Chapter 7

Solid Oxide Fuel Cell Fabrication and Testing

We have seen compatibility study of electrolyte and electrode materials with LTCC in the earlier Chapter. Different sintering aids in the form of oxides and low melting temperature glasses were used to make the SOFC materials compatible with each other and with LTCC. The focus was also on improvement of the properties through this inevitable addition of sintering aid. This target could be achieved for the oxygen ion conductor, but the properties of proton conducting electrolyte were found to be deteriorating with the addition of sintering aid. The effect of alkali oxide in glass resulted in improved properties of GDC electrolyte and compatibility with LTCC. This glass also used for electrode materials and their compatibility with LTCC was also studied in earlier Chapter.

This Chapter presents fabrication of fuel cell using these LTCC compatible electrode and electrolyte materials, fabrication of LTCC integrated SOFC and reliability of its sealing and testing using in laboratory developed SOFC test set up. It may be noted that this attempt was aimed mainly at confirming the feasibility of fabrication and not at optimizing the cell design for power output and efficiency.
7.1 Fabrication of solid oxide fuel cell

The SOFC fabrication process consists of putting together all three components, \textit{viz.} two electrodes and the electrolyte, physically and chemically. These three components are initially attached to each other physically, forming a sharp boundary at both side of electrolyte. There are three known types of SOFC based on their fabrication process \textit{viz.} anode supported, where, anode is made into a thick substrate over which the electrolyte and cathode electrodes are applied by various physical and chemical methods. The other two are electrolyte supported and cathode supported SOFC fabrication processes. Mostly, anode or cathode supported SOFCs are more favorable SOFC fabrication process as electrolyte thickness can be controlled and is possible to keep it low, if required. In electrolyte supported SOFCs, thickness of the electrolyte is grater and hence may reduce performance of the cell. These materials must be chemically compatible \textit{i.e.} should not react with each other and form impurity phases due to diffusion during firing process. The electrodes must by porous enough to create ample surface area for the Triple Phase Boundary (TPB), as it plays important role in fuel cell performance. These issues must consider during fabrication of cell.

The earlier Chapter demonstrated the compatibility of cathode material \textit{i.e.} Samarium and Strontium doped Cobaltite (SSC) with the electrolyte made of Gadolinium doped Ceria and BKPV glass composite. These two materials with doped glass was initially pressed co-axially to
stack. The fabrication of the cell was initiated by first grounding the SSC nanocrystalline powder in agate pestle mortar. 40 wt% BKPV glass frit was then added to SSC and mixed well. Polyvinyl Alcohol (PVA: Molecular weight 10000, Sigma Aldrich) was added as binder and was again mixed. The mixture was put into pelletizer. Similarly GDC powder was also ground and mixed well with glass and PVA to form homogeneous mixture. This mixture was also added into pelletizer. These two powders were then pressed together to form a pellet by applying 285 MPa co-axially pressure. This pellet was fired at 1000°C for 40 min. Observation of the fired pellet showed fine interface and no evidence of inter-diffusion could be seen. However, a minor crack was observed at one side of pellet, which was due to slight thickness variation of GDC. The Copper Zinc Oxide pellet was pressed from the other side onto the electrolyte. However, due to dense and flat surface of electrolyte the CuZnO pellet could not stick physically to the electrolyte. Hence, the electrolyte surface was partially scratched to the depth of 10-12 µm using a diamond tool. The pressed pellet was fired at 900°C for 40 min and observed under microscope. The optical images of fired cell are shown in Figure 7.1
A close look at the button cell shows change in color at both ends of the electrolyte. This attributed to chemical reaction of the materials with each other interface. Shrinkage of the pellets was seen matching with each other. In this button cell, the thin GDC-composite electrolytes had a fired thickness of 0.9mm, the SSC-glass composite cathode was 1.8mm thick and the CuZnO anode had a thickness of 2.2mm.

### 7.2 SOFC set up development

This cell was used to measure fuel cell performance using lab made SOFC testing unit. This set up consists of two parts viz. LTCC package to hold the already fired button cell and Stainless steel supports on either side. The LTCC package was used to embed kanthal heaters, a K-type Alumel-Chromel temperature sensors and Platinum wires for current collection. This LTCC part was designed and fabricated in-house. Figure 7.2 (a) and (b) present the isometric view of the base and lid design of the
LTCC package respectively. The base package consist of hollow channels for heater wire, burried as well as open channel at top for electrical interconnects, cavity for button cell and central hole for fuel flow. The isometric view of the lid is shown in Fig. 7.2 (b) from the top side. This package also includes hollow heater chennel and hole for oxidant flow. Figure 7.2 (c) presents a cross sectional view of the package featuring arrangement of lid, base and button cell for testing. Small openings denoted by black arrows indicate gaps through which electrical contacts using Platinum wires were taken out of the package. Internal surface of cell cavity and bottom surface of lid was screen printed by DuPont 5731 conductor Gold paste for current collection. This square package is of 3 cm per side and 1mm in thickness including base and lid.

Figure 7.2: Schematic of LTCC fabricated package for SOFC testing (a) Base of package (b) lid, and, (c) cross-sectional view of package showing, heater channels and cell fitted in cavity (Navy blue color)
This package was supported by stainless steel supports from both sides. This support was designed and fabricated considering Methanol would be used as fuel and Air as oxidant. The SS support consists of two square plates of 50mm side and 1mm thickness. These plates can be clamped together after inserting the LTCC package. The plates also have a central hole with attached, long tubing for fuel and air supply. The LTCC package is placed between these two plates along with ceramic wool insulation to prevent heat desipition. The schematic diagram and photograph of this setup is presented in Figure 7.3.
7.3 SOFC cell testing and results

Setup in Figure 7.3 was used to test fabricated composite fuel cell. Methanol fuel (HPLC grade; Merck) was diluted to 10 volume % by adding...
fresh DI water (Millipore ELIX 10) and was kept in a bubbler to pass the fuel to the cell from anode side. Humidified compressed air was passed from cathode side as an oxidizer. The cell was heated to 500°C using kanthal wires wound through the LTCC structure. An heater arrangement was made in such a way that air and oxidant are heated before passing to the cell. Air back pressure from both side was 0.1Bar. The Cell output was measured across electrical load having range 0.1-100 Ω using multimeters. Figure 7.4 presents I-V characteristic of cell measured at 500°C for the composite fuel cell using fuel cell set up.

Figure 7.4 indicates Open Circuit Voltage (OCV) of the cell measured was 5.6mV, Short Circuit current measured was 0.4mA. The maximum power generated by the cell was 1.5µW. The maximum power density of the cell was 2.84µW.cm⁻². The fill factor was calculated to be 0.67. It is seen that the efficiency of the cell is very low as compared to literature where direct methanol was used as fuel and performance measured at 550°C. The power densities reported using methanol in literature are tabulated in Table 7.1
Figure 7.4: I-V characteristics of composite fuel cell measured at 500°C, using methanol as fuel and humidified air as oxidant

<table>
<thead>
<tr>
<th>Fuel Cell component materials</th>
<th>Methanol supply</th>
<th>Operating temperature (°C)</th>
<th>Power density (mW/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-YSZ</td>
<td>GDC</td>
<td>LSCF</td>
<td>direct methanol</td>
<td>550</td>
</tr>
<tr>
<td>Activated carbon doped Copper oxide:SDC</td>
<td>Carbonate doped SDC</td>
<td>Copper-Nickel-Zinc oxide</td>
<td>direct methanol</td>
<td>580</td>
</tr>
<tr>
<td>Activated carbon doped Copper oxide:SDC</td>
<td>Carbonate doped SDC</td>
<td>Direct methanol</td>
<td>560</td>
<td>250</td>
</tr>
<tr>
<td>CuZnO</td>
<td>GDC+BKVP glass</td>
<td>SSC +BKVP glass</td>
<td>10% humidified Methanol</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 7.1: Comparison of power drawn by SOFC with values given in literature using methanol as fuel

Table 7.1 indicates that low temperature operating SOFC’s operated using direct methanol as fuel shows power output in the range of a few mW at about 550°C. In this work the power output is found to be very low.
This may be due to multiple factors acting simultaneously. Firstly, operating temperature is low, there is dilution of methanol, air has been used as oxidant. Structurally, it is known that the density of cathode is high at this sintering temperature, causing reduced surface area and consequently drop in the catalytic performance of the electrode.

The cell was tested further at 600°C. However, it was found that the output decreased further at higher operating temperature. This cell showed promising $V_{oc}$ of 150mV, however, the power output of the cell degraded drastically after some time. The post analysis shows internal cracks and possible diffusion of anode material in the electrolyte. Figure 7.5, presents pictures of the cell after cutting center using diamond cutting tool of dicing machine.

The pictures indicates that CuZnO may have diffused through electrolyte and cracks are developed possibly due to extreme temperature differences developed during the operation. The cell was found unstable at temperature above 600°C. The diffusion of anode in electrolyte may be due to very high local temperature at the tripple phase boundary (TPB) that could have been close to the melting point of CuZnO. It may be noted that the reduction reaction happenning at this electrode is exothermic. This study implies that, composite cell with CuZnO as anode is unstable at higher (≥600°) operating temperature.
7.4 **SOFC cell packaging and sealing**

SOFC cell with GDC-glass composite electrolyte was fabricated using above illustrated method to study effect of thermal cycling on LTCC embedded SOFC cell. This study includes post fire packaging of SOFC in LTCC. An appropriate cell structure was designed and fabricated in LTCC. A standard cell having electrolyte pellet with Pt applied on both sides was fabricated and fired separately. This cell was then enclosed in the fabricated LTCC structure and then sealed using DuPont 9616 glass paste. It was then fired according to the given temperature profile. The cell showed good quality hermetic sealing across the edges. This package was placed in SOFC testing unit and operated at 600°C. This fuel cell package showed structural stability and cracks or any physical damage was not observed. This package also observed using 3D X-ray (XRADIA Micro XCT 400) after thermal cycling at 600°C. Figure 7.5 presents pictures of LTCC-

![Figure 7.5: Degradation of the SOFC composite cell when operated at 600°C in humidified methanol, (b) close view of the anode diffusion in electrolyte](image)

Contaminated electrolyte

SSC cathode

CuZnO anode

Figure 7.5: Degradation of the SOFC composite cell when operated at 600°C in humidified methanol, (b) close view of the anode diffusion in electrolyte
embedded SOFC, its side view to showing sealing and 3D X-ray images after thermal cycling.

Figure 7.6:(a) LTCC embedded fuel cell with Pt wires for contacts, (b) side view of the sealed of cell, and, (c) 3D X-ray image of cell placed inside LTCC structure

Thus, it can be concluded from above discussion that, hermetic sealing technology used in LTCC is suitable with the GDC-glass composite electrolyte. The package shows good stability and has sturdy structural performance. The sealing was hermetic and stable at 600°C operating temperature. However, this package yet to be tested for fuel cell performance with methanol fuel. Further, the on-going work includes using platinum paste as heater and more reliable contacts through via made in LTCC and sturdy electrode contacts through brazing. This will impart more stability to the structure and simplicity in fuel cell operation.

7.5 Conclusions

The very initial attempts for the fabrication of SOFC button cell packaged into LTCC has been presented here. The cell used glass ceramic
composite anode (Copper Zinc oxide), glass composite electrolyte (GDC-BKVP) and glass-ceramic composite cathode material (SSC-BKVP) respectively. The fabricated cell was tested in laboratory developed fuel cell testing set up using 10% diluted methanol as fuel and air as oxidant. The cell has shown 1.5µW power output at 500°C. The cell became unstable above at 600°C due to diffusion of CuZnO in electrolyte resulting in decrease in output of cell and internal cracks due to extreme temperature variation. The standard GDC-BKVP glass composite electrolyte with platinum electrode was placed in glass sealed LTCC package. This package showed good stability during temperature cycling up to 600°C with humidified environment.

It is clear from the initial experiments that the cell needs more structural stability, better thermal management and improved anode material that is stable at high temperatures. It is felt that the inherent advantages of LTCC would come handy for most of these requirements.

7.6 References


2. Development of cathodes for methanol and ethanol fuelled low temperature (300–600°C) solid oxide fuel cells. Mahmut D. Mat,