CHAPTER 5

Synthesis and characterization of NiO–GDC composite for SOFC anode

5.1 Introduction

The performance of a SOFC depends on the internal resistance of a cell during operation. The internal resistance mainly depends on the electrolyte resistance and the polarisation resistance at the electrode-electrolyte interface. In an electrode supported cell thin electrolyte can be integrated to minimize the resistance coming from electrolyte. The electrolyte resistance depends on the material and thickness of the electrolyte layer. For dense GDC electrolyte of nominal thickness of about 20 µm the area specific resistance is about 0.1 Ω.cm². Anode supported cell having thin electrolyte has been reported extensively in the literature [184-192]. Nickel has good catalytic property towards hydrogen oxidation and is widely used in the anode structure in the form of a composite of nickel and the electrolyte material. Nickel has higher coefficient of thermal expansion compared to GDC electrolyte. However, in the nickel–GDC composite the thermal
expansion coefficient matches quite well with the electrolyte material. Also, presence of electrolyte material in the anode structure extends the triple phase boundary area. Therefore, Ni-GDC composite is a potential anode material for GDC electrolyte based IT-SOFC [193-194].

Apart from the electrode composition the microstructure plays an important role. The electrochemical reaction at the anode is heterogeneous in nature. The heterogeneous reactions at the anode takes place at the triple phase boundary (TBP) area where the pores, the Ni phase and the YSZ electrolyte meet. Hence the triple phase boundary should be as large as possible for better catalytic activity. At the same time the continuity of nickel phase need to be maintained throughout the anode structure in order to keep TBPs active through better current collection. Fine microstructure is expected to have better TBP area. Also fine NiO particle ensures electrical percolation in the sintered anode structure. Therefore it is required to have ultrafine NiO powder with narrow size distribution for effective control over latter stage processing and sintering properties i.e control over final microstructure and performance of the fuel cell. Increase in the Ni amount increases the conductivity, however thermal expansion coefficient (TEC) also changes drastically. Conductivity value decrease with decrease in nickel content and there exist a threshold value below which the conductivity falls drastically. NiO was taken as precursor for the Ni-GDC anode fabrication. At the high operating temperature and reducing atmosphere of the anode NiO transforms into Ni. NiO-electrolyte composite close to 1:1 weight ratio has been used by many authors [195,196]. After reduction of NiO in the anode, there should be continuity among the nickel particle for better current collection. The minimum amount of nickel to GDC ratio for which there will be a
continuous network among Ni particles is called percolation ratio which is around 30 weight %.

GDC powder for preparation of anode structure has been described in Chapter 3. Fine NiO powders can be prepared by various wet chemical methods [197-200]. Gel combustion method is an attractive method for preparing fine powders without calcination. Optimization of fuel to oxidant leads to final product in a single step in many occasions. In the present investigation ultra fine NiO has been synthesized by combustion route and physical characterization of the powder was carried by x-ray diffraction, laser scattering, scanning electron microscope, transmission electron microscope, and EDS. Electrical conductivity of NiO-GDC has been measured in H₂ atmosphere.

5.2 Experimental

5.2.1 Synthesis of fine NiO powder

Fine NiO has been synthesized by solution combustion route using nickel nitrate as oxidant and citric acid as fuel. Calculated amount of Ni(NO₃)₂·6H₂O was dissolved in deionised water. Required amount of citric acid as calculated from propellant chemistry was added to the metal nitrate solution with constant stirring on a hot plate. After dehydration, a viscous gel is formed and further heating of the gel leads to an exothermic reaction with evolution of large amount of gaseous molecules. The flowchart for the preparation of fine NiO powder through combustion route is shown in Figure 5.1. The
decomposition behaviour of the dried precursor gel from combustion synthesis was carried out on a TG-DSC instrument (SETARAM: SETSYS evolution) in flowing air atmosphere. X-ray diffraction of the as synthesized powder was taken in an X-Ray diffractometer (Philips, model: PW1830) in the 2θ range from 20 – 80° with a step size of 0.02°. The as-synthesized powder was calcined at 700 °C and X-ray diffraction pattern of the calcined powder was recorded. The particle size of the calcined powder was taken in a laser diffraction particle size analyzer (HORIBA, Model: LA500). The morphology of the calcined powder was observed using a scanning electron microscope (Model: SERON 2000, South Korea) and a transmission electron microscope (TEM).

![Flowchart for the preparation of fine NiO powder through combustion route](image)

Fig. 5.1: Flowchart for the preparation of fine NiO powder through combustion route
5.2.2 Preparation of NiO-GDC powder

NiO and GDC powders were taken in weight ratio 1:1 and mixed in a ball mill in ethanol medium for 6 h. After mixing, the powder was dried under IR lamp. Pellets of 12 mm in diameter were prepared by uniaxial die compaction at a pressure of 180 MPa. The green pellets were sintered at 1350 °C and the densities of the sintered pellets were measured by water displacement method. The micrographs of the sintered pellets were taken in a scanning electron microscope (Model: SERON 2000). Distribution of the NiO and GDC phases in the sintered pellet was confirmed by energy dispersive X-ray spectroscopy (EDS) (Oxford make). Rectangular bar pellets of ~20 mm length and 6×6 mm² cross sectional area were prepared by cold compaction in a rectangular die pressing at a pressure of 180 MPa. The bar pellet was sintered at 1350 °C and treated in hydrogen atmosphere to facilitate reduction of NiO into metallic Ni. Electrical conductivity measurement of Ni-GDC bar specimen was carried out by dc four probe technique in hydrogen environment using a source meter. Microstructure of the reduced pellet was carried out by a SEM.

5.3 Results and Discussion

5.3.1 Synthesis and characterisation of fine NiO powder

In the synthesis of NiO powder, nickel nitrate and citric acid were taken in molar ratio 9:5 as per propellant chemistry. Nickel nitrate acts as an oxidiser and citric acid acts as
fuel to enable combustion reaction. TG-DSC graph of the dried gel-precursor in the combustion route is shown in Fig. 5.2. The initial mass loss in the range 80-200 °C is attributed to the loss of water molecules left in the gel. There was a sudden mass loss at 370 °C and an exothermic peak corresponding to the mass loss is an indicative of combustion reaction. After the combustion there is gain in mass as reflected in the TG pattern. The as-synthesized powder in the solution combustion route using citric acid as fuel was calcined at different temperatures. A minimum calcination temperature of 700 °C is required for phase formation as indicated in the X-ray diffraction pattern. The X-ray diffraction patterns of the as-synthesized powder and calcined powder are shown in Fig. 5.3. Peaks corresponding to NiO and metallic Ni phases are present in the XRD pattern of as-synthesized powder. This is attributed to the reducing environment prevailing in the combustion reactor. Initial Ni content in the as synthesized powder is converted to NiO leading to a mass gain in the TG-DSC graph. It may be noted that for taking right quantity of NiO powder to get NiO-GDC mix powder it is required to have single NiO phase in the powder. From the XRD pattern of the calcined powder it is observed that only NiO peaks are present. Therefore, calcination at 700 °C fully oxidises Ni particles that were present in the as-synthesized powder. Particle size distribution of calcined powder was measured by laser diffraction particle size analyzer and the median particle size is found to be 0.69 micron. From XRD line broadening the crystallite size has been calculated to be 7 nm. These results suggest that the calcined powder is agglomerates of nm size crystallites.
Fig. 5.2: TG-DSC pattern of gel precursor of NiO in the combustion method

Fig. 5.3: X-ray diffraction pattern of as-synthesized (black line) and calcined (red line)

NiO powder
The SEM micrograph of the calcined powder is shown in Fig.5.4. Submicron size agglomerates are observed in the SEM micrograph. The size of the agglomerate
corroborates the results obtained from laser diffraction particle size analyser. Though submicron size particles are observed in the SEM micrographs, finer details are not clear. Nano size primary particles are clearly observed in the TEM micrographs as shown in Fig. 5.5. The average size of the primary particles in the calcined powder is about 15 nm. These nano size particles are bound by weak van-der-waals force forming agglomerates that can break easily during compaction of powder.

5.3.2 Characterisation of NiO-GDC sintered pellet

Fig. 5.6 shows the scanning electron micrograph of the sintered NiO-GDC pellet. Two different phases are distinctly identified in the micrograph. One phase has networked structure of larger grains of size in the range of 1 to 2 µm. The grain size of other phase is relatively finer (<1 µm). The finer grains also form a networked structure. At some places the finer grains are present in agglomerated form. Pores are present in the microstructure and the porosity is 15% as measured by water displacement method. The porosity is expected to increase in the Ni-GDC cermet structure after reduction. In order to identify the phases in the composite structure EDS analysis has been carried out. It is observed from the micrograph that the GDC electrolyte particles have grown up to micron size though fine nano size particles are used as initial material. The EDS element scan of the NiO-GDC surface and the corresponding secondary electron micrograph is shown in Fig. 5.7. The element scans indicate that larger grains correspond to GDC phases and smaller grains are of NiO phase.
Fig. 5.6: SEM micrograph of NiO-GDC pellet sintered at 1250 °C

Fig. 5.7: EDS element scan of the NiO-GDC surface and the corresponding SE image
5.3.3 Characterisation of Ni-GDC cermets

The electrical conductivity of the Ni-GDC bar specimen measured by four probe DC technique is shown in Fig. 5.8. Metallic behaviour is observed in the conductivity plot, where conductivity decreases with increasing temperature. The electronic conductivity of GDC is very low compared to Ni in the cermet composition. Hence total conductivity is controlled by the conductivity of networked nickel phase in the anode. At temperatures below 400 °C conductivity value more than 1500 S.cm\(^{-1}\) has been obtained. The conductivity remains around 1200 S.cm\(^{-1}\) even at 800 °C which is the upper temperature limit of IT-SOFC operation. Ni coarsening has been addressed in the literature when Ni cermet is used for prolonged time. This leads to decrease in conductivity of the anode as well as reduces the triple phase boundary area. In the present study the conductivity has been measured at 800 °C for 72 h continuously. No appreciable decrease in the conductivity has been observed. Low temperature operation as well as uniform distribution of GDC phases prevents coarsening of nickel particles. The SEM micrograph of a sintered and reduced NiO-GDC pellet is shown in Fig. 5.9. More than 30% porosity was observed in the reduced pellet as confirmed from the water displacement data.
Fig: 5.8 Variation of conductivity with temperature of a reduced NiO-GDC bar pellet

Fig: 5.9 SEM micrograph of the reduced Ni-GDC pellet
5.4 Summary

Phase pure nano-size NiO powder has been prepared by gel combustion and subsequent calcination at 700 °C. NiO-GDC anode prepared by mixing combustion synthesized GDC and NiO powders followed by sintering at 1250 °C shows networked structure of both GDC and NiO phases. The electrical conductivity of Ni-GDC cermet is well above 1200 S.cm⁻¹ and the electrical conductivity is found to be stable over long time. The results suggest that Ni-GDC cermet prepared using nano-sized starting powder can form an anode structure having long term stability.