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One-step synthesis and microstructure of CuO-SDC composites

(Síntese em uma etapa e microestrutura de compósitos CuO-SDC)

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Abstract

An *in situ* one step synthesis route based on the polymeric precursor method was used to produce dual phase CuO-samaria doped ceria (SDC) nanocomposite powders. This chemical route allowed to obtain composite powders with reduced particle size and uniform distribution of Cu, Ce and Sm elements. The particulate material was characterized by powder X-ray diffraction (XRD) combined with Rietveld refinement. CuO-SDC sintered in air between 950 to 1050 °C and subsequently reduced to Cu-SDC cermets were further characterized by XRD and scanning electron microscopy. The open porosity was measured using the Archimedes' principle. Suitable microstructures for both charge transfer and mass transport processes (30 to 45% porosity) were attained in Cu-SDC cermets previously fired at 1000 to 1050 °C. Overall results indicated that CuO-SDC composites and Cu-SDC cermets with potential application as anodes for solid oxide fuel cells (SOFCs) can be obtained by microstructural design. An anode supported half-cell was prepared by co-pressing and co-firing gadolinia doped ceria (CGO) and the herein synthesized CuO-SDC nanocomposite powder.
Keywords: one-step synthesis, nanocomposites, microstructure, Cu-SDC cermets.

Resumo

Uma rota de síntese em uma etapa baseada no método dos precursores poliméricos foi usada para produzir pós do nanocompósito contendo as fases CuO e céria dopada com samária (SDC). Esta rota química permitiu obter pós compósitos com reduzido tamanho de partícula e uniforme distribuição dos elementos Cu, Ce e Sm. O material particulado foi caracterizado por difração de raios X (DRX) combinado com refinamento Rietveld dos dados de difração. Compósitos CuO-SDC sinterizados em ar entre 950 e 1050 °C e em seguida reduzidos a Cu-SDC foram caracterizados por DRX e microscopia eletrônica de varredura. A porosidade aberta foi medida usando o princípio de Arquimedes. Microestruturas adequadas para os processos de transferência de carga e transporte de massa (30 a 45% de porosidade) foram obtidas em cermets Cu-SDC previamente sinterizados a 1000 a 1050 °C. Os resultados indicaram que compósitos CuO-SDC e cermets Cu-SDC com potencial aplicação como anodos de células a combustível de óxido sólido (CCOS) podem ser obtidos por projeto microestrutural. Meia célula suportada no anodo foi preparada por coprensagem e cossinterização de céria dopada com gadolínia (CGO) e o nanocompósito obtido neste trabalho.
***Palavras-chave**: síntese em uma etapa, nanocompósitos, microestrutura, cermets Cu-SDC.*

INTRODUCTION

Ni-based composite materials, especially Ni-YSZ (yttria stabilized zirconia) cermets are the most used materials for solid oxide fuel cell (SOFC) anodes. In these cermets, Ni metal offers good electronic conductivity and catalytic activity for fuel oxidation, while the ceramic phase provides ionic conductivity, structural support, and reduces the Ni agglomeration during fuel cell operation at 800 to 1000 °C [1-3]. It is well known that the cermet performance depends on content, distribution and grain size of both metallic and ceramic phases, which together with the gaseous phase make up the triple phase boundaries, electrochemical sites where the fuel oxidation reactions take place [4-6]. Although widely used, Ni-based anodes have some disadvantages, especially the carbon deposition on the nickel surface, a poisoning phenomenon commonly observed when hydrogen fuel is replaced by hydrocarbons. This problem causes the decrease of Ni electrocatalytic activity for the electrochemical oxidation of fuels such as methane or natural gas [2-4]. Poisoning due to carbon can be avoided or reduced by replacing Ni with another electrical conductor having lower potential to catalyze the carbon formation. Copper (Cu) is well known for such a replacement which is being used alone or in combination with Ni anodes in obtaining bimetallic electrodes [3]. Even though the catalytic activities for the formation of C-C bonds is not in the expected range, Cu provides the required electrical conductivity for the anodes in comparison with Ni [7, 8].

The main disadvantage of YSZ as compared to the ceria-based ceramics, such as gadolinia (CGO) or samaria (SDC) doped ceria, is its reduced ionic conductivity at lower operating temperatures [3]. In ceria-based cermets, the ceramic phase (regardless the type of metal) not only exhibits high ionic conductivity (between 600 and 800 °C), but also is an excellent catalyst for hydrocarbon oxidation [7, 8]. These kind of anodes have demonstrated effective behavior with a variety of hydrocarbon fuels, and are highly resistant to deactivation by carbon deposition, even considering the direct conversion of hydrocarbons without prior reform in CO and H_2 [9]. Cu-based anodes have the additional advantage of being reasonably tolerant to sulfur [10].

The anode precursor particulate materials are generally prepared by the conventional mechanical mixing of powders, which results in a heterogeneous distribution of elements that compromises the electrode performance. The use of nanopowders obtained by chemical routes, allowing a homogeneous distribution of elements and a controlled grain growth in the final microstructure, has been an effective alternative to circumvent this problem. One-step synthesis methods allow the preparation of nanopowders with regular grain size and size distribution, contributing to maximize the number of triple phase boundaries and, as a result, improving the electrochemical performance [11-14]. This work aimed to prepare CuO/Cu-SDC composites through one-step synthesis technique as potential anode materials for SOFCs fed with hydrocarbons. The microstructure of the one-step nanocomposite powder and the effects of firing temperature on open porosity and microstructure of composites were investigated. Aiming to prepare CGO/CuO-SDC half cells at lower firing temperatures, CGO powder was co-pressed with the herein synthesized CuO-SDC nanocomposite and co-fired at 1100 °C.

EXPERIMENTAL

Copper oxide-samaria doped ceria with nominal composition of $CuO\text{-}Ce_{0.9}Sm_{0.1}O_{1.95}$ (CuO-SDC) was prepared by a one-step synthesis route based on the polymeric precursor method. Cerium, samarium and copper nitrates (Sigma Aldrich, 99.9%), citric acid and ethylene glycol (Synth, Brazil) were used as starting materials. To produce the composite by one step synthesis, the precursor resins of the SDC and CuO phases were previously obtained by the polymeric precursor method and then mixed to form a homogeneous resin. The resultant resin was expanded at 350 °C at a heating rate of 1 $°C.min^{-1}$ and dwell time of 2 h. Further details of the powder preparation were previously described in [14]. A final firing at 700 °C for 1 h was used to obtain a crystalline powder which was uniaxially pressed at 125 MPa and fired in air between 950 and 1050 °C for 1 h at a heating rate of 3 $°C.min^{-1}$. CuO-SDC composites were further reduced in hydrogen (flow rate of 20 $mL.s^{-1}$) at 700 °C for 1 h to transform copper oxide into Cu.

The crystal structures of calcined and reduced powders were identified by powder X-ray diffraction (XRD) technique using a Bruker D2 PHASER diffractometer (CuKα radiation, with 40 kV and 30 mA). The diffraction patterns were obtained within the angular range of $20° \leq 2\theta \leq 70°$ in step-scanning mode (0.02 °/step, 2 s/step). The lattice parameters were estimated by Rietveld refinement of the XRD data using the MAUD computer program. The morphology of the calcined powder and the surface fracture of fired and reduced samples were analyzed using a scanning electron microscope (SEM, LEO 1430). The apparent porosity of CuO/Cu-SDC composites was obtained by the Archimedes' method.

An anode supported half-cell comprising a gadolinia doped ceria (CGO with nominal composition of $Ce_{0.9}Gd_{0.1}O_{1.95}$ synthesized by Pechini method and calcined at 600 °C) electrolyte film on a porous CuO-SDC substrate was prepared by a dry co-pressing method (under 125 MPa) followed by co-firing at 1100 °C for 1 h. The cross-sectional microstructure of the CGO/CuO-SDC interface was observed by SEM.

RESULTS AND DISCUSSION

The XRD pattern of the CuO-SDC powder calcined at 700 °C and results from Rietveld refinement of the diffraction data are shown in Fig 1. The SDC and CuO phases were indexed using JCPDS files n° 75-0157 (SDC with cubic fluorite type structure) and 48-1548 (CuO with monoclinic tenorite type structure), indicating that there were no peaks from phases other than CuO and SDC in the one-step synthesized composite powder. The lattice parameters calculated for each crystalline phase were close to those in their respective crystallographic files (for SDC, a = 0.5423 nm; for CuO, a = 0.4688 nm, b = 0.342 nm, c = 0.5131 nm, and β = 99.506°). The SDC crystallite size, D_{XRD} = 24 nm, was comparatively lower than those reported in the literature for doped ceria powders synthesized by hydroxide co-precipitation (27.3 nm), combustion (40 to 50 nm) and citrate complexation (53.7 nm), obtained under similar firing conditions [12, 15, 16]. CuO crystallite (D_{XRD} = 60 nm) seemed to grow nearly three times faster than that of SDC phase in the composite. A similar trend was previously observed for NiO crystallites in one-step NiO-CGO synthesized powders [14]. The obtained low $\chi^2 = R_{WP}/R_{EXP}$ (3.91/3.40 ~ 1.15) value indicated the good fit quality.

The morphology of particles/agglomerates of the CuO-SDC powder calcined at 700 °C for 1 h was studied by scanning electron microscopy (Fig. 2). The particulate material had a microstructure consisting of micrometric and sub-micrometric clusters of particles (Fig. 2a) with an average size lower than 100 nm (Fig. 2b). These powder microstructures were expected since the chemical route used in this work provides nanosized powders with strong tendency to agglomeration due to high surface energy. The reduced particle size associated to the relatively low melting point of the CuO (~1300 °C) may contribute to the high sinterability of CuO-SDC composites, resulting in mechanical consolidation with good structural stability at firing temperatures as low as 1000 °C.

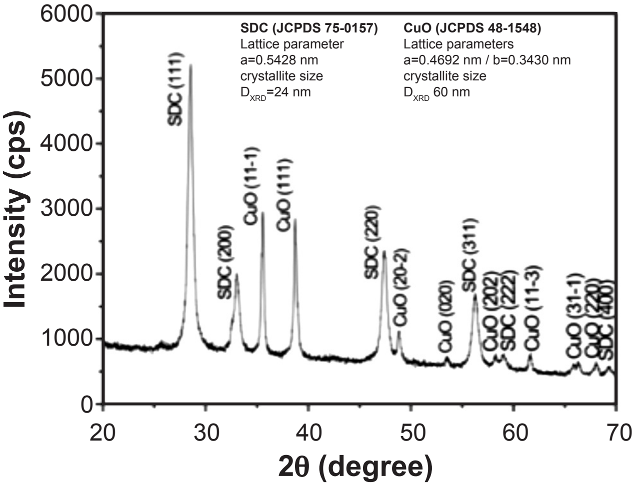

Figure 1: X-ray diffraction pattern of the CuO-$Ce_{0.9}Sm_{0.1}O_{1.95}$ (CuO-SDC) powder calcined at 700 °C.
[Figura 1: Difratograma de raios X do pó de CuO-$Ce_{0,9}Sm_{0,1}O_{1,95}$ (CuO-SDC) calcinado a 700 °C.]

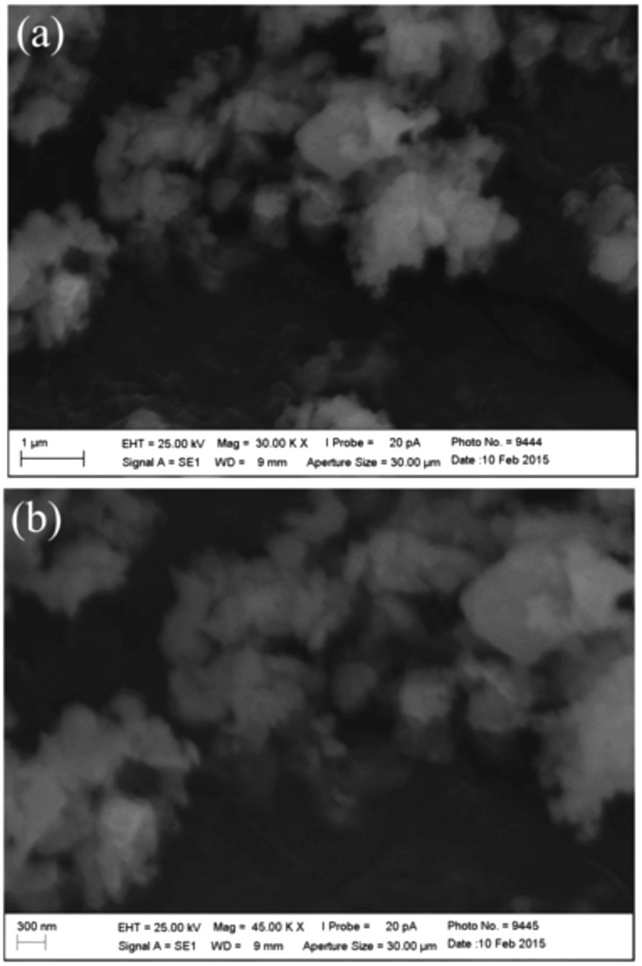

Figure 2: SEM micrographs of the calcined powder.
[Figura 2: Micrografias obtidas por microscopia eletrônica de varredura do pó calcinado.]

The fracture surface microstructures of CuO-SDC composites fired at 950 and 1000 °C for 1 h are shown in Fig. 3. Although it is reported that this kind of material begins to densify at 700 °C [13], a microstructure with low densification even after firing at 950 °C for 1 h was observed (Fig. 3a). The faster growth of CuO in comparison with SDC which was observed in structural analysis (by Rietveld refinement) is further confirmed in the microstructural analysis (Fig. 3a). While the CuO particle size ranged from 1 to 2 μm, SDC remains essentially nanosized after firing at 950 °C. It is clear from Fig. 3a that the number of CuO-CuO (dark gray grains) contacts was reduced due to the large amount of well dispersed SDC particles (light gray grains), which resulted from the intimate mixture of phases provided by one step synthesis. The composite structural stability was improved by firing at 1000 °C (Fig. 3b), an enough temperature to maximize the CuO-CuO contacts and increase the composite densification. The increase in firing temperature from 950 to 1000 °C had little effect on the SDC grain size, suggesting that CuO obstructed the grain growth of the doped ceria phase. Based on these microstructural observations, CuO-SDC composites fired above 950 °C were expected to have suitable microstructures to obtain Cu-SDC cermets via CuO reduction in hydrogen.

Fig. 4 shows a typical XRD pattern of the Cu-SDC cermet derived from composite after firing at 1050 °C. As can be seen, there were no peaks from phases other than Cu (ICSD 06-4699) and SDC, indicating that CuO was successfully reduced to Cu after heat treatment in hydrogen at 700 °C. Fig. 5 shows a typical micrograph for the cermet fired at 1050 °C and then reduced in H_2 at 700 °C for 1 h. The increase in Cu grain size (ranging between 2.5 and 3 μm) compared with the CuO grain in the composite fired at 950 °C (Fig. 3a) could be mainly associated to the higher firing temperature (1050 °C) than that of the reduction of CuO to Cu. The uniform distribution of pores and grains maximized the number of triple phase boundaries (Cu/SDC/gas) in cermet anodes, increasing their electrochemical performance for fuel oxidation and charge transfer processes.

The apparent porosity values of CuO/Cu-SDC composites with respect to the firing temperature are shown in Fig. 6. It can be observed that the porosity was significantly decreased with increasing firing temperature. Further heat treatment in a reducing atmosphere resulted in an increase in porosity of up to 10% for the composite fired at 950 °C. For those samples prepared at 1000 and 1050 °C, porosity changes were only up to 3% due to reduction. As expected, the oxygen loss associated with the CuO reduction process leaded to an additional increase in porosity, especially for those composites obtained in the lowest firing temperature. It is clear from Fig. 6 that only the Cu-SDC cermets derived from samples fired at 1000 and 1050 °C had suitable porosities

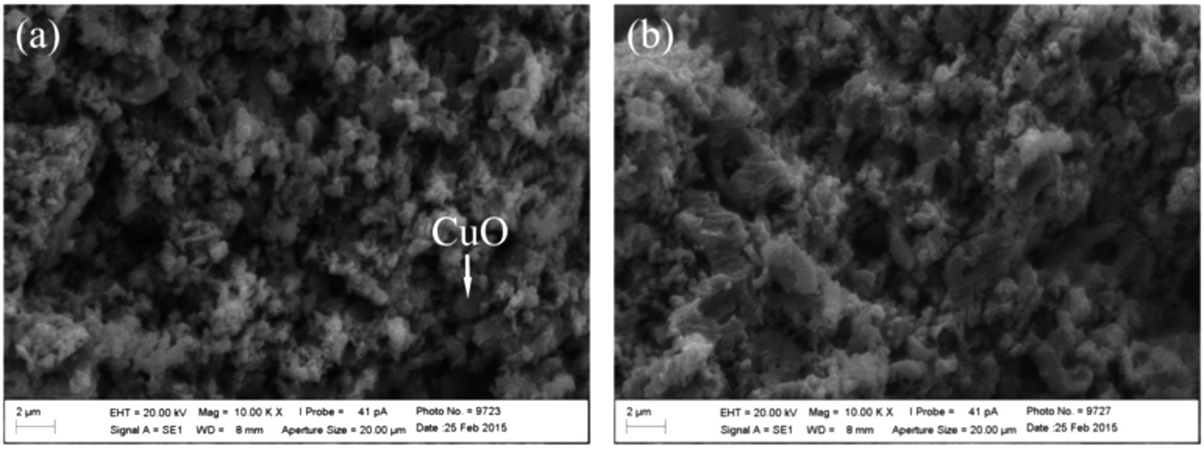

Figure 3: SEM micrographs of fracture surfaces of CuO-SDC composites fired at (a) 950 °C and (b) 1000 °C.
[Figura 3: Micrografias obtidas por microscopia eletrônica de varredura da superfície de fratura de compósitos sinterizados a (a) 950 °C e (b) 1000 °C.]

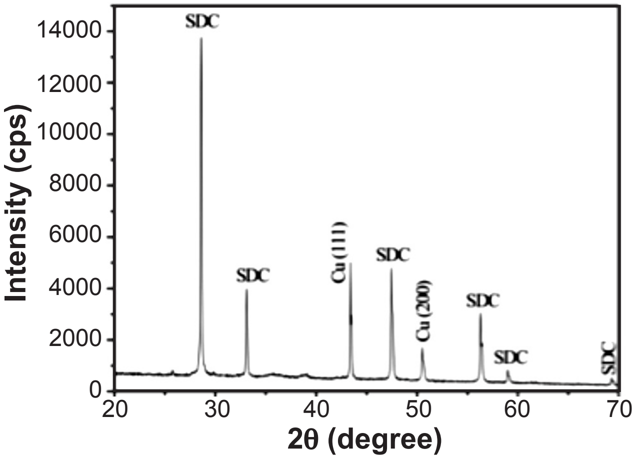

Figure 4: X-ray diffraction pattern of the composite fired at 1050 °C and reduced in H_2.
[Figura 4: Difratograma de raios X do compósito sinterizado a 1050 °C e reduzido em H_2.]

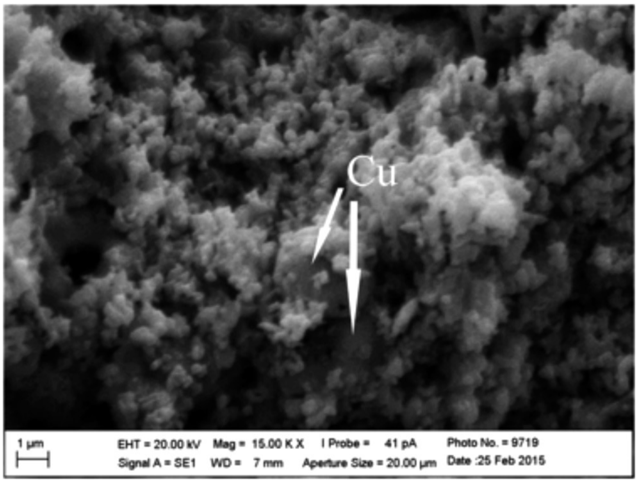

Figure 5: SEM micrograph of fracture surface of the Cu-SDC cermet fired at 1050 °C and reduced in H_2.
[Figura 5: Micrografia obtida por microscopia eletrônica de varredura da superfície de fratura do cermet Cu-SDC sinterizado a 1050 °C e reduzido em H_2.*]*

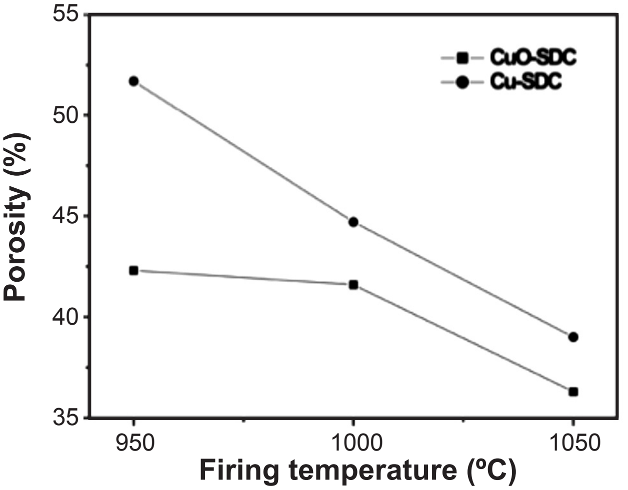

Figure 6: Porosity of CuO/Cu-SDC composites fired between 950 and 1050 °C.
[Figura 6: Porosidade de compósitos CuO/Cu-SDC sinterizados entre 950 e 1050 °C.]

(35 to 45%) for application as solid oxide fuel cell anodes. As the porosity values were above 20%, a slightly higher mass transfer resistance is expected for these cermets. Due to the presence of carbon residue in powders obtained by chemical routes, as reported in [11, 14], cermets derived from these powders typically require no pore forming agents to achieve the optimal porosity range for use as anode material. This remarkable advantage of the herein used one-step synthesis method provided additional flexibility in microstructural design, allowing the mechanical consolidation of cermets with controlled porosity. In general, the porosity of Cu-SDC cermets fired above 1000 °C was close to those reported by [3] for samples of same nominal composition prepared by the mechanical mixing method, fired at 1000 °C and reduced in H_2 at 600 °C.

Fig. 7 shows the cross-sectional SEM micrograph of the anode supported half-cell prepared by co-pressing and co-firing processes. It can be seen that the CGO electrolyte has relatively uniform thickness (~150 µm) and was well adhered to the porous CuO-SDC substrate. This SEM image also demonstrates that crack-free CGO electrolyte films can be successfully prepared on porous substrates of the herein synthesized CuO-SDC nanocomposite powder by co-pressing and co-firing at temperatures as low as 1100 ºC.

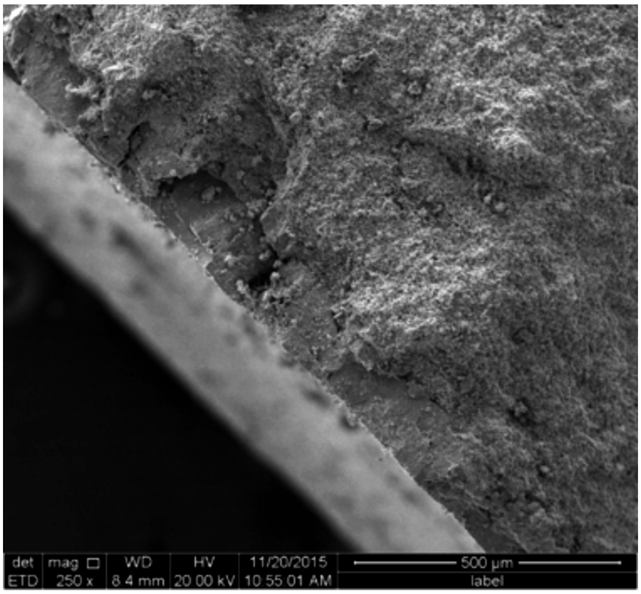

Figure 7: Cross-sectional SEM micrograph of the CGO/CuO-SDC half-cell prepared by co-pressing and co-firing at 1100 °C.
[Figura 7: Micrografia obtida por microscopia eletrônica de varredura da seção transversal da meia célula CGO/CuO-SDC preparada por coprensagem e cossinterização a 1100 °C.]

CONCLUSIONS

Dual phase CuO-SDC nanocomposite powders with average crystallite sizes of 24 nm (SDC) and 60 nm (CuO) were prepared through an *in situ* one-step synthesis technique. The crystal structure, microstructure and porosity of calcined and fired materials for SOFC anodes were investigated. The XRD patterns of CuO/Cu-SDC composites showed that there was no secondary phase in the anode precursor material (CuO-SDC), and CuO was successfully reduced to Cu. Despite the level of agglomeration (in both micro- and submicrometric ranges), the nanopowders had good sinterability which resulted in consolidation with good structural stability at firing temperatures as low as 1000 °C. The low firing temperature significantly decreased the porosity of CuO/Cu-SDC samples, with suitable microstructures for both charge transfer and mass transport processes being attained in Cu-SDC cermet anodes derived from CuO-SDC composites fired at 1000 to 1050 °C. CGO electrolyte films on porous CuO-SDC substrates could be successfully prepared by simple and rapid co-pressing and co-firing processes. These results indicated that one-step CuO-SDC nanocomposite materials are potential candidates to prepare anode supported SOFCs at relatively low firing temperatures.

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