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NONSTOICHIOMETRIC COMPOUNDS

An investigation of the interfacial stability between the anode and electrolyte layer of LSGM-based SOFCs

**Jong-Ho Lee · Kwang Nyeon Kim ·
Ji-Won Son Joosun Kim · Byung-Kook Kim ·
Hae-Weon Lee · Jooho Moon**

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Abstract LSGM is known to have very serious interfacial reactivity with other unit cell components even though it is one of the most favorable solid electrolytes for intermediate-temperature SOFCs. Above all, the formation of a La-deficient La-Sr-Ga-O phase at the LSGM/NiO or the LSGM/CeO_2 interface is most problematic in LSGM-based SOFCs due to the very resistive nature of its electrical property in fuel cell operating conditions. In this study, we investigated the interfacial reactions in LSGM-based SOFCs under various fabrication conditions, in order to discern a method to either avoid or diminish the undesirable influence of these interfacial reactions. Microstructural evolution due to the chemical reactions between the anode and electrolyte layer were characterized with an Environmental Scanning Electron Microscopy (ESEM-PHILIPS XL-30) and an Energy Dispersive X-ray (EDX-Link XL30) analysis. The spatial distributions of each constituent element at the interfaces were thoroughly investigated with an Electron Probe Micro-Analyzer (EPMA-JEOL. JXA-8600).

Introduction

Solid oxide fuel cells (henceforth SOFCs) are the most feasible candidate for a new generation power system due to their high efficiency, high level of waste-heat utilization, and their greater fuel flexibility [1, 2]. Nevertheless, SOFCs still have many drawbacks concerning their long term stability and fabrication cost, and these factors are very critical issues for those working toward the commercialization of a SOFC system. It is well known that many kinds of technical problems are chiefly originated from its higher operating temperatures nearing 1000 °C [2]. Thus, most researchers have focused on the development of reliable and cost effective SOFCs that can be operated in a more moderate temperature range of 600–750 °C [3].

The main advantages of lower temperature SOFCs have to do with the practical application of an inexpensive metallic bipolar-plate, as well as the assurance of the material's long-term stability. It is generally believed that the most critical factor in reducing the operating temperature is to secure a proper electrolyte material, which can be utilized at a lower temperature without any performance loss [4–6]. In the relevant research, various electrolyte materials, including scandia-doped zirconia (ScSZ), $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC), $Ce_{1-x}Sm_xO_{2-\delta}$ (SDC), or $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM) have been suggested for low-temperature SOFCs [7]. Among these materials, LSGM may be the most popular choice due to its favorable advantages such as (i) a higher ionic conductivity of 0.15 S cm^{-1} at 800 °C (which is about five times higher than that of a conventional yttria-stabilized zirconia (YSZ)); (ii) its reasonable material

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J.-H. Lee (✉) · K. N. Kim · J.-W. S. J. Kim ·
B.-K. Kim · H.-W. Lee · J. Moon
Nano-Materials Research Center, Korea Institute of
Science and Technology, Seoul 136-791, Korea
e-mail: jongho@kist.re.kr

J. Moon
School of Advanced Materials Engineering, Yonsei
University, Seoul 120-749, Korea

cost; and (iii) its superior electrolytic and mechanical stability [8, 9]. However, it has been reported that there is a serious interfacial reaction between a NiO-based anode and the LSGM electrolyte, resulting in a substantial loss in unit cell performance, even though NiO-based materials are the most promising anode materials for SOFCs [10–15]. According to the previous studies [10–15], NiO in an anode substrate reacts strongly enough with the LSGM electrolyte to form an unwanted interfacial layer. The most problematic interfacial reaction is the formation of a very resistive La-Sr-Ga-O phase at the LSGM and Ni–CeO_2 interface due to the La migration out of the LSGM phase.

In this study, we investigated the interfacial reactions in LSGM-based SOFCs under various fabrication conditions in order to discern a method to either avoid or diminish the undesirable influence of these interfacial reactions. We traced all possible interfacial reactions between the anode and the electrolyte and addressed the key factors in determining such intricate interfacial reactions.

Experimental

In order to precisely investigate the effect of a buffer layer on the interfacial reaction between the anode and electrolyte different anode supported cells were prepared, some with and some without a buffer layer. For the fabrication of the anode supported cells, commercial $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC, Rhodia, USA) and NiO (Sumitomo, Japan) powders were used for NiO–GDC anode substrate. The granules of NiO–GDC composite powders were compacted by way of uni-axially pressing them into a green anode substrate. Gd-doped ceria (Rhodia, USA) was deposited on the NiO–GDC substrate as a buffering layer via screen printing and the LSGM electrolyte layer was also screen printed on the buffer layer. The entire assembly of anode/functional/electrolyte-layer was co-fired in a temperature-controlled electric furnace. We investigated the interfacial stability between the anode and electrolyte as functions of the co-firing temperature and duration time in an air atmosphere. Microstructural evolution due to the chemical reactions between the anode and electrolyte layer was analyzed with an Environmental Scanning Electron Microscopy (ESEM XL-30, FEI Company, The Nertherlands) and Energy Dispersive X-ray Spectroscopy (EDS Genesis, TSL, Utah, USA). The spatial distributions of each constituent element at the interfaces were also investigated with an Electron Probe Micro-Analyzer (EPMA-JEOL. JXA-8600).

Results and discussion

Figure 1 shows a typical interfacial morphology of the NiO–GDC anode and the LSGM electrolyte cell. According to the EDS analysis in Fig. 2, two reaction products were detected. The first one was $LaSrGa_3O_7$ and the second one was a NiO rich phase. As shown in Fig. 1, a dark gray-colored NiO phase was located very close to the anode substrate and has a fairly continuous form along the interfacial boundary. On the other hand, a gray-colored $LaSrGa_3O_7$ phase was located at a more interior section of the LSGM layer.

Determining the origin of this unexpected NiO phase is beyond the scope of this study, nonetheless we suspect the occurrence of this phase was due to the decomposition of the $LaNiO_3$ during the heat-treatment. It has been suggested that a $LaNiO_3$ phase is not thermodynamically stable at relatively high temperature; thus, it is very possible that the $LaNiO_3$ phase decomposed into another new La_2NiO_4 phase and NiO [16]. Additionally in this study, another interesting finding was noted: if the GDC was next to the $LaNiO_3$ during the decomposition, all of the La in the $LaNiO_3$ phase completely dissolved into the GDC. Thus, only NiO phase remained as a second phase at the end. This could very well be the origin of the continuous NiO phase at the interface as shown in Fig. 1.

On the other hand, according to the EDS and EPMA analyses on the interfacial layer, the formation of the $LaSrGa_3O_7$ phase was closely related to the migration of La out of the LSGM electrolyte into a ceria-based anode, resulting in a La-deficient phase at the LSGM side. From the separate measurements of

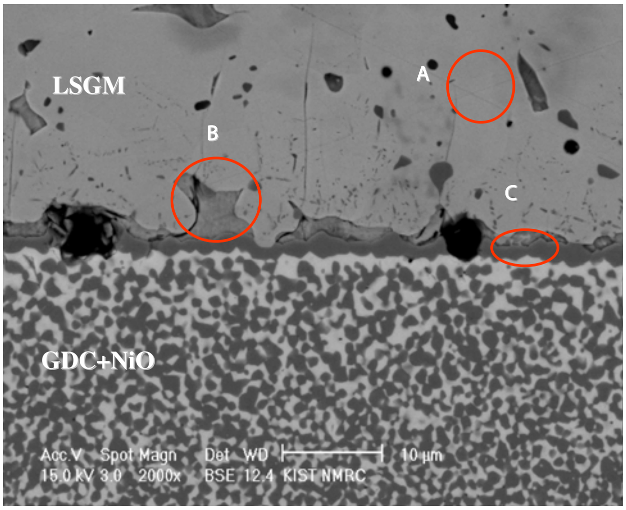


Fig. 1 Typical interfacial morphology of the NiO-GDC based anode and LSGM electrolyte cell

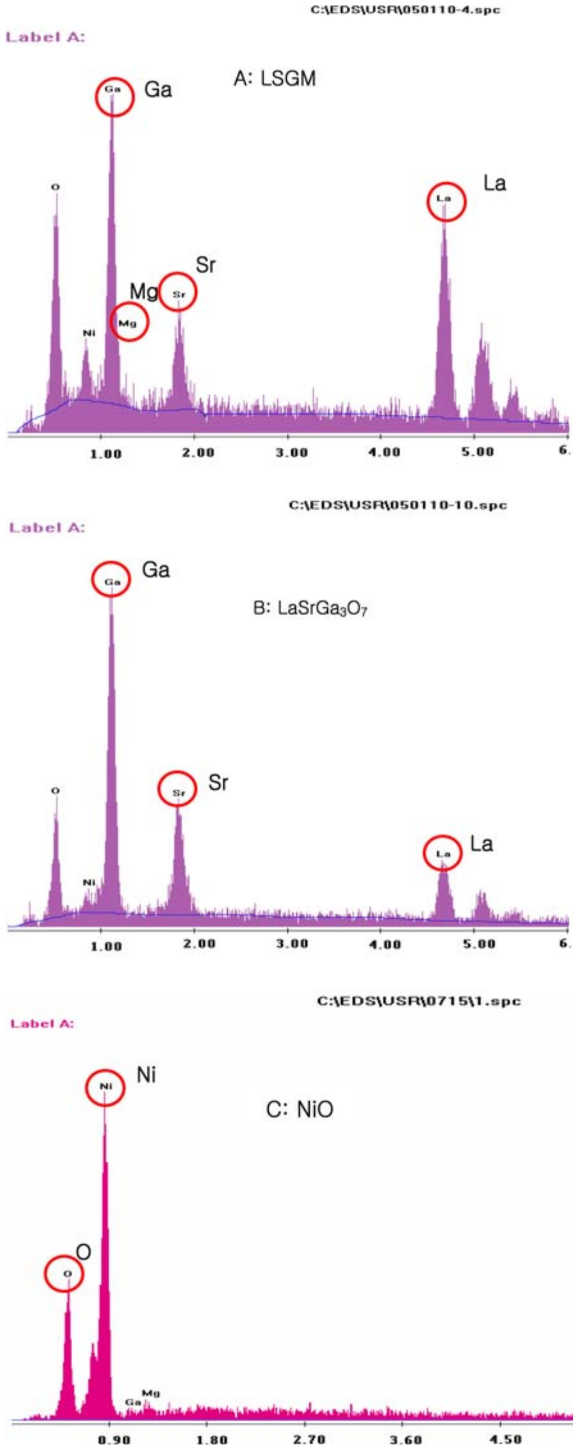


Fig. 2 Results from EDS analysis for the sites A, B and C at the interface between NiO-GDC based anode and LSGM electrolyte

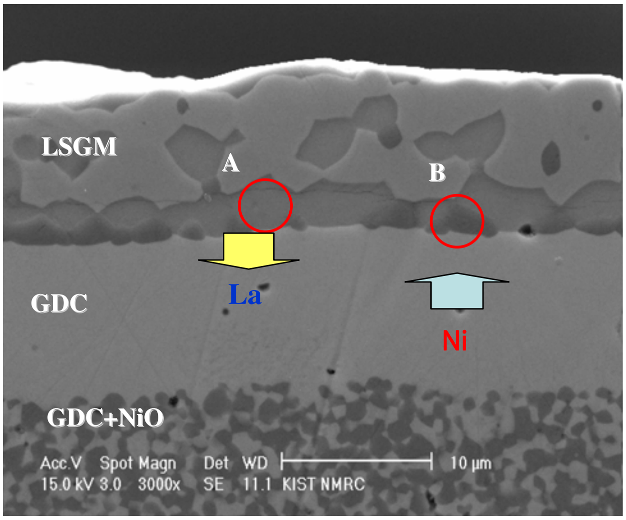


Fig. 3 Typical interfacial morphology of the NiO-GDC anode, GDC buffer and LSGM electrolyte cell

the electrical conductivity via DC 4-probe technique, we found that this $LaSrGa_3O_7$ phase was very resistive compared to other unit cell components [17].

Figure 3 shows a typical interfacial morphology from the anode supported cell with the GDC buffer layer. As shown in Fig. 3, an exceptionally strong interfacial reaction was observed at the interface of the LSGM electrolyte and the GDC buffer. According to the EDS analyzing results in Fig. 4, the reaction product was identified as a $LaSrGa_3O_7$ phase, which indicated that the ceria buffer layer might occasion another instance of an interfacial reaction even though the ceria buffer was originally introduced to suppress the chemical reaction between the electrode and the electrolyte. Moreover, the ceria buffer layer did not so much as halt the Ni migration across the LSGM/GDC/NiO–GDC interface, which, in the end, resulted in the formation of the Ni rich phase at the LSGM side.

According to our study, such an interfacial reaction was closely related to the heat-treatment conditions such as the heating temperature and the duration time. As shown in Figs. 5 and 6, the gray-colored reaction zone became extended as the heating temperature increased and as the duration time increased, which strongly indicated that this type of interfacial reaction is controlled by a conventional thermally-activated diffusional process of corresponding species.

Figures 7 and 8 show the results of the EPMA line mapping for the La and Ni concentration across the GDC buffer layer as a function of heat-treatment time. In Fig. 7, one can find a fairly distinct concentration profile of La through the GDC buffering layer. The clear moving appearance of the front end of the La concentration profile, in terms of heat-treatment time, verifies the aforementioned thermally-activated diffusional process of the La. In the mean time, as shown in Fig. 8, there was no clear concentration profile of Ni through the GDC layer, even though an abundant Ni concentration was detected at the interface of the GDC/LSGM. At present, we are at a loss as to how to

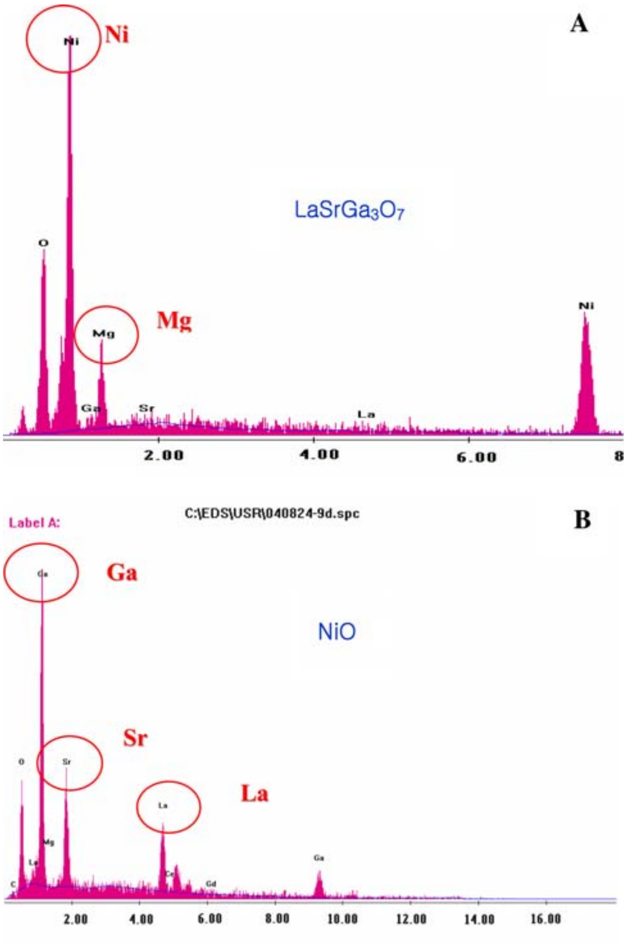


Fig. 4 Results from EDS analysis for the sites A and B at the interface between GDC buffer and LSGM electrolyte layer

explain the crossing mechanism of this Ni component. For the time being we can only conclude that the Ni was somehow moved through the GDC layer via a solid state diffusion rather than by any other ways, such as by evaporation and condensation via a gas phase. The authors of this paper plan to undertake additional studies to explain this phenomenon.

This unwanted interfacial layer at the LSGM/GDC interface presented a further detrimental influence above and beyond its already negative influence on the electrical property. This second influence was on the mechanical stability of the multilayered structure. As shown in Fig. 9, there is a continuous crack along the gray-colored zone of the $LaSrGa_3O_7$ phase. From the measured data of the thermal expansion coefficients of each constituent phase in Table 1, this interfacial crack was positively caused by the mismatch of the thermal expansion coefficients of the neighboring phases.

In this study, we found that the interfacial problem between the anode and the electrolyte could not be solved with the GDC-based buffer layer. According to our electrochemical characterization [18], such an interfacial reaction had a detrimental influence on the unit cell performance by not only reducing an OCV (open cell voltage) of the cell, but also increasing the internal cell resistance of the unit cell. The OCV of the cell was sharply decreased down to less than 40% of theoretical value as Ni migration reached higher levels; in addition, the internal ohmic resistance of the cell was greatly increased up to two order of magnitude higher value than normal case, as the amount of

Fig. 5 Microstructural evolution at the interface of GDC/LSGM with respect to the co-firing temperature: (**a**) 1450 °C, (**b**) 1400 °C, (**c**) 1350 °C and (**d**) 1300 °C

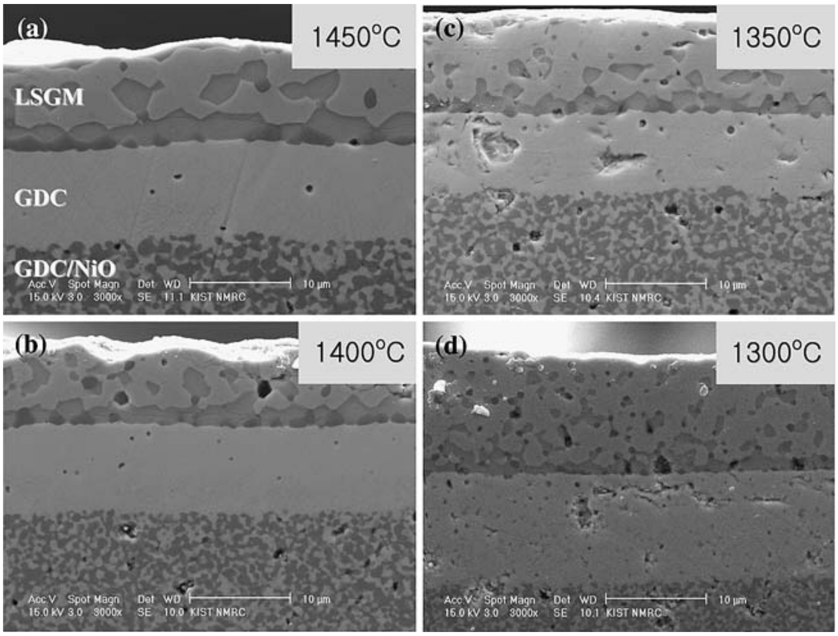


Fig. 6 Microstructural evolution at the interface of GDC/LSGM with respect to the duration time at the co-firing temperature of 1450 °C: (**a**) 0 h (**b**) 2 h, (**c**) 4 h and (**d**) 6 h

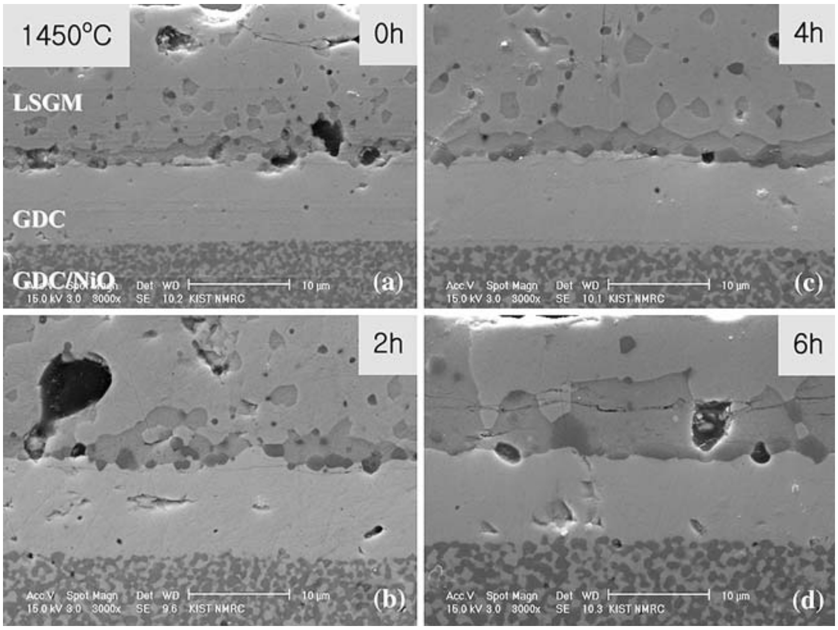
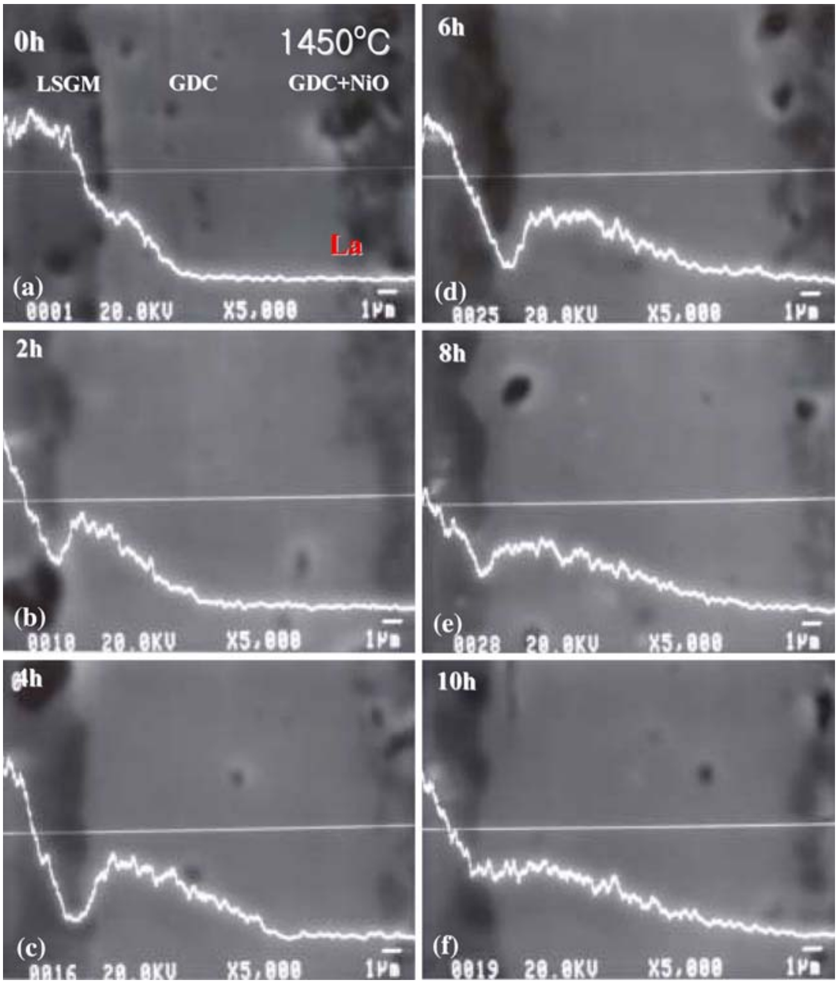


Fig. 7 Temporal variation of the EPMA line profiles of La concentration across the GDC buffer layer which was co-fired at 1450 °C with different duration time: (**a**) 0 h (**b**) 2 h, (**c**) 4 h, (**d**) 6 h, (**e**) 8 h and (**f**) 10 h



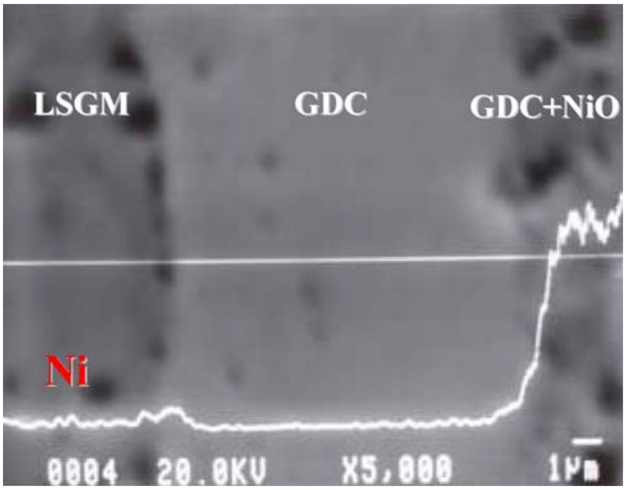


Fig. 8 EPMA line profile of Ni concentration across the GDC buffer layer of the cell co-fired at 1450 °C

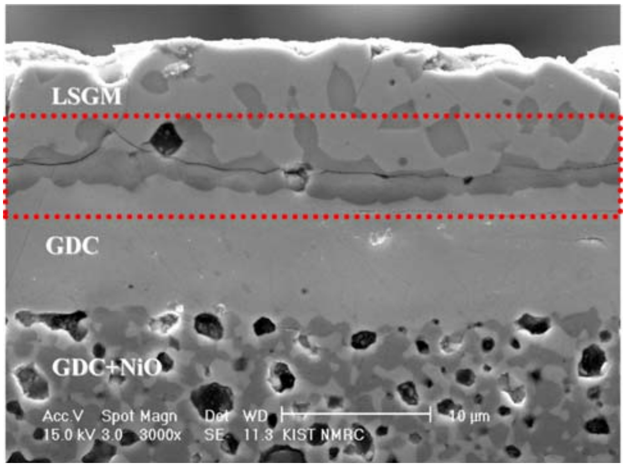


Fig. 9 Cross sectional view of the NiO-GDC/GDC/LSGM cell with a crack visible along the interface of the GDC and the LSGM, which was induced by the mismatch of the thermal expansion coefficients of neighboring phases

Table 1 Thermal expansion coefficients of the corresponding components of LSGM-based SOFCs

	Thermal expansion coefficient ($\times10^{-6}$)
LSGM	11.4
$LaSrGaO_7$	8.6
GDC	13.4

interfacial reaction increased. Taking these results as a whole, we can conclude that the most important thing to consider when assuring the best possible performance of a LSGM based SOFC is to avoid or at least reduce such unwanted interfacial reaction in all cases where it is possible.

Conclusions

According to the analyses on the interfacial reactions at the anode and the electrolyte interface in LSGM based SOFCs with Environmental Scanning Electron Microscopy (ESEM XL-30, FEI Company, The Nertherlands) and Energy Dispersive X-ray Spectroscopy (EDS Genesis, TSL, Utah, USA), a strong interfacial reaction was observed. The interfacial reaction was induced not only from the NiO-based anode but also from the GDC buffer, which was initially introduced to suppress the reaction between the NiO and the LSGM. The reaction zone of the LSGM/GDC was extended as the heating temperature increased and the duration time increased, which showed the typical characteristics of a thermally-activated diffusional process. The interfacial reaction between the anode and electrolyte severely deteriorated not only the electrical properties but also the mechanical property of the unit cells.

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