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CHARACTERIZATION OF NiO-YSZ NANOCOMPOSITE SYNTHESIZED BY COMBUSTION METHOD

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Abstract

Homogeneous mixture of nanocrystalline powder of NiO–YSZ composite is preferred as the precursor of Ni-YSZ anode in solid oxide fuel cell. Combustion synthesis is an economically viable technique for the preparation of advanced ceramics and nano-materials. In present work, Nickel Oxide–Yttria stabilized Zirconia (NiO–YSZ) composite of composition, mNiO–(1–m) $Zr_{0·9}Y_{0·1}$ $O_{1·95}$ (m = 0·4), was successfully synthesized by combustion process using glycine as fuel and nitrate as oxidizer. The study of prepared Nano-composites has been done by DTA-TGA and FTIR to determine the powder properties.

Keywords

Anode, NiO-YSZ, Combustion Method, FTIR, TGA-DTA.

1. INTRODUCTION

A solid oxide fuel cell (SOFC) is an electrochemical device that converts chemical energy of a fuel and an oxidant gas (air) directly into electricity [1-2]. It has high operating temperature of about 600°C-1000°C [3]. Main components of SOFC are electrolyte, cathode, anode and interconnect. Fuel such as hydrogen is brought into the anode side and an oxidant, usually oxygen, into the cathode side. This oxygen is reduced to oxygen ions and migrats through the electrolyte via ionic conduction to the anode. At the anode side these oxygen ions combine with the hydrogen and produce water and electrons [4-5]. Solid oxide fuel cells have many advantages over other types of fuel cells such as high energy conversion efficiency, low emission of pollutants, and fuel flexibility which makes it a suitable alternative of non-renewable energy resources [2, 6].

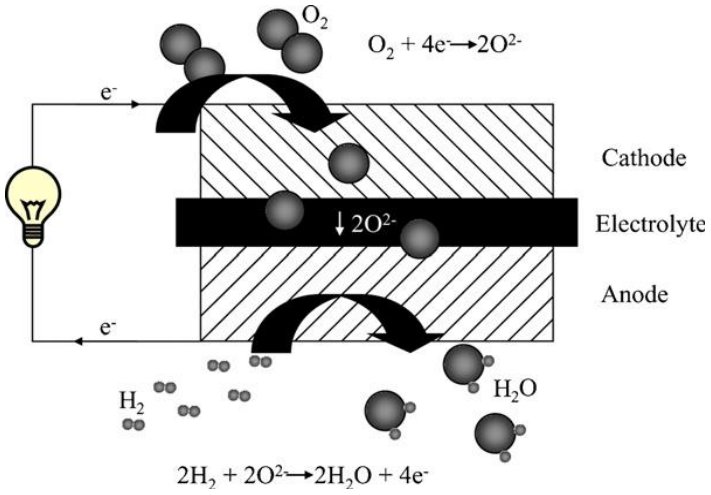


Figure 1: Schematic diagram of SOFC with its working principle [7].

Different materials used for anode are CeO_2 (rare-earth doped), Doped $SrTiO_3$, $La_{0.7}Sr_{0.3}Cr_{0.8}Ti_{0.2}O_3$, $La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3$, Ni–YSZ etc., but Ni/YSZ cermet is still the most preferred anode material. An anode must have high electrical conductivity, good adherence to other cell components, high electrochemical or catalytic activity, and high porosity [1-2, 8-9]. Ni/YSZ cermet satisfies these conditions. Ni-YSZ consists of three different phases such as: a metallic Ni, an YSZ ceramic and pores resulting in very complicated structural features. Nickel acts as an electron conductor and the catalyst for the anode reactions. The functions of YSZ are to support the nickel-metal particles, and to provide an anode the thermal expansion coefficient that acceptably close to those of the other cell components [10-12]. It is reported that the volume % of Ni must be in the ratio between 40%-60% to achieve high conductivity, good porosity and mechanical strength [2, 6, 8, 12-13]. The finer microstructure of Ni-YSZ consisting of uniformly arranged Ni, YSZ and pore phases would result in increase in Triple Phase Boundary (TPB) and better electrochemical performance [9, 14-15].

Ni–YSZ porous cermets for SOFCs are conventionally prepared by reduction of NiO–YSZ ceramic composites [16]. The different methods of preparation of NiO-YSZ nano-composite are: Sono-chemical preparation [17], Co-precipitation [18], Electro-less co-deposition [13, 19], Hydro-thermal synthesis [20], Spray pyrolysis [21-22], Tape casting [5, 15, 23], Combustion synthesis [24-27] etc. Among these methods the combustion synthesis is a low cost and simple technique providing homogeneous powder with nanometric and submicronic particles, with high specific surface area [24, 28]. The present work reports the synthesis of homogeneous NiO-YSZ powders by combustion method using different ratio of fuel.

2. EXPERIMENTAL

Chemicals such as Yttrium Oxide (Y_2O_3, CDH, New Delhi), Zirconyl Nitrate hydrated ($ZrO(NO_3)_2.xH_2O$, CDH, New Delhi), Nickel Nitrate Hexa-hydrate ($Ni(NO_3)_2.6H_2O$, CDH, New Delhi) are used as metal nitrates, Glycine (GR) (H_2NCH_2COOH, LOBA Chemie, Mumbai) is used as fuel, Nitric Acid (HNO_3) and distilled water are used in the combustion process. All the chemicals were dissolved in distilled water in the stoichiometric ratio that the resultant solution can produce NiO-YSZ of composition $mNiO–(1–m)\ Zr_{0·9}Y_{0·1}\ O_{1·95}$ (m = 0·4). Three batches of solutions were made. The amount of glycine corresponding to 0.8 mol of solution to first batch, 1.1 mol of solution to second batch and 1.2 mol of solution was added to third batch of the solution. The resulting solutions were stirred on magnetic stirrer until clear green solutions were obtained. This green solutions were heated on hot plate until all the solvent was evaporated then the combustion took place just like volcanic eruption shown in figure 2 yielding very fine and porous NiO-YSZ powder. During combustion reaction of zirconium nitrate and glycine, gases such as NO_2, N_2, H_2O and CO_2 are produced. The complete combustion reaction can be represented as [29]:

$$5Zr(NO_3)_4 + 8H_2NCH_2COOH \rightarrow 5ZrO_2 + 8CO_2 + 20H_2O + 15NO_2 + 13/2N_2$$ [29]

Figure 2: Combustion of NiO-YSZ powder.

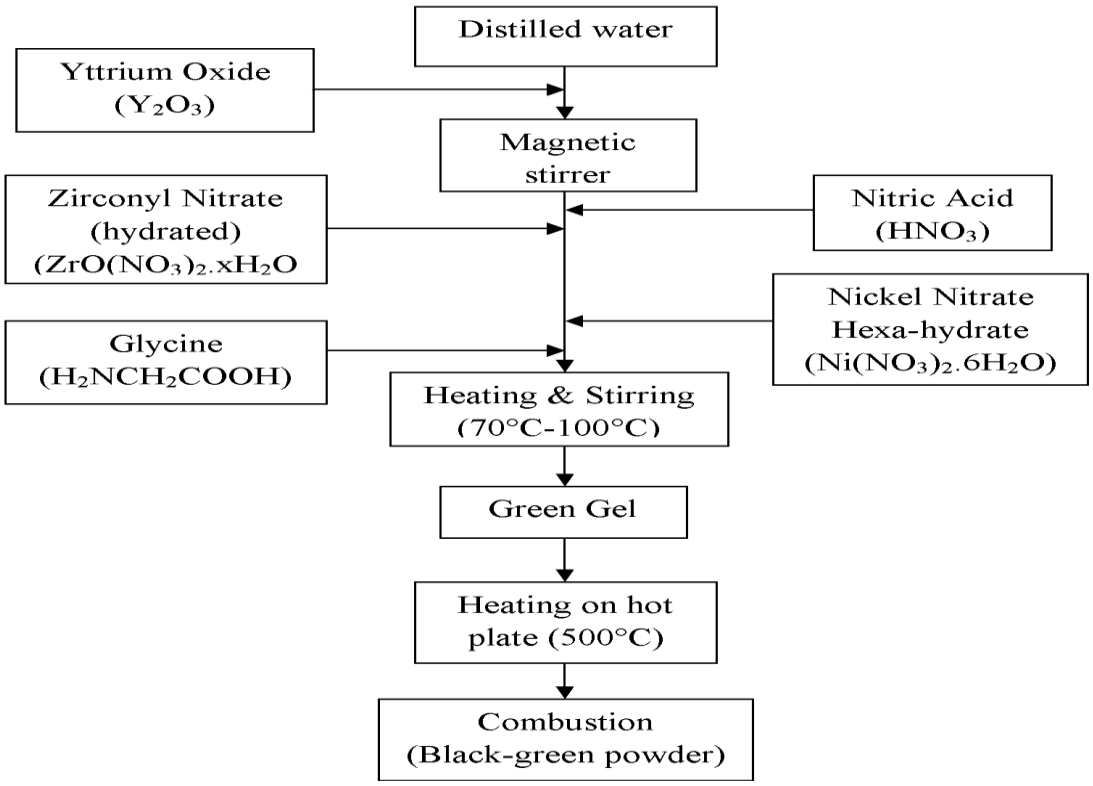


Figure 3: Combustion Synthesis Process

The prepared powder is calcined at 700°C for 6 hours. The study of prepared powder and calcined powder has been done FTIR and DTA-TGA.

3. RESULTS & DISCUSSIONS

Spectral measurements were carried out by using a FTIR spectrometer that was operated in the transmittance mode (%T). Spectra were acquired with resolution over the wave number range of 400-3500 cm-1. FTIR spectrum of uncalcined and calcined powder with glycine 0.8 mol, 1.1 mol and 1.2 mol are shown in figure 4 and 5 respectively. FTIR analysis was used to investigate the chemical and structural changes that take place during the combustion process. Figure 4 shows the amount of unburnt carbon is more in product obtained with 1.2 mol glycine as compare to that of product obtained with 0.8 mol glycine and 1.1 mol glycine, which is due to incomplete combustion of fuel.

The two sharp peaks between 2700 and 3000 cm^{-1} are attributed to vibrations involving $–CH_2$ and $–CH_3$ groups. The intensity of the same peaks is diminished after the calcination process as shown in figure 5 [17]. The absorption bands at 1380 cm^{-1} and 822 cm^{-1} corresponds to the $NO^{-3}$and ZrO^{2+} ions, respectively. The vibration of glycine NH_2 group is

the cause of absorption bands at about 1100 cm^{-1}. The absorption bands at about 1620 cm^{-1} and 1750 cm^{-1} corresponds to the deformation vibration of NH_2 and stretching vibration of C=O [28]. Large amount of carbonate species are present in the powder as can be seen from the absorption in the spectral region from 1200cm^{-1} to 1700 cm^{-1}. By comparing figures 4 and 5, it is clearly seen that the amount of carbon is diminished due to calcination process [28, 30]. The absorption peak of the Ni-O vibration is at 410 cm^{-1} [17].

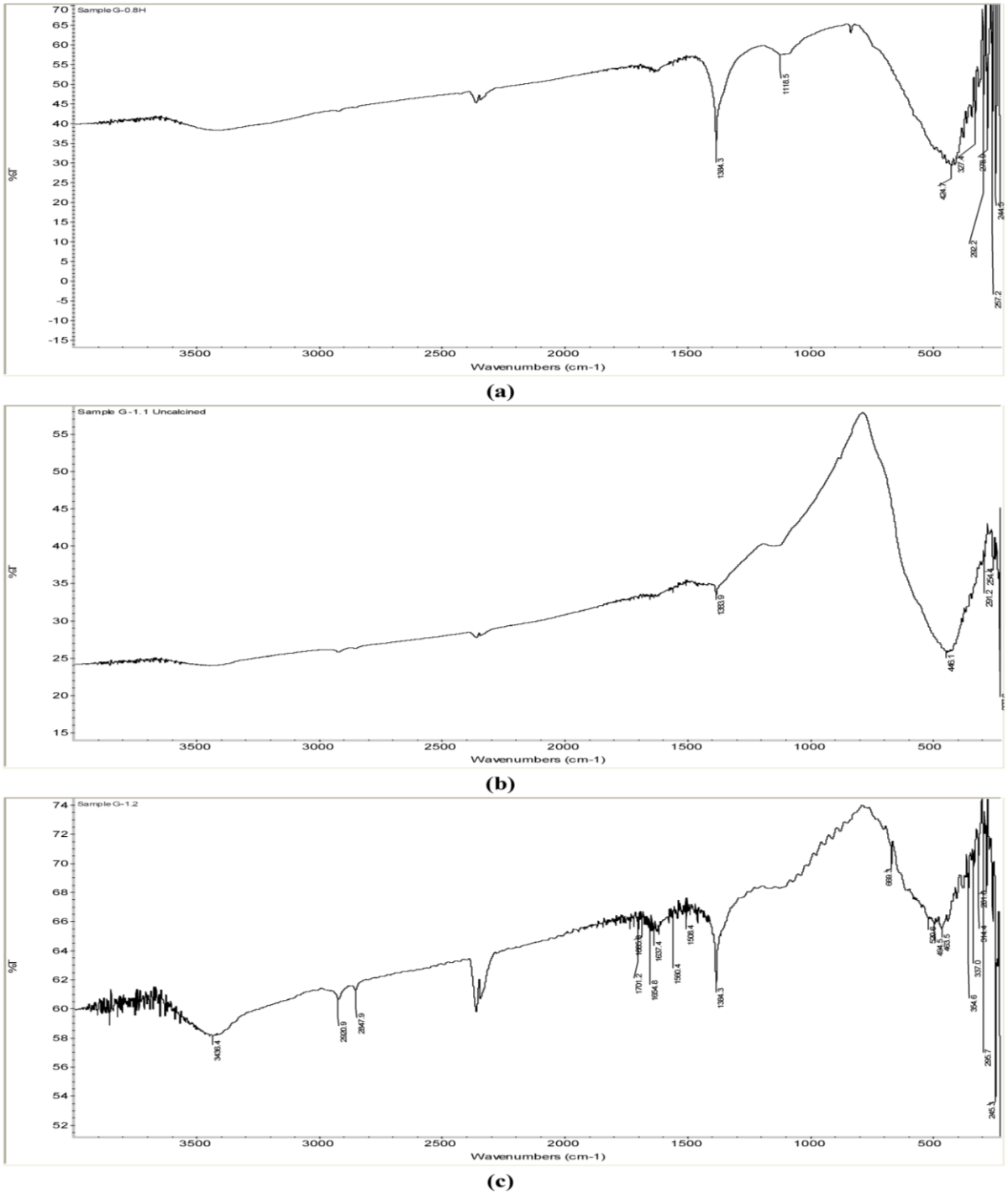
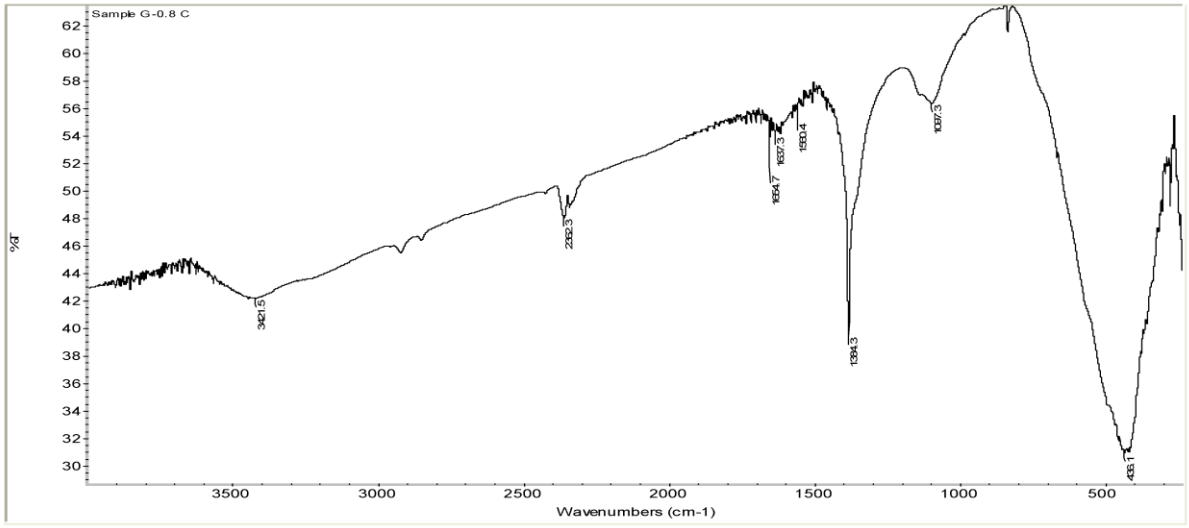
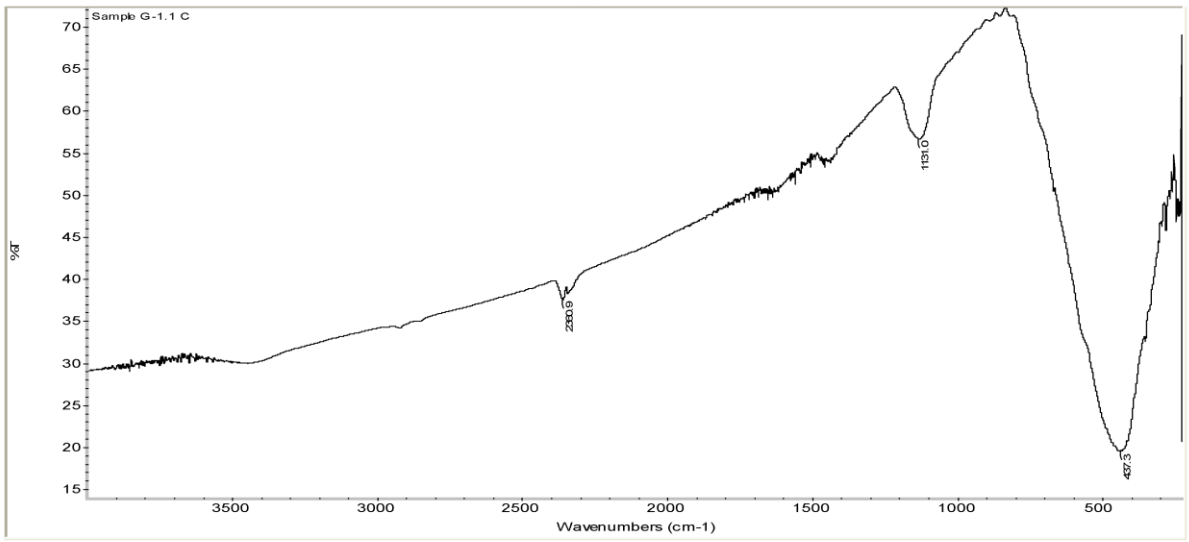


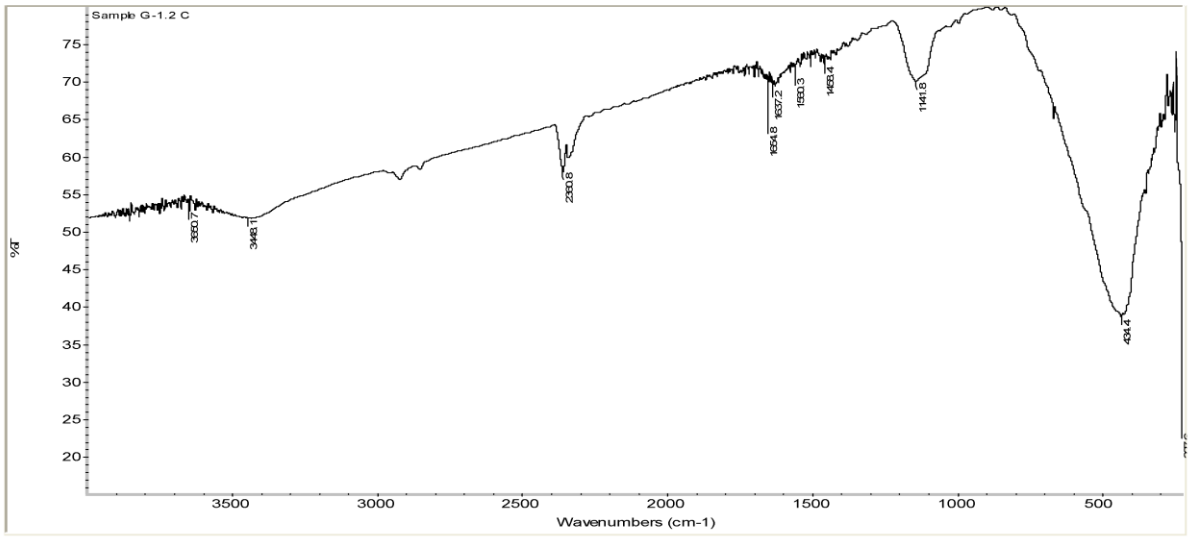
Figure 4: FTIR spectra of Uncalcined NiO-YSZ powder **(a)** glycine 0.8 mol and **(b)** glycine 1.1 mol and **(c)** glycine 1.2 mol



(a)



(b)



(c)

Figure 5: FTIR spectra of Calcined NiO-YSZ powder for 6 hours at 700°C **(a)** glycine 0.8 mol and **(b)** glycine 1.1 mol and **(c)** glycine 1.2 mol

The thermal decomposition of the prepared powder with glycine 0.8 mol was analyzed by simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in the temperature range from 20°C to 995°C in air environment with a heating rate of 20°Cmin^{-1}. The DTA-TGA data for uncalcined powder with glycine 0.8 mol is shown in figure 6. Dotted line shows DTA curve and continues line shows TGA curve. In the beginning small weight gain has been observed that might be due to oxidation in air environment. Afterwards continues weight loss is observed between 80°C to 700°C. The weight loss may be due to dehydration of water molecules and decomposition of residual glycine in the powder [11, 31-32]. A slight weight gain is observed above 700°C that may be attributed to further oxidation in air atmosphere.

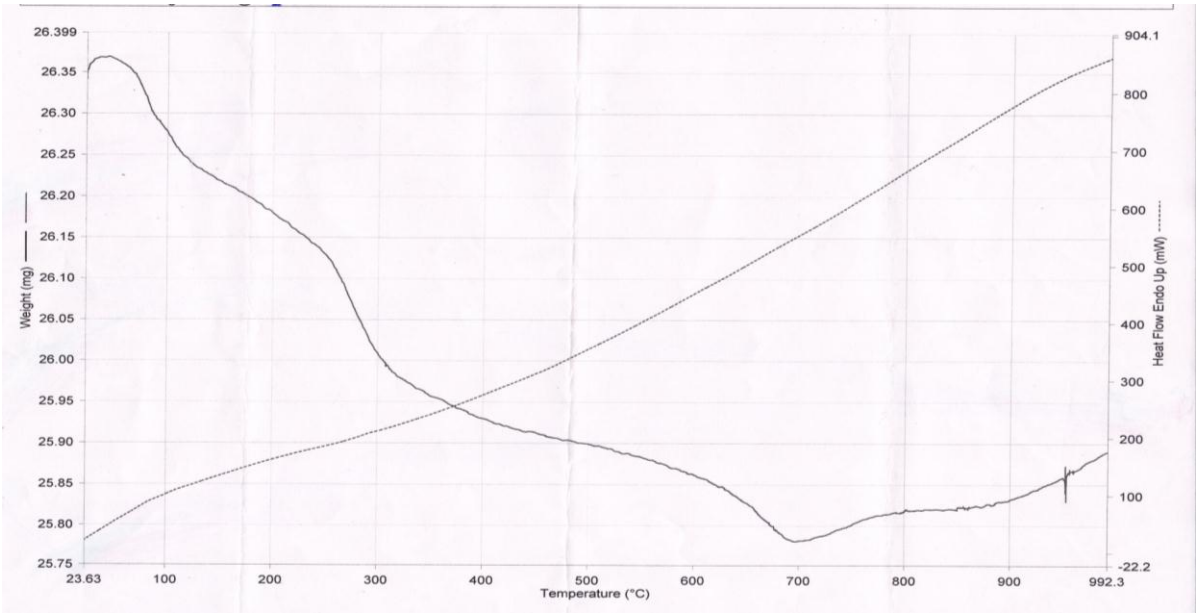


Figure 6: Thermo Gravimetric and Differential Thermal Analysis data for NiO-YSZ powders with glycine 0.8 mol.

4. CONCLUSIONS

Combustion synthesis is a low cost process used to prepare very fine and homogeneous powders of NiO-YSZ. Amount of glycine plays an important role for the combustion process. In present case three different precursors of NiO-YSZ were prepared using 0.8, 1.1 and 1.2 mol glycine. FTIR result shows that the calcinations process leads to the reduction in the amount of carbon present in NiO-YSZ powder. It is evident from the DTA-TGA result that there is no decrease in weight of prepared NiO-YSZ nanocomposite powder above 700°C. Therefore the calcination is done at 700°C.

5. ACKNOWLEDGEMENT

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