a nano-voltmeter. Current to voltage response
of the cells were recorded at 800 °C. The cell resistance (ohmic + interfacial polarization) was measured from the linear portion of the I-V curve. After the testing of the cells, the microstructures of the complete cells were observed in scanning electron microscope (Seron Technology, Korea).

8.3 Results and discussion

8.3.1 On the fabrication of anode supported half cell through doctor blade tape casting

The electrode and electrolyte thickness in the sintered half cell depend on the corresponding thicknesses in the green co-cast tape. The thickness of a green tape can be controlled by the blade gap (opening between the doctor blade and the cast surface). Table 8.2 shows the variation of thickness of the tape at different blade gap adjusted. Based on the results a blade gap of 200 µm was used for casting the electrolyte layer. Thereafter, anode layer was cast over the green electrolyte tape using a blade gap of 800 µm.
Table 8.2: Variation in the thickness of the tape in drying and at sintering stage for NiO-GDC anode and GDC electrolyte tape

<table>
<thead>
<tr>
<th></th>
<th>Blade gap (µm)</th>
<th>Thickness of green tape (µm)</th>
<th>Thickness of the sintered tape (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>~70</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>~160</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>~450</td>
<td>360</td>
<td></td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>~90</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>~230</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>~580</td>
<td>460</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8.3: Anode and electrolyte layer of green tape and sintered single cell

Fig. 8.3 (a-b) shows the photographs of the green bilayer tape. The NiO-GDC anode layer appears to be green in colour and the GDC electrolyte layer is off-white in colour.

Fig. 8.3 (c) shows the photograph of a single cell obtained after co-firing the bilayer and subsequently integrating with cathode layers.
A lateral shrinkage of around 20% is observed in the sintered cell. In the sintered cell the electrolyte layer becomes transparent. Black cathode layer was applied over the electrolyte layer leaving a 2 mm wide rim at the periphery. The cell is fixed with the alumina tube of test assembly by applying glass sealing material along the rim of dense electrolyte.

Fig. 8.4 shows the SEM micrograph of anode-electrolyte half cell at low magnification. As shown in Fig. 8.4(a) the thickness of electrolyte and anode layers are about 50 µm and 400 µm, respectively. Good adherence is observed between the anode and electrolyte layers as seen in the SEM micrograph of Fig. 8.4(b). Fig. 8.5 (a) and (b) show the SEM micrographs of the sintered electrolyte and anode layers at higher magnification. Impervious electrolyte layer and porous anode layer is clearly visible in the micrographs.

Fig. 8.4: SEM micrograph of anode-electrolyte half cell at low magnification; (a) 230 X, (b) 970 X.
Fig. 8.5 SEM micrographs of (a) GDC electrolyte and (b) NiO-GDC anode of the sintered bilayer

8.3.2 I-V characteristics of anode supported cell prepared by uniaxial die pressing

The I-V characteristics of the cell prepared though die-pressing route is shown in Fig. 8.6. A maximum power density of 80 mW/cm² was obtained at 800 °C from this cell. The SEM micrograph of the cell after testing is shown in Fig. 8.7. Dense electrolyte of 70 – 90 µm thickness was observed in the microstructure. The non-uniformity in thickness is due to the defects generated during uniaxial pressing. The electrolyte layer has good adherence with both the cathode and anode layer. The lower value of power density of this cell may be due to deficiency in current collection.
Fig. 8.6: I-V characteristics of single cell fabricated by tape casting

Fig. 8.7: SEM micrograph of single cell fabricated by die pressing (after cell testing)

8.3.2 I-V characteristics of anode supported cell prepared by tape casting
The I-V characteristics of the cell prepared by doctor blade tape casting method is shown in Figure 8.8. A maximum power density of 85 mW/cm² was obtained from this cell. Figure 8.9 shows the SEM micrograph of the cell after the cell testing. Dense electrolyte of uniform thickness (~50 µm) is observed in the microstructure. The electrolyte layer has good adherence with both the cathode and anode layer.

Fig 8.8: I-V curve of single cell fabricated by tape casting
8.4 Summary

Planar anode supported single cells have been formed by uniaxial die pressing and doctor blade co-casting method. Electrolyte thickness could be maintained in the range of 70 to 90 µm in case of pressing technique. Dense electrolyte layer of uniform thickness around 50 µm has been obtained by tape casting. Good adherence is obtained in the cells formed by both the techniques. The cells fabricated by pressing route and co-casting route delivered power @ 80 mW/cm² and 85 mW/cm², respectively. As per calculation, using the data generated on electrolyte resistance and area specific interfacial polarisation resistance, the power density is expected to be much higher than the above values. The low power density in the present study is primarily due to the defficiency in current collection.