Pertanika J. Sci. & Technol. 22 (1): 35 - 42 (2014)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

A Comparative Study of Yttrium Doped Ceria Ceramics Synthesized using Mechanochemical and Solid State Methods

Ong, P. S.[1], Tan, Y. P.[1,2]*, Taufiq-Yap, Y. H.[1,2] and Zainal, Z.[1,2]

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Putra Laboratory for Catalysis Science and Technology, Department of Chemistry, Faculty of Science,Universiti Putra Malaysia, UPM Serdang, Selangor, Malaysia

ABSTRACT

In this work, 10 mol% yttrium-doped ceria powders, $Ce_{0.9}Y_{0.1}O_{1.95}$, were synthesised using a new mechanical technique, mechanochemical reaction, in which both impact action and shearing forces were applied for efficient fine grinding, subsequently leading to higher homogeneity of the resultant powders. $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared using this new technique was systematically compared with a sample of the same prepared using conventional solid-state methodology. X-ray diffraction analysis showed all prepared samples were single phase with a cubic fluorite structure. Generally, Y_2O_3-doped CeO_2 electrolytes prepared by mechanochemical reactions were stable at a lower temperature (1100 °C) compared with a sample of the same synthesised using the conventional solid-state method. Characterisations using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) showed no thermal changes and phase transitions, indicating all materials were thermally stable. The electrical properties of the samples investigated by AC impedance spectroscopy in the temperature range 200–800 ˚C are presented and discussed. Scanning electron microscopy (SEM) was used to study the morphology of the materials. Fine-grained powders with uniform grain-size distribution were obtained from the mechanochemical reaction.

Keywords: Oxide ion conductor, yttrium, ceria

Article history:
Received: 26 March 2011
Accepted: 15 August 2013

E-mail addresses:
poh_shing@hotmail.com (Ong, P. S.),
typ@upm.edu.my (Tan, Y. P.),
taufiq@upm.edu.my (Taufiq-Yap, Y. H.),
zulkar@upm.edu.my (Zainal, Z.)
*Corresponding Author

INTRODUCTION

Doped ceria is a solid electrolyte which is becoming increasingly attractive for use in solid oxide fuel cells because of its high oxygen ion conductivity at low temperature. Solid oxide fuel cells continue to attract wide interest due to their high energy conversion and low pollution capacity. Currently,

ISSN: 0128-7680

stabilised zirconia electrolytes are considered the main or established choice of electrolyte in solid oxide fuel cells under restricted conditions (Dudek. 2008). This is in spite of the short life-span of materials of cells at operation temperature range of 900–1000 ˚C. In attempting to reduce the operation temperature, several researchers have turned their attention to the application of doped-ceria electrolytes as an alternative to the conventional stabilised zirconia electrolytes. The top variants of doped-ceria systems are comprised of products resulting from a substitution of lower-valent metals such as Y, Sm, Gd and Ca (Huang *et al*., 1997). Y_2O_3-doped ceria is considered a potential solid electrolyte for use in intermediate temperature solid oxide fuel cells (IT-SOFC). Wang *et al*. (2006) have studied the relationship between defect structures in Y_2O_3-doped ceria by diffusion and electrical conduction in order to understand the conduction mechanisms of this electrolyte.

Powders of nano-scale have excellent properties suited for various applications as highlighted by Singh and Hegde (2008). This study was carried out because no systematic research has yet been conducted on the mechanochemical synthetic route, better known as the ball-milling method, due to drawbacks encountered using mechanical synthesis compared to the wet chemical approach in terms of sinterability and densification (Li *et al.,* 2002). However, this study was conducted with the main purpose of contributing to the construction of a solid-state method basis by addressing this matter, which might then enable us to draw more reliable conclusions about the potential as well as the limitations of this synthetic route.

MATERIALS AND METHODS

Yttrium oxide-substituted ceria samples were synthesised using two methods i.e. the conventional solid state method and the mechanochemical method with starting materials CeO_2 (99.9% Acros Organics) and Y_2O_3 (98% Fluka-Garantie). All starting materials were dried at 500-600 ˚C prior to weighing. Stoichiometric amounts of these materials were mixed. The mechanochemical method used a total mass of approximately 15.0 g of stoichiometric mixtures of CeO_2 with Y_2O_3, placed in an agate bowl (99.9 % SiO_2) with agate balls of 10 mm diameter. Ethanol was added as a milling medium to prevent excessive abrasion. The mixture was milled using a planetary ball mill (Model Pulverisette 4 vario-Planetary mill) for one hour. The slurry was dried at 60–70 ˚C to evaporate the ethanol. In the conventional solid state method, mixtures of required molar ratios of materials were weighed and wet-mixed manually with acetone as the wetting medium using an agate mortar and pestle. The materials were subjected to heat treatments at different temperatures and durations to ensure the formation of single phase materials.

Phase purity was characterised by X-ray diffraction analysis (XRD) (Shimadzu diffractormeter XRD 6000, CuKα radiation) in 2θ range of 10–60 ˚ at 2 ˚/minute. The CHEKCELL refinement programme was used to obtain lattice parameters of the structure. Thermal events were recorded from room temperature to 1000 ˚C on heat and cool cycles (10 ˚C/minute) using differential thermal analysis (DTA, Perkin-Elmer DTA 7) and thermogravimetric analysis (TGA, Perkin Elmer TGA 7).

The electrical conductivity of sintered ceramic pellets was measured. The pellets were pressed uniaxially and sintered at a temperature range of 1200–1500 °C. The densities of the

pellets (85 %) were determined through the Archimedes method using deionised water as the medium. The electrical properties were determined by AC impedance spectroscopy using a Hewlett Packard Impedance Analyzer, HP4192A, over the frequency range 5 Hz to 13 MHz. Measurements were made from 100 ˚C to 800 ˚C by incremental steps of 50 ˚C on a heating cycle with 30 min equilibration time. Scanning electron microscopy (SEM) analysis was carried out using SEM JEOL JSM-6400 operated at 15 kV, with a working distance of 13 mm.

RESULTS AND DISCUSSION

XRD Analysis

X-ray diffraction analysis (XRD) was used to identify the crystalline phases as well as the lattice parameters of solid solution powders. The diffracted X-rays were collected over 2θ range 10 ˚–60 ˚ using a step width of 0.02 ˚. The diffractometer was calibrated using Si standard. The XRD spectra of the 10 mol% yttrium-doped CeO_2 powders are illustrated in Fig.1 and Fig.2. X-ray diffraction analysis showed that all the yttrium-doped ceria samples were monophase materials. (JCPDS powder diffraction File No. 34-0394). Bragg peaks for the unreacted Y_2O_3 phase were found in the XRD spectra of compounds prepared using the conventional solid-state method after calcination at 800-–1200 ˚C. The Y-doped CeO_2 prepared using the mechanochemical method showed the presence of strong XRD Bragg peaks of a fluorite-type phase, indicating the presence of CeO_2 (JCPDS card No. 34-0394) at a lower temperature compared to that of the material synthesised using the conventional solid-state method. X-ray diffraction analysis also showed all doped ceria powders obtained in $Ce_{1-x}Y_xO_{2-\delta}$ ($0.05 \leq x \leq 0.3$) ceramics were monophasic material (Fig.3). These results demonstrated that successful synthesis was achieved at a temperature ~200 ˚C lower than previously reported by Zhang *et al*. (2003) using the same mechanical synthesis approach.

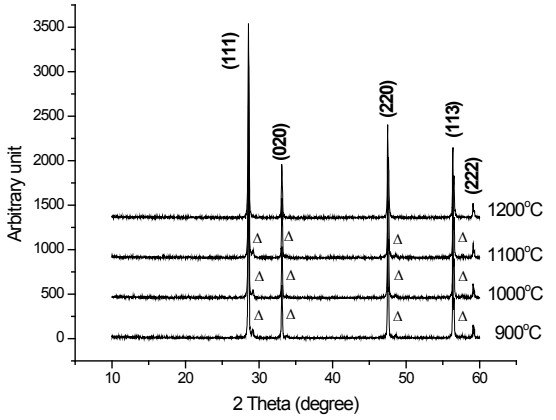

Fig.1: XRD diffraction patterns of Y_2O_3 doped CeO_2 system prepared by conventional solid-state method. Δ denotes the unreacted Y_2O_3 (JCPDS powder diffraction File No. 19-1448).

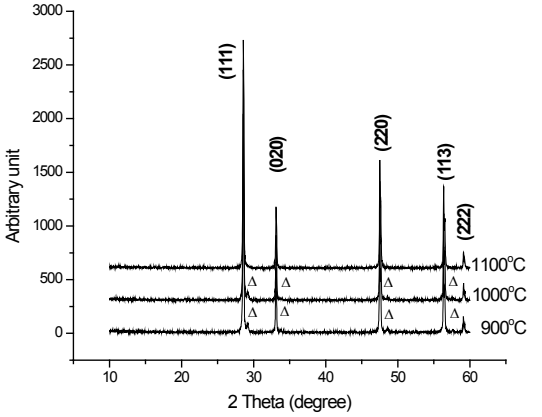

Fig.2: XRD diffraction patterns of Y_2O_3 doped CeO_2 system prepared by mechanochemical method. Δ denotes the un-reacted Y_2O_3 (JCPDS powder diffraction File No. 19-1448).

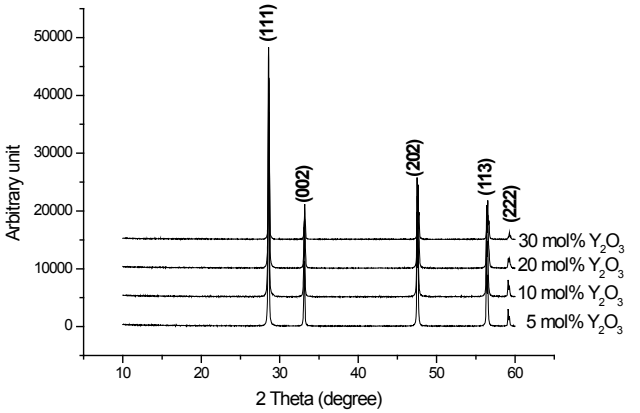

Fig.3: Powder XRD (CuKα) patterns of $Ce_{1-x}Y_xO_{2-\delta}$ ($0.05 \leq x \leq 0.3$) prepared by mechanical syntheses.

Calculation of the cell parameters was done using the main reflection of a material having a typical fluorite structure with an fcc cell, corresponding to the (1 1 1) plane at ~ 28.5˚. Comparison of lattice parameters as a function of yttrium content is shown in Fig.4. The lattice constants of $Ce_{1-x}Y_xO_{2-\delta}$ samples synthesised by both methods decreased linearly with increasing yttrium content in the investigated substitution range x = 0.05 - 0.3. The results in Fig.4 further suggest that all the doped ceria samples in this work are ceria-based solid solutions. Incorporation of Y_2O_3 into the CeO_2 system caused an almost linear decrease of cell parameter and is in good agreement with effective ionic radii for which the radius of Y^{3+} (0.1019 nm) is smaller than the radius of Ce^{4+} (0.1111 nm) (Shannon, 1976). It was also found that the 2θ values of the doped ceria shift slightly towards higher angles when x varies from 0.05 to 0.3 (Fig.3). Dissolution of a smaller radius cation into the ceria system is testimony that yttrium is soluble into the ceria crystal lattice and is in good agreement with Vegard's rule of lattice parameter linear dependence against the composition.

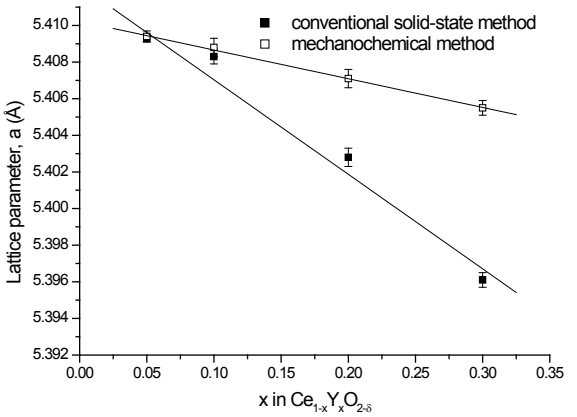

Fig.4: Variation of cell parameters with x in$Ce_{1-x}Y_xO_{2-\delta}$ solid solutions prepared by both mechanochemical and solid state methods

Thermal Analysis

Thermal analysis showed no significant thermal events, verifying that all the compounds are thermally stable at a temperature range from room temperature to 1000 ˚C.

Impedance Analysis

The conductivity data measured in air below 1073 K for Y-doped ceria samples prepared by solid-state and mechanochemical methods were analysed using Arrhenius' equation:

$$\sigma = \frac{\sigma \circ}{T} \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where E is the activation energy of electrical conduction, k Boltzmann's constant, T the absolute temperature and σ_o the pre-exponential factor.

This study showed the conductivity measurement upon $Ce_{0.9}Y_{0.1}O_{1.95}$ samples synthesised using both methods, which were sintered at 1200 – 1500 ˚C (Fig.5 and Fig.6). The optimum temperature for the highest conductivity for $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by the solid-state method was determined to be 1400 ˚C, whereas for samples prepared using the mechanochemical method, comparable conductivity occurred at 1300 ˚C. Both samples showed similar values at 600 ˚C (~ 10^{-3} S cm^{-1}) with activation energy, E_a ~ 0.89 eV, in agreement with the value reported previously (Van Herle *et al*., 1996).

Morphology Analysis

The powder samples were pelletised and sintered at 1200 ˚C overnight with a programmed heating and cooling rate of 5 ˚C/minute. Fig.7 and Fig.8 show typical micrographs of samples prepared by the solid-state reaction and the mechanochemical method. $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by solid-state reaction revealed poor densification. It was difficult to distinguish the

grain boundaries and to estimate the corresponding grain size. The sample prepared by the mechanochemical method, however, appeared dense with low intergranular porosity. The solid-state reaction method yields higher particle size and larger intergranular porosity due to high-firing temperature. The average grain size measured from the sample prepared by the mechanochemical method is 1.04 μm compared to 4.25 μm, prepared by solid-state reaction.

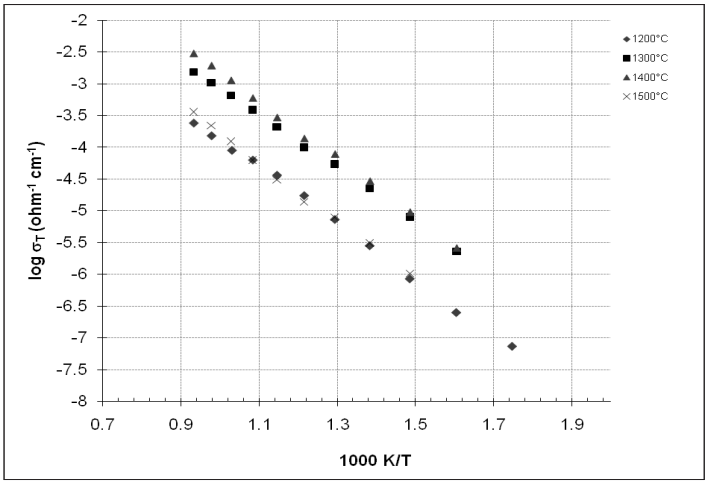

Fig.5: Arrhenius conductivity plot of the ionic conductivity of $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by conventional solid-state method.

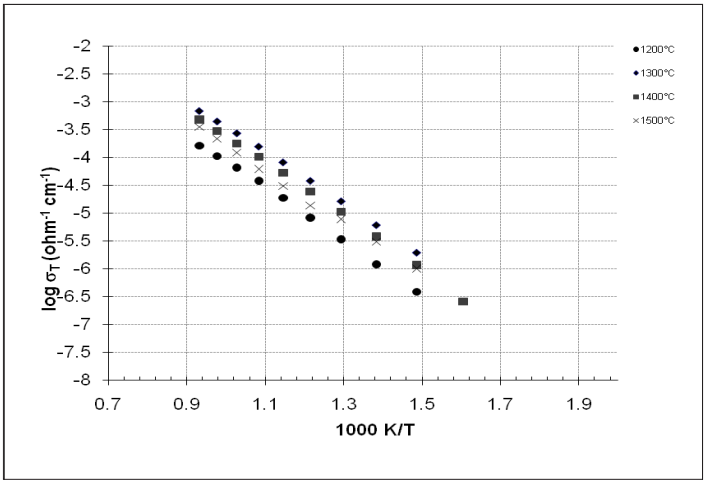

Fig.6: Arrhenius conductivity plot of the ionic conductivity of $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by mechanochemical method.

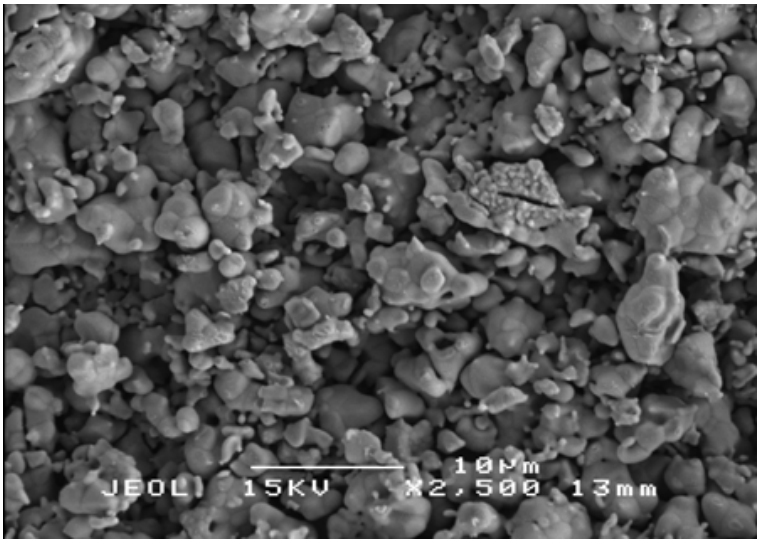

Fig.7: Scanning electron micrograph of $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by conventional solid-state method

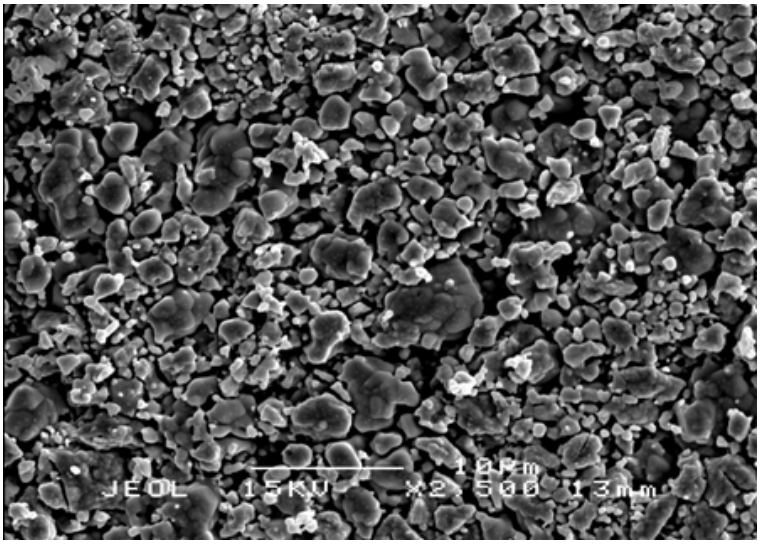

Fig.8: Scanning electron micrograph of $Ce_{0.9}Y_{0.1}O_{1.95}$ prepared by mechanochemical method

CONCLUSION

The yttrium-doped ceria solid solutions, $Ce_{1-x}Y_xO_{2-\delta}$ ($0.05 \leq x \leq 0.3$) with fluorite structure, were successfully prepared using different mechanical syntheses. The results of X-ray diffraction showed that all samples were single phase with a cubic fluorite structure. The employment of the mechanochemical synthetic route had proven promising in terms of phase stability. The best conductivity of the $Ce_{0.9}Y_{0.1}O_{1.95}$ studied prepared by the conventional solid-state method ($\sigma_{600^\circ C} \sim 2.97 \times 10^{-3}$ S cm^{-1}) was close to those previously recorded by Zhang *et al*. (2003) and

Yamashita *et al*. (1995) ($\sigma_{600^{\circ}C} \sim 10^{-2}$ S cm^{-1}) and one order of magnitude higher than that of stabilised zirconia, the most commonly used solid electrolyte at the corresponding temperatures ($\sigma_{600^{\circ}C} \sim 10^{-4}$ S cm^{-1}) (Marques *et al*., 2006).

ACKNOWLEDGEMENTS

The authors wish to thank Yayasan Khazanah for funding this research work through the Yayasan Khazanah Watan Scholarship and the Ministry of Science and Technology for financial support through Research Grants.

REFERENCES

Dudek, M. (2008). Ceramic oxide electrolytes based on CeO_2 - Preparation, properties and possibility of application to electrochemical devices. *Journal of the European Ceramic Society*, *28*, 965-971.

Huang, W., Shuk, P., & Greenblatt, M. (1997). Properties of sol-gel prepared $Ce_{1-x}Sm_xO_{2-x/2}$ solid electrolytes. *Solid State Ionics*, *100*, 23-27.

Li, J. G., Ikegami, T., Wang, Y., & Mori, T. (2002). Nanocrystalline $Ce_{1-x}Y_xO_{2-x/2}$ ($0 \leq x \leq 0.35$) Oxides via Carbonate Precipitation: Synthesis and Characterization. *Journal of Solid State Chemistry*, *168*, 52–59.

Marques, F. M. B., Kharton, V. V., Naumovich, E. N., Shaula, A. L., Kovalevsky, A. V., & Yaremchenko, A. A. (2006). Oxygen ion conductors for fuel cells and membranes: Selected developments. *Solid State Ionics, 177*, 1697-1703.

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, *32A*, 751.

Singh, P., & Hegde, M. S. (2008). Controlled synthesis of nanocrystalline CeO_2 and $Ce_{1-x}M_xO_{2-\delta}$ (M = Zr, Y, Ti, Pr and Fe) solid solutions by the hydrothermal method: Structure and oxygen storage capacity. *Journal of Solid State Chemistry, 181*, 3248–3256.

Van Herle, J., Horita, T., Kawada, T., Sakai, N., Yokokawa, H., & Dokiya, M. (1996). Sintering behaviour and ionic conductivity of yttria-doped ceria. *Journal of the European Ceramic Society*, *16*, 961-973.

Wang, Y., Kageyama, H., Mori, T., Yoshikawa, H., & Drennan, J. (2006). Local structures around Y and Ce cations in 10 mol% Y_2O_3 doped ceria ceramics by EXAFS spectroscopy. *Solid State Ionics, 177*, 1681-1685

Yamashita, K., Ramanujachary, K. V., & Greenblatt, M. (1995). Hydrothermal synthesis and low temperature conduction properties of substituted ceria ceramics. *Solid State Ionics*, *81*, 53-60.

Zhang, T. S., Ma, J., Huang, H. T., Hing, P., Xia, Z. T., Chan, S. H., & Kilner, J. A. (2003). Effects of dopant concentration and aging on the electrical properties of Y-doped ceria electrolytes. *Solid State Sciences*, *5,* 1505–1511.