

Electrical characterization of NiO-CGO composites- SOFC anode precursor- prepared via combustion synthesis route

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Abstract: A precursor to SOFC anode was made via solution combustion technique that is NiO-GDC (Gadolinia doped Ceria) composites by mixing nitrates of cerium, gadolinium and nickel in stoichiometric ratio of composition to form the final precursor product as $Ce_{0.90}Gd_{0.10}O_{1.95}$ - 0.40 NiO. The fuel for the combustion synthesis that is glycine's concentration was varied between 0.5 mole% to 1.4 mole%. The temperature of the resultant sintered pellets was varied between 30 to 800°C and electrical properties of the NiO-CGO composite was studied by means of admittance plots between conductivity & susceptance. The results showed that the composite precursor varied in conductivity and activation energy depending on the concentration of the fuel.

Keywords: Cermet, NiO-CGO composites, SOFC, Electrical conductivity

I. LITERATURE REVIEW

Various techniques are available for the preparation of nanomaterials include methods such as Laser abrasion, Plasma synthesis, Chemical vapor deposition, Mechanical alloying or High-energy milling and Sol-gel synthesis. All these techniques are involved, require special chemicals and equipments. Solution combustion method involves low temperature initiated, self-propagating, gas producing combustion technique. Solution combustion method have been previously being used for preparation of nanosize alumina, yttria, zirconia, CeO_2 - ZrO_2 , t - ZrO_2 - Al_2O_3 and Y_2O_3 - ZrO_2 etc. using corresponding metal nitrate, ammonium nitrate and glycine redox mixtures in stoichiometric amounts. Stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valencies of the oxidizer and the fuel keeping the Oxidiser/Fuel ratio close to unity. The process is fast (instantaneous) and yields high purity, homogenous crystalline products with desired composition and structure.

The anode is the part of the SOFC that has main focus in this research work. 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. The reducing conditions present on the fuel side of a SOFC permit the use of a metal such as nickel as the fuel electrode. 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. However there exist several problems when nickel-Yttria stabilized zirconia is used as anode material.

In high temperature SOFC, the state of the art material yttria stabilized zirconia (YSZ) exhibits sufficient ionic conductivity at 900-1000°C. This high temperature requires expensive materials for interconnects and also due to high operating temperatures results in high operating cost and accelerate degradation of fuel cell systems. It is therefore desirable to lower the operating temperature to intermediate temperature. But as the operating temperature is lowered the ionic conductivity of the anode decreases resulting in a rapid deterioration of the performance of SOFCs.

Conventional SOFC based on NiO-YSZ electrode although has adequate ionic conductivity above 700°C,

becomes ineffective and unattractive at lower temperature due to increase in bulk resistance. More-over YSZ is brittle in planar SOFCs; there is thermal mismatch of YSZ in stainless steel which exhibits appreciably large expansion than YSZ upon heating. 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.

Ceria based anode have been acknowledged to be the most promising anode for intermediate temperature (500°C-800°C) SOFC since its ionic conductivity is higher than that of YSZ at intermediate temperature range. The Gd^{3+} doped ceria ceramics have been seen to have highest conductivity due to smallest 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 in the conventional sintering. With this objective Nano- Nickel Oxide- Gadolina doped Ceria was synthesized by solution combustion method and its properties were studied as a precursor to SOFC anode [1].

II. INTRODUCTION

Solid oxide fuel cells (SOFCs) are of two types: high temperature SOFCs and low temperature or intermediate temperature SOFCs (i.e. IT-SOFCs). The problem encountered in commercializing HT-SOFC has motivated researchers to develop materials that could allow the SOFC operation at intermediate temperatures. Various groups around the world are involved in developing cathode, anode and electrolyte materials for IT-SOFC. For IT-SOFC, the anodic material must have high ionic conductivity at comparatively lower temperature.

The conventional YSZ ($Y_2O_3-ZrO_2$) anode shows the required ionic conductivity (i.e. $0.001 S\text{-cm}^{-1}$) at 1000°C; hence, it requires a higher operating temperature. In order to reduce the operating temperature, two approaches are widely applied. The resistance of dense anode membranes is decreased by decreasing thickness of the traditional YSZ electrolyte or using alternative materials of higher ionic conductivity at comparatively lower temperatures (Mogensen et al 2000; Singhal 2000; Steele 2000). An alternative SOFC anode capable of efficient operation under methane and hydrogen uses CeO_2 which exhibits both ionic and some electronic conduction under reduced conditions and thereby avoids the problems Ni-YSZ based cermet anode. Nevertheless, this material presents a drawback, which is a redox change in volume for ceria as a consequence of partial reduction of Ce^{4+} to Ce^{3+} due to release of oxygen from the lattice. By partially doping CeO_2 with 10 mol% Gd, this redox change in volume of ceria can be reduced to a considerable extent. The Gd^{3+} doped ceria ceramics have the highest conductivity due to the low 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 decreases [2].

Cerium Gadolinium oxide (CGO) is one of the most promising anode for SOFCs to be operated below 650°C [3]. In view of the various advantages over the conventional electrolytes, YSZ and recently developed BICUMVOX material, it is planned to develop gadolinium doped ceria oxide as an SOFC anode. Various synthesis and processing methods have been used to prepare doped ceria with desired properties, including hydrothermal synthesis, homogeneous precipitation, sol-gel process [3]. Further, glycine-nitrate process (GNP) a simple and cost-effective method, is often adopted to prepare bulk electrolyte materials [4] and cathode samples. In the present paper, the preparation of $Ce_{0.90}Gd_{0.10}O_{1.95} - 0.40 NiO$ as anode via combustion synthesis route has been done. After sintering at 1100°C [5], the electrical properties of the composite have been studied and the effect of varying glycine concentration has been evaluated.

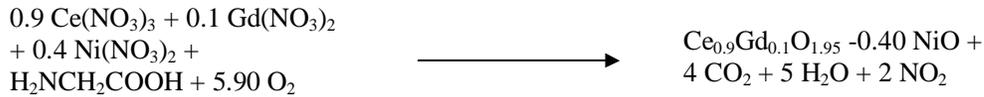
III. EXPERIMENTAL

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 400 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 4 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 and 1.4 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 overall combustion reaction may be represented by



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 uni-axial hydraulic press at 150 MPa pressure. The pellets sintered at 1100 °C, were polished and electroded with silver paste on both sides. Then the pellets were heated at temperature 900°C for 12 hrs for better adhering of silver paste on the surface of pellets. The conductivity measurements were made by complex impedance spectroscopy method in the frequency range 100Hz to 5 MHz using LCR METER (HIOKI 3532-50 LCR Hi TESTER, Japan). In these measurements the temperature was varied from room temperature to 800°C the variation of temperature was ±1°C. The experimental arrangement used is shown in fig.1.

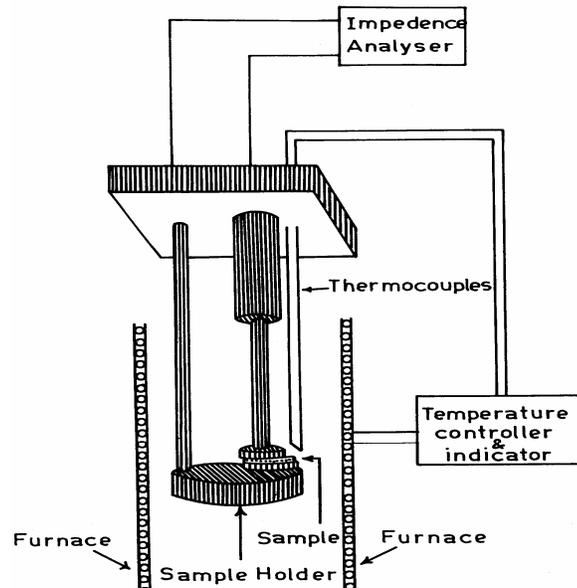


Fig 1: Experimental set-up for electrical conductivity measurement

IV. 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 1.

S. No.	Glycine	Nitrate	fuel/oxidant	Color before calcination	Color upon calcination	Density of sintered pellet (g/cc)
1	0.5	2.6	0.1923	Dark Brown	Brown	5.927
2	1.0	2.6	0.3486	Brown Light	Brown	5.4477
3	1.2	2.6	0.4615	Light Brown	Creamish brown	6.1014
4	1.4	2.6	0.5385	Creamish brown	Off-white	4.5152

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

In complex impedance spectroscopy, a low amplitude a.c. signal (sinusoidal) is applied to the cell consisting of the solid Anode. The real and the imaginary parts of the impedance/admittance are measured over a wide frequency range. The impedance (Z) / admittance (Y) is a complex quantity and can be written as

$$Z(\omega) = Z'(\omega) - jZ''(\omega)$$

and $Y(\omega) = 1/Z(\omega) = G(\omega) + jB(\omega)$

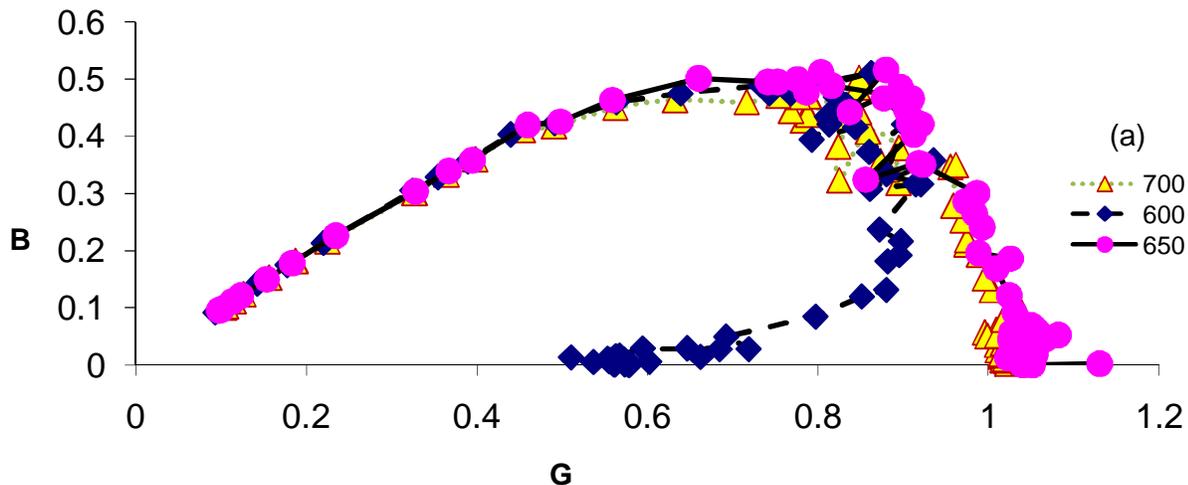
where Z' and Z'' are the real and imaginary parts of the impedance, G is the conductance, and B the susceptance. Two semi-circles or arcs can be obtained in the admittance plots of the samples at various temperatures, one at lower frequencies and the other at higher frequencies. The intercept of the lower frequency semi-circle gives the value of dc conductance (G_{dc}) whereas the intersection of the lower and the higher frequencies semi-circles on the G-axis gives the value of the bulk conductance (G_{bulk}). The blocking conductance (G_{block}) at the grain boundaries is obtained from the following relation:

$$G_{block} = G_{bulk} - G_{dc}$$

Since the admittance plot of the 1.4 mole glycine/mole nitrate sample could not be obtained in proper shape, therefore it has not been considered for further analysis. The admittance plots for 0.5, 1.0 and 1.2 mole fr. fuel/oxidant are shown in the fig2.

The Conductivity corresponding to σ_{dc} , σ_{bulk} , σ_{block} have been found by

$$\sigma = G \times (l/A)$$



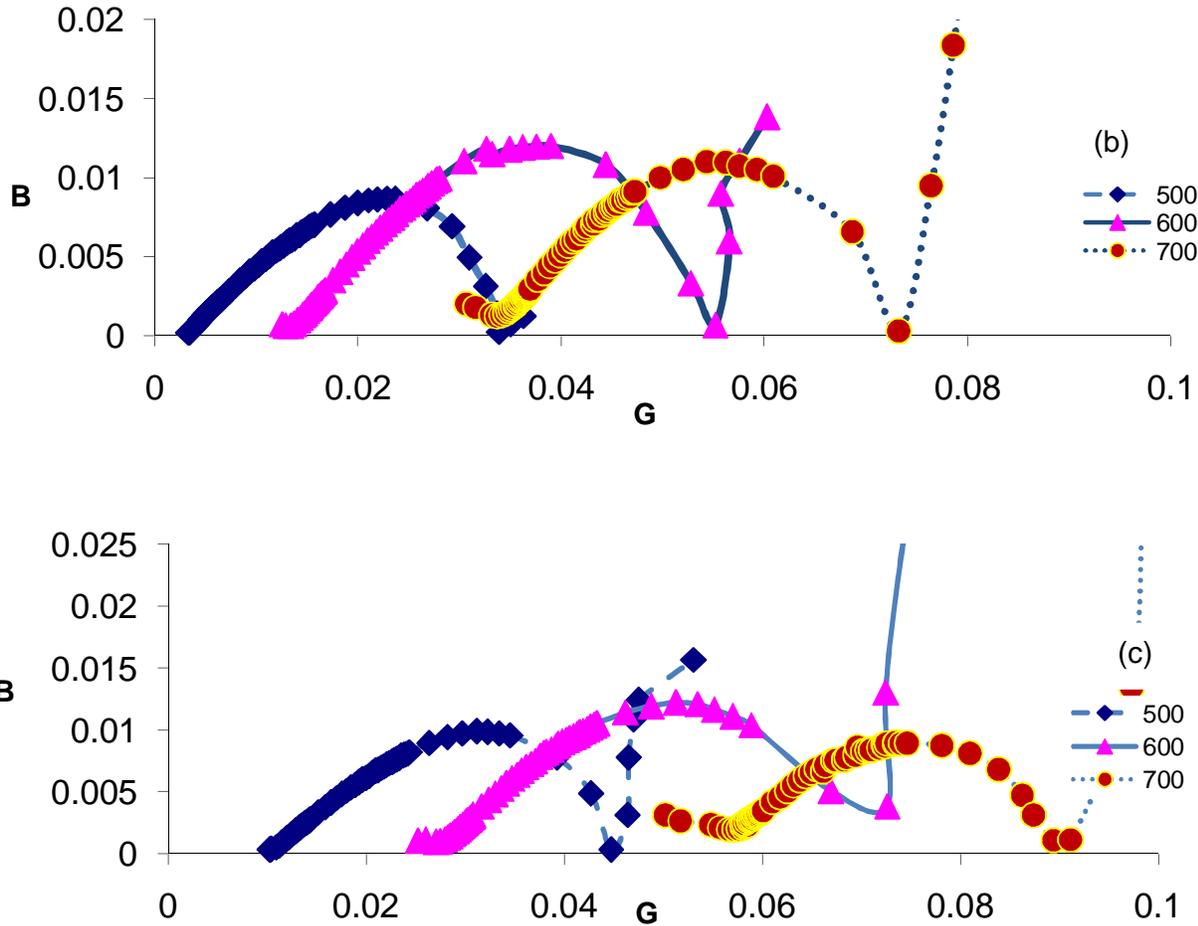


Fig2. Admittance plots for (a) 0.5 mole fr. fuel/oxidant (b) 1.0 mole fr. fuel/oxidant (c) 1.2 mole fr. fuel/oxidant

The temperature variations of σ_{dc} , σ_{bulk} , σ_{block} for all the different samples is obtained by plot between $\ln \sigma_{dc}$, σ_{bulk} , σ_{block} vs. $1000/T$ as shown in fig 3. From the figure, two distinct variations of activation energy with temperature can be seen, one in the temperature range of 623K to 848K and the other in 848K to 1073K. From the slopes of graphs, the activation energies for the various samples were calculated from the following formulas:

$$\begin{aligned} \sigma &= \sigma_0 \exp[-(E_a/kT)] \\ \ln \sigma &= \ln \sigma_0 - (E_a/1000k) \times (1000/T) \\ \text{Slope} &= - (E_a/1000k) \\ E_a &= - (\text{slope}) \times 1000k \end{aligned}$$

where k is the boltzman's constant (8.616×10^{-5} eV/K.) and E_a is the activation energy.

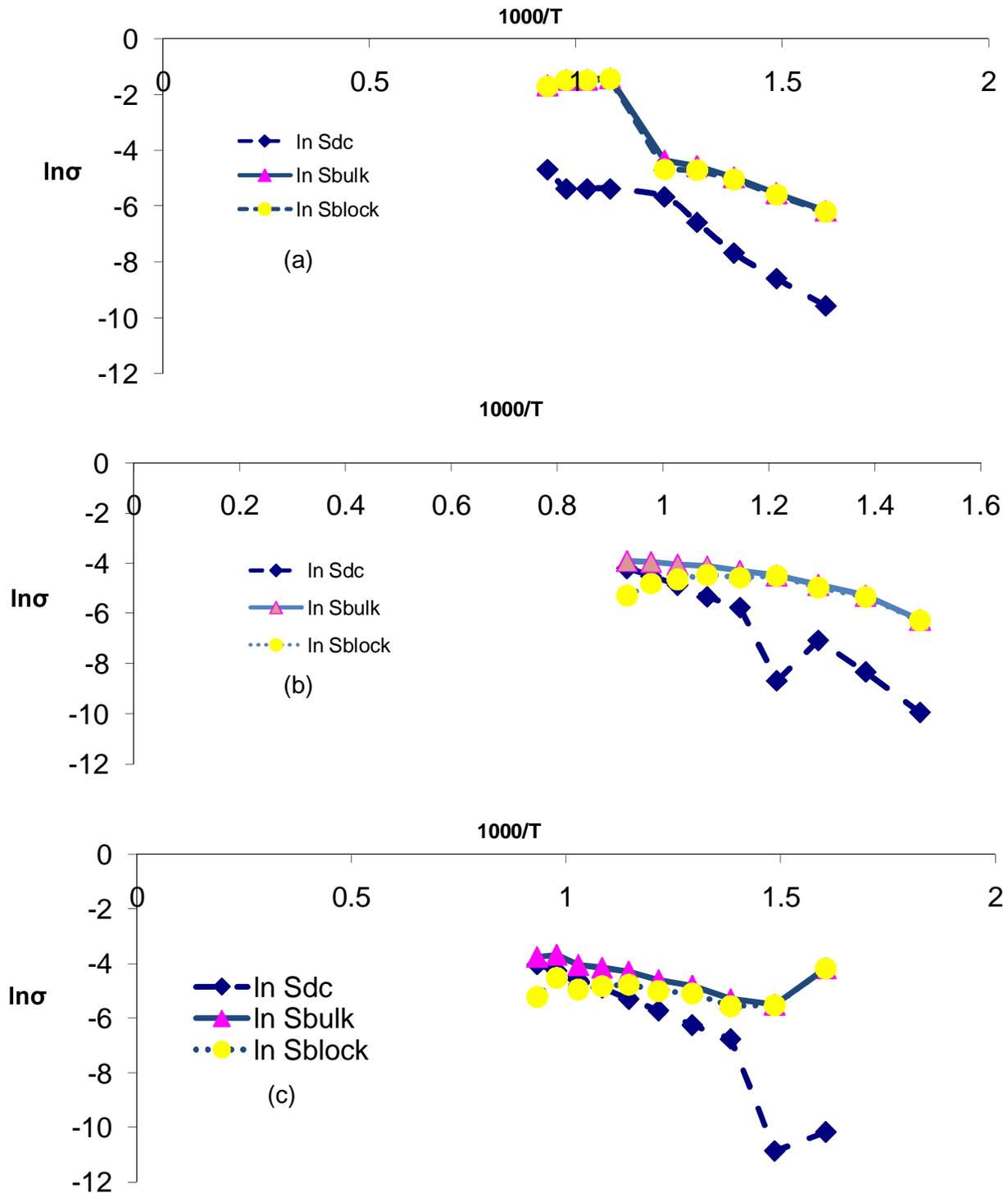


Fig3. Activation energy by plots between $\ln \sigma$ and $1000/T$ for (a) 0.5 g/n (b) 1.0 g/n (c) 1.2 g/n

From the graphs between $\ln \sigma$ vs $1000/T$ activation energies for different samples for dc and bulk for two typical temperature ranges is summarized in table 2 below.

Sample	Temperature Range	Activation Energy (dc) Ea(electron Volts)	Activation Energy (bulk) Ea(electron Volts)
0.5 mole glycine	623K - 848K	2.28324	1.63704
	848K- 1073K	0.47388	0.99084
1.0 mole glycine	623K - 848K	1.1750	1.98168
	848K- 1073K	0.62662	0.68928
1.2 mole glycine	623K - 848K	0.60312	1.33548
	848K- 1073K	0.17232	0.15385

Table 2 Activation energy dc and bulk for different samples for the two temperature ranges

V. CONCLUSIONS

$Ce_{0.90}Gd_{0.10}O_{1.95} - 0.40 NiO$ - a precursor to SOFC anode - was synthesized for different concentrations of glycine (fuel) and a study of properties of the precursor so obtained was compared for various concentration of fuel. The combustion characteristics of the solution of nitrates during synthesis step was dependent on glycine (fuel). The solution with 1.2 mole glycine/mole nitrate burnt explosively forming a very fluffy product which erupted like a volcano. A large volume of reddish-brown gas (NO_2) was evolved. The pellets formed for 1.2 mole glycine/mole nitrate had maximum density under same pelleting pressure due to highly porous microstructure.

Electrical conductivity was measured from admittance plots which reveal that 1.2 mole glycine/mole nitrate has the best electrical conductivity for both dc and bulk. However, with increasing temperature the difference in electrical conductivity was reduced and the conductivity was nearly constant with increasing glycine concentration in most compositions above $500^\circ C$. The graphs for activation energy variation with temperature show that 1.2 mole glycine sample possesses the lowest activation energy for a given frequency for both dc as well for bulk. Therefore making a practical SOFC Anode 1.2 mole glycine per mole nitrate can be used to synthesize NiO on CGO.

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