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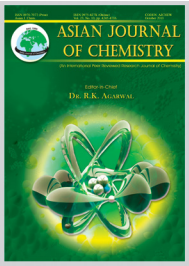

Chemical Synthesis and Characterization of $Ce_{0.8}Y_{0.18}Ca_{0.02}O_{1.89}$ as Electrolyte for Solid Oxide Fuel Cells†

CHANGAN TIAN*, WEITAO BAO, JIHAI CHENG, QIYI YIN, DIFANG ZHAO, YU WANG and FAN WU

Department of Chemistry and Materials Engineering, Hefei University, Hefei 230022, P.R. China

*Corresponding author: E-mail: tianchangan@tom.com

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The synthesis of nano-sized $Ce_{0.8}Y_{0.18}Ca_{0.02}O_{1.89}$ (YCDC) powders by citrate gel route has been investigated. The details of gel's combustion were investigated by TG-DSC and the structure of as-synthesized powders from auto-combustion was characterized by XRD. The results show that single phase YCDC powders with average size of 50 nm can be synthesized by citrate gel route. The as-synthesized powders exhibited high sinter activity, it can be sintered to 95 % of its theoretical density at 1250 ºC for 4 h. The YCDC composition exhibits a total conductivity of 0.02 S/cm at 700 ºC.

Key Words: $Ce_{0.8}Y_{0.18}Ca_{0.02}O_{1.89}$, Electrolyte, Citrate gel route, Solid oxide fuel cells.

INTRODUCTION

Solid oxide fuel cells (SOFCs) transform chemical energy to electrical energy with high conversion efficiency and low pollution. Research and development of SOFCs have received much attention recently. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte in SOFCs, which requires operating temperature around 1000 ºC. However, the high temperature leads to a series of complicated material problems such as high-temperature gas seal, thermal expansion mismatch and interface reaction between components in SOFCs. Therefore, a major challenge in reducing the operating temperature of SOFCs is to develop alternative electrolyte materials that can operate at intermediate-temperatures (500-800 ºC) with high oxygen-ion conductivity. CeO_2-based oxides with a fluorite type structure showed much higher oxide-ion conductivities than ZrO_2-based oxides and thus are expected to be candidates for the electrolyte of the SOFCs operated at intermediate temperature range of 500-800 ºC[1-3].

In this study, Y and Ca doped CeO_2 electrolyte ($Ce_{0.8}Y_{0.18}Ca_{0.02}O_{1.89}$, YCDC) powders were synthesized *via* the citrate gel route and the single-phase ceramics were obtained by sintering of the powders at lower temperature. In order to elucidate the performances, the sinterability and electrical conductivity were evaluated.

EXPERIMENTAL

The nano-crystalline YCDC was synthesized by the citrate gel route. In this method, stoichiometric amount of $Ce(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were dissolved in distilled water and an aqueous solution of citric acid ($C_6H_8O_7{\cdot}H_2O$) were added with constant stirring until a homogenous solution was achieved, with the Ge^{4+}, Y^{3+} and Ca^{2+}-to-citric acid molar ratio of 1:2. Then the solution was stirred, heated slowly to form a glutinous colloid. The colloid was then dried, grinded and calcined at 600 ºC for 2 h.

The as-synthesized YCDC powders were mixed with an appropriate amount of 5 wt % polyvinyl alcohols as the binder and granulated using a 180-mesh sieve, after which the granulated powders were uniaxially pressed at a pressure of 200 MPa to form green-specimens. After burnt out at 600 ºC for 2 h, the specimens were sintered at different temperatures 1100, 1150, 1200, 1250 and 1400 ºC for 4 h in the air. The densities of the sintered samples were determined using Archimedes method.

The thermal analysis was done using differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TG) techniques with a heating rate of 10 ºC/min in air environment to study the different reaction steps and temperatures of the YCDC precursor gel. The phase identification of the

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as-synthesized products was recorded by X-ray diffractometer (XRD) with CuK_α radiation (λ = 0.15406 nm). The ionic conductivity of sintered sample was obtained from two probe impedance spectroscopy in the frequency range of 0.1 Hz to 100 kHz.

RESULTS AND DISCUSSION

TG-DSC curves of the citrate gel are presented in Fig. 1. Considering the thermal gravimetry analysis results, we can observe the following characteristics: The first regime(I) up to T = 190 ºC shows a decrease in mass of approximately 10 %. At the same temperature range, an endothermic reaction can be detected at the DSC signal, which can be named to the evaporation of water. The second regime(II) in a temperature ranges between T = 190 and 400 ºC shows a decrease in mass that indicates the decomposition of organics. The exothermic DSC-peak at T = 370 ºC indicates the crystallization of YCDC. From T = 400 ºC, a constant mass can be detected considering the thermogravimetry signal; the crystallization of YCDC is finished.

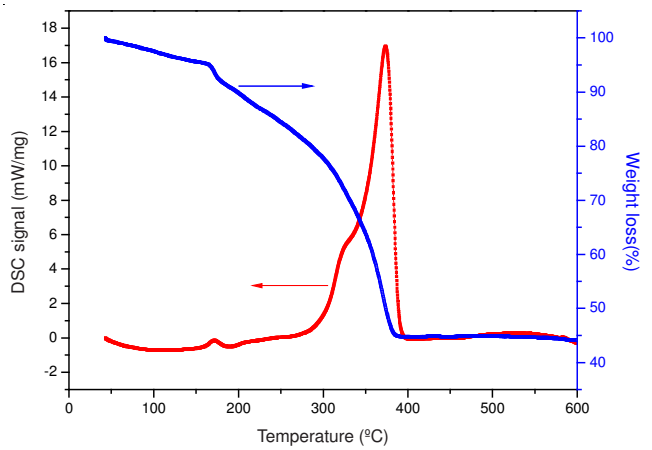

Fig. 1. TG and DSC curves of the dried citrate gel

Fig. 2 shows the XRD patterns of the as-synthesized powder by the citrate gel route. Reflections matched with those in CeO_2 (JCPDS PDF # 65-2975) of fluorite type structure can easily be identified. In addition, no diffraction peak that could be assigned to a secondary phase was observed in the sample. This result indicates that the pure phase YCDC with fluorite type structure directly synthesized by the citrate gel route. The peaks are broad indicating nano-crystalline nature of the powders. The crystallite size has been calculated from FWHM (full width at half maximum) data using Scherrer formula:

$$D = \frac{0.89\lambda}{\beta\cos\theta} \quad (1)$$

where D is the crystallite size in nm, λ is the radiation wavelength, 2θ is the diffraction angle and β is the corrected line width at half peak intensity. The calculated average crystallite size was *ca.* 40 nm for powders by the citrate gel route.

The as-synthesized YCDC powders *via* the citrate gel route have fine sinterability. Fig. 3 shows the relative densities of the sintered specimens as a function of the sintering temperature. It was seen that the specimens sintered at 1250 ºC for 4 h

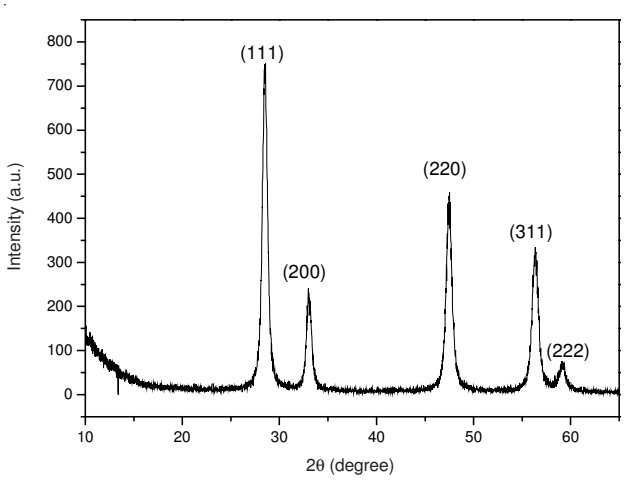

Fig. 2. X-Ray diffraction of the as-synthesized powders

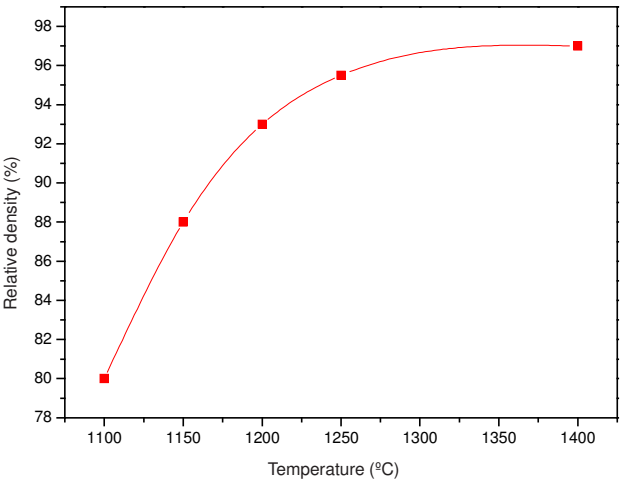

Fig. 3. Effect of temperature on density

had relative density of 95.5 %, indicating that the densification temperature of the YCDC powders by the citrate gel route is 150 -250 ºC lower than that of CeO_2-based electrolytes powders prepared by solid-state synthesis[4,5].

Fig. 4 is the AC impedance spectra of the sintered YCDC specimen tested at 700 ºC in air.The spectrum consists of an incomplete semicircle and an inclined line shown as Fig. 4. Based on the spectra Fig. 4 and eqn. 2, the bulk conductivities of YCDC specimen can be estimated to be 0.02 S/cm at 700 ºC.

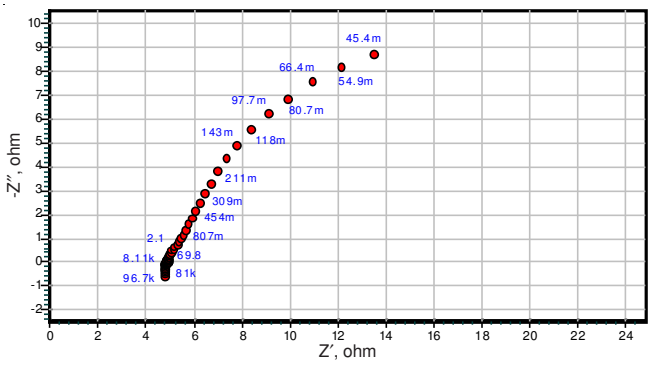

Fig. 4. AC impedance curve of pellet tested at 700 ºC

$$\delta = \frac{L}{RS} \quad (2)$$

where L is the thickness of the pellet, S is the area of the pellet and R is the resistance of the sample.

Conclusion

Single phase ultrafine YCDC powders of fluorite type structure with average size of *ca.* 40 nm have been prepared successfully by the citrate gel route. The density measurements reveal the formation of the samples with relative density more than 95 % at comparatively lower sintering temperature (1250 ºC). The as-synthesized YCDC showed low temperature sinterability, which in fact could assist co-firing of other cell components of SOFC at reduced temperature. The sintered YCDC specimens possess high ionic conductivity of 0.02 S/cm at 700 ºC in air.

ACKNOWLEDGEMENTS

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