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Reducing sintering temperature of yttria stabilized zirconia through addition of lithium nitrate and alumina

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Abstract

Reducing sintering temperature of yttria stabilized zirconia (YSZ) has been achieved through doping with alumina and lithium nitrate at levels below 1 mol%. Sintering experiments of pure and doped samples have been conducted with the same profile using an optical dilatometer. All samples exhibited anisotropic sintering over a wide range of temperatures but final shrinkage values were comparable in axial and radial directions. Sintering temperature has been reduced by as much as 110 °C. We believe that the reduction in sintering temperatures is due to viscous flow in the first stage sintering. Bimetallic doping (mixture of alumina and lithium nitrate doping) is more effective in reducing sintering temperature than single doping possibly due to better distribution of doping material throughout the matrix material. Separate sintering experiments for 5 h have been conducted at 1250 °C and 1170 °C on doped 8 mol% and 3 mol% YSZ, respectively, and have shown that near full density (∼96%) is reachable.

Keywords: A. Sintering; Doping; Zirconia; Sintering aids

1. Introduction

Lowering sintering temperature is useful not only because it reduces the processing cost (and also processing time) and improves the quality control, by avoiding abnormal and excessive grain coarsening, but also because it may serve as an unavoidable solution to certain applications. For example, the electronic packaging industry has long strived for co-sintering multiple layers including ceramics and metals. Lowering sintering temperature of ceramic substrate used in some electronic structure was a breakthrough and an excellent alternative to the traditional HTCC (high temperature co-fired ceramics) as gold and silver could now be used as metallization layers [1]. The so-called Low temperature co-fired ceramics (LTCC) technology is nowadays used to produce multichip ceramic modules MCM-C for packaging integrated circuits, sensors and actuators, MEMS and MOEMS packages [2].

Solid oxide fuel cell is among many other applications where lowering sintering temperature is beneficial. Here gadolinium doped ceria is a promising electrolyte material due to its good electrochemical performance. However, ceria requires very high sintering temperature usually above 1500 °C [3–7]. For an anode supported fuel cell this presents a problem as the anode sintering temperature is lower than the electrolyte sintering temperature. The anode that is presintered at a lower temperature is going through a second sintering process above 1500 °C that may cause it to disintegrate. Thus, the need for reducing the sintering temperature of electrolyte is pressing from a technological point of view. Additionally, reducing the sintering temperature has an obvious economic benefit.

The traditional SOFC electrolyte is yttria stabilized zirconia (YSZ). This electrolyte is not as conductive as ceria but it showed good stability and performance over a long period of time and therefore is most celebrated in industry. Here the sintering temperature is matching that of the anode but much higher than that of the cathode. The latter component shall not be heated above 1200 °C. Lowering sintering temperature of the YSZ electrolyte to the cathode sintering temperature shall reduce the cost and open the opportunity for developing co-sintering protocol including anode, electrolyte and cathode.

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This requires reducing temperature from 1400 °C to below 1200 °C. Although sequential sintering of the layers (anode, electrolyte and cathode) is currently the standard process, it may run up to a prohibitively high cost and time. For example, if a sintering cycle last a working day, the whole fuel cell stack including anode, anode current collector, electrolyte, cathode current collector and cathode requires a whole week for fabrication. Another day is required for sintering glass-ceramic which is usually used as sealant. Therefore, co-sintering of fuel cell components shall be a very attractive process to develop.

It is the aim of this paper to reduce the sintering temperature of YSZ. Sintering additives are used at very small concentrations in order to avoid compromising physical properties of the host material such as ionic conductivity.

2. Experimental procedure

Commercial powder 3 mol% YSZ (MEL chemicals) and 8 mol% YSZ (Tosho Corporation) were used in the experiments. Lithium nitrate and aluminum nitrate were used as sintering aid precursors. For 8 mol% YSZ systems, lithium nitrate was used as sintering aid at concentration of 0.3, 0.5 and 1 mol% and aluminum nitrate was introduced alone at concentration of 0.25 mol% in one case and along with 0.5 mol% lithium nitrate in a second case. For 3 mol% YSZ, only lithium nitrate were considered at a concentration of 0.5 mol% lithium nitrate. Table 1 summarizes the various experiments along with sample designations.

The sintering aid precursors are first dissolved in water. The solution is brought to 40 °C onto a hotplate and stirred using a magnetic bar. Zirconia powder is added slowly to the solution while stirring. The resulting slurry is stirred overnight at 40 °C. The powder is then dried and calcined at 500 °C in a furnace. After calcination the powder is mixed in ethanol and ball milled for several hours. Thereafter the powder is dried, placed into a mortar and mixed with binder solution. After being well mixed, the powder is made into a pellet at low consolidation pressure (~0.5 ton). The pellet is weighted and its dimensions measured before being sintered at 5 °C/min to 1500 °C. The dilatometry tests were conducted in an optical dilatometer (ISC Frauenhofen). The weight and dimensions of the pellet were again determined after sintering.

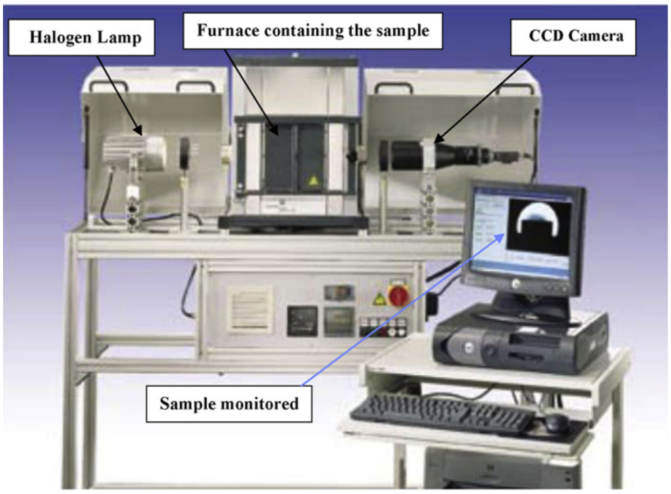

Fig. 1. Optical dilatometer set-up including halogen lamp, high-temperature furnace, CCD camera and connected computer with integrated image software.

The optical dilatometer is shown in Fig. 1. The sample is placed in a chamber furnace which has two openings on both sides. On one side a halogen lamp illuminates the sample while on the other side a CCD camera records the sample silhouette. This recording is conducted by an optical system that takes into account the sample distortion without loss of accuracy and with a resolution within at most 2 μm. Vertical and horizontal shrinkage can be determined with the help of an image analysis software. Here any potential shift, although not corrected by the optical system, is well compensated by the image software. The advantage of this optical dilatometer is not only because images are taking during heat treatment and thus observing sample changes instantaneously but also because measurement is preformed remotely without contacting sample so possible deformation due to push rod pressure is excluded. Moreover, the optical dilatometer permits capturing all details of dimension changes including anisotropic sintering as linear shrinkages in axial and radial directions could be in situ monitored.

3. Results and discussion

Doping of 8YSZ with lithium nitrate was restricted to doping level up to 1 mol%. Alumina was added only at a level of 0.25 mol% either to pure 8YSZ or to 0.5 mol% lithium

Table 1
Designation, material composition and sintering temperature of the tested samples.

Designation	Mol% lithium nitrate	Mol% aluminum nitrate	Matrix material	Sintering temperature
3YSZ	–	–	3 mol%YSZ	1500
05LN-3YSZ	0.5	–	3 mol%YSZ	1500
05LN-3YSZ-1170	0.5	–	3 mol%YSZ	1170
8YSZ	–	–	8 mol%YSZ	1500
03LN-8YSZ	0.3	–	8 mol%YSZ	1500
05LN-8YSZ	0.5	–	8 mol%YSZ	1500
1LN-8YSZ	1	–	8 mol%YSZ	1500
025A-8YSZ	–	0.25	8 mol%YSZ	1500
025A-05LN-8YSZ	0.5	0.25	8 mol%YSZ	1500
1LN-8YSZ-1250	1	–	8 mol%YSZ	1250
025A-05LN-8YSZ-1250	0.5	0.25	8 mol%YSZ	1250

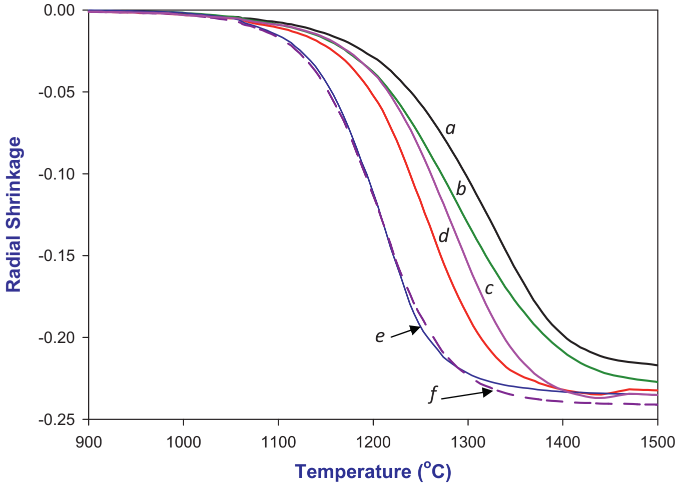

Fig. 2. Radial shrinkage versus temperature: (a) pure 8YSZ, (b) 025A-8YSZ, (c) 03LN-8YSZ, (d) 05LN-8YSZ, (e) 1LN-8YSZ and (f) 025A-05LN-8YSZ.

nitrate doped 8YSZ. A comparison of linear radial and axial shrinkage results of doped and undoped 8YSZ is given is Figs. 2 and 3, respectively. Table 2 lists the maximum shrinkage values at 1500 °C for every experiment for both linear shrinkages in axial and radial directions and their percent variations. Although there is a difference between linear shrinkage in axial and radial directions at final sintering process, this difference is small enough to assume that final shrinkage is isotropic. Except for the sample 05LN-8YSZ where the shrinkage variation is ∼6.5%, the variations for the rest are less than 1.5%. Note, however, that the axial and radial sintering profiles vary at lower temperatures and the difference is quite considerable over a wide range of temperatures. An example of such anisotropic shrinkage over wide range of temperatures is shown in Fig. 4 for the sample 03LN-8YSZ. Thus, although the final axial and radial shrinkage values are comparable, an obvious anisotropy in sintering is observed during intermediate sintering stage.

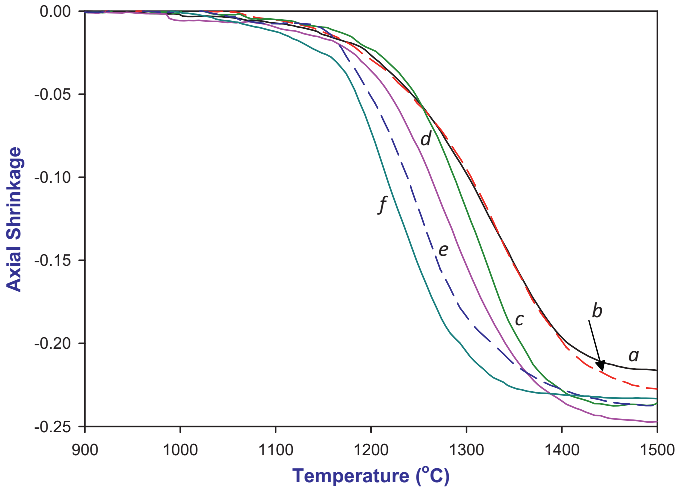

Fig. 3. Axial shrinkage versus temperature: (a) pure 8YSZ, (b) 025A-8YSZ, (c) 03LN-8YSZ, (d) 05LN-8YSZ, (e) 1LN-8YSZ and (f) 025A-05LN-8YSZ.

Table 2
Shrinkage values in the radial and axial directions and their percent variations at the maximum sintering temperature.

Material	Radial shrinkage	Axial shrinkage	Percent variation
Pure 8YSZ	21.7%	21.63%	0.32%
03LN-8YSZ	23.51%	23.6%	0.4%
05LN-8YSZ	23.2%	24.7%	6.46%
1LN-8YSZ	24.1%	23.76%	1.4%
025A-8YSZ	22.73%	22.75%	0.1%
025A-05LN-8YSZ	23.5%	23.3%	0.85%

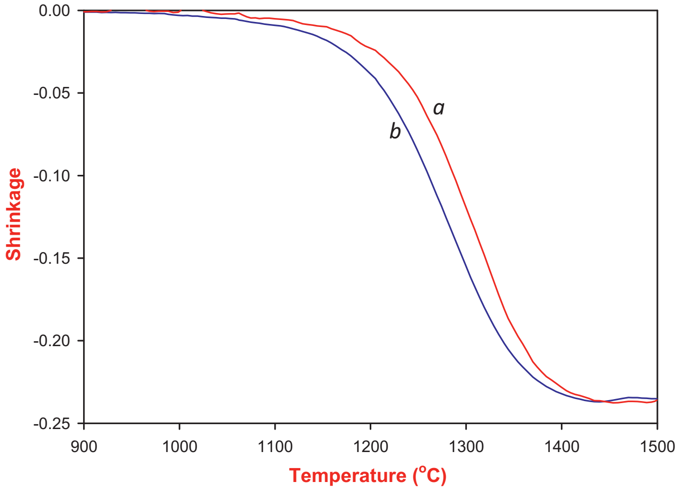

Fig. 4. Axial and radial shrinkage of 03LN-8YSZ versus temperature: (a) axial shrinkage and (b) radial shrinkage. Although the final shrinkage values are similar, there is quite a big difference in shrinkage values in axial and radial directions over a considerable range of temperatures.

As shown in Fig. 2 the onset of sintering is hardly changed for all the samples under investigation. However, if we refer to the transition to the rapid sintering stage (assumed here to be the intermediate sintering stage), then we can clearly see a considerable shift of this stage toward lower temperatures as doping levels are increased.

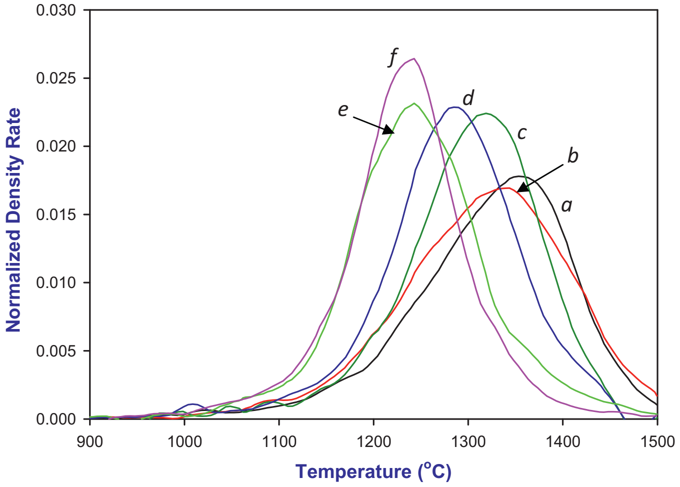

Fig. 5. Normalized density rate versus temperature: (a) pure 8YSZ, (b) 025A-8YSZ, (c) 03LN-8YSZ, (d) 05LN-8YSZ, (e) 1LN-8YSZ and (f) 025A-05LN-8YSZ. Note that the normalized density rate is the opposite of the volumetric strain rate, thus the data shown are positive.

The anisotropic sintering over a wide range of temperatures prevents using linear sintering rates to evaluate the sintering process as these rates vary quite considerably in axial and radial directions. Instead volumetric sintering rate is used. The volumetric sintering rate is given by:

$$\dot{\varepsilon}_v = -\frac{\dot{\rho}}{\rho} \tag{1}$$

The volumetric sintering rate is thus simply the opposite of the density rate normalized by the density itself. Fig. 5 shows the volumetric sintering (normalized density) rate versus temperature. As shown, the temperature at which sintering rates are at maximum progressively reduces in the following order:

$$T_{\max}^{\text{undoped}}(1353\,^{\circ}\text{C}) > T_{\max}^{\text{025A-8YSZ}}(1344\,^{\circ}\text{C}) > T_{\max}^{\text{03LN-8YSZ}}(1319\,^{\circ}\text{C}) > T_{\max}^{\text{05LN-8YSZ}}(1285\,^{\circ}\text{C}) > T_{\max}^{\text{1LN-8YSZ}}(1243\,^{\circ}\text{C}) \cong T_{\max}^{\text{025A-05LN-8YSZ}}(1243\,^{\circ}\text{C}).$$

This observation clearly indicates that addition of lithium nitrate and alumina at very low levels significantly reduces the sintering temperature of 8YSZ. Moreover, the addition of sintering aids progressively increases the densification rate of 8YSZ (see Fig. 5). The larger is the doping content, the higher is the densification rate. We believe that the reduction of sintering temperature is due to viscous sintering predominantly taking place in the early stage sintering, as it was reported elsewhere for other materials [7–9]. Lithium oxide and alumina easily diffuse on the particle surfaces of 8YSZ to form very thin amorphous layers. These thin layers coat host material particles and act as lubricant that facilitates flowing of particles past one another with least friction. Thus, particles at low temperature are able to rearrange easily and thus provide large contact area between them which favors fast sintering.

The high diffusivity of both lithium oxide and alumina during the early stage sintering (at ~1000 °C) is due to various reasons. According to Chen and Chen [10] severely undersized doping ions will be able to migrate fast in materials with either fluorite or C-type structures. In this investigation aluminum ion [atomic radius $(\text{Al}^{3+}) = 67.5$ pm] is much smaller than zirconium ion [atomic radius $(\text{Zr}^{4+}) = 86$ pm] and yttrium [atomic radius $(\text{Y}^{3+}) = 104$ pm]. Thus, doping 8YSZ with alumina shall help reduce the sintering temperature. Similarly, diffusivity of lithium oxide strongly depends on the mobility of metal ions. Due to the high volatility of lithium oxide at low temperature, the mobility of lithium is quite high and we expect to have high diffusivity in the early stage sintering. Van Arkel et al. [11] observed an apparent volatilization of LiO_2 in the presence of oxygen at 1000 °C. They showed that there are small losses of oxide at 1000 °C in either vacuum or dry oxygen. These losses increase dramatically in a medium containing oxygen and small amount of moisture. Since our sintering experiments were carried out in open air, thus in presence of oxygen and moisture, we believe that the volatility of lithium oxide at the early stage sintering is high. These high diffusivity rates of both aluminum and lithium metals on YSZ particles promote viscous sintering at the early and intermediate sintering stage.

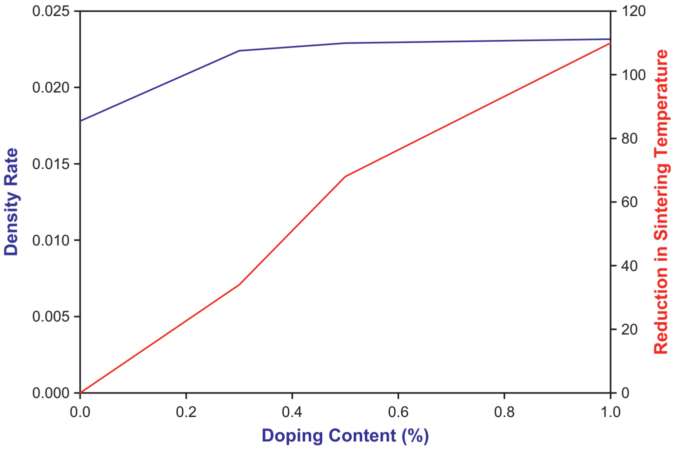

Fig. 6. Maximal values for the normalized density rate versus doping content of lithium nitrate. Also shown is the extent of reduction in sintering temperature versus doping content. The graphic illustration suggests that introducing lithium nitrate in excess of 1 mol% becomes ineffective in reducing sintering temperature.

Interesting to note that the trend of $T_{\max.}$ with mol% addition of lithium nitrate is nearly linearly approximated, as shown in Fig. 6. Addition of 0.25 mol% alumina has clearly less impact on reducing sintering temperature than that of 0.3 mol% of lithium nitrate. If we presume that there is total independency of the effects of both alumina and lithium nitrate in reducing $T_{\max}$, i.e. the effects of both types of doping materials are additive, we would expect that $T_{\max}$ for 025A-05LN-8YSZ would have been reduced to 1270–1280 °C. Even if we would assume that the effect of introduction of alumina is same as that of addition of lithium nitrate then we would expect that $T_{\max}$ for 025A-05LN-8YSZ would have been reduced by 90 °C (temperature reduction corresponding to ~0.75 mol% lithium nitrate in Fig. 6). However, the reduction in temperature is much higher! The actual reduction is as high as 110 °C. Thus, there must be a coupling effect between both alumina and lithium nitrate that has contributed to this unexpected higher reduction in $T_{\max}$. We thus conclude that bimetallic doping is more effective than single metal doping. This is a very interesting observation that shall trigger a rather more attentive investigation on the benefit of bimetallic doping versus single metal doping.

Looking back to Fig. 5, it seems that the coupling effect is occurring in both the early and intermediate sintering stages. The first stage sintering rate for 025-05LN-8YSZ is clearly higher than that of 05LN-8YSZ and nearly approaching that of 1LN-8YSZ. The maximum sintering rate exhibited in the intermediate sintering stage for 025-05LN-8YSZ is higher than that of 1LN-8YSZ although the doping level for the former sample is lower than that of the latter. For both cases, doping level provide sintering aid material to coat particles at the early stage sintering that help rearrangement of particles with least energy requirement. However, it seems that bimetallic doping favors more uniform distributions of doping additives in the host material than single material doping.

As shown in Fig. 6, the maximum magnitude for the sintering rates increases with increasing doping contents of lithium nitrate before progressively flattens for high doping contents. This indicates that with further increase of sintering

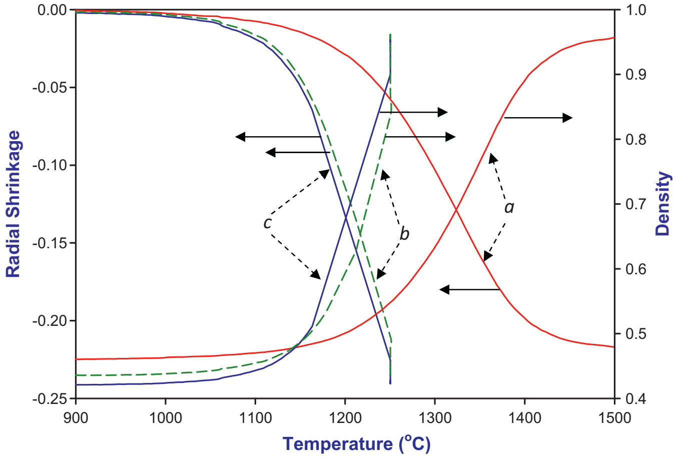

Fig. 7. Density and radial shrinkage of pure and doped 8YSZ versus temperature: (a) pure 8YSZ sintered at 1500 °C for 1 h, (b) 1LN-8YSZ-1250 sintered at 1250 °C for 5 h, and (c) 025A-05LN-8YSZ-1250 sintered at 1250 °C for 5 h.

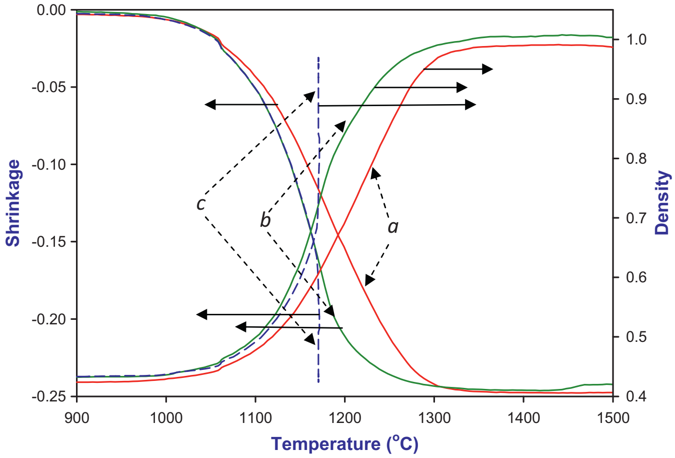

Fig. 8. Density and radial shrinkage of pure and doped 3YSZ versus temperature: (a) pure 3YSZ sintered at 1500 °C for 1 h, (b) 05LN-3YSZ sintered at 1500 °C for 1 h, and (c) 05LN-3YSZ-1170 sintered at 1170 °C for 5 h.

aid no more reduction of sintering temperature in foreseen. Our motivation for not introducing high level of doping was to avoid affecting the chemical and physical properties of 8YSZ especially the ionic conductivity, if any, only by small amount. Thus, we have restricted the doping level to no more that 1 mol%. Nevertheless, this observation indicates that the benefit of introducing higher amount of doping may not be significant anyway. Although, this observation is only approximate based on few experimental data and technically has no solid basis, it was shown by other studies that increasing doping levels will eventually get ineffective in reducing sintering temperatures. For example, Zhang has reported that doping ceria with more than 2 wt.% does not further reduce sintering temperature [7,12].

According to Fig. 5 the temperatures at maximum shrinkage rate are shifted toward lower temperatures indicating that the introduced sintering aids helped reducing sintering temperatures. For the case of introducing either 1 mol% Lithium nitrate or 0.25 mol% alumina and 0.5 mol% lithium nitrate the temperature at maximum shrinkage rate has been reduced from 1353 °C to 1243 °C. Thus, it is anticipated that a temperature as low as 1250 °C could be sufficient for attaining complete sintering. To verify this observation, we have sintered 1LN-8YSZ and 025A-05LN-8YSZ at 1250 °C for 5 h. Fig. 7 shows the results of these experiments compared with that of pure 8YSZ sintered at 1500 °C for 1 h. The density at sintering temperature after 5 h dwell is around 96% (near full density). At this density level, although some isolated pores may be present, no interconnecting pores are possible. As 8YSZ is routinely used as electrolyte for a solid oxide fuel cell (SOFC), reducing its sintering temperature to 1250 °C is a big step toward including cathode in the co-sintering process.

Although 3YSZ has lower ionic conductivity than its 8YSZ counterpart, it has a better sinterability. It is not uncommon that 3YSZ is used commercially as the electrolyte of SOFC [13]. We have doped pure 3YSZ with only 0.5 mol% lithium nitrate in an attempt to reduce the sintering temperature below 1200 °C. Fig. 8 shows shrinkage results for the pure 3YSZ sintered at 1500 °C for 1 h and that of doped 3YSZ sintered at 1500 °C for 1 h and at 1170 °C for 5 h. As shown the sintering temperature for 3YSZ doped with sintering aid as low as 0.5 mol% can be reduced below 1200 °C. Hence electrolyte can be co-sintered with cathode without interdiffusion between both layers.

4. Conclusions

Yttria stabilized zirconia have been doped with lithium nitrate and alumina at different levels below 1 mol%. Shrinkage results show that sintering temperature can be lowered by as much as 110 °C. Mixed doping of lithium nitrate and alumina is more effective than single doping of either type of sintering aids. Separate sintering experiments on 8YSZ and 3YSZ doped with 1 mol% and 0.5 mol% lithium nitrate, respectively, have shown that near full density can be reached at 1250 °C for 8YSZ and 1170 °C for 3YSZ.

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