



# Effect of flash sintering on microstructure of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte fabricated by tape-casting



Jonathan Usuba Valdebenito<sup>a,\*</sup>, Ali Akbari-Fakhrabadi<sup>b</sup>, Mangalaraja Ramalinga Viswanathan<sup>a,\*</sup>

<sup>a</sup> Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, Faculty of Engineering, University of Concepcion, Concepcion 407-0409, Chile  
<sup>b</sup> Advanced Materials Laboratory, Department of Mechanical Engineering, University of Chile, Beauchef 851, Santiago, Chile

## ARTICLE INFO

### Article history:

Received 2 June 2017

Received in revised form 27 July 2017

Accepted 28 July 2017

Available online 29 July 2017

### Keywords:

Gadolinium doped ceria

Electrolyte

Tape-casting

Flash sintering

## ABSTRACT

Flash sintering technique was applied to  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (10GDC) electrolyte fabricated by tape-casting at different temperatures under various electric fields. Densification of the electrolyte at constant electric field depended mainly on the current passing through the sample. The applied electric field influenced the temperature at which the flash sintering occurred. To achieve the microstructure with high densification, a suitable current density must be selected. The temperature for flash sintering varies with the materials and the contact area between the particles, which changes with the particle size, the porosity and the inhomogeneity.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Solid oxide fuel cells (SOFCs) based on yttria-stabilized zirconia (YSZ) operate only at high temperature (>800 °C). Such SOFCs require expensive structural components which prohibit their commercialization [1]. To reduce the operating temperature, gadolinium doped ceria (GDC) has been considered as a suitable solid electrolyte for low temperature SOFCs [2].

Generally, SOFC support is manufactured by tape-casting technique, which is a cost-effective method and therefore suitable for mass production [3]. Traditional tape-casting method needs organic solvents. Due to the environmental safety and the economic reasons, aqueous-based tape-casting method is adopted [4].

It was found that the sintering by electrical field requires short time. Especially in flash sintering method, densification occurs within a few seconds at threshold condition (at specific electric field, ceramics and furnace temperature). The research focused on YSZ [5,6] indicates the existence of a critical electric field ( $E_{crit}$ ) that depends on the nature of the material, and accordingly, two types of behaviors are observed. When  $E < E_{crit}$ , the sintering rate gradually increases (field assisted sintering technique, FAST). Suppose  $E > E_{crit}$ , the sintering rate increases abruptly along with sud-

den increase in the conductivity, which in turn achieves the densification in a few seconds (FLASH sintering). Xao et al. [7] prepared a densified 20%GDC (20 mol% gadolinium doped ceria) microstructure by flash sintering technique under a field of 70 V/cm with the sintering temperature of 545 °C. Biesuz et al. [8] also prepared GDC at 550 °C with a field of 75 V/cm. In both cases, the powders were previously compacted and heated by flash sintering technique.

Herein, we applied flash sintering technique on  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (10GDC) tapes manufactured by aqueous tape-casting method. The effect of electric field, current density and time on the formation of GDC microstructure was determined.

## 2. Experimental

### 2.1. Tape casting

All the required chemicals were obtained from Sigma-Aldrich.  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (10 mol%, 10GDC) was synthesized by nitrate combustion method [9]. An aqueous tape-casting [10] was carried out using distilled water, polyacrylic acid (PAA,  $M = 1800 \text{ gmol}^{-1}$ ), polyvinyl alcohol (PVA,  $M = 70.000\text{--}100.000 \text{ gmol}^{-1}$ ) as the solvent, dispersant and binder respectively. Polyethylene glycol (PEG,  $M = 200 \text{ gmol}^{-1}$ ) and glycerol were used as plasticizer. Octanol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate were selected as the defoamer and surfactant respectively. The composition of the slurry is given in Fig. 1a. The pH of the suspension was adjusted by  $\text{NH}_4\text{OH}$  and  $\text{HNO}_3$ .

\* Corresponding authors.

E-mail addresses: [jusuba@udec.cl](mailto:jusuba@udec.cl) (J.U. Valdebenito), [mangal@udec.cl](mailto:mangal@udec.cl) (M.R. Viswanathan).

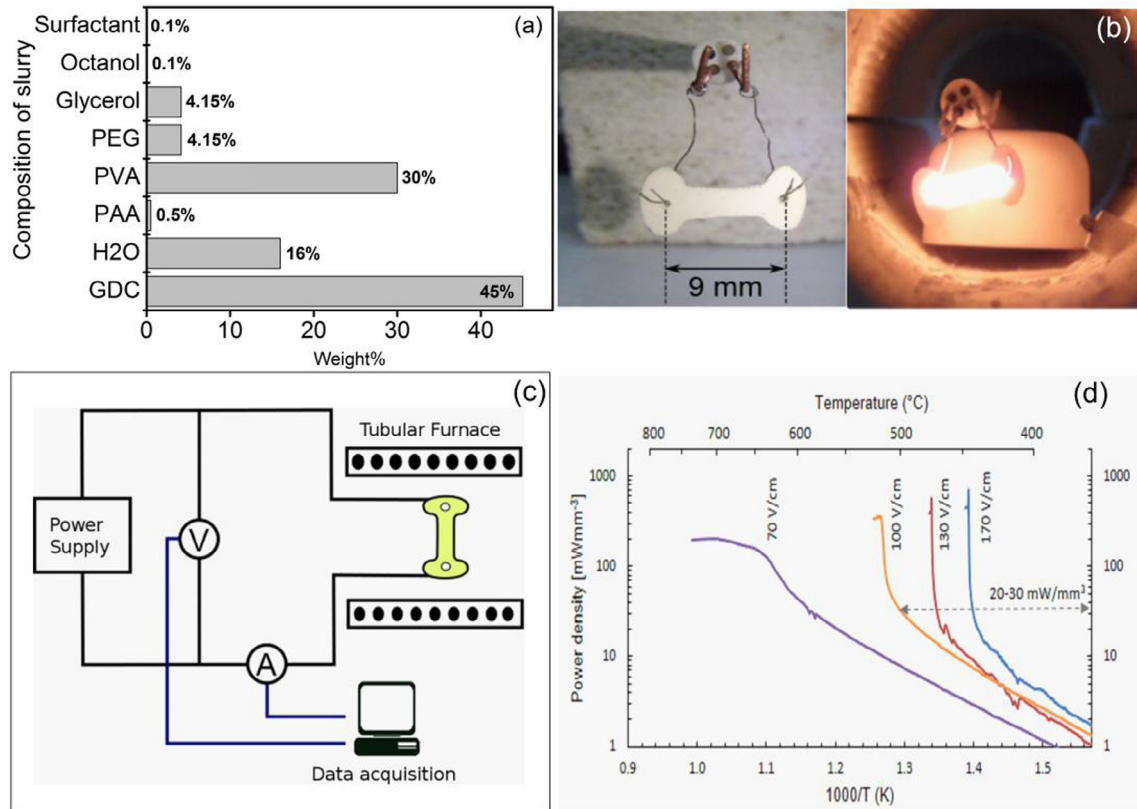


Fig. 1. (a) Composition of slurry, (b) photographs of sample, (c) flash sintering set-up, and (d) power density versus temperature plot.

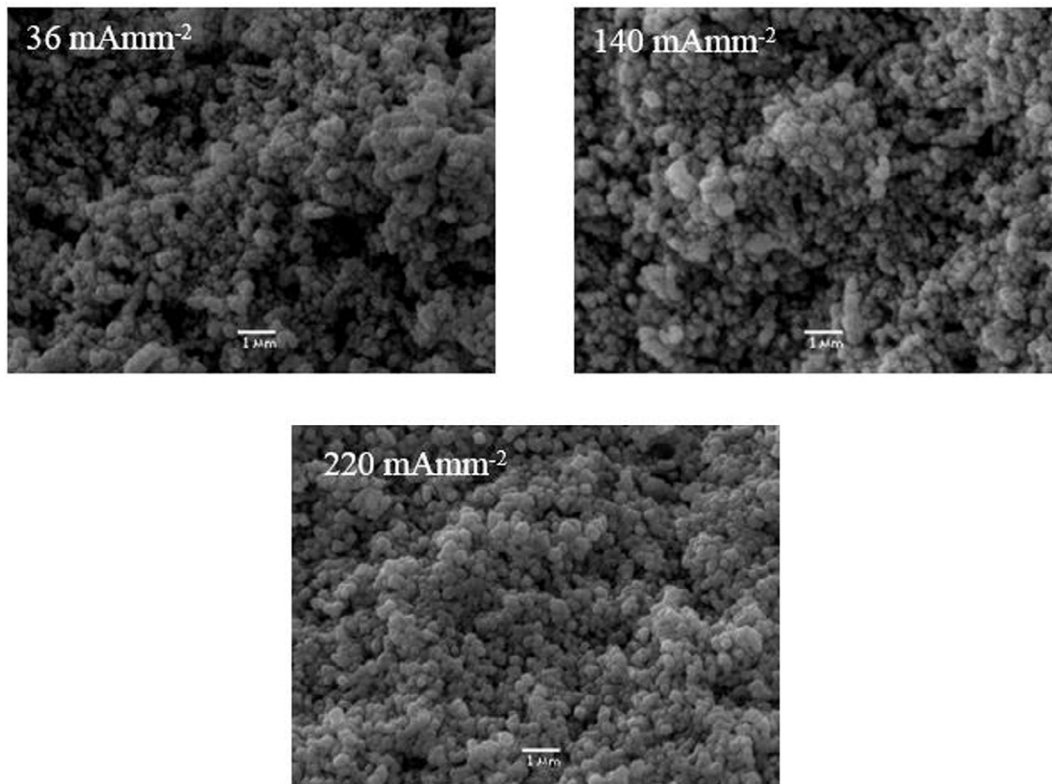


Fig. 2. Effect of current density on the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  microstructure.

## 2.2. Flash sintering

Dog bone samples were insulated by green tape along with two holes at the end and heated at 600 °C for 1 h to eliminate any organic additives, and then pre-sintered at 1000 °C for 1 h to increase the mechanical strength. Then, two platinum wires (diameter = 0.2 mm) were placed in each holes and filled with silver paste to improve the electrical contact (Fig. 1b). Then the sample is kept into the tube furnace (Thermo Scientific Linderberg Blue M 1100 °C) that is connected to the (Sorensen DLM 300–2) power source (Fig. 1c). The furnace heating rate was 10 °C/min. Two multimeters were connected to measure the current (Tektronix DMM 4050) and the voltage (DMM Yokogawa 7162). The electric field ( $E$ ) is calculated by Eq. (1):

$$E = V/l \quad (1)$$

where  $V$  is the voltage and  $l$  is the separation between electrodes. On the other hand, current density is expressed by Eq. (2):

$$j = I/wt \quad (2)$$

where  $I$  is the current,  $w$  and  $t$  are the width and the thickness of the sample respectively. The power density ( $p$ ) can be calculated by:

$$p = Ej \quad (3)$$

The density of the sintered samples was measured by Archimedes method and the morphology of the samples was analyzed by JEOL 6460 LV scanning electron microscopy.

## 3. Results

The power density versus temperature input curves for different electric field is shown in Fig. 1d. Nonlinear power dissipation is observed at above 100 V/cm, which is considered as a flash sintering behavior. The 70 V/cm curve corresponds to FAST regime where the power dissipation increases smoothly.

The effect of current density on GDC microstructure was evaluated under a constant electric field of 100 V/cm. The current densities of 36, 140 and 220 mA/mm<sup>2</sup> were applied, and the percentage of densification obtained was 60, 68 and 90%, respectively (Fig. 2). Densification of particles increased with the current density. Especially, the sample at 220 mA/mm<sup>2</sup> reached higher density with homogeneous and smaller grain size.

Fig. 3a–f shows the dissipated power curve under isothermal conditions (600 °C) for different times along with the resulting microstructures. 10 s was required for the occurrence of flash sintering. The power density at the steady state was 1500 mWmm<sup>−3</sup> for the three cases studied, and then gradually decreased to 1200 mWmm<sup>−3</sup> as the time progresses especially the sample was exposed to 300 s. In turn, the microstructures generally have an acceptable degree of densification but still possess porosity in small areas, which is more evident in the samples subjected to 120 s. The samples possessed with a homogeneous microstructure with the density around 90%.

## 4. Discussions

There will be significant differences even for the materials whose composition is very similar. For instance, 20GDC experi-

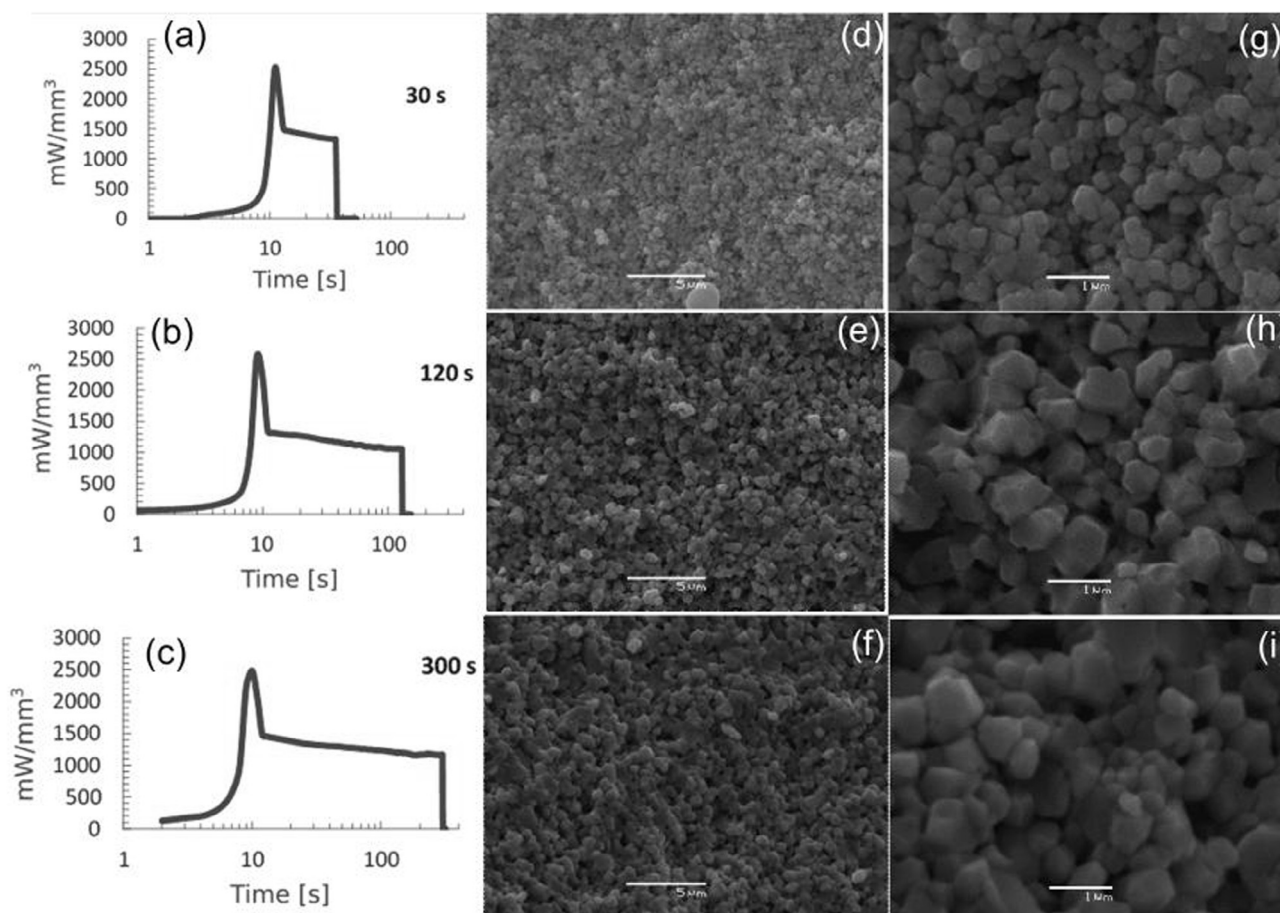


Fig. 3. (a–f) Time effect and (g–i) difference in the grain size under isothermal flash sintering at 600 °C on Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> tape.

enced the flash sintering under a field of 70 V/cm at 545 °C [7]. Under the same electric field, 10GDC samples of this work did not experience flash sintering, but rather had a FAST behavior, i.e., a gradual densification between 600 to 700 °C. Moreover, the critical electric field for 20GDC was around 30 V/cm [7], whereas for 10GDC, it is 70–100 V/cm. It seems that the increase in the vacancy sites decreases the electric field required to occur flash sintering phenomena. This is consistent with the mechanism described by Narayan [11], which proposed the interaction between the electric field and high concentration of intrinsic and extrinsic defects in oxide ceramics that lead to enhance the conductivity and rapid heating.

On the other hand, the high degree of porosity was obtained under different electric fields, which indicates that the electric field did not impact significantly on the densification process that seems to depend more heavily on the current density. Under a given electric field and a certain temperature by the field itself, the conductivity rises abruptly, which suggested that the field along with the temperature has acted synergistically. However, if the current density is not enough, not only the material densification is incomplete but also biased densification areas are achieved (Fig. 2). Based on the theory of Narayan [11], it could be concluded that the current densities of 36 and 140 mA/mm<sup>2</sup> were not enough to achieve the avalanche effect that generate adequate melt grain boundaries, and therefore it is too low to achieve the homogeneous material densification. As the current density increases, the porosity decreases. According to Narayan [11], the sites of the selective melting increased to reach an acceptable degree of densification for the samples under a current density of 220 mA/mm<sup>2</sup>.

Under the flash sintering for 30 s, the samples could be densified satisfactorily with homogeneous and fine sized grains. It is known that the electric fields have a low magnitude retarding effect on the grain growth. In particular, a lower critical field (within the FAST type) produces a microstructure with lesser grain size than those samples sintered under normal conditions [12]. In flash sintering technique, the same phenomenon also occurs. The 20GDC samples sintered under different electric fields conclude that the application of high electric fields significantly reduces the grain size [7]. However, the prolonged application of the technique shows a significant increase in the grain size (Fig. 3g–i). Especially, larger grain size is observed for the samples exposed to 120 and 300 s. The estimated transient regime temperature was found to be 1500 °C using Eq. (4) (black body model):

$$T = \left( T_0^4 + \frac{W}{A\sigma\epsilon} \right)^{\frac{1}{4}} \quad (4)$$

where T is the sample temperature, T<sub>0</sub> is the furnace temperature, W is the power dissipated (W), A is the emissive area of the sample

(m<sup>2</sup>), σ is Stefan Boltzmann constant (5.67 × 10<sup>-8</sup> W/m<sup>2</sup> K<sup>4</sup>) and ε is the emissivity (for ceramic oxides, ε = 0.9). Generally, the Eq.4 subestimates the temperature of the samples at 100–200 °C that is above the actual temperature, because it is generally assumed that the emissivity of the oxide is equal to one [13].

By considering the dissipated power in this system that was 1500 mW/mm<sup>3</sup>, the measured temperature is slightly higher than the traditional 10GDC sintering temperature (1400 °C). The high temperature was reached and the fact that there was a significant densification with longer application indicates that the predominant processes of mass transport in the transient, after a certain period of time, were coalescing, favoring the grain growth but without necessarily improving the densification of the sample.

## 5. Conclusion

The temperature required to sinter 10GDC fabricated by tape-casting can be significantly reduced using an accurate electric field. It is possible to sinter at 445 °C under an electric field of 170 V/cm. However, in order to obtain a dense microstructure, it is necessary to select a suitable current density. As the current density increases, the densification increases with decreasing porosity. Moreover, the time at applied power influences the microstructure of the material, promoting the grain growth after the occurrence of flash sintering phenomena.

## Acknowledgment

JU thanks CONICYT, Government of Chile, Santiago for providing National Doctoral Scholarship (Folio No.: 21150095).

## References

- [1] E. Wachsman, T. Ishihara, J. Kilner, *MRS Bull.* 39 (2014) 773–779.
- [2] R.V. Mangalaraja, S. Ananthakumar, M. Paulraj, K. Uma, M. López, C.P. Camurri, R.E. Avila, *Proc. Appl. Ceram.* 3 (2009) 137–143.
- [3] F. Tietz, H. Buchkremer, D. Sto, *Solid State Ionics* 153 (2002) 373–381.
- [4] L.H. Luo, A.I.Y. Tok, F.Y.C. Boey, *Mater. Sci. Eng. A* 429 (2006) 266–271.
- [5] J.S.C. Francis, R. Raj, *J. Am. Ceram. Soc.* 95 (2012) 138–146.
- [6] M. Cologna, A.L.G. Prette, R. Raj, *J. Am. Ceram. Soc.* 94 (2011) 316–319.
- [7] X. Hao, Y. Liu, Z. Wang, J. Qiao, K. Sun, *J. Power Sources* 210 (2012) 86–91.
- [8] M. Biesuz, G.D. Agli, L. Spiridigliozzi, C. Ferone, V.M. Sglavo, *Ceram. Int.* (2016) 1–6.
- [9] R.V. Mangalaraja, S. Ananthakumar, A. Schachtsiek, M. López, C.P. Camurri, R.E. Avila, *Mater. Sci. Eng. A* 527 (2010) 3645–3650.
- [10] A. Akbari-Fakhrabadi, R.V. Mangalaraja, F.A. Sanhueza, R.E. Avila, S. Ananthakumar, S.H. Chan, *J. Power Sources* 218 (2012) 307–312.
- [11] J. Narayan, *Scr. Mater.* 69 (2013) 107–111.
- [12] R. Raj, M. Cologna, J.S.C. Francis, *J. Am. Ceram. Soc.* 94 (2011) 1941–1965.
- [13] R. Raj, *J. Eur. Ceram. Soc.* 32 (2012) 2293–2301.