



Synthesis and Characterization of $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ as Electrolyte for Solid Oxide Fuel Cells†

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In this study, ultrafine $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ ($x = 0$ to 0.1) powders have been successfully prepared by the sol-gel method. The samples were characterized by TG-DSC, XRD and AC impedance. Experimental results indicated that highly phase-pure cubic fluorite electrolyte $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ powders were obtained. The $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ series electrolytes have higher relatively dense over 96 % can obtained after sintered at $1400\text{ }^\circ\text{C}$. Among all the samples, $Ce_{0.8}Y_{0.1}Ca_{0.1}O_{1.85}$ shows excellent ionic conductivity of 0.041 S/cm measured at $800\text{ }^\circ\text{C}$ and lower conductive activation energy of 0.89 eV .

Keywords: CeO_2 , Electrolyte, Sol-gel, Solid oxide fuel cells.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are an appliance which can transform chemical energy to electrical energy. Research and development of solid oxide fuel cells has received considerable attention recently due to its high conversion efficiency and environmental friendship¹. One of the key component of solid oxide fuel cells is solid electrolyte, which requires high ionic conductivity, low electronic conductivity and high stability in an oxidizing and reducing atmosphere². So far, the most common study of electrolyte materials is yttria-stabilized zirconia (YSZ) with higher operating temperature around $800\text{--}1000\text{ }^\circ\text{C}$ ³. However, such high temperature leads to a series of material problems such as thermal degradation, high-temperature gas seal, thermal expansion mismatch and solid reaction between components in solid oxide fuel cells⁴. Therefore, it becomes increasingly important to reduce the operating temperature of solid oxide fuel cells and the major challenge is to develop alternative electrolyte materials that can operate at intermediate temperature ($500\text{--}800\text{ }^\circ\text{C}$) with superior oxide ionic conductivity^{5,6}.

EXPERIMENTAL

The nano-crystalline $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ was synthesized by the sol-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 then added citric acid and ethylene

glycol as complexing agent to form a homogeneous solution with the citric acid-to-metal ions molar ratio of 1.5:1 and the ethylene glycol-to-citric acid molar ratio of 1.2:1. After this stage, the solution was stirred, heated slowly to form a glutinous colloid. The colloid was then dried, grinded and calcined at $600\text{ }^\circ\text{C}$ for 2 h.

The as-synthesized $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ powders were mixed with an appropriate amount of 5 wt % poly(vinyl 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 $600\text{ }^\circ\text{C}$ for 2 h, the specimens were sintered at different temperatures for 4 h in the air. The densities of the sintered samples were determined using Archimedes method. The thermal analysis was done using DSC-TG techniques with a heating rate of $10\text{ }^\circ\text{C/min}$ in air environment to study the different reaction steps and temperatures of the $Ce_{0.8}Y_{0.2-x}Ca_xO_{2-\delta}$ precursor gel. The phase identification of the as-synthesized products was recorded by X-ray diffractometer (XRD). The ionic conductivity of sintered sample was obtained from two probe impedance spectroscopy in the frequency range of 0.1 Hz to 1 MHz.

RESULTS AND DISCUSSION

TG-DSC curves of the dried gel are presented in Fig. 1. Considering the thermal gravimetry analysis results, we can observe the following characteristics: The first regime (I) up to $T = 250\text{ }^\circ\text{C}$ shows a decrease in mass of 20 %. At the same

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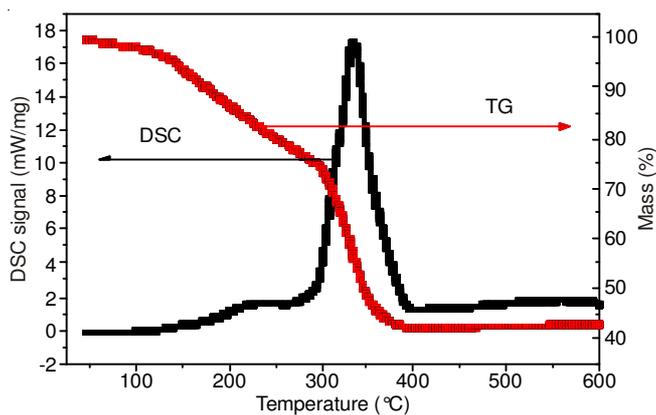
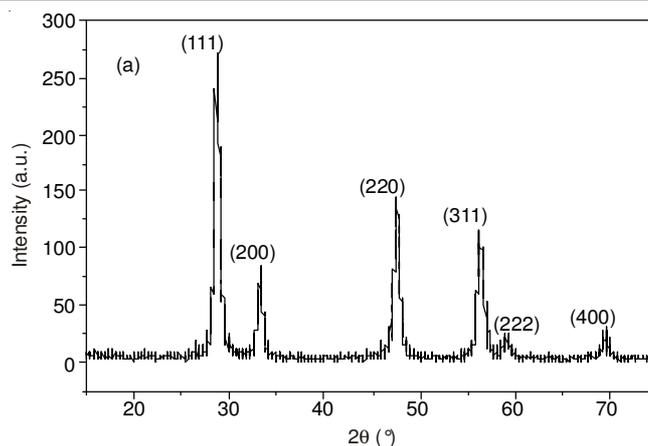
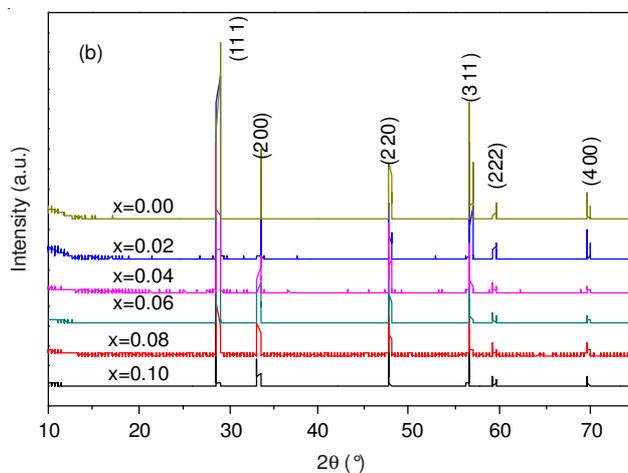


Fig. 1. TG-DSC curves of the dried gel

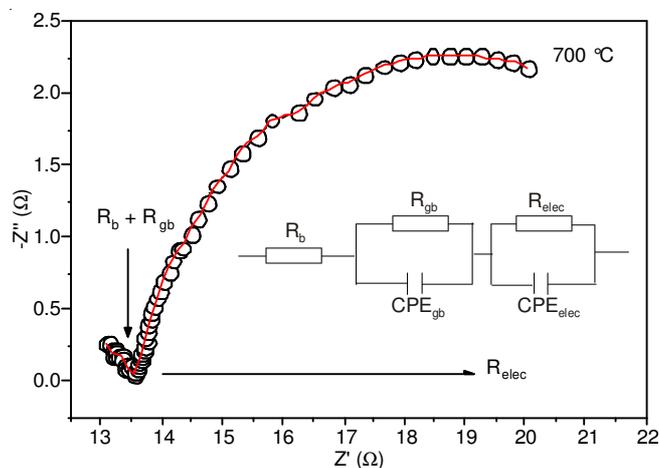
temperature range, an endothermic reaction can be detected at the DSC signal, which can be named to the evaporation of water. The second regime(II) in a temperature ranges between $T = 250$ and 400 °C shows a decrease in mass that indicates the decomposition of organics. The exothermic DSC-peak at $T = 330$ °C indicates the crystallization of $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$. From $T = 400$ °C, a constant mass can be detected considering the thermogravimetry signal, implying only the presence of crystalline $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$. It was further confirmed by XRD studies.

Fig. 2 shows the XRD patterns of the as-synthesized powders of $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ by the sol-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 $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ with fluorite type structure directly synthesized by the sol-gel route. The peaks are broad indicating nanocrystalline nature of the powders. Fig. 3 shows the XRD patterns of the $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$ solid solutions prepared by the the sol-gel and calcined at 1400 °C for 4 h. It can be seen that all powders were single phase with a cubic fluorite structure and space group $\text{Fm}\bar{3}\text{m}$ (JCPDS powder diffraction file no. 65-2975). No other peaks attributable to impurities or other phases were detected. Table-1 shows the relationship between the Properties (such as lattice parameter, relative densities, electrical conductivity, activity energy) for $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$ and the doping content. It was seen that the as-synthesized powders exhibited high sintering activity, achieving over 96 % of its theoretical relative density at 1400 °C for 4 h, over 200 °C lower than the sintering temperature for the powders derived from traditional solid reactions.

TABLE-1 PROPERTIES OF $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$ ($0.00 \leq x \leq 0.10$) SAMPLES				
$\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$	Lattice parameter (Å)	Relative densities (%)	Electrical conductivity, σ_{800} (S cm^{-1})	Activity energy, E_a (eV)
$x = 0.10$	5.396 17	98.3	0.041	0.81
$x = 0.08$	5.392 69	97.5	0.038	0.82
$x = 0.06$	5.391 49	97.8	0.035	0.83
$x = 0.04$	5.388 81	97.2	0.034	0.85
$x = 0.02$	5.386 32	96.9	0.030	0.89
$x = 0.00$	5.382 53	97.4	0.025	0.92

Fig. 2. XRD patterns of $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ sintered at 600 °C for 2 hFig. 3. XRD patterns of $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2.8}$ sintered at 1400 °C for 4 h

AC impedance spectroscopy is widely employed to obtain information related to the electrical behaviour of grains, grain boundaries and electrode response. A typical impedance spectrum measured at 700 °C under air for the $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ pellets. The conductivities can be calculated using the resistance obtained by fitting the impedance spectra with equivalent circuit models (Fig. 4) using ZSimpWin software. The total electrical conductivity at 800 °C and the activation energy values are given in Table-1. It can be seen from Table-1 that

Fig. 4. AC impedance curve of $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ at 700 °C

the activation energy increases with increasing Y dopant content x and the addition of Ca improves the electrical conductivity. As shown in Table-1, the electrical conductivity of $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ can reach as high as 0.041 S/cm at 800 °C, which are among the highest values observed in electrolytes considered as candidates for IT-solid oxide fuel cells.

Conclusion

Single phase ultrafine $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2-\delta}$ powders of fluorite type structure have been prepared successfully by the sol-gel route. The density measurements reveal the formation of the samples with relative density more than 96 % at comparatively lower sintering temperature (1400 °C). The as-synthesized $\text{Ce}_{0.8}\text{Y}_{0.2-x}\text{Ca}_x\text{O}_{2-\delta}$ showed low temperature sinterability, which in fact could assist co-firing of other cell components of solid oxide fuel cells at reduced temperature. Among all the samples, $\text{Ce}_{0.8}\text{Y}_{0.1}\text{Ca}_{0.1}\text{O}_{1.85}$ shows excellent ionic conductivity of 0.041 S/cm measured at 800 °C, lower conductive activation energy of 0.89 eV.

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