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Fabrication and Characterization of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ Nanostructured Anode Material for SOFC Applications by using Mechanochemical Technique

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Keywords

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Abstract

Solid oxide fuel cell (SOFC) works by converting chemical energy into electrical energy due to reforming, and it is one of the promising alternative sources of energy for the future. In the present work, emphasis was given on increasing the electronic conductivity of anode material for SOFC. The $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ was prepared by mechanochemical (ball milling) route, with and without pore former. The effect of pore former on the electrical and structural characterization was studied in detail, and found that the $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ ceramic anode prepared by using pore former is more effective from structural and electrical points of view. The crystallite size is 58 nanoscales and DC conductivity after reduction is $9.50 \times 10^{-1} \text{ Scm}^{-2}$. Thus, the $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ prepared by ball milling using pore former technique could be an emerging potential anode material for SOFC.

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1. Introduction

Fuel cell technology has been identified as a base for future energy economy. It receives a great deal of attention from research community as well as manufacturers, as elaborated by Atkinson et al. (2004). Solid oxide fuel cell (SOFC) converts chemical energy into electrical energy with negligible emission of pollutions. SOFCs are attractive due to high conversion efficiency, fuel flexibility, less pollution, and a possibility to recover exhaust (Tsipis et al., 2008). SOFCs can work on high as well as intermediate temperatures (from 600 °C to 1000°C) and hence are more efficient as compared to low temperature fuel cell such as proton exchange membrane fuel cell (PEMFC). They do not require external reformer as the reforming of fuel takes place internally (Gorte et al., 2004). Since 40 years nickel-zirconia cermet has become dominant over other single phase anodes. But due to

the disadvantage of Ni cermet anode, there is increase in the promotion of competitive catalytic cracking of hydrocarbon reactions. Since carbon deposition (and the resulting rapid coke formation) is a serious problem in Ni-cermet anode, the direct oxidation of methane is not technically feasible in Ni-based SOFCs. Atkinson et al. (2004) tried to replace Ni with Co and Fe, but it was observed that there was formation of carbon deposition layer which hindered the electrochemical reactivity at the anode/electrolyte interface and in the anode for SOFC. Utilizing natural gas as fuel needs Cu, which has been found to be good alternative to prevent carbon deposition in Ni based cermet. Also, Cu-cermets are observed to be good catalyst due to its low cost as compared to other metals such as Au and Ru which are very expensive and commercially unfeasible (Gorte et al., 2008). Thus, the present study focuses on Cu-cermet anode for SOFC, prepared by using mechanochemical technique with improved structural and electrical properties. Another approach being used in the development of cermet anodes that allows the use of fairly dry hydrocarbon is to use a relatively inert metal such as Cu for electrical conductivity and a metal oxide to provide catalytic activity and ionic conductivity in the composite anode such as Cu/CeO₂/YSZ and Cu/YZT.

More specifically the Cu/CeO₂/YSZ anode system is interesting and has been shown to be very effective for the direct utilization of a variety of hydrocarbon fuels including butane and decane. Also they are highly resistant to deactivation via carbon deposition. In these composite anodes Cu acts as a current conductor while ceria (cerium oxide) primarily acts as an oxidation catalyst. The target for electronic conductivity for anode materials is often set to be 100 Scm⁻¹, but the actual requirement depends on the cell design and particularly the length of the current path to the current collection locations. Thus this could be relaxed to as low as 1 Scm⁻¹ for a well-distributed current collection. Similarly, if the material is porous and as an efficient current collector with thickness of 0.5 mm the conductivity should be greater than 1 Scm⁻¹ to maintain losses below 0.1 Ω cm². Thus by replacing Ni cermet with composites containing Cu and ceria, reforming can be avoided. Cu is relatively inert towards the carbon-formation reactions that occur on Ni cermet anode, and stable operation has been observed with even large hydrocarbons over Cu-based anodes. The prime strategy for developing SOFC that can operate directly on hydrocarbon fuels involves anodes made from electronically conductive ceramics, since these anodes are also tolerant towards carbon formation. In recent years, there are major advances in SOFC anode development, which open doors for new electrodes for second generation commercial fuel cells, with improved redox tolerance and better resistance to carbon deposition. However, there is need to optimize these materials in terms of composition and microstructure, in order to maximize electronic conductivity without disturbing the chemical stability under reducing conditions (Atkinson et al., 2004) In Cu-CeO_{2- δ} anode Cu acts as a catalyst as well as a good electronic conductor. Cu-Cermet acts as a mixed ionic electronic conductor (MIEC). On the other hand, the ability of ceria to store, release and transport oxygen makes it very attractive as a catalyst in oxidation reactions. Ferreira et al. (2010) suggested that ceria is capable of adjusting its electronic configuration and cerium itself has catalytic activity for the oxidation of methane.

The promoting effect of ceria on the performance of precious metal catalysts in the three-way catalytic converter has been intensively investigated in the past decades by (2008). Dictor and Roberts (1989) suggested that the role of ceria is to enhance the metal dispersion. The promoting effect of ceria on base metals is also prominent, especially in copper-based catalysts. Chen et al. (2008) observed that Cu/CeO₂ and Ce_{1-x}Cu_xO_{2-δ} have received special attention due to the unique redox behavior of CeO₂, and their strong copper-ceria interactions. Gorte et al. (2002) suggested that the Cu-cermet based anode materials are more attractive and efficient for SOFC, since they are highly resistant to carbon deposition and improve the electrochemical performance. More intensive research is in progress, to develop materials with good mechanical properties and electronic conductivity (Gorte et al., 2008). Thus by considering the aforementioned problem with anode, there is significant scope for development of Cu-based ceria anode for SOFCs. In the present work, the

Cu_xCe_{1-x}O_{2-δ} anode materials were synthesized using mechanochemical route for SOFC. The samples were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and four probe DC conductivity. In addition to DC conductivity the sample is reduced in presence of 10%H₂+90%N₂.

2. Experimental Method

The initial reagents CuO and CeO₂ (Aldrich Chemicals, USA) of purity ≥99.9% were used for the synthesis of Cu_xCe_{1-x}O_{2-δ} by mechanochemical route with and without using pore former; graphite was also procured from Aldrich USA. To remove the traces of moisture, all the initial reagents were dried at 120°C for 24h. Initially, the reagents of 20g batch in the required stoichiometric ratio were taken into a tungsten carbide (TC) bowl of 80-ml capacity. Then, 2wt. % of process control agent (PCA) ethanol was added to the mixture. Later, 35 balls (TC) of 10 mm diameter were added into it and closed with a TC lid. The mixture was then ball-milled for 3h with 600 revolutions per minute (rpm) by using a Pulverisette-6 planetary monomill (Fritsch, Germany). The obtained powder material was calcined at 650°C. Later the milled samples were compressed uniaxially (3tons/cm²) to obtain pellets with diameter and thickness of 9 and 1–2 mm, respectively, with a Specac (UK) stainless steel die-punch and hydraulic press. The pellets were finally sintered at 700°C for 2h.

To study the effect of pore former on structural and electrical performances, similar synthesis steps were followed to prepare Cu_xCe_{1-x}O_{2-δ} anode material by adding pore former graphite. The powdered samples were subjected to the structural characterization by XRD and PANalytical X'pert PRO (Philips, Netherlands) by using Cu-Kα radiations. A curved graphite crystal was used as monochromator. The XRD measurements were carried out in the 2θ range from 20° to 80° with the step size and time per step as 0.020° and 5s, respectively. The X'pert Highscore plus software was used for the XRD data analysis and Rietveld refinement. The microstructure of the sintered samples was examined with JEOL JSM-6380A, scanning electron microscope. A thin platinum film on both flat surfaces of the sintered pellet which was obtained by DC sputtering resulted in good ohmic contacts for DC electrical conductivity measurements. Prior to the conductivity measurements, the sample was spring-loaded in a ceramic cell holder (Amel, Italy) and heated to

700°C for 1h to homogenize the charge carriers. The resistance as a function of temperature was measured using four-probe method during the cooling cycle with the help of computer-controlled Keithley 6221 current source and 2182A nanovoltmeter in delta mode. The temperature of the sample was controlled with an accuracy of $\pm 1^\circ\text{C}$ by using Eurotherm 2216e temperature controller. The tip of a calibrated thermocouple was kept in the vicinity of the sample to measure its actual temperature.

3. Results and Discussion

3.1. X-ray Powder Diffraction

The X-ray diffraction patterns of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$, synthesized by ball milling with and without pore former (graphite) sintered at 700°C are depicted in Figures 1(a) and (b) respectively. The obtained XRD data were profile fitted with X'pert Highscore plus software and then indexed. The broadening of peaks is attributed to the nanocrystalline nature of the materials. Figure 1 reveals that all the potential characteristic diffracted lines matches 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. In general, all the diffracted lines are broader than the usual ones. These results are in good agreement with those reported by Gorte et al. (2002) and Shaikh et al. (2012). Table 1 summarizes the comparison of properties of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$, synthesized with and without pore reformer. The crystallite size is smaller for the sample prepared with pore former. The crystallite size is approximately in the range 45-58 nm, the lower being observed without pore former. The observed intensity values (Fig.1) of XRD pattern of CuO and CeO_2 confirm the phase identity with the JCPDS standard (File Nos. 00-001-1117 and 00-001-0800 respectively). This confirms the cubic fluorite structure of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ anode. The dispersion of the CuO in the cubic fluorite lattice shifts the peaks to small angles, which is the reflection of the change in lattice constant, due to ion mismatch.

The average crystallite size (t) of the prepared $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ samples were calculated from XRD pattern by using Debye Scherrer relation (Eq. 1), as adopted in the authors' previous works (Shaikh et al., 2011&2012):

$$t = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where ' λ ' is the x-ray wavelength, ' β ' is FWHM and ' θ_B ' is the Bragg's angle. Here, β is obtained by:

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

where β_m and β_s are the measured and standard full width of half maxima (FWHM) respectively, of the diffracted lines. The XRD pattern obtained experimentally by a standard silicon sample (PANalytical X'Pert Pro, Netherlands) was used to estimate the value of β_s . A close scrutiny of the data in Table1 suggests that all the samples under study are nanocrystalline in nature.

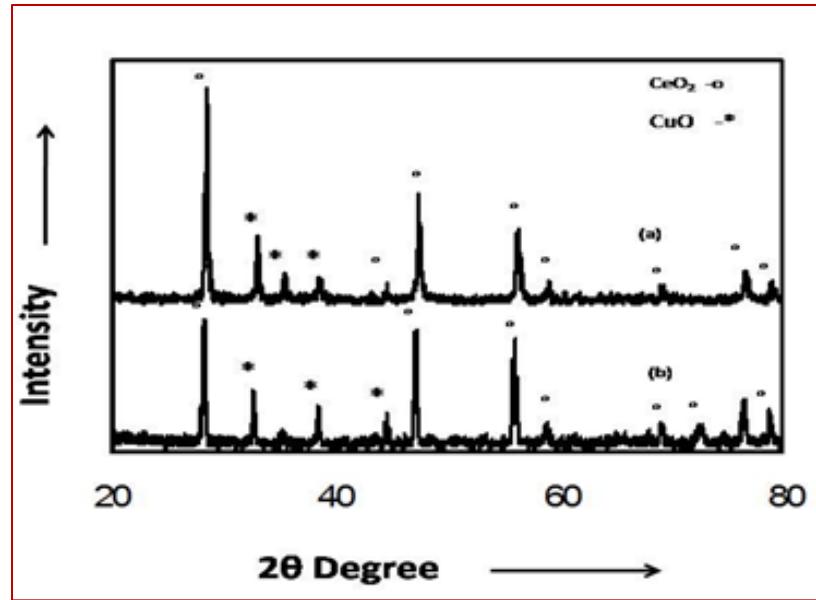


Figure 1. X-ray diffraction of $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ prepared by mechanochemical route before reduction: (a) with pore reformer and b) without pore former

Table 1: Comparison of properties of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ synthesized with and without pore former, before reduction

Sample	Crystallite size (nm)	Lattice parameter 'a' (nm)	Cell volume 'V' (nm)	Relative Density (gm/cm ³)	Porosity (%)	Hardness HV
$\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$	45.4	0.5386	15.625	2.543	47.88	54.38
$\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ with pore	58.0	0.5386	15.625	2.117	56.61	50.21

3.2. Scanning Electron Microscopy

The SEM images of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ prepared by mechanochemical route with and without pore former before reduction are shown in Figure 2. The grains in both the cases are in nano size. Furthermore, agglomerated grains (Figure 2a) resulted in micropores, which are uniformly distributed throughout the sample. A comparative study of Figures 2(a) and 2 (b) suggests increased grain size at the cost of pores.

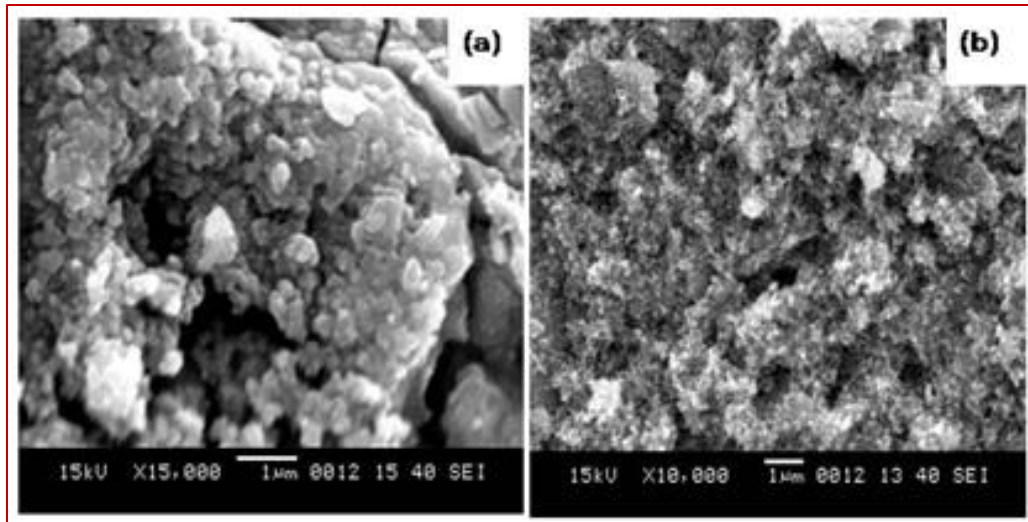


Figure 2. Scanning Electron micrographs of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ prepared by mechanochemical route before reduction: (a) with pore former and (b) without pore former.

The reduction in $10\%\text{H}_2+90\%\text{N}_2$ at 700°C for 2h leads to the grain growth having more porosity than before reduction as shown in Figure 3 (a & b), which substantiates the XRD results discussed earlier. The small agglomerated lumps of grains of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ leads to uniformly distributed micro-pores throughout the anode, whereas Figure 3a reveals moderate grain growth within the agglomerated lumps leaving adequate porosity. On the other hand, the grain grows considerably (Figure. 3b) at the cost of porosity on the addition of pore former graphite in pure $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ during synthesis.

3.3. DC Conductivity

The temperature dependent DC conductivity of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ synthesized with and without pore former before and after reduction are shown in Figure 4(a & b); both these plots obey the Arrhenius law (Eq. 3):

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \quad (3)$$

where σ_0 , K , T and E_a are the pre-exponential factor, Boltzmann constant, absolute temperature and activation energy respectively. Furthermore, the conductivity is higher for the sample prepared by using pore former than without pore former.

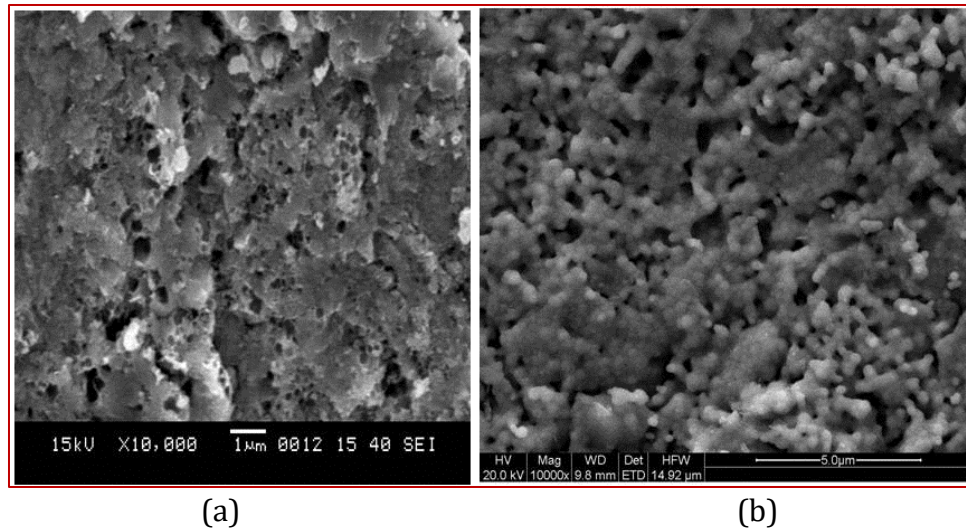


Figure 3. Scanning Electron micrographs of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ prepared by mechanochemical route after reduction: (a) with pore former and (b) without pore former.

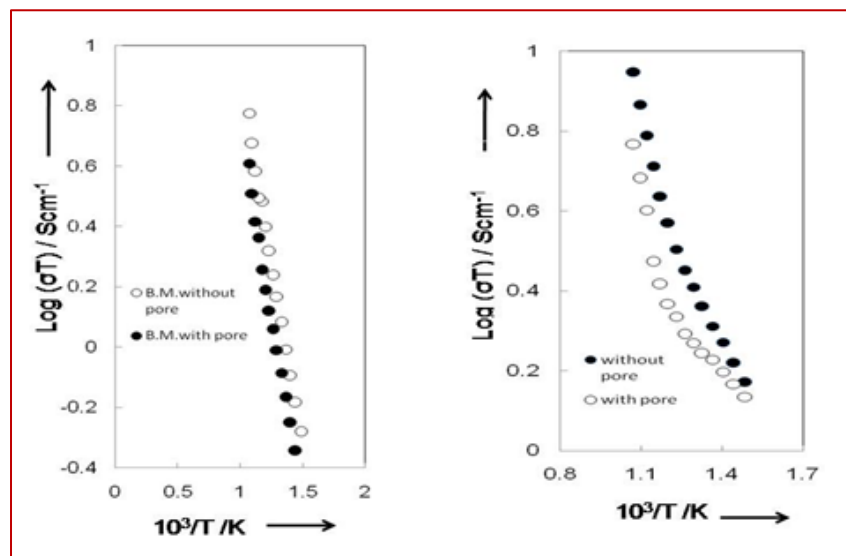


Figure 4. Arrhenius plots of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ synthesized with and without pore former: (a) before reduction and (b) after reduction.

From the Arrhenius plots, it can be seen by Paatsch et al (1991) 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, which demonstrates that Cu particles are not sintered (Shaikh et al., 2012). The D.C. conductivity increases with the synthesis technique of $\text{Cu}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ for both before and after reduction. The activation energy decreases on

addition of graphite as a pore former while ball milling the initial reagents before and after reduction in 10% H_2 +90% N_2 respectively as shown in Table 2.

Table 2: Comparison of properties of $Cu_{0.5}Ce_{0.5}O_{2-\delta}$ in 10% H_2 +90% N_2 synthesized with and without using pore former, before and after reduction

Sample	DC Conductivity ' σ ' (Scm^{-2})		Activation energy ' E_a ' (eV)	
	Before Reduction	After Reduction	Before Reduction	After Reduction
$Cu_{0.5}Ce_{0.5}O_{2-\delta}$	0.00436	0.628	0.488	0.159
$Cu_{0.5}Ce_{0.5}O_{2-\delta}$ with pore	0.00639	0.950	0.479	0.118

4. Conclusion

The mechanochemical route is found to be one of the emerging techniques for producing good Cu-cermet anode materials for SOFC. In the present work the effect of pore former on the properties of $Cu_{0.5}Ce_{0.5}O_{2-\delta}$ was studied with the help of mechanochemical route. The experimental results are in good agreement with the earlier reported data. The DC electronic conductivity of $Cu_{0.5}Ce_{0.5}O_{2-\delta}$ prepared by ball milling by using pore former after reduction in 10% H_2 +90% N_2 at 700°C for 2h, is found to be $0.950 Scm^{-1}$ with sufficient crystallite size and porosity; this proves the present method to be better than the UNP technique reported by Gorte et. al. (2000). The microstructure or pore structure of anode material, and hence the anodic properties, are greatly influenced by the size, shape and amount of pore former (graphite) used. Thus, from the SOFC application point of view, $Cu_{0.5}Ce_{0.5}O_{2-\delta}$ prepared by mechanochemical route with pore former, has proved to be a promising anode material.

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