Catalyst-Infiltrated Supporting Cathode for Thin-film SOFCs

Keiji Yamahara[+], Craig P. Jacobson[+], Steven J. Visco[+], and Lutgard C. De Jonghe[*+#]

[+]Materials Science Division, Lawrence Berkeley National Laboratory,
University of California, Berkeley, CA 94720, USA
and
#Department of Materials science and Engineering
University of California at Berkeley
Berkeley CA 94720

Abstract

The fabrication and electrochemical performance of co-fired, LSM-SYSZ [*i.e.* $La_{0.65}Sr_{0.30}MnO_3$ (LSM) - $(Sc_2O_3)_{0.1}(Y_2O_3)_{0.01}(ZrO_2)_{0.89}$] supported thin-film cells were examined using humidified hydrogen as a fuel. Co-firing of bi-layers and tri-layers was successful at 1250°C by optimizing the amount of carbon pore formers. A power density of a factor of 2.5 higher than that recently reported for the same type of cell at 800°C [3] was obtained for a cell with cobalt infiltration into the supporting cathode: the peak power densities were 455, 389, 285, 202, 141 mW/cm^2 at 800, 750, 700, 650, 600°C, respectively, and in most cases power densities at 0.7V exceeded more than 90 % of the peak output. Increasing the cathode porosity from 43 to 53 % improved peak power densities by as much as 1.3, shifting the diffusion limitation to high current densities. Cobalt infiltration into the support improved those by as much as a factor of 2 due to a significant reduction in non-ohmic resistance. These results demonstrate that cobalt catalyst-infiltrated LSM can be effective and low-cost supporting electrodes for reduced temperature, thin film SOFCs.

---

*Corresponding author. Tel.: +1-510-486-6138; fax: +1-510-486-4881.
E-mail address: dejonghe@lbl.gov.

Introduction

Cost reduction has been frequently identified a key issue for successful commercialization of fuel cells. For solid oxide fuel cells, SOFCs, one approach to cost reduction is lowering the operational temperature from 1000˚C to 600-750˚C, so that inexpensive metallic alloys may considered for interconnects, heat exchangers, and structural components. Reducing raw materials and manufacturing costs of the SOFC membranes   is equally important. For thin-film SOFCs, using $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) supporting cathodes instead of thick nickel-zirconia cermets supporting anodes can be an attractive alternative, because the cost of LSM is estimated to be less than $1/3^{rd}$ of that of yttria stabilized zirconia (YSZ) [1]. Co-firing multi-layered cells can further lower manufacturing costs by requiring less operations. LSM cathode-supported thin-film electrolytes would have further advantages for SOFCs. For example, the difficulties associated with volume contraction and expansion resulting from accidental anode redox cycles may be avoided, since now the anode can be thin and is not dominating the mechanical integrity of the membrane. Also, the risk of Ni-oxidation by water produced at high current densities, potentially more problematic at lower operation temperatures, is less for thinner anodes.

It was demonstrated earlier that a co-fired LSM supported YSZ cell could perform quite well as an oxygen pump, *e.g.* a current of 1.55 A/cm^2 could be sustained at a cell voltage of 0.5 V, at 800°C [2]. There have, however, been few studies evaluating the performance of co-fired LSM supported SOFCs [3,4]. One of these studies reported a peak power density of 180 and 830 mW/cm^2 at 800 and 1000˚C, respectively [3], with these performances limited by the supporting LSM cathode. At 800˚C, this power density is marginal for practical use. Recently, it was reported [5, 6] that the LSM cathode activity can be dramatically improved by infiltrating nano-

sized catalyst particles into its pores after the firing process. It may therefore be expected that the performance of LSM-supported thin-film SOFC cells could equally be improved by this procedure.

In this study, we evaluate the electrochemical performances of co-fired LSM-SYSZ composite cathode-supported thin-film SOFCs, where the cathode is subsequently infiltrated with cobalt nitrate to produce additional catalyst sites. While this does not yet address the lowering of the zirconia content of the cell electrodes, it is an assessment of the potential benefit that electrode catalyst infiltration may provide. It can also be envisioned that the zirconia-containing active layer need only be 20-50 microns thick so that the remainder of the cathode can be LSM only. In the fabrication of these cathode-supported cells, the following issues should be considered: (1) Chemical reactions between LSM and zirconia, which occurs significantly above 1200°C and causes electrical degradation of the LSM/YSZ interfaces [7,8].   (2) Excessive coarsening of LSM particles, with loss of triple phase boundaries for oxygen reduction reaction. (3) Gas diffusion through the continuous pores of the supporting cathode. Thus, the co-firing temperature and the amount of pore formers included in the cathode are chosen to be compatible with both these requirements. In addition, co-firing requires appropriate matching of the electrolyte film shrinkage with that of the supporting electrode.   The electrochemical performance of the cells, using flowing, humidified hydrogen fuel and stagnant air as oxidant, is then evaluated.

2. Experimental

$La_{0.65}Sr_{0.30}MnO_{3-\delta}$ (LSM) powder (d_{50}=1.3 μm, surface area ~4.71 m^2/g) was obtained from Praxair Specialty Ceramics. $Sc_{0.2}Y_{0.02}Zr_{0.89}O_{1.78}$ (SYSZ) powder   (d_{50}=0.55 μm, surface

area 11.2 m^2/g) was supplied by Daiichi Kigenso Kagakukogyo, and Timrex KS4 graphite (d_{50}=2.4 μm, surface area 26 m^2/g) and KS15 graphite (d_{50}=8 μm, surface area 12 m^2/g) pore formers were obtained from Timcal Ltd. 20g of an LSM-SYSZ mixture in a weight ratio of 1:1 was attritor-milled with Menhaden fish oil (MFO, 3 wt% of the LSM-SYSZ) using zirconia milling balls, in iso-propanol (IPA), for 1 hr, at 550 rpm. After milling, 35 to 60 wt% (relative to ceramics) of the graphite pore former, 3 wt% (relative to ceramics) of polyvinyl butyral and dibutyl phthalate were added and dispersed by a ultrasound, for 5 min. The mixture was dried, ground with mortar and pestle, and passed through a 150 μm mesh sieve. The powders were then uniaxially pressed into disks with a diameter of 2.5 cm at 103 MPa (15 kpsi) using a stainless steel die. The resulting green LSM-SYSZ disks were either used as is, or pre-fired in air at 750°C, for 4 hrs, to remove the binder and graphite before depositing the electrolyte film.

Thin-films of the electrolyte and the anode were formed on the LSM disks by colloidal deposition [9]. The SYSZ suspension was prepared by ultrasonically dispersing 2g of powder into 50 ml of IPA with 0.1g of MFO. The mixture of SYSZ-NiO(J. T. Baker) was prepared similarly, and was attritor-milled for 1 hr, at 550 rpm. These suspensions were sprayed on the LSM-SYSZ disks in sequence, with an aerosol spray gun. The deposited disks were then co-fired in air, at 1150-1350°C, for 4 hrs.

For electrochemical testing, a Pt mesh current collector was attached with Pt paste on both sides of the disks. Cobalt nitrate was infiltrated into the LSM-SYSZ supporting cathodes by dropping on a few drops of a cobalt nitrate solution (0.5 g-Co nitrate/ml), sufficient to flood the pores without excess. The DC current-voltage (I-V) characteristics of completed cells were recorded with a potentiostat-galvanostat (Princeton Applied Research Model 371), between 600-800°C, using humidified hydrogen (about 3% water) as fuel, and stagnant air as oxidant. AC

impedances were measured between 0.1Hz-1 MHz with a frequency response analyzer and a potentiostat (Solartron 1260 and 1286, respectively). Densification of the powders was also recorded with a dilatometer (Orton model 1600D).

3. Results

3.1. Fabrication of Co-Fired Cells

Linear shrinkage as a function of temperature was measured for separate compacts of SYSZ and LSM-KS4 (35 wt% relative to LSM), as shown in Fig. 1. The LSM-KS4 showed a larger linear shrinkage than the SYSZ compact. The sintering profiles of the support and the electrolyte powders can be matched, so that the supporting electrode assists the densification of the electrolyte film during co-firing. If the supporting cathode is made to dominate the densification of the supported electrolyte film, then full density for the electrolyte film should be reached at about $1250\,^0C$.

The amount of carbon pore-formers (KS4 and KS15) was also varied to increase the supporting electrode porosity at the firing temperature of 1250°C, Fig. 2. As expected, residual porosity increased with increasing amounts of carbon pore formers, while maintaining necessary linear shrinkage. In this study, 45 and 50 wt % of carbon relative to ceramic was chosen for KS4 and KS15, respectively. Fig. 3 a shows cross-sectional SEM image of an LSM-SYSZ supported thin-film SOFC, after co-firing at 1250°C. Dense SYSZ electrolyte films were obtained on homogeneous, porous LSM-SYSZ supporting cathodes.

3.2. Electrochemical Performance

Fig.4 shows the characteristics of the cells following cobalt infiltration of the cathodes as a function of temperature. Fig 4.a shows the power and I-V performance of an LSM-SYSZ

supported cell using KS4 (45 wt% relative to ceramic powders), for with the cathode, electrolyte, and anode layers were co-fired at 1250˚C. Fig. 4.b shows the performance for an LSM-SYSZ supported SOFC, cell B, using KS15 (50 wt% relative to ceramic powders), for which the cathode and the electrolyte were co-fired at 1250˚C, with subsequent application of the anode. The cell polarization curves were almost linear in a low current density range, which is a characteristic of cobalt-infiltrated LSM-SYSZ supported cells. This will be discussed later when comparing with a cell without cobalt infiltration. The power drops after the peak are characteristic of gas diffusion limitation. The improvement in gas diffusion limitation for cells B may be attributed to the increase in cathode porosity from 43 to 53 % by increasing the amount of the pore former and to larger pore sizes. As a result, power densities of as much as a factor of 1.3 higher were obtained for cell B. Table 1 summarizes electrochemical performance for cells A and B with those of a co-fired LSM supported cell reported recently [3]. While the ASRs at 0.7 V were comparable for cells A and B, the peak power densities were higher for cell B because the diffusion limitation was reduced. The power density of cell B was a factor of 2.5 higher than that reported at 800˚C in Ref. [3]. It should be also noticed that because of the absence of significant activation polarization, power densities of more than 90 % of peak were obtained at 0.7 V in most cases for both cells A and B. The contribution of ohmic resistances to the ASRs was 20-32 %, thus at high current densities non-ohmic resistance was significant in addition to the gas diffusion limitation .

The influence of cobalt infiltration into an LSM-SYSZ support on electrochemical characteristics was investigated by comparison of identically prepared cells with cobalt infiltration (cell A) and without cobalt infiltration (cell C). Fig. 5 shows remarkable differences in characteristics. The polarization curves of cell C (no infiltration) show a more rapid drop

than cell A (with infiltration) especially at low current densities. As a result, the difference in peak power density between A and C was as much as a factor of two. Particularly noteworthy are also the significant improvements in performance at 0.7V, which are of more practical value than the peak power densities. These dramatic improvements by cobalt infiltration was mainly due to a significant reduction in non-ohmic resistance, as seen in the Cole-Cole plots of AC impedance in Fig. 6. The authors previously reported [5] that Co_3O_4 nano-particles with an average size of 25 nm were found by TEM in the pores of infiltrated LSM-SYSZ composites heated up to an operational temperature of 650˚C. The improvement by cobalt infiltration might be attributed to enhancement of surface exchange processes on the LSM itself, such as discussed by Kilner, Steele. and co-workers,[10] or to the creation of new oxygen reduction sites and additional triple phase boundaries with the cobalt spinel particles. The performance improvement and the reduction in non-ohmic resistance by cobalt infiltration for these cathode-supported cells was consistent with most of the results reported for Ni-SYSZ anode supported SYSZ cells [5], in which cobalt was infiltrated into a thin-film LSM-SYSZ cathode.

4. Conclusion

Co-fired LSM-SYSZ cathode-supported solid oxide fuel cells were successfully fabricated at 1250˚C by optimizing the amount of carbon pore formers. The electrochemical performances of cells with cobalt infiltration into LSM support-cathode were examined in the temperature range of 600-800˚C using humidified hydrogen and stagnant air for anode and cathode sides, respectively. Substantial improvements in power output at 0.7V and at peak were evident. The best peak power densities obtained, were 455, 389, 285, 202, 141 mW/cm^2 at 800, 750, 700, 650, 600˚C, respectively. The peak power density at 800˚C was a factor of 2.5 higher than that of 180 mW/cm^2 recently reported elsewhere for the same type of cell [3]. The porosity of the cathode significantly influenced power densities. An increase in porosity from 43 to 53 % with some increase in pore size improved the peak power density by as much as a factor of 1.3, while maintaining comparable ASRs at low current densities. Cobalt infiltration into the support improved peak power density by as much as a factor of 2 due to a considerable reduction in non-ohmic resistance, evident in Cole-Cole plots of AC impedance. Because of the strong lowering of the apparent activation polarization, power densities of more than 90 % of peak were obtained at 0.7 V in most cases. Non-ohmic resistances from gas diffusion and other, as yet not clearly identified processes, still constituted up to 80 % of the ASRs for all cells. This remains an area for further investigation.

The results demonstrated that LSM cathode-supported intermediate temperature SOFCs can be effective, and potentially lower cost, alternatives to the anode -supported ones.

Acknowledgements

References

1. M. Ippommatsu, H. Sasaki, and S. Otoshi, *Int. J. Hydrogen Energy,* **21**, No. 2, 129-135 (1996).

2. S. J. Visco, C. P. Jacobson, L.C. De Jonghe, in *SOFC VI*, S. C. Singhal and M. Dokiya, Eds, **PV 99-19**, p.861-8, Electrochem Soc. Proc. Series, Pennington, NJ, (1999).

3. H. Ohrui, K.Watanabe, M. Arakawa, *J. Power Sources*, **112**, 90 (2002).

4. H. Ohrui, T. Matsushima, T. Hirai, J. Power Sources, **71**,185 (1998).

5. K. Yamahara, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, submitted to Solid State Ionics.

6. R. Chiba, F. Yoshimura, Y. Sakurai, Y. Tabata, M. Arakawa, in *Extended Abstracts of 14th Int. Conf. on Solid State Ionics*, p.14 (2003).

7. O. Yamamoto, Y. Takeda, R. kanno, in SOFC I, S.C. Singhal Editor, p. 242, The Electrochem. Soc., Proc. Series, Pennington, NJ, (1989).

8. M.C. Brant, L. Dessemond, *Solid State Ionics*, 138, 1 (2000).

9. S.J. Visco, C.P. Jacobson and L.C. De Jonghe, U.S. Pat. No. 6458170, October 1 (2002).

10. S. Carter, A. Selcuk, R.J. Chater, J. Kajda, J.A. Kilner and B.C.H. Steele, *Solid State Ionics*, **53-56** (1992) 597.

Table and figure captions

Table 1 Electrochemical characteristics of the co-fired LSM-SYSZ-supported SOFCs and those of a co-fired LSM-supported cell in the reference [3].

Fig. 1 Sintering profiles of SYSZ and an LSM-KS4 (35 wt% relative to LSM) mixture.

Fig. 2 Linear shrinkage and porosity of an LSM support sintered at 1250°C as a function of the

amount of KS4 or KS15 carbon pore formers.

Fig. 3 Cross-section SEM images of co-fired LSM-SYSZ-supported SYSZ cells. The top picture, cell A, was a co-fired tri-layer of Ni-SYSZ/SYSZ/LSM-SYSZ (45 wt% KS4 relative to ceramics) at 1250°C for 4 hrs and was infiltrated with a cobalt nitrate. The bottom picture, cell B, was a co-fired bi-layer of SYSZ/LSM-SYSZ (50 wt% KS15 relative to ceramics) at 1250°C for 4 hrs, with the Ni-SYSZ applied subsequently.

Fig. 5 Current-voltage and power density characteristics for co-fired LSM-SYSZ-supported SOFCs with cobalt infiltrated cathodes.   The top plot is for cell A; the bottom plot is of cell B

Fig. 6 Current-voltage and power density characteristics for co-fired LSM-SYSZ supported SOFCs with cobalt infiltration (cell A) and without cobalt infiltration (Cell C).

Fig. 7 Cole-Cole plots of AC impedance for cells A (with cobalt infiltration) and C (without cobalt infiltration). Cells A and C were co-fired tri-layers of Ni-SYSZ/SYSZ/LSM-SYSZ (45 wt% KS4 relative to ceramics) at 1250°C, for 4 hrs.

Table 1

T (°C)	Peak power (mW/cm²)			Power at 0.7V (mW/cm²)			ASR at 0.7V (Ω cm²)			R$_{ohmic}$* (Ω cm²)		
	A	B	Ref [3]	A	B	Ref [3]	A	B	Ref [3]	A	B	Ref [3]
800	350	455	180	350	446	126	0.73	0.64	1.93	0.17	0.19	0.75
750	324	389		319	366		0.78	0.78		0.19	0.21	
700	267	285		237	255		0.94	1.14		0.24	0.26	
650	182	202		145	185		1.46	1.61		0.30	0.40	
600		141			132			2.31			0.75	

*Ohmic resistance was determined from the high frequency intercept of Cole-Cole plots of AC impedance.

Fig. 1

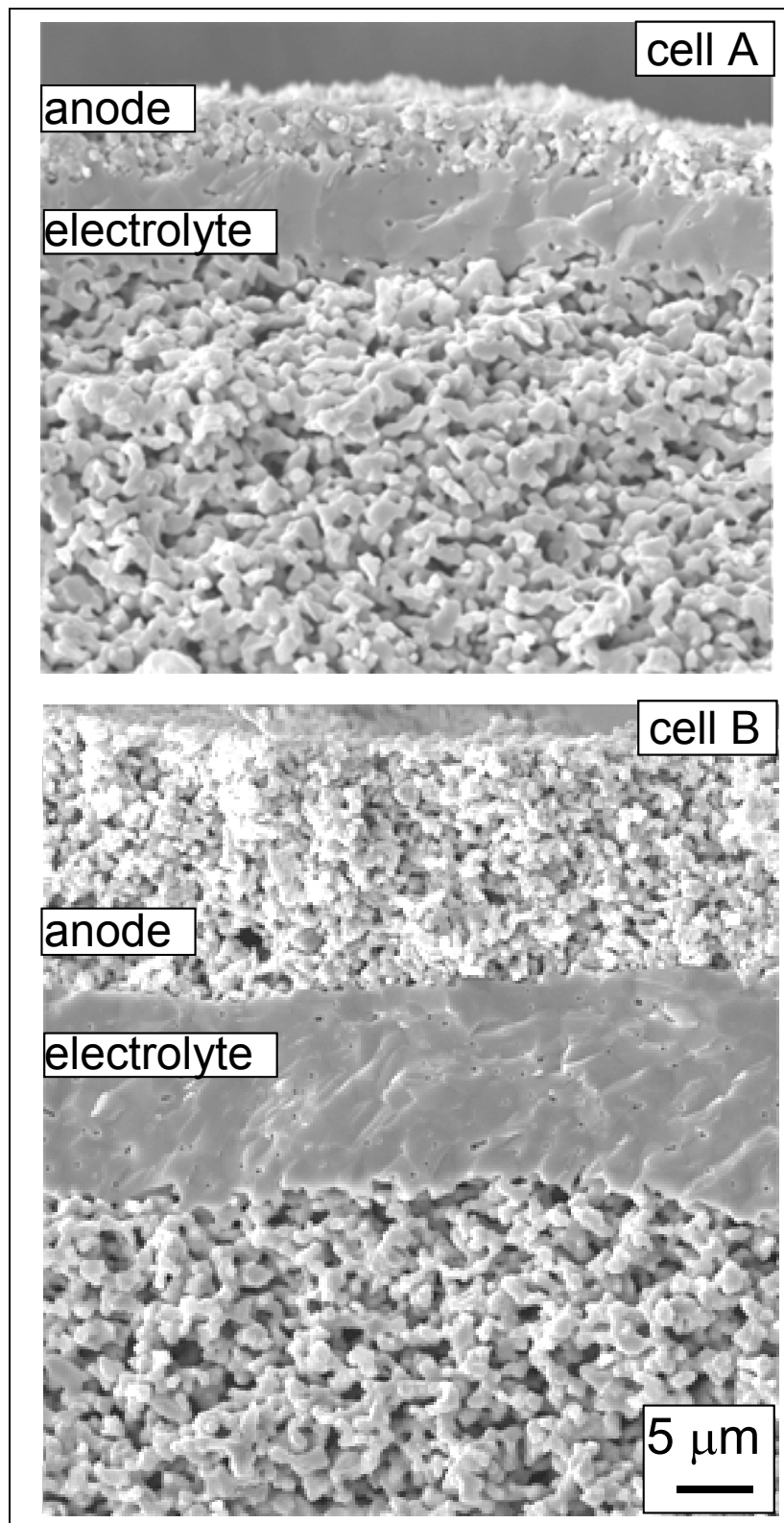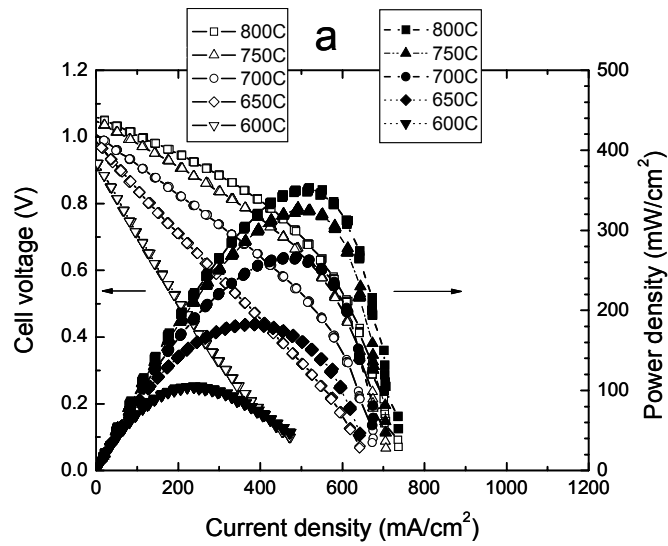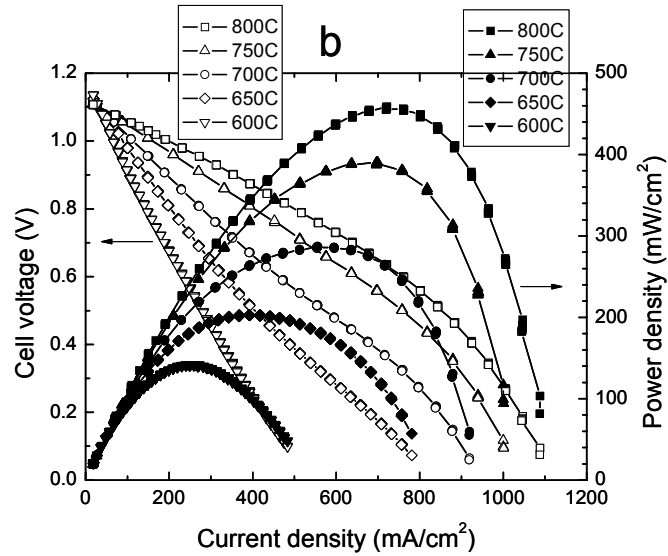Fig. 2

cell A
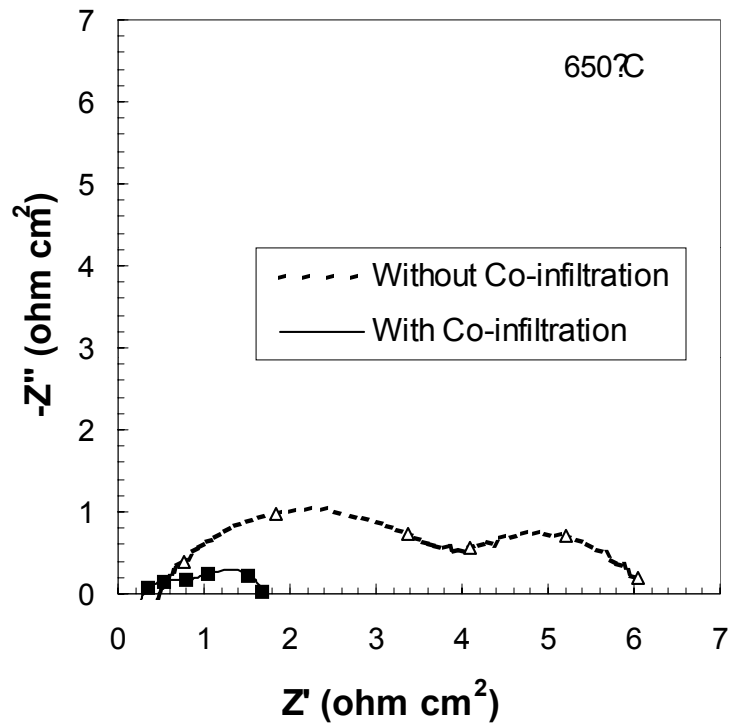
anode

electrolyte

cell B

anode

electrolyte

5 μm
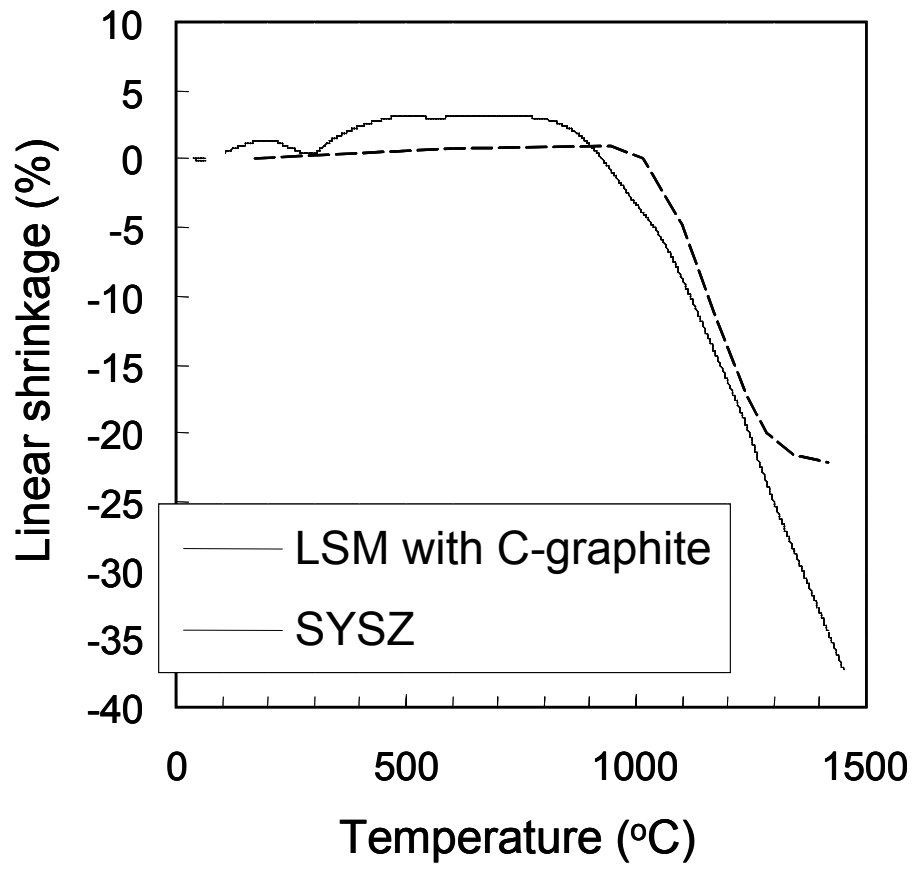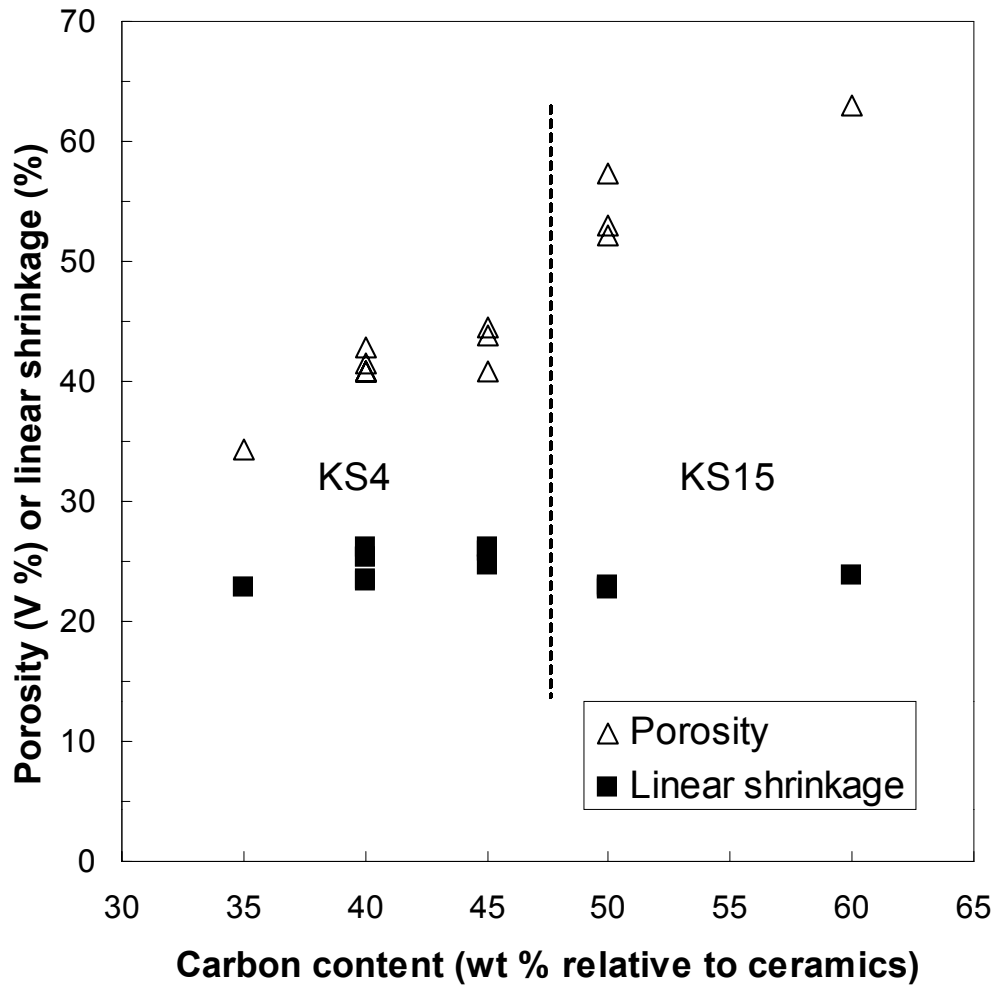
Ig 3

Fig. 4a

Fig. 4b

Fig. 5

Fig 5

Fig. 6