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CERIA-CARBONATE SOLID ELECTROLYTE COMPOZITE FOR INTERMEDIATE TEMPERATURE FUEL CELL

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ABSTRACT. Ceria based nanocomposites consisting of calcium doped ceria and Na_2CO_3 have been prepared for their use as solid state electrolyte in solid oxide fuel cells by a direct co-precipitation method followed by a thermal treatment at 700 ^{0}C. The decomposition course of the precursor, the thermal stability, the morphology, and the composite formation succession were studied by thermogravimetric analyses (TG), FT-IR spectroscopy, SEM and XRD analyses. The only identified crystalline phase is cerium oxide, in which the cerium ions are partially substituted by the calcium ions. The absence of any carbonate phase in the XRD pattern is indicative for its amorphous character. The calcium doped ceria crystallites, with an average size of about 50 nm, have a uniform distribution in the matrix. The temperature dependence of the conductivity between 300-600 ^{0}C was performed on the composite pellets, exhibiting an exponential behavior of the electrical conductivity with values intermediate between the calcium doped ceria and Na_2CO_3. The activation energy decreases from 1.693 eV for pure ceria to 0.79 eV for the calcium doped ceria nanocomposite

Key words: *ceria, co-precipitation, electrical conductivity, SOFC*

INTRODUCTION

Solid Oxide Fuel Cells (SOFC) still represent a promising class of electrochemical devices which transform the chemical energy into electrical energy by using solid oxide materials for electrolytes and electrodes (Lapa et al., 2010; Liu et al., 2010; Velciu et al., 2011; Raza et al., 2012; Chen et al., 2014; Fan et al., 2014). Conventional fuel cells with solid electrolyte operate at over 750 ^{0}C, temperature which generates the solid electrolyte degradation and, thus, a faulty operation of the fuel cell, low chemical energy conversion yield and, last but not least, environmental damages by waste generation (Shawuti and Gulgun, 2014). Some recent researches (Ma et al., 2012) were directed towards the development of composite materials for fuel cells with solid electrolytes which operate in the range below 600 ^{0}C based on cerium oxide composites consisting of two phases: undoped or doped-ceria as the host phase and carbonate or a mixture of carbonates as a second phase. In this context, by using a versatile co-precipitation method, various ceria-based composites, such as: CeO_2/Na_2CO_3, $Ce_{0,8}Sm_{0,2}O_{1,9}/Na_2CO_3$ (Wang et al., 2008), $Ce_{0,9}Gd_{0,1}O_{2-x}/Na_2CO_3$ (Raza et al., 2010) and $Ce_{0,8}Ca_{0,2}O_{2-x}/Na_2CO_3$ have been synthetized and tested. Calcium has been selected as a dopant due to its availability, and the replacement of Ce^{4+}/Ce^{3+} by a cation with a lower valence and an appropriate ionic radius (Ca^{2+} = 100 pm vs Ce^{3+}=102 pm, Ce^{4+} =92 pm) stabilizes the fluorite structure (Truffault et al., 2010).

In this paper, we report our preliminary results on a new approach with respect to the synthesis by co-precipitation of calcium doped ceria nanocomposites, aiming towards a correlation between structure and a tunable conduction behavior.

EXPERIMENTAL

Synthesis

The $Ce_{0.8}Ca_{0.2}O_{2-x}$ (CDC) sample was prepared by a co-precipitation method using sodium carbonate Na_2CO_3 as a precipitation agent. All the chemicals were used as received, without any further purification. The initial solution was prepared by dissolving the cerium nitrate hexahydrate ($Ce(NO_3)_2•6H_2O$, 99.99 %, Alfa Aesar) and the calcium nitrate tetrahydrate ($Ca(NO_3)_2•4H_2O$, 99.95%, Fluka BioChimika) in distilled water at a molar ratio Ce:Ca=4:1. A 0.5M sodium carbonate (Na_2CO_3, 99.00 %, Nordic Chemicals) aqueous solution was directly added under stirring into the salt mixture solution forming a white precipitate instantaneously. The precipitate was washed several times with ultrapure water and then dried at 80^{0}C in air for 24 h in order to obtain the precursor powder. The as-obtained CDC precursor powder was mixed under stirring with a 2M Na_2CO_3 solution at a CDC: Na_2CO_3=4:1 weight ratio. Finally, the resulting slurry was dried at 80^{o}C in air for 24 h. To obtain the final $Ce_{0.8}Ca_{0.2}O_{2-x}/Na_2CO_3$, CDC/$Na_2CO_3$ composite only one thermal treatment has been performed at 700 ^{0}C in air for 1 h. The CDC composite powders were uniaxially pressed (250 MPa) into pellets of 10 mm in diameter, and 2.5 mm in thickness. For reference, pure Na_2CO_3 carbonate and calcium doped ceria were considered, as well.

Instruments

The thermal analyses of the precursors were performed in air, from ambient temperature up to 950 ^{0}C, at a rate of 10 ^{0}C/min, using computer-controlled equipment.

The FTIR absorption spectra of the samples in the 400-4000 cm^{-1} spectral range were performed using a Tensor 27 Bruker FTIR spectrometer.

The samples were structurally characterized by means of X-ray diffraction using a Bruker AXS D8 Discover diffractometer, with a graphite monochromator for the CuKα_1 radiation (λ=1,54056 Å).

The SEM analysis was carried out by using a Quanta Inspect F microscope from FEI Company with field emission gun (FEG) and a 1.2 nm resolution, equipped with an energy-dispersive X-ray spectrometer (EDXS) with a resolution at Mn Ka of 133 eV.

A Keithley 2400 Source Measure Unit has been used for measuring the conductivity of the solid electrolyte.

RESULTS AND DISCUSSIONS

Precursor characterization

The thermal analyses of the CDC precursor powders and of the CDC/ Na_2CO_3 composite were carried out in air in the temperature range from 25-950 ^{0}C at a heating rate of 10 ^{o}C/min. The TG curves are shown in figure. 1a.

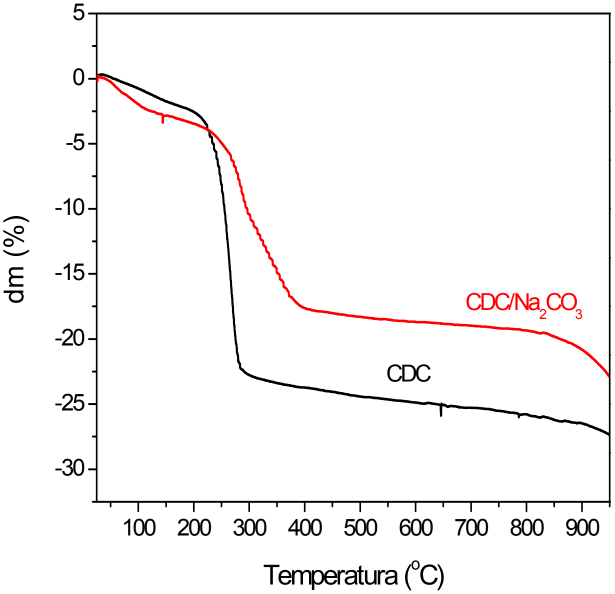

Fig. 1a. *The TG curve for the CDC precursor powder and CDC/Na_2CO_3 composite precursor powder*

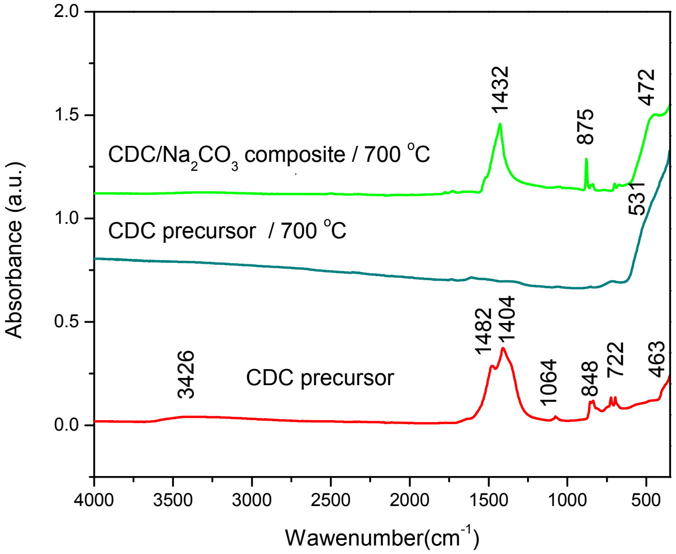

Fig. 1b. *The FT-IR spectra for: CDC precursor powder, CDC precursor powder heat treated at 700 °C and CDC/Na_2CO_3 composite at 700 °C*

The weight loss, as determined from the experimental data, is 27.2 wt. %, (see figure 1a). The weight loss below 170 °C (2.2 wt. %) is due to the evaporation of adsorbed water. In the temperature range 170-700 °C the weight loss is 26.6 wt. %, and it is attributed to the simultaneous and successive decomposition of both $Ce_2(CO_3)_3$ and CaCO3 with the formation of CeO_2 and CaO. The experimental weight loss of 27.2 wt. % is in a good agreement with the theoretical value of 27.8%, as calculated from the global reaction:

$$Ce_2(CO_3)_3 + CaCO_3 + 2O_2 \rightarrow 2CeO_2 + CaO + 7CO_2$$

The thermal stability of the CDC/Na_2CO_3 composite precursor (see figure 1b) has been studied in air in the temperature range 25-950 ^{0}C. The weight loss, as determined from the experimental data, is 24.5 wt. %. It results that at a temperature as high as 700 °C the $Ce_2(CO_3)_3$ and the $CaCO_3$ decomposition can be considered completed.

The functional groups in the composition of the precursor powders, were determined using the FT-IR spectroscopy. The spectra are shown in figure 1(b). The absorption bands localized at 3400 cm^{-1} range can be attributed to the O-H vibration corresponding to the adsorbed water. The CDC precursor spectrum presents bands corresponding to the carbonate species: the asymmetric (1482, 1410 cm^{-1}), and the symmetric (1064 cm^{-1}) stretching vibrations, the out-of-plane (848 cm^{-1}), and in plane (722 cm^{-1}) bending vibration (Andersen, 1991; Li et al., 2014). In the CDC/Na_2CO_3 composite the carbonate vibration bands have almost completely dissappeared, confirming the total decomposition of carbonates into cerium/calcium oxide – the band in the 500 cm^{-1} region. In the heat treated CDC/Na_2CO_3 composite the IR absorbtion bands at 1432, 875 cm^{-1} are assigned to the carbonate species in Na_2CO_3 (Su and Suarez, 1997).

Structural and morphological characterization

The structural characterization of the CDC/Na_2CO_3 composite was performed by X-ray diffraction (see figure 2). All the diffraction lines in the sample were indexed with the diffraction lines of the fluorite-type cubic structure of CeO_2, JCPDS (034-0394), and no peak for the crystalline Na_2CO_3 is found, indicating that the Na_2CO_3 is in an amourphous state in the CDC/Na_2CO_3 composite (Wang et al., 2008). The absence of diffraction lines specific to CaO indicates that the Ca^{2+} ions are substitutionally incorporated into the CeO_2 structure. The peak broadening of the XRD patterns indicates the small size of the crystallites. The average crystallite sizes of the sample have been calculated using Scherrer formula:

$$D_p = \frac{0.9 \cdot \lambda}{\beta \cdot \cos\theta}$$

where Dp is the average crystallite size, λ is the wavelength of the Cu Kα line, θ is the Bragg angle, and β is the full-with at half-maximum (FWHM) of the diffraction peak in radians, resulting 24.4 nm.

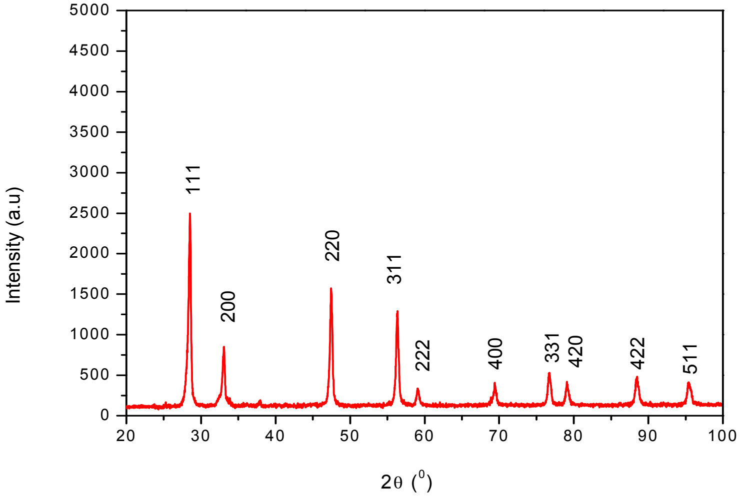

Fig. 2. *The X-ray diffraction pattern for the CDC/Na_2CO_3 composite heat treated at 700 °C*

The morphological characteristics of the CDC precursor powder, and CDC/Na_2CO_3 composite are investigated by SEM - fig. 3. It can be observed that the CDC precursor particle size (figure 3a) is in the 29 - 63 nm domain, while the CDC/Na_2CO_3 composite presents particles in the 16 - 36 nm range (figure 3b). The smaller particle size of the CDC/Na_2CO_3 composite can be attributed to the presence of Na_2CO_3 which acts as a barrier in preventing the particle growth.

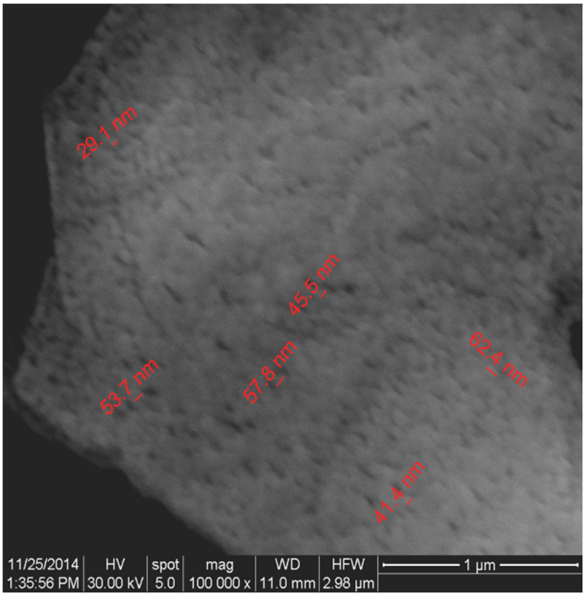

Fig. 3a. *The SEM image of the CDC precursor powder cross-section surface at 1 µm*

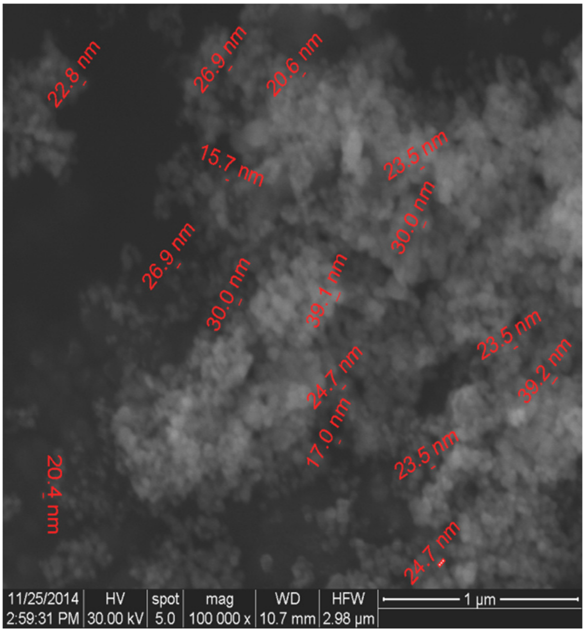

Fig. 3b. *The SEM image of the CDC/Na_2CO_3 composite cross-section surface at 1 µm*

Electrical characterization

Pure ceria is a mixed ionic-electronic conductor transporting electrons via n-type small polaron hopping and oxygen ions via oxygen vacancies (Ristoiu et al., 2012). It is possible to enhance the electrical conduction of the ceria, by substituting the cerium ions with Ca^{2+}, when the concentration of oxygen vacancies increases. The electrical conduction in ceria is a thermally activated process in which the conductivity σ is expressed by:

$$\sigma T = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is a pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature.

The temperature dependence of the conductivity between 300-600 ^{0}C is exhibiting an exponential behavior of the electrical conductivity with values intermediate between the calcium doped ceria and Na_2CO_3. The activation energy decreases from 1.693 eV for pure ceria to 0.79 eV for the calcium doped ceria nanocomposite suggesting that the Na_2CO_3 amorphous layer on the surface of CDC improves the overall conductivity. The Arrhenius plots $\ln[\sigma T(Scm^{-1})]$ vs $10^3/T$ for CDC precursor powder, CDC/Na_2CO_3 and Na_2CO_3 are shown in figure 4.

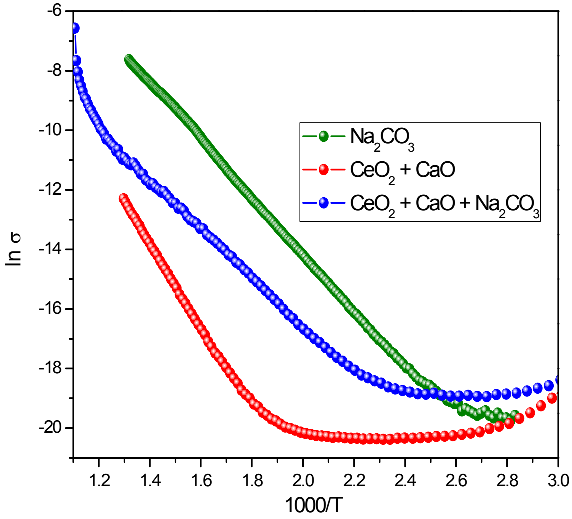

Fig. 4. *The Arrhenius plot for Na_2CO_3, CDC precursor powder, and CDC/Na_2CO_3 composite*

The CDC precursor powder shows improved activation energy values as compared to pure ceria. The calculated activation energy for CDC precursor powder is 1.204 eV, while for the pure ceria it is 1.639 eV. The decrease of the activation energy value for CDC precursor powder suggests that it might be used as a potential precursor powder for the CDC/Na_2CO_3 composite solid electrolyte for intermediate temperature SOFC.

CONCLUSIONS

CDC/Na_2CO_3 composites have been successfully synthesized by the co-precipitation method followed by a wet mixing and a single heat treatment at 700ºC. The precursor and the composite were studied by TG, FT-IR, SEM and XRD analyses. The as-obtained composite is characterized by an improved conduction and an activation energy of 0.79 eV due to the small size of the particles and the two-phase composite system. It may be suggested that the amorphous Na_2CO_3 plays an important role in the conductivity and thus influencing the fuel cell performance.

ACKNOWLEDGEMENT

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