

A Study of Electrical Characterization of Nano-structured Copper Cermet Anode Material for ITSOFC through GNP*

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Abstract: The samples belonging to $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ ($x = 0.05, 0.1, 0.3, 0.4, 0.5$ and 0.6) series prepared by glycine-nitrate process (GNP) using copper nitrate, cerium nitrate and glycine as a fuel. The XRD confirms the formation of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$. The solid solubility limit for $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ is up to $x = 0.3$. The crystallite size of anode materials decreases with the increasing content of Cu. The addition of Cu increases the porosity. The highest conductivity $3.4 \times 10^{-2} \text{ Scm}^{-1}$ is achieved for $x = 0.6$ and that of $x = 0.5$ is $2.5 \times 10^{-2} \text{ Scm}^{-1}$ at 660°C before reduction. It is found that from mechanical strength point of view $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ anode material for $x = 0.5$ is suitable than other compositions. The electrochemical performance and anode /electrolyte/anode interface of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ anode is studied after reduction in $10\%\text{H}_2+90\%\text{N}_2$ and in humidified $10\%\text{H}_2+90\%\text{N}_2$ using impedance spectroscopy. The conductivity is maximum for the Cell-800 at Cell-700 $^\circ\text{C}$ having lowest ASR 155.24 and 54.65 ohm cm^2 in $10\%\text{H}_2+90\%\text{N}_2$ and humidified $10\%\text{H}_2+90\%\text{N}_2$ respectively. Thus, the combustion synthesis method is found to be more promising for obtaining the suitable anode material for solid oxide full cell (SOFC) application.

Keywords: SOFC, Anode, GNP, XRD, SEM, EIS, Reduction in $10\%\text{H}_2+90\%\text{N}_2$ and humidified $10\%\text{H}_2+90\%\text{N}_2$. Copper-cermet etc.

1. Introduction

Solid oxide fuel cells (SOFCs) have gained importance in the recent past, due to their high efficiency, low emission and excellent fuel flexibility¹. The major disadvantages of SOFCs viz. cell-cracking, need of expensive non-metallic interconnects, etc. have been mostly due to high operating temperatures. Intermediate temperature solid oxide fuel cells (IT-SOFCs) have, thus, in the near past, attracted great deal of attention². Achieving high cell performance at reduced temperature has increased the thirst for new materials.

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A potential anode material must exhibit high electronic conductivity, sufficient electro catalytic activity for fuel oxidation reaction, chemically stable, thermally compatible with other cell components and sufficiently porous for efficient gas transportation³. The Ni/YSZ cermet materials, with and without catalyst modification have been extensively studied for the internal reforming of methane. However, sulphur poisoning and carbon deposition caused by the cracking of methane have been the major drawback⁴. On the other hand, it has excellent electrocatalytic properties for H₂ fuel. It has been suffering from number of drawbacks in system, where natural gas has been used as fuel. Furthermore, Ni/YSZ cermet has been unsuitable for IT-SOFC (300-700 °C) due to low ionic conductivity of YSZ at that temperature⁵. The Ni/GDC has, thus, received much importance due to higher ionic conductivity of gadolinia doped ceria (GDC) than that of YSZ over a temperature range of 300-700 °C^{6, 7}. Joerger and Gauckler have reported the higher electrical conductivity and electrocatalytic activity of Ni/GDC cermet over Ni/YSZ cermet⁸. According to them improved performance of Ni/GDC has been due to an increased effective reaction area resulting from high ionic conductivity of oxide.

The Ni-based anodes have been not suitable in case of dry hydrocarbon fuels because carbon deposits on Ni during the catalysis. Alternatively anodes based on Cu-CeO₂ have been developed for direct oxidation of dry hydrocarbon fuels^{9, 10}. Copper has been relatively inert metal for carbon deposition reactions, and provides electrical conductivity to the anode. However, ceria, an active phase has been added to Cu in order to achieve improved electrochemical performance¹¹. Furthermore, Cu-based anodes being reasonably tolerant to sulphur has been an added advantage. Gorte et al have studied on Cu/CeO₂/YSZ and Cu/CeO₂/SDC anodes for H₂, methane and butane oxidation¹².

All above factors evoked enough interest to undertake a systematic study on the influence of Cu substitution on the structural, electrical and electrochemical properties of Cu-CeO₂ cermet anode material. In this work, various compositions of Cu_xCe_{1-x}O_{2-δ} were prepared by glycine nitrate combustion process. The prepared samples were characterized using x-ray powder diffraction, scanning electron microscopy, and four-probe dc conductivity. In addition, electrochemical impedance spectroscopy (EIS) studies were carried on the symmetric cells Cu_{0.5} Ce_{0.5} O_{2-δ} / GDC / Cu_{0.5} Ce_{0.5} O_{2-δ} sintered at various temperatures.

2. Experimental

The initial reagents, namely cerium nitrate hexahydrate, copper nitrate trihydrate and glycine (Aldrich Chemicals, USA) were of purity 99.99%. All the reagents were dried at 120 °C for 24 h to remove the traces of moisture. All the nitrates were dissolved in 100 ml double-distilled deionised water, separately, in the required stoichiometric ratios. The homogenous aqueous solution was then heated at 100 °C while subjecting it to constant stirring using rota-mentle to facilitate the evaporation of water. The glycine was added to this solution by maintaining the fuel to oxidizer ratio as 1:1.5. The solution was heated further till the formation of gel. The resultant gel was then charred at about 400 °C by introducing it to an electric muffle furnace. The nitrates act as an oxidizer for further combustion, which results in foamy solid product in less than 10 min.

The residue obtained was then pulverized to form powders. Pellets of diameter and thickness 9 and 1-2 mm, respectively, were obtained by uniaxially compressing the ground powder at a pressure of 3 tons cm⁻² with a Specac (UK) stainless-steel die-punch and hydraulic press. The resulting pellets were initially calcined at 600 °C for 5 h in an electric furnace. Subsequently, they were crushed, and pellets were made in a similar manner as described above before final sintering at 700 °C for 2 h. The samples were allowed to cool to room temperature in the furnace.

All the prepared samples were subjected to structural characterization by X-ray powder diffraction (XRD) with a PANalytical X'pert PRO (Philips, the Netherlands) using Cu K α radiation. A curved graphite crystal was used as a monochromator. The X-ray diffraction measurements were carried out in a 2 θ range from 20 to 80° with a step size and time per step of 0.020° and 5s, respectively. The XRD data were refined with X'pert Highscore plus software. The sintered densities of all the samples were determined using Archimedes' principle using Metler Toledo with density kit. The microstructures of the sintered samples were examined with a JEOL JSM-6380A scanning electron microscope. Microhardness was measured by the Vickers indentation technique (HVM-2 microhardness tester, Shimadzu, Japan). A thin platinum film on both flat surfaces of the sintered pellet was obtained by d.c. sputtering and resulted in good ohmic contacts for d.c. electrical conductivity measurements. The sample was spring-loaded in a ceramic high temperature sample (cell) holder (Amel, Italy) in the hydrogen partial pressure (10% H₂ + 90% N₂) and in humidified (10% H₂ + 90% N₂) separately around the cell during the conductivity measurements was

maintained using electronic mass flow meters and controllers (Teledyne-Hastings, USA). The hydrogen partial pressure was maintained during the measurements to achieve the reduction of anode materials. Prior to the conductivity measurements, the spring-loaded samples were heated to 700 °C for 2 h to homogenize the charge carriers. The temperature was varied in steps 0.5 K/min. The resistance during the cooling cycle was measured as a function of temperature using the four-probe method with a computer-controlled Keithley 6221 current source and a 2182A nano-voltmeter in delta mode. The temperature of the sample during the measurement was controlled with an accuracy of ± 1 °C with a Eurotherm 2216e temperature controller. The tip of a calibrated thermocouple was kept in the vicinity of the sample to measure its actual temperature. Nitrogen was used as the carrier gas. For electrochemical investigations, the initial slurry/ink of the $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ anode was obtained as follows. A gram of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ powder was mixed with 3 wt% polyvinyl butral binder, sodium free corn oil, and ethyl methyl ketone. The mixture was then ball-milled using a Pulverisette-6 (Fritsch Germany) for 1 h with 300 revolutions per minute. Thirty-five tungsten carbide balls of diameter 10 mm and 80 ml bowl of the same material were used. The GDC (10 mol% gadolinium-doped ceria) nano-powder was pressed in a similar manner to obtain pellets of diameter 9 mm and thickness 1-2 mm. GDC pellets were then sintered at 1400 °C for 6 h. A sintered density of about 6.377gm/cm^3 was achieved. The slurry/ ink of anode material was then spin-coated at 3000 rpm for 60 s on both flat surfaces of the sintered GDC electrolyte to obtain the following symmetric cell configurations.



The symmetric cells were initially baked in microwave oven at power 800 watt to burn out the organic binders, and finally sintered at 700 and 800 °C for 3 h. The cells sintered at 700 and 800 °C are abbreviated as Cell-700 and Cell-800, respectively.

Electrochemical impedance measurements on the sintered symmetric cells were carried out using a computer-controlled Solartron 1255B FRA in combination with a Solartron SI 1287 electrochemical interface, impedance analyzer. Prior to the impedance measurement, the spring-loaded samples were heated to 700 °C for 2 h. During the cooling cycle, a dwell time of 30 min was given to ensure the thermal equilibrium in the cells. The 10 m prior to the end of the dwell time, the real and the imaginary parts of the impedance were measured as a parametric function of frequency and

temperature in the range of $0.01 - 1 \times 10^6$ Hz and $500 - 700$ °C, respectively. The ac signal amplitude was 50 mV. The EIS data obtained were analyzed using software developed by Scribner advanced software for electrochemical research and development¹³.

3. Results and Discussion

3.1 X-ray powder diffraction (XRD)

The X-ray diffraction patterns $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ with $x = 0.05, 0.1, 0.3, 0.4, 0.5$ and 0.6 are shown in figs. 1(a-e), respectively. The obtained XRD data were profile fitted with X'pert Highscore plus software and then indexed. In addition to the lines due to CeO_2 , the characteristic diffracted lines due to initial reagents are also clearly seen in fig. 1(a). On the other hand, fig. 1(b) revealed that all the potential characteristic diffracted lines matched with the Joint Committee for Powder Diffraction Standard (JCPDS) data (File No. 00-001-0800 and 00-001-1117) corresponding to CeO_2 and CuO with small deviations with cubic fluorite structure. Absence of lines due to pure CuO rules out the possibility of its presence in the sample, i.e. CuO goes into the cubic fluorite structure of CeO_2 thereby forming a solid solution. Almost similar results are observed for composition with $x \leq 0.3$. In contrast, in addition to the diffracted lines due to CeO_2 some feeble peaks corresponding to CuO are clearly seen for $x = 0.4$ (Fig. 1(d)). Furthermore, it is evident from fig. 1(e) that the diffraction peaks due to CuO become more distinct for $x = 0.5$ than for $x = 0.4$. In general, all the diffracted lines were broader than the usual ones. This broadening is attributed to the nano crystalline nature of the materials.

A close look at figs.1 (d-e) reveals that CuO peaks goes on increasing with increase in copper content x of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ synthesized by GNP. These results are in good agreement with the results of reference¹⁴. To ascertain the formation of a solid solution and its consequence on the host lattice structure, the lattice cell constant for all samples under study were determined using unit cell computer software¹⁵. Fig.5 indicates the comparison of the crystallite size of all compositions under study goes on decreasing non-linearly with increase in x , determined using the X'pert Highscore plus Software. The variation of lattice cell constants and cell volume with x is depicted in fig.6 It can be seen that the lattice cell constant decreases linearly up to $x = 0.6$. These results substantiate the solid solubility limit up to $x = 0.3$ discussed above. On the other hand there is a negligible change in lattice constant ' a ' with increase in ' x '. The

$\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ shows the absence of XRD peak corresponding to Cu dopant concentration up to less than $x = 0.4$; which confirms the formation of complete solid solution. The single-phase XRD patterns shows that the high dispersion of copper species at the surface of CeO_2 crystallites for $x = 0.05$ and 0.3 , whereas, for $x = 0.4$, it reveals the composite nature. A close look at fig.5 indicates that the crystallite size goes on decreasing with increase in x of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$. The observed ' d ' values of XRD pattern of CuO and CeO_2 confirms the phase identity with the standard JCPDS data having file number 00-001-1117 and 00-001-0800 respectively. This confirmed the cubic fluorite structure of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$. The dispersion of the CuO in the cubic fluorite lattice shifts the peaks to small angles. This shift is the reflection of the change in lattice constant, due to ion mismatch. The average crystallite sizes of the prepared $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ samples were calculated from XRD pattern using Debye Scherer relation.

$$(3.1.1) \quad t = \frac{0.9 \lambda}{\beta \cos \theta_B},$$

where ' t ' is the crystallite size, ' λ ' is the x-ray wavelength, ' β ' is FWHM and ' θ_B ' is the Bragg's angle. Here β is obtained by

$$(3.1.2) \quad \beta^2 = \beta_m^2 - \beta_s^2,$$

where, β_m and β_s are the measured and standard full width at half maxima (FWHM) respectively, of the diffracted lines. The XRD pattern obtained by running the experiment on a standard silicon sample provided by PANalytical (Netherlands) is used to estimate the value of β_s . Furthermore, the crystallite size, lattice parameters and porosity of various composition of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ before reduction are given in table1. The crystallite size is obtained approximately between the 40-80 nm as shown in fig.5. A close scrutiny of the data in table1 suggests that all the compositions under study are nanocrystalline materials. The porosity of the sample increases as the composition of copper increases for the various composition of $x = 0.05$ to $x = 0.6$ wt % of copper. The relative density of the sample before reduction for $x = 0.05$ to $x = 0.6$ wt % of copper goes on decreasing for which the conductivity is increased as shown in the table1.

3.2 Microstructure Characterization

The scanning electron morphographs (SEM) of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ with $x = 0.5$ before and after reduction is shown in figs. 2(a) and 2(b) respectively. A

close look at the figure also reveals that the grains are agglomerated with sufficient porosity having uniform distribution in such a way that the electrode structure becomes highly porous. It is observed that the cerium oxide is highly porous, but experimentally the porosity of the CuO/CeO₂ material was found to be in the range 29-60% which is in close agreement to the earlier reported data ^[16] as shown in the table1. The micrographs shown in the figs. 2(a) and 2(b) are observed to be denser due to the sintering of the sample Cu_xCe_{1-x}O_{2-δ}. The porosity of Cu_xCe_{1-x}O_{2-δ} is highest for $x = 0.6$ wt% of copper. A close scrutiny of table1 shows that the porosity goes on increasing with increase in copper content x due to which the mechanical strength of the sample Cu_xCe_{1-x}O_{2-δ} goes on decreasing (Fig.7). The particle size in nm range is in good agreement with the resulted XRD. These nano particles were agglomerated due to the sintering of anode materials. Microphotograph of both the sample Ce_{0.5}Cu_{0.5}O_{2-δ} before and after reduction reveals the grains are in nanometer range. The CuO particles dispersed in nanosized particle over the CeO₂ matrix. A close look at the figs. 2(a) and 2(b) reveals that the nano-crystallites of Cu_xCe_{1-x}O_{2-δ} have agglomerated to form a porous electrode. Furthermore such agglomerates are uniformly distributed in such a way that the electrode structure becomes sufficiently porous. The microstructure of reduced sample Cu_xCe_{1-x}O_{2-δ} in 10%H₂+90%N₂ also studied which is found to be more porous than the structure of the sample before reduction as revealed in fig. 2(b). Also, after the performance test the cell was cooled down to room temperature under the testing environment cross sectioned and polished down to 1μm platinum finish. The SEM photographs of cross section and a fractured surface of the electrode/electrolyte interface of the symmetric cell-800 after the four thermal cycles in 10%H₂+90%N₂ and in humidified 10%H₂+90%N₂ are depicted in fig.3 and 4 respectively. As seen from the fig 3 the electrode and electrolyte formed intimate contact across the interface. Moreover, electrode/electrolyte interface is homogeneous. From the microphotographs of the fractured surface of the Cell-800 reduced in 10%H₂+90%N₂ and in humidified 10%H₂+90%N₂ revealed that the grains are more agglomerated and porous in case of the Cell-800 reduced in humidified H₂/N₂. Despite, with repeated thermal cycles at 700-30°C no cracks or separation between the electrode and electrolyte are found at the interface. The electrode layer thickness while reduction in 10%H₂+90%N₂ and in humidified 10%H₂+90%N₂ are approximately 8.70 and 4.27 μm respectively (Figs. 3(a) & 3(b)). Sintering of a symmetric cell at 800°C facilitates the fusion of nanocrystalline grains of Cu_{0.5}Ce_{0.5}O_{2-δ} leading to grain growth. The electrolyte 10GDC is more dense having negligible oxide vacancies due to reduction in moist H₂/N₂ than in H₂/N₂ as depicted in figs. 3(a) and 3(b) with

and without moist at 700°C for 2h. The microstructure of the electrode and electrolyte layers was characterized using an analytical scanning electron microscope (SEM) which revealed the anode/electrolyte adherence is good at this sintering temperature and it may be advantageous to lower the sintering temperature still further to promote higher anode porosity.

3.3. D.C. Conductivity

The conductivity measurement of any electrode plays a very important role particularly in fuel cell based research. In the present work, four-probe method was used to measure the D.C. conductivity of the samples before and after reduction in 10%H₂+90%N₂. Two of the probes were used to source D. C. current and the other two probes were used to measure voltage. This technique involved bringing four equally spaced probes into contact with the material of unknown resistance. The probe array was placed in the center of the material. The D.C. conductivity measurement was done in the temperature range 400-700 °C for cooling run only. Using Ohm's law, the resistance (R) of the sample is estimated. The conductivity σ is calculated using the equations

$$(3.3.1) \quad R = V/I,$$

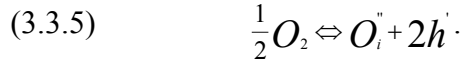
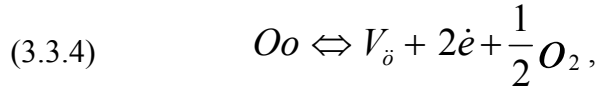
$$(3.3.2) \quad \sigma = 1/R.$$

Activation energy follows the opposite behavior to that of the conductivity with 'x'. The variation of D. C. conductivity before and after reduction in 10%H₂+90%N₂, with temperature for all sample of Cu_xCe_{1-x}O_{2- δ} under study is shown in fig.8 and fig.9 with $x = 0.05$ to 0.6 which exhibits the Arrhenius plots. All the samples obey the Arrhenius law

$$(3.3.3) \quad \sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right),$$

where σ_0 , K , T and E_a are the pre exponential factor, Boltzman constant, absolute temperature and activation energy respectively. From the Arrhenius plot (Fig. 8 and Fig.9) it can be seen that the equation fits the data over the temperature range studied and that the electrical conductivity decreases with temperature, which is a characteristic from a pure metallic electronic conductor. This behavior verifies again the continuity of the copper phase with predominant Cu-Cu contact, demonstrates that there is not sintering of Cu particles.

The D.C. conductivity increases with increase in 'x' of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ in case of both before and after reduction. Intrinsically electron and holes can be produced in $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ lattice by following two point defect equilibria.

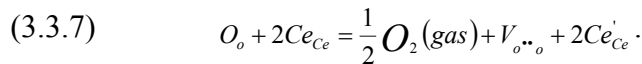


Coupled with intrinsic ionization

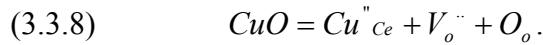


When CeO_2 is reduced to CeO_{2-x} defects are formed in the form of Ce^{3+} , which in the Korger-Vink notation is written as Ce_{Ce}' as the Ce^{3+} has one negative charge compared to the normal lattice. In early work, such as those of Kofstad and Hed¹⁷, Kevane¹⁸, Blumenthal et al¹⁹ and Iwasaka and Katsura²⁰, it was discussed whether these substitutional negative defects were balanced by some of the Ce^{3+} going on interstitial sites as Ce'' or by oxide ion vacancies, V_o'' .

Later works using oxygen self-diffusion studies²¹⁻²³ in nonstoichiometric CeO_2 appear to show that the behavior was consistent with the oxygen vacancy model. Now it is generally agreed that the main compensating defects in CeO_{2-x} are oxygen vacancies. Faber et al²² examined the electron density distribution using x-ray diffraction (XRD) and they concluded that the amount of interstitial Ce is less than about 0.1% of the total defect concentration in CeO_{2-x} . The process of ceria reduction may be written as



The oxide vacancies may also be introduced by doping with oxides of metals with lower valency by dissolution of CuO ²³



Further, the activation energy before and after reduction for the different compositions are depicted in table 1. The conductivity of all samples under study, in general, increases with the percentage of Cu from $x = 0.05$ to 0.6 , which is in close agreement with the reported data in the reported literatures^{14,16}. The Arrhenius plot represents the behavior of conductivity of the sample $\text{Ce}_{1-x}\text{Cu}_x\text{O}_{2-\delta}$ as shown in the figs. 8 and 9 respectively.

3.4 Cell operation in Hydrogen/Nitrogen and with moist Hydrogen/Nitrogen

The symmetric Cell-700 and Cell-800 were first fed with $10\%\text{H}_2+90\%\text{N}_2$ and humidified $10\%\text{H}_2+90\%\text{N}_2$ at 700°C separately in order to reduce CuO to Cu in the anode. During the cooling cycle, a dwell time of 30min was allowed at each set temperature ($T_2, T_3, T_4, \dots$) to ensure that thermal equilibrium was achieved in the cells²⁴. Ten minutes prior to the end of the dwell time (t_{s1} in fig.11). Prior to the impedance measurement, the spring-loaded samples were heated to 700°C (T_1) for 2 h in $10\%\text{H}_2+90\%\text{N}_2$ and in humidified $10\%\text{H}_2+90\%\text{N}_2$ separately, as shown in fig.11. The reduction gas mixture was controlled by mass flow meter, and the gas stream was humidified by passing the outlet of the gas line through a water bubbler. The bubbler was placed in a water bath allowing the steam content to be varied by controlling the water temperature. The real and the imaginary parts of the impedance were measured as a parametric function of frequency and temperature in the range of $0.01-1 \times 10^6$ Hz and $500-700^\circ\text{C}$, respectively, with signal amplitude of 50 mV. Results were corrected for the ohmic loss due to the thick electrolyte pellet at high frequency and normalized to electrode area. fig.14 and fig.15 shows the presence of two semicircles for the symmetric cell $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}/\text{GDC}/\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ on the cole- cole plots for the Cell-700 and Cell-800 reduced in $10\%\text{H}_2+90\%\text{N}_2$ and in humidified $10\%\text{H}_2+90\%\text{N}_2$. The impedance spectra consisted of two semicircles (arc), this indicated that there were at least two electrode processes corresponding the two arcs during molecular reduction. The high frequency incomplete arc (HF) ($\text{freq} > 100\text{Hz}$) was relatively independent of the hydrogen concentration whereas low frequency (LF) arc was strongly affected by the content. Effectively the LF arc resistance exhibits on approximate (PH_2) dependency. This suggests that the LF feature might be dominated by mass transport limitation arising from transport in the gas phase within the anode. The influence of the anode gas phase diffusion at LF is also consistent with the anode's fine pore structure and highlights the need for optimization of the anode pore structure to improve anode performance. The impedance spectra are successfully fitted by equivalent circuit as shown in fig.10, here; L

represents the inductance which might be the consequences of current/voltage probe or the high frequency phase shift of the electrochemical device. The overall ohmic resistance R_{Ω} includes the electrolyte resistance, the electrode ohmic resistance and the lead resistance. The resistance at the high frequency is probably associated with the charge transfer process R_{E1} which include the ion-transfer process occurring at the electrode/electrolyte interface and the electron transfer process accompanying with the reduction process. The low frequency arc can be attributed to the diffusion processes R_{E2} which include the adsorption-desorption of H_2/N_2 gases. The difference between the real axes intercepts of the impedance plot is considered to be the electrode polarization resistance $R_p = R_{E1} + R_{E2}$ the fitting results of the three parts resistance obtained from a Z-view program (Scribener associated Inc) parameters Q_1 and Q_2 are constant phase elements. The anode specific resistance was determined by the relation

$$(3.4.1) \quad ASR = R_{\text{interface}} * \frac{A}{2},$$

where, $R_{\text{interface}}$ and 'A' is the diameter of the low frequency semicircle (electrode). The activation energy is reduced with the increased in temperature as shown in fig.11 and fig.12 which suggests that the hopping mechanism is due to the transfer of charge within the electrode and across the electrode/electrolyte interface.

4. Conclusions

The glycine-nitrate combustion process (GNP) is less time consuming, more easy and quick method to prepare copper cermet anode materials for SOFC. It is clear that the observed and the calculated values are in good agreement with the reported one. The Cu peak intensities were found to increase in the Ce-Cu anode material. Thus, from mechanical strength point of view $Cu_xCe_{1-x}O_{2-\delta}$ anode material with $x = 0.5$ is suitable than other composition, which also possesses sufficient electronic conductivity. The spin coating method is also one of the good techniques for obtaining the homogeneous coating of anode layer on the electrolyte to form a symmetric cell. The D.C. conductivity of $Cu_xCe_{1-x}O_{2-\delta}$ observed to a high value with the increasing percentage of Cu. Further on addition of copper content ($x > 0.5$), the bulk CuO particles are formed which do not contribute to catalytic activities. The activation energy of the $Cu_xCe_{1-x}O_{2-\delta}$ anode material decreases with the increase in content 'x' before and after reduction. Though the D.C. conductivity is maximum for $x > 0.6$, its mechanical strength is less as

compared to that for $x = 0.5$. Mechanical strength is an important parameter for the cell fabrication and its operation. The D.C. conductivities is higher after reduction of copper cermet in 10% H_2 + 90% N_2 . Also the activation energy of Cell-800 in humidified H_2/N_2 is less as compared to that for H_2/N_2 . The ASR of Cell-800 reduced in moist H_2/N_2 is lowest. The lowest ASR of $Cu_{0.5}Ce_{0.5}O_{2-\delta}/GDC/Cu_{0.5}Ce_{0.5}O_{2-\delta}$ in humidified 10% H_2 + 90% N_2 is due to the optimum smaller grain size and sufficient porosity. Thus, it is concluded that fine grain size, adequate porosity and sufficient Cu content in the anode are essential to achieve the high performance. Thus this Ce-Cu sample may be used as an anode materials as well as a catalyst for SOFC. Also the influence of the anode gas phase diffusion low frequency (LF) is consistent with the anode's fine pore structure and highlights the need for optimization of the anode pore structure to improve the performance of anode. Therefore, the GNP technique considerably reduces the sintering temperature and time. Also yields nanostructured $Cu_xCe_{1-x}O_{2-\delta}$. The $Cu_xCe_{1-x}O_{2-\delta}$ prepared using the combustion technique, promises to be a potential anode material for ITSOFC application point of view.

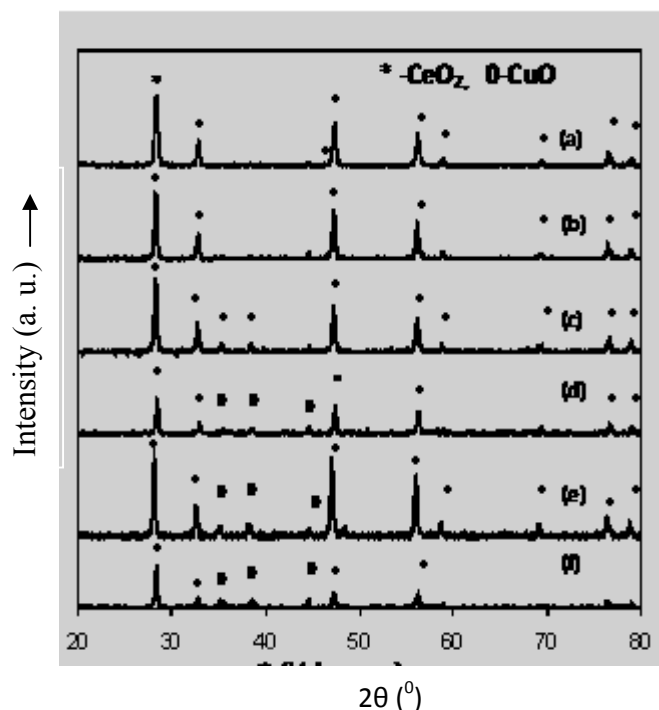


Fig.1: X-ray diffraction patterns of $Cu_xCe_{1-x}O_{2-\delta}$ sintered at 700 $^{\circ}$ C for 90 min for x =(a) 0.05 (b) 0.1 (c) 0.3 (d) 0.4 (e) 0.5 and (f) 0.6 respectively before reduction

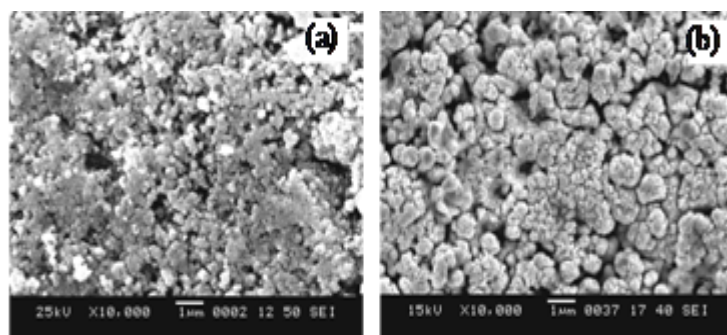


Fig.2: Scanning electron microphotographs of $\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}$
(a) Before reduction and (b) after reduction

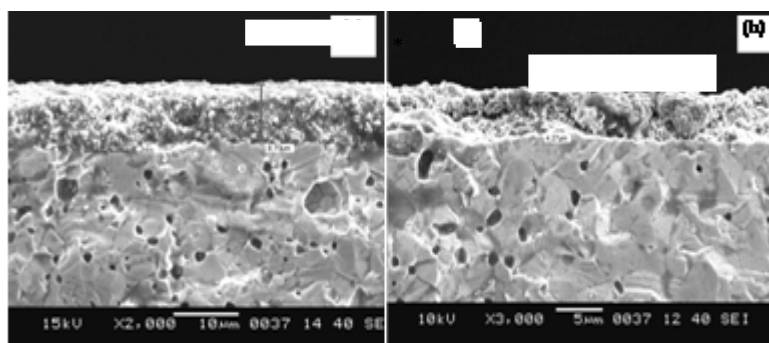


Fig.3: A cross sectional view (Scanning electron microphotographs) of $\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}/\text{GDC}/\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}$ of cell-800 after reduction

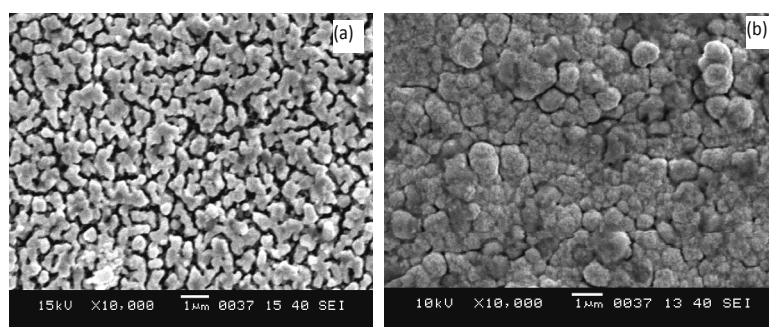


Fig. 4: A surface view (SEM) of $\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}/\text{GDC}/\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}$ for Cell-800

a) After reduction $10\%\text{H}_2+90\%\text{N}_2$ b) after reduction in humidified $10\%\text{H}_2+90\%\text{N}_2$

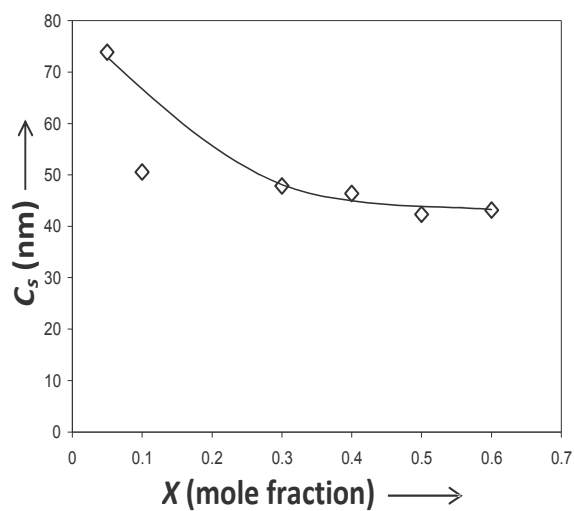


Fig.5: Variation plot of crystallite size C_s with content x of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ before reduction

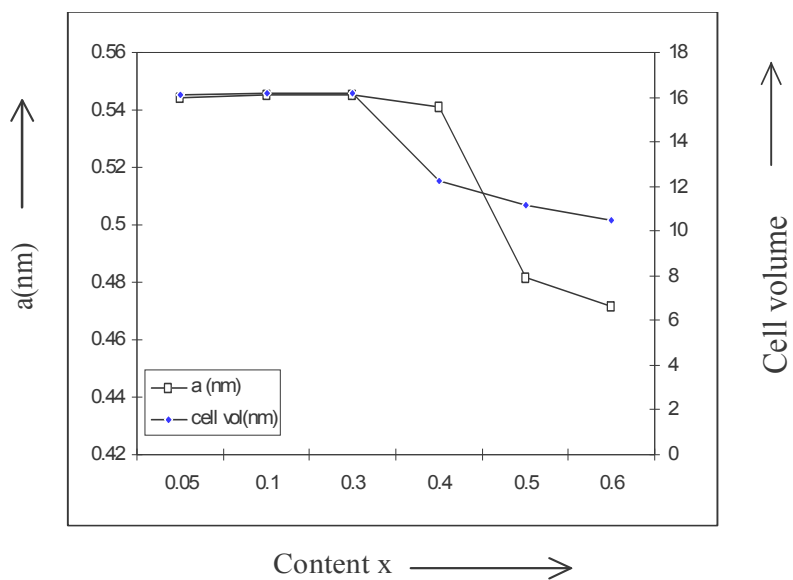


Fig. 6: Variation plot of Lattice constant a and cell volume v with x of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ before reduction

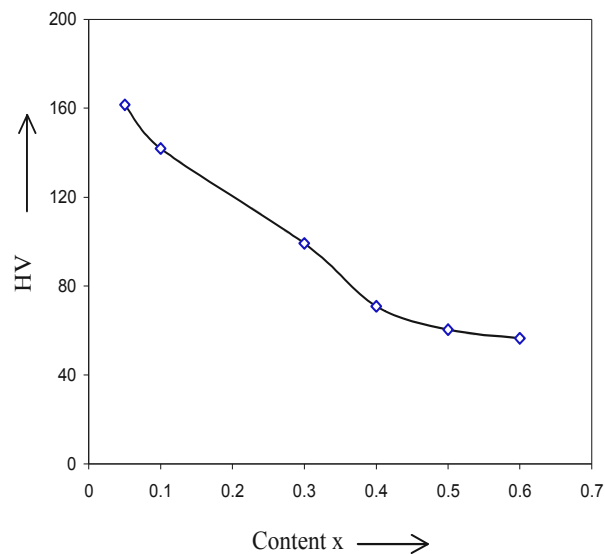


Fig. 7: Variation of (Hardness) Mechanical Strength HV with content x of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ before reduction

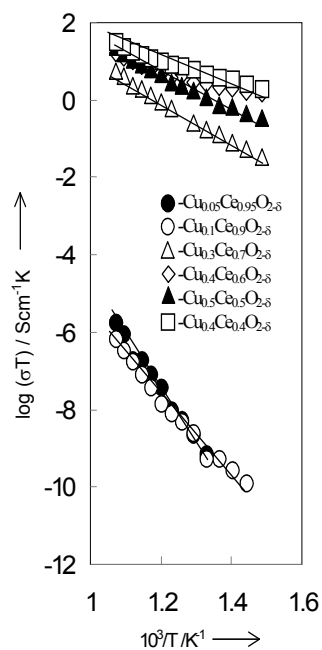


Fig. 8: Arrhenius plots of $\log(\sigma T)$ vs. $10^3/T$ for $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$

with $x = 0.05, 0.1, 0.3, 0.4, 0.5$ and 0.6 before reduction

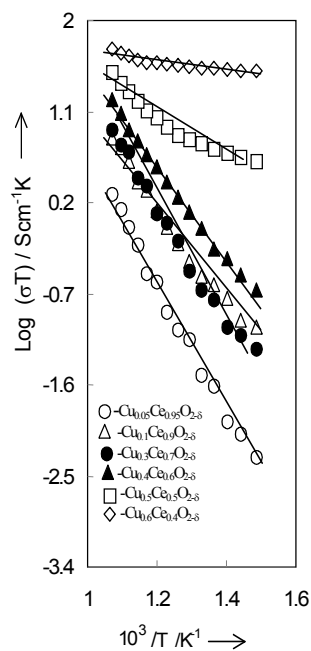


Fig.9: Showing Arrhenius plot of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ for

$x = 0.05$ to 0.6 after reduction in $10\%\text{H}_2 + 90\%\text{N}_2$

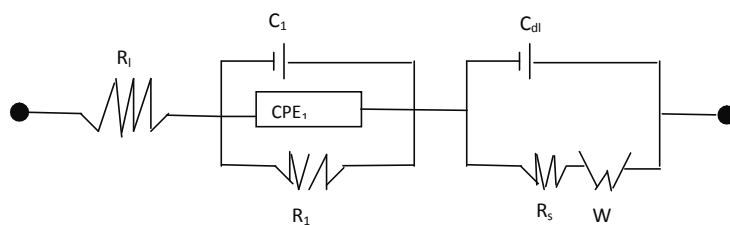


Fig.10 Electrical equivalent circuit for EIS measurement of symmetric cell

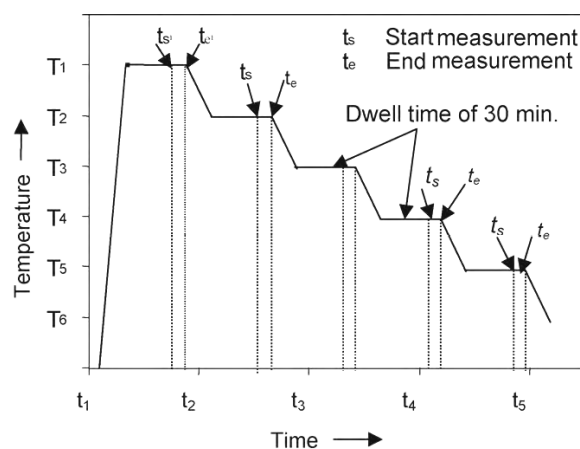
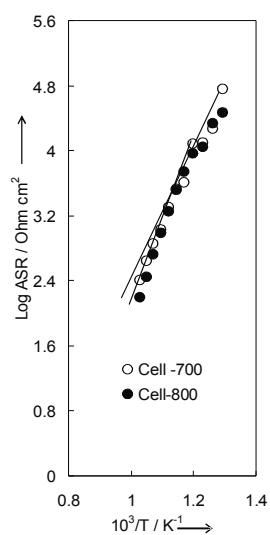
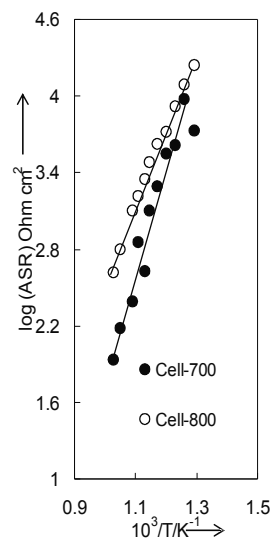


Fig. 11 Temperature profile during EIS measurements

Fig.12: Arrhenius plot of Log ASR Vs. $10^3/T$ of Cell-700 and Cell-800 reduced in 10% H_2 +90% N_2 Fig.13: Arrhenius plot of log ASR Vs $10^3/T$ of Cell-700 and Cell-800 reduced in humidified 10% H_2 +90% N_2

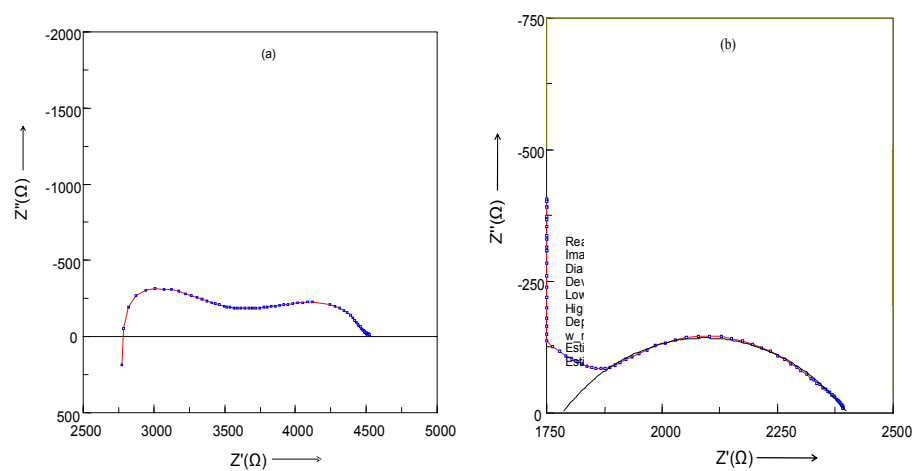


Fig.14: Impedance plot at $T = 700^{\circ}\text{C}$ reduced $10\%\text{H}_2 + 90\%\text{N}_2$ of

(a) Cell-700 and (b) Cell-800 $\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}/\text{GDC}/\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}$

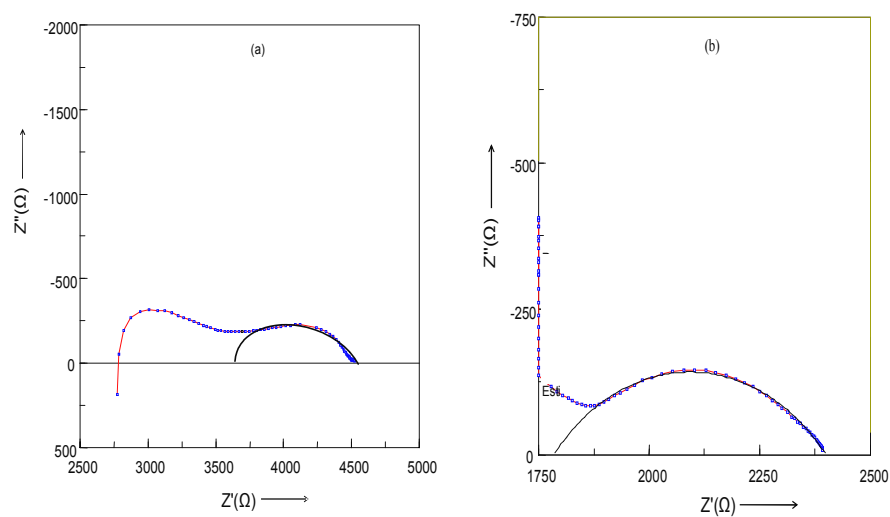


Fig.15: Impedance plot at $T = 700^{\circ}\text{C}$ reduced in humidified $10\%\text{H}_2 + 90\%\text{N}_2$ of (a) Cell-700 and (b) Cell-800 $\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}/\text{GDC}/\text{Ce}_{0.5}\text{Cu}_{0.5}\text{O}_{2-\delta}$

Table 1: Porosity, density, crystallite size, activations energy and D. C. Conductivity of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ before and after reduction in $10\%\text{H}_2+90\%\text{N}_2$

X	Porosity before reduction (%)	Relative density gny/cm ³ before reduction	Activation energy (E _a) before reduction (eV)	Activation energy (E _a) after reduction (eV)	D.C. Conductivity σ (S/cm ²) before reduction	D.C. Conductivity σ (S/cm ²) after reduction
0.05	29.13	4.227	2.565	1.260	-1.16×10^{-5}	2.0×10^{-5}
0.1	31.4	4.035	2.007	1.091	1.0×10^{-5}	7.2×10^{-5}
0.3	35.61	3.985	1.051	0.927	5.7×10^{-5}	8.9×10^{-5}
0.4	41.74	2.477	0.867	0.908	1.6×10^{-2}	1.7×10^{-2}
0.5	55.81	2.155	0.546	0.535	2.5×10^{-2}	3.2×10^{-2}
0.6	60.34	2.086	0.488	0.093	3.4×10^{-2}	5.51×10^{-2}

Table2. Activations energies from EIS of Cell-700 and Cell-800 reduced in $10\%\text{H}_2+90\%\text{N}_2$ and in humidified $10\%\text{H}_2+90\%\text{N}_2$

Symmetric Cell	E _a in $10\%\text{H}_2+90\%\text{N}_2$ from ASR _s (eV)	E _a in humidified $10\%\text{H}_2+90\%\text{N}_2$ from ASR (eV)
Cell-700	1.65	1.51
Cell-800.	1.45	1.19

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