Structural Properties of NiO-CGO Composites Precursor Prepared via Combustion Synthesis Route

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Solution combustion technique was used for the preparation of NiO-CGO (Ceria Gadolinia Oxide) composites – a precursor to SOFC anode by mixing cerium nitrate, gadolinium nitrate and nickel nitrate in stoichiometric ratio of composition Ce0.90Gd0.10O1.95 - 0.40 NiO. The concentration of glycine, was varied between 0.5 mole% to 1.6 mole% and its effect was studied on the crystallite size and agglomerate of resulting NiO-CGO composite. The products formed were characterized by XRD, SEM and Particle Size Analysis. The results showed that the composite precursor varied in combustion characteristics, crystallite size and agglomerated particle size depending on the concentration of the fuel.

Key Words: cermet; NiO-CGO composites; SEM; SOFC; XRD.

INTRODUCTION

The anode of an SOFC must be stable in the reducing environment of the fuel, should be electronically conducting and must have sufficient porosity to allow the transport of the products of fuel oxidation away from the electrolyte/fuel electrode interface (Raymond *et al* 2004). The excellent catalytic properties of nickel-yittria stabilized zirconia (YSZ) for breaking hydrogen bonds, the low reactivity with other components and fairly low cost has led to its widespread use as anode. Ni-YSZ exhibits sufficient ionic conductivity at 900-1000°C, but it becomes ineffective and unattractive at lower temperature due to increase in bulk resistance.(Ringuede *et al* 2001).YSZ is also brittle in planar SOFCs and there is thermal mismatch of YSZ in stainless steel which exhibits appreciably large expansion than YSZ upon heating. (Koide H. 2000)

An alternative solid oxide fuel cell anode capable of efficient operation under methane and hydrogen and which avoids the problems, that the Ni-YSZ based cermet anode presents, is CeO_2 which exhibits both ionic and some electronic conduction under reduced conditions. Nevertheless, this material presents a drawback, which is a redox change in volume for ceria as a consequence of part of the present Ce^{4+} being reduced to Ce^{3+} due to release of oxygen from the lattice(Chavan *et al* 2007). By partially doping CeO_2 with 10 mol% Gd, this redox change in volume of ceria can be reduced to considerable extent. The Gd^{3+} doped ceria ceramics have been seen to have the highest conductivity due to the small association enthalpy between dopant cations and the oxygen vacancies in

the lattice. It has also been observed that doping CGO with transition metal like nickel, the sintering temperature of CGO decreases.

EXPERIMENTAL

AR grade Cerium Nitrate [$Ce(NO_3)_3.6H_2O$], Gadolinium Nitrate [$Gd(NO_3)_3.6H_2O$]and Nickel Nitrate [$Ni(NO_3)_2.6H_2O$] were mixed in stoichiometric ratio to prepare 500 ml of aqueous solution having a composition $Ce_{0.90}Gd_{0.10}O_{1.95}$ - 0.40 NiO. Metal Nitrates were employed both as metal precursors and oxidizing agents. The solution was divided into 5 equal 100ml samples. Amino acid glycine [NH_2CH_2COOH] as fuel was added to each of these five samples corresponding to 0.5 mole, 1.0 mole, 1.2 mole, 1.4 mole and 1.6 mole/ mole nitrate solution. The resulting clear and transparent green colored solution was heated on a hot plate and concentrated till gel formation took place. The viscous solution on further heating swelled and ignited automatically with a rapid evolution of large volume of gases producing highly voluminous powder.

The powder obtained after auto-ignition was calcined at 600°C for 3 hrs to remove traces of undecomposed glycine, nitrates (if any) and to obtain the chemically pure and well crystalline powder. The consolidated powder was sintered in the furnace at a temperature of 1100°C for 4 hrs. The powder after combustion was consolidated by uniaxial hydraulic press at 150 MPa pressure. The overall combustion reaction may be represented by

$$0.9\ Ce(NO_3)_3 + 0.1\ Gd(NO_3)_2 + 0.4\ Ni(NO_3)_2 + H_2NCH_2COOH + 5.90\ O_2 \rightarrow Ce_{0.9}Gd_{0.1}O_{1.95}\ \text{-}0.40\ NiO + 4\ CO_2 + 5\ H_2O + 2\ NO_2$$

X-ray diffraction (XRD) analysis was carried out on heat treated powders for crystalline phase identification and crystallite size determination at room temperature using a step scan procedure (0.02°/2θ step, time per step 0.5 or 1 s) in the 2θ range of 10° to 70° on a X-ray diffractometer (Model Bruker AXS, D-8 Advance, Switzerland) equipped with a crystal monochromatic employing Cu Kα radiation. Agglomerated particle size analysis of samples was determined by suspending the particles in glycerol (viscosity=1.850 cp and Index of refraction=1.45082) by means of dynamic light scattering using NICOMP 380ZLS (NICOMP particle sizing system, Santa Barbara, CA, USA). Microstructural analysis was carried out using a JEOL JSM-840A Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

The rate of auto-ignition was dependent on the concentration of glycine (fuel). The 1.2 mole glycine sample auto-ignited explosively forming highly voluminous product. The rate of auto-ignition decreased for both other fuel-deficient and fuel propellent ratios. The product formed for this glycine concentration was finest, light in color and had the maximum density for its

sintered pellet. Various characteristics of the samples prepared are given in table 1.

Table 1 Characteristics of NiO-CGO with variation in glycine concentration

S.No.	Glycine	Color before calcination	Color upon calcination	Density of sintered pellet
1	1.0	Brown	Light Brown	5.4477 g/cm^3
2	1.2	Light Brown	Creamish brown	6.1014 g/cm^3
3	1.4	Creamish brown	Off-white	4.5152 g/cm^3
4	1.6	Blackish brown	Brown	4.7093 g/cm^3

XRD study for both the uncalcined and calcined precursors of $Ce_{0.90}Gd_{0.10}O_{1.95}$ - 0.40 NiO having glycine concentrations of 1.0 mole glycine, 1.2 mole glycine, 1.4 mole glycine and 1.6 mole glycine/mole nitrate were done for crystallite size determination. Figure 1(a) and (b) shows the XRD patterns of uncalcined and calcined CGO precursor for different concentrations of glycine. The presence of cubic phases of ceria and NiO have been identified from (111) and (200) peak. Considerable peak broadening was observed which was due to very fine crystallite sizes. In each of the figures, (111), (200),(220), (311),(400)and (331) peaks are the characteristic peaks of CeO_2 and (220), (420), (422) peaks are characteristic peaks of NiO (Rosch B. *et al* 2004). The XRD patterns of both uncalcined and calcined samples show that with increasing glycine concentration, the sharpness of the XRD peaks increases resulting in an increase in the crystallanity of the product.
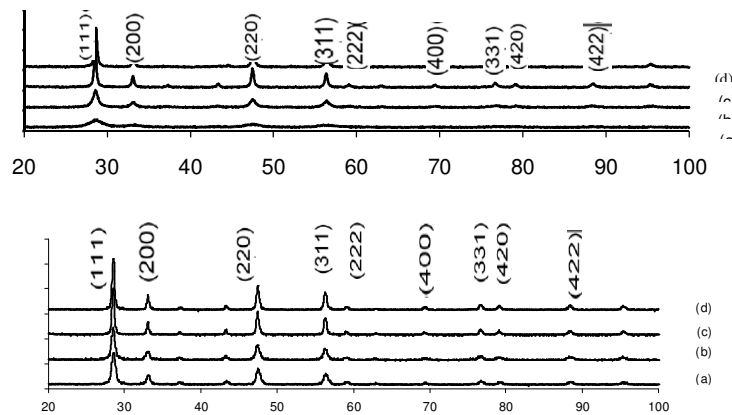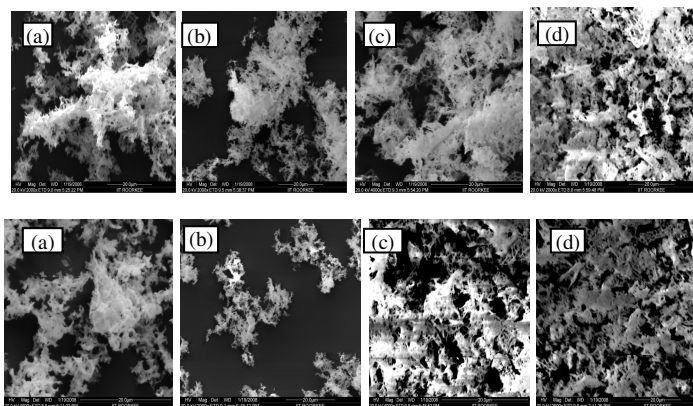

Fig1(a) and 1(b). XRD patterns of the uncalcined and calcined CGO precursor respectively with (a) 1.0 mole glycine (b) 1.2 mole glycine (c)1.4 mole glycine and (d) 1.6 mole glycine/mole nitrate

The crystallite size for both the uncalcined and calcined CGO samples was determined by X-ray line broadening using Scherrer formula. Table 2 gives the crystallite sizes alongwith agglomerated particle sizes as determined by NICOMP ZLS Particle size Analyzer.

Table 2: Crystallite size of Uncalcined and calcined NiO-CGO samples alongwith agglomerated Particle size

Samples	Crystallite Size (uncalcined) (Scherrer Equation)	Crystallite Size (Calcined) (Scherrer Equation)	Agglomerated particle size(Mean) NICOMP article Size Analyzer
1.0 mole	122.3nm	166.42nm	5.27µm
1.2 mole	26.72nm	153.25nm	6.39µm
1.4 mole	264.35nm	274.08nm	3.73µm
1.6 mole	255.32nm	224.80nm	4.82µm

It is evident that the crystallite particle size obtained was minimum for the uncalcined and calcined 1.2 mole glycine sample. Further, the synthesized samples had an average grain size of about 100 to 300 nm. A number of forces are responsible for the nanosize of the resulting powder. Before the reaction, all the reactants were uniformly mixed in solution at atomic and molecular level. During combustion, nucleation process may occur through the rearrangement and short-distance diffusion of nearby atoms and molecules. Large volume of gases evolves during the combustion reaction and the reaction occurs at a fast rate so that sufficient time and energy are not available for long- distance diffusion or migration of atoms and molecules which would result in the growth of crystallites (Virkar A.V. 2000). Consequently, the initial particle size is retained after the combustion reaction. It was observed that the agglomerated particle size is maximum for a 1.2 mole glycine sample which may be understood as the crystallite particle size decreases, the tendency towards agglomeration increases.

2(b).Scanning micrographs of uncalcined and calcined CGO precursor respectively with (a) 1.0 mole glycine (b) 1.2 mole glycine (c) 1.4 mole glycine and (d) 1.6 mole glycine/mole nitrate.

The Scanning electron micrographs of NiO-CGO precursors of both uncalcined and calcined composites are shown in fig 2(a) and fig 2(b) respectively. The prepared powders are highly porous and particles are linked together in agglomerates of different shapes and sizes. The particle size of samples calcined at 600°C increases, but the structure remains highly porous. It is

also evident from fig 2(a) and 2(b) that both for uncalcined and calcined NiO-CGO, visual appearance show that the pore size is small and the particles are agglomerated. The 1.2 mole uncalcined glycine sample photograph given in fig 2(a) shows very high degree of porosity. The particles are agglomerated to a larger extent due to reduction in the crystallite size. Upon calcination the porosity has increased a bit but the degree of agglomeration almost remains the same. For a fuel propellant ratio glycine concentration above 1.2 mole glycine, the micrographs depict that the particle void space has reduced with smaller agglomerated particle complexes and the porosity is decreased considerably. It was also be observed that the particles do not have a very firm structure.

Conclusions

$Ce_{0.90}Gd_{0.10}O_{1.95}$ - 0.40NiO a precursor to SOFC anode was synthesized for different concentrations of glycine (fuel) and a study of properties of the precursor so obtained was made for various concentration of fuel. The cermet obtained for 1.2 mole glycine/mole nitrate during combustion synthesis showed the most optimal properties. The solution with this concentration of fuel formed a very fluffy powder which erupted like a volcano. The pellets formed from this fuel concentration had maximum density under the same pelletizing pressure due to highly porous microstructure. The crystallite size revealed finest nano-crystalline particle size. Degree of agglomeration was maximum supported by its largest agglomerated particle size. The porosity for 1.2 mole glycine fuel concentration was maximum which would allow oxygen ions to diffuse through NiO-CGO composite and react in the triple points with hydrogen ions. Thus the NiO-CGO composite may be a promising alternative precursor for SOFC anode.

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