

Structural Properties of Anode Composites Precursor of A Solid Oxide Fuel Cell Prepared Via Combustion Synthesis Route

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Abstract - 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 to form a precursor of composition $Ce_{0.90}Gd_{0.10}O_{1.95}$ - 0.40 NiO. The concentration of oxidant i.e. glycine, was varied between 0.5 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 X-Ray Diffraction, Scanning Electron Microscope and Particle Size Analyzer. The results showed that the composite precursor varied in combustion characteristics, crystallite size and agglomerated particle size depending on the concentration of the fuel.

Keywords : Cermet, NiO-CGO composites, SEM, SOFC, XRD

I. INTRODUCTION

Solid oxide fuel cells (SOFC) are being considered as the premium power generation devices in the future as they have demonstrated high energy conversion efficiency, high power density, extremely low pollution, in addition to flexibility in using hydrocarbon fuel. The anode i.e. the fuel electrode 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 [9]. The excellent catalytic properties of nickel-yttria 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. Although, yttria stabilized zirconia (YSZ) exhibits sufficient ionic conductivity at 900-1000°C, such a high temperature requires expensive materials for interconnects, resulting in high operating cost and accelerate degradation of fuel cell system. It is therefore desirable to lower the operating temperature to intermediate temperature [1].

Ni-YSZ becomes ineffective and unattractive at lower temperature due to increase in bulk resistance. Moreover YSZ is brittle in planar SOFCs and also there is thermal mismatch of YSZ in stainless steel which exhibits appreciably large expansion than YSZ upon heating [7]. Using other type of anode with higher oxide ionic conductivity to increase SOFC performance is a possibility at reduced operating temperature (500°C-800°C). Therefore, some alternative anodic material must be developed that can replace YSZ.

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 and can be used as anode without forming a composite. 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 [10]. 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.

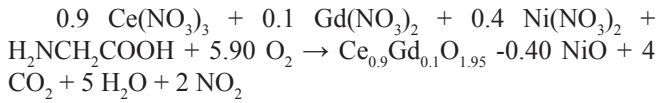
II. EXPERIMENTAL

A. Powder Synthesis

AR grade Cerium Nitrate [$Ce(NO_3)_3 \cdot 6H_2O$], Gadolinium Nitrate [$Gd(NO_3)_3 \cdot 6H_2O$] and Nickel Nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] 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/mole nitrate, 1.0 mole/ mole nitrate, 1.2 mole/ mole nitrate, 1.4 mole/ mole nitrate and 1.6 mole/ mole nitrate. 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 temperature of 600°C was chosen as the minimum required temperature for calcinations, as below this temperature some carbon may be still left. An additive (pore-former) is generally added to the precursor during consolidation, which is removed on heating. The traces of carbon which may be present in the sample would itself work as pore former. The powder after combustion was consolidated by uniaxial hydraulic press at 150 MPa pressure. The consolidated powder was sintered in the furnace at a

temperature of 1100°C for 4 hrs. The overall combustion reaction may be represented by:



B. Characterization

X-ray diffraction (XRD) analysis was carried out on heat treated powders for crystalline phase identification and crystallite size determination. Powder XRD patterns were recorded 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). Prior to analysis, a thin layer of Pt or carbon was evaporated onto the SEM specimens for electrical conductivity.

III. 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 propellant 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 I.

XRD study for both the uncalcined and calcined precursors of Ce_{0.90}Gd_{0.10}O_{1.95} - 0.40 NiO obtained from combustion synthesis having glycine concentrations of 1.0 mole glycine/mole nitrate, 1.2 mole glycine/mole nitrate, 1.4 mole glycine/mole nitrate and 1.6 mole glycine/mole nitrate were done for crystallite size determination. Figure 1(a) and 1(b) shows the XRD patterns of uncalcined and calcined CGO precursor for different concentrations of glycine. In figure 1(a) and 1(b), 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 CeO₂ and (220), (420), (422) peaks are characteristic peaks of NiO [9]. The XRD patterns of both uncalcined and calcined samples show that with increasing glycine concentration, the sharpness of the XRD peaks increases. Thus with an increase in the glycine concentration, the crystallinity of the product also increases.

The crystallite size for both the uncalcined and calcined

TABLE I CHARACTERISTICS OF NiO-CGO WITH VARIATION IN GLYCINE CONCENTRATION

S.No.	Glycine	Nitrate	g/n	Color before calcination	Color upon calcination	Density of sintered pellet
1	0.5	2.6	0.1923	Dark Brown	Brown	5.927g/cm ³
2	1.0	2.6	0.3486	Brown	Light Brown	5.4477 g/cm ³
3	1.2	2.6	0.4615	Light Brown	Creamish brown	6.1014 g/cm ³
4	1.4	2.6	0.5385	Creamish brown	Off-white	4.5152 g/cm ³
5	1.6	2.6	0.6154	Blackish brown	Brown	4.7093 g/cm ³

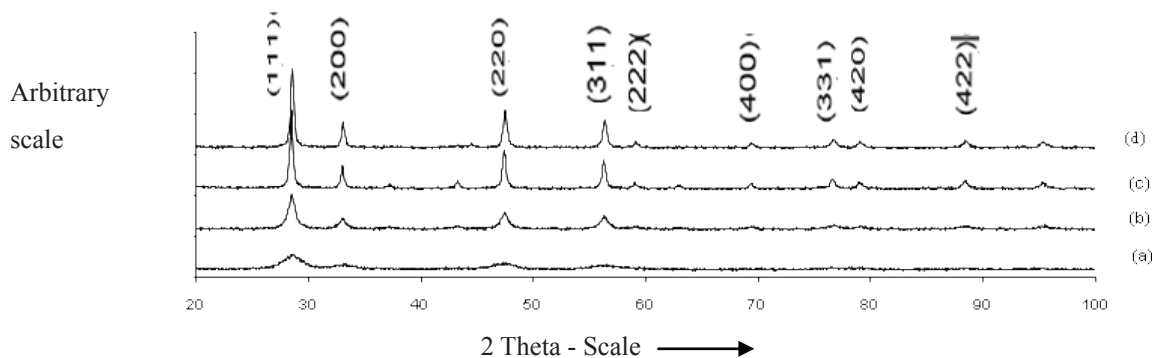


Fig. 1(a) XRD patterns of the uncalcined CGO precursor by combustion synthesis with (a) 1.0 mole glycine/mole nitrate (b) 1.2 mole glycine/mole nitrate (c) 1.4 mole glycine/mole nitrate and (d) 1.6 mole glycine/mole nitrate

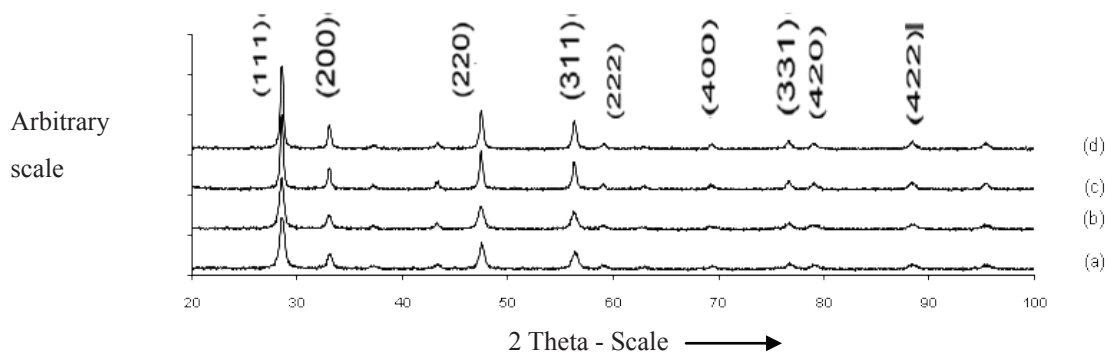


Fig.1(b) XRD patterns of the calcined CGO precursor by combustion synthesis with (a) 1.0 mole glycine/mole nitrate (b) 1.2 mole glycine/mole nitrate (c) 1.4 mole glycine/mole nitrate and (d) 1.6 mole glycine/mole nitrate

TABLE II 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 Particle Size Analyzer
1.0 mole glycine	122.3nm	166.42nm	5.27 μ m
1.2 mole glycine	26.72nm	153.25nm	6.39 μ m
1.4 mole glycine	264.35nm	274.08nm	3.73 μ m
1.6 mole glycine	255.32nm	224.80nm	4.82 μ m

CGO samples was calculated by X-ray line broadening using Scherrer formula. The crystallite sizes of uncalcined and calcined NiO-CGO samples alongwith agglomerated particle sizes as determined by NICOMP ZLS Particle size Analyzer are given in Table II.

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 [11]. 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. The reason for this agglomerated particle size may be understood as the crystallite particle size decreases, the tendency towards agglomeration increases. Therefore the size of agglomerated particle was maximum for the 1.2 mole glycine/ mole nitrate sample.

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. It is evident from the figures that the prepared powders are highly porous and particles are linked together in agglomerates of different shapes and sizes. Also, substantial particle growth

is observed upon calcination of samples for 3 h at 600 °C or higher temperatures. The particle size of samples calcined at 600°C increases, but the structure remains highly porous.

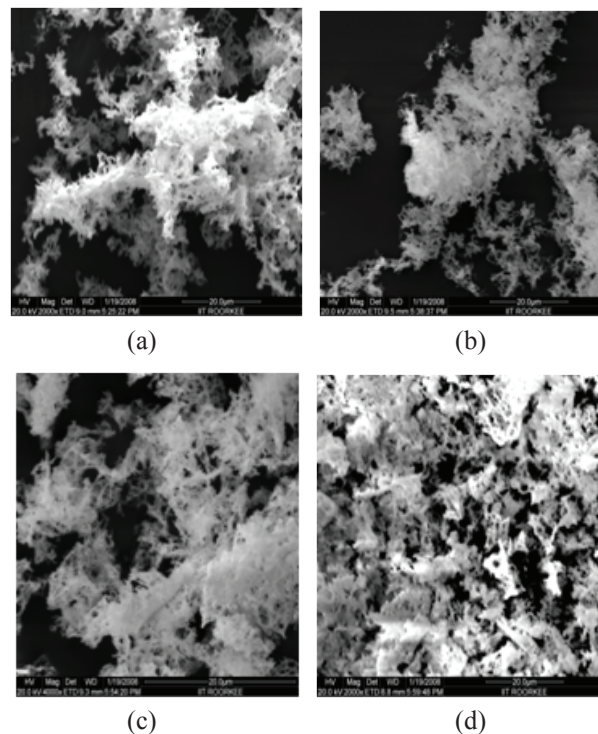


Fig. 2(a) Scanning micrographs of uncalcined CGO precursor by combustion synthesis with (a) 1.0 mole glycine/mole nitrate (b) 1.2 mole glycine/mole nitrate (c) 1.4 mole glycine/mole nitrate and (d) 1.6 mole glycine/mole nitrate.

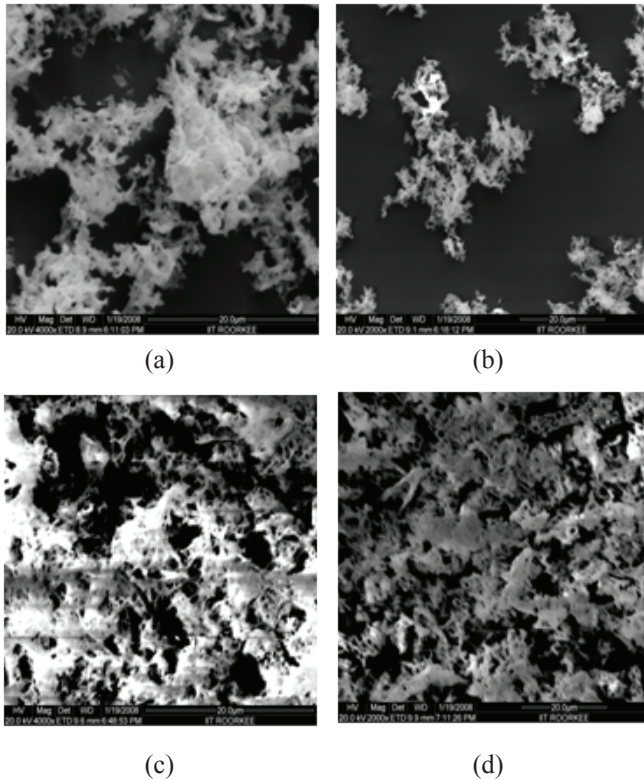


Fig. 2(b) Scanning micrographs of calcined CGO precursor by combustion synthesis with (a) 1.0 mole glycine/mole nitrate (b) 1.2 mole glycine/mole nitrate (c) 1.4 mole glycine/mole nitrate and (d) 1.6 mole glycine/mole nitrate

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. With 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 observed that the particles do not have a very firm structure.

IV. 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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