

Consumptive coating layer synthesis by a sol-gel technique on a stainless steel substrate for an IT-SOFC separator

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The manufacturing costs of solid oxide fuel cells (SOFCs) could feasibly be reduced by using ferritic stainless steel (SUS) interconnectors. However, the stainless steel interconnector suffers from poor oxidation resistance at the IT-SOFC operating temperature. In order to solve this problem, we coated LaCrO_3 or strontium-doped LaCrO_3 on SUS444 as an oxidation protective layer by a sol-gel technique. Precursor solutions with different metal ion concentrations (0.1, 0.3, and 0.5 mol/l) were prepared from metal nitrates, ethylene glycol, and nitric acid. Dense coating layers with a thickness of 0.8 to 2 μm could be obtained upon heat-treatment of gel films at 700 °C in an air atmosphere. It was found that the thickness and microstructure of the coating layers depended on the concentration of the precursor solution. The oxidation behavior of the LaCrO_3 or strontium-doped LaCrO_3 -coated SUS444 was compared with that of bare SUS444. Area specific resistances (ASR) of the SUS444 substrates were measured as a function of temperature. The ASR monotonically decreased with an increase in the concentration of the precursor solution.

Key words: Solid oxide fuel cell, LaCrO_3 , Interconnector, SUS444, Oxidation protective coating.

Introduction

Solid oxide fuel cells (SOFCs) have some advantages over other types of fuel cells, because they are able to operate at high temperatures (usually 800 °C to 1,000 °C). SOFCs can use various fuels such as hydrocarbons, gasoline, etc, and their efficiency is about 90% including heating value efficiency [1, 2]. In addition, solid electrolytes do not cause migratory problems, which are sometimes serious in fuel cells using liquid electrolytes. However, SOFCs require an expensive ceramic interconnect material and there is also a glass sealing issue at high temperatures [3]. To overcome these problems, numerous studies focusing on lowering the SOFC operating temperature have been reported. If the operating temperature of SOFCs could be reduced to around 600~800 °C, cheap metallic alloys could be used as an interconnect material instead of LaCrO_3 based ceramics. A metallic interconnect design is approximately 45% less expensive than the ceramic construction.

The electrical conductivity of metallic alloys is several orders of magnitude greater than that of ceramic interconnects and their high thermal conductivity can readily eliminate the presence of a thermal gradient along the interconnect plane. In addition, metallic alloys can better accommodate a thermal stress, and they show excellent mechanical strength and creep resistance and are easy

to fabricate. Applicable candidate alloys are Ni-based, Cr-based, and Fe-based alloys [4-7]. In Cr_2O_3 forming alloys, volatile Cr(VI) is present under the operating environments of the SOFC; this leads to Cr-poisoning at the interface of the perovskite type cathode and YSZ electrolyte [8, 9]. Generally, a Cr_2O_3 scale has a high electrical resistance, that is, $1 \times 10^2 \Omega \cdot \text{cm}$ at 800 °C [10]. For SOFC interconnect materials, the area specific resistance (ASR) is required to be smaller than $0.1 \Omega \cdot \text{cm}^2$ for 40,000 h at 750 °C [11]. Therefore, the substrate surface should be modified in order to prevent a voltage drop caused by its poor oxidation resistance.

In our previous study, it was found that a lanthanum chromite (LaCrO_3)-based conductive layer acts as a protective coating to mitigate the oxidation of stainless steels [12]. LaCrO_3 shows high electrical conductivity, low oxygen ion diffusivity, chemical compatibility to adjacent stack components even at high temperature, and a good thermal expansion coefficient matched to the substrate alloy. Various techniques such as plasma-spray coating [13], EB-PVD [14], and RF-magnetron sputtering [15] have been applied to deposit LaCrO_3 on a stainless steel substrate. A sol-gel process has also been developed over the past few years, as it is economical. Furthermore, it can be used to prepare coatings with a wide variety of chemical compositions and the microstructure of the coating layer can be varied from porous to dense.

In this study, we synthesized various precursor solutions with different concentrations and compositions for the preparation of oxidation protective coatings. LaCrO_3 and strontium-doped LaCrO_3 were deposited on stainless

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Table 1. Chemical composition (wt%) of SUS444

Elements	C	Si	Mn	Cr	Mo	Ti	Ni	Nb	Fe
Composition	0.01	0.44	0.26	17.75	1.89	0.20	0.23	0.26	78.96

steel substrates (SUS444). The effects of the concentration of the precursor solution and strontium doping on the phase evolution and microstructural change of the LaCrO_3 -coated stainless steel substrate during oxidation in air were investigated.

Experimental Procedure

A commercial stainless steel, SUS444, was used as a substrate for the coating; its chemical composition is given in Table 1. A SUS444 plate was cut into rectangular pieces of about $19 \text{ mm} \times 23 \text{ mm} \times 1.5 \text{ mm}$. The sample surfaces were then polished with a series of increasingly finer SiC grit papers (from #400 to 2000) and finally with a diamond paste (from 3 to $1 \mu\text{m}$) in order to obtain a mirror surface. The polished substrates were ultrasonically washed in acetone for 20 minutes, rinsed in distilled water, soaked in ethanol for 10 minutes, and dried with a nitrogen gas gun.

Precursor solutions for the LaCrO_3 and strontium-doped LaCrO_3 coating were prepared from lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, GFS chemicals Inc., 99%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, KANTO Chemical Co., 98%), chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ACROS Organics, 99%), ethylene glycol, and nitric acid. In the case of the LaCrO_3 (LC) thin film, the atomic ratio of La and Cr was 1 : 1 and the atomic ratio of La, Sr, and Cr was 0.8 : 0.2 : 1 for the $(\text{La}_{0.8}\text{Sr}_{0.2})\text{CrO}_3$ (LSC) thin film. The concentration of the precursor solution was 0.1, 0.3 and 0.5 M. Appropriate quantities of the starting materials were dissolved in 40 ml ethylene glycol, and 0.9 ml nitric acid was subsequently introduced. The solutions were stirred and heated on a hot plate controlled at a temperature of 80°C for 24 h.

La-Cr-O and (La,Sr)-Cr-O films were deposited on the SUS444 substrate by a dip-coating technique. The speed at which the substrate was withdrawn from the precursor solution was 0.3 cm/minute. The La-Cr and La-Sr-Cr film-coated substrates were dried on a hot plate at 80°C to form gel films. The gel films were then heat-treated at 300°C for 10 minutes. The coating and drying process was repeated three times. The resulting amorphous films were finally heat-treated at 700°C for 1 h. The oxidation treatment was examined at 700°C for 100 h in air. For comparison, a non-coated SUS444 sample was oxidized simultaneously.

A thin film X-ray diffractometer (XRD, Philips, X'pert MPD) using Ni filtered $\text{CuK}\alpha$ radiation was used in order to confirm the phases developed in the crystallized and subsequently oxidized thin films. The surface and cross-sectional morphology of the coated samples were observed by field emission scanning electron microscopy

(FESEM, HITACH, S-4200). The cross-sections of the samples were polished using SiC papers and diamond paste ($\sim 1 \mu\text{m}$) to estimate the thickness of the coated layer. The area specific resistance (ASR) of the oxidized samples was measured via the two probe, four-wire probe method at 500, 600, 700 and 800°C . Platinum paste was screen-printed on both surfaces of each of the samples ($10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$), which were oxidized at 700°C for 100 h. Platinum meshes were then placed onto the platinum electrode and platinum wires were connected to the platinum mesh.

Results and Discussion

Figure 1 shows X-ray diffraction patterns of LC (a) and LSC (b) thin films on the SUS444 substrates, which were heat-treated at 700°C for 1 h. The surface of the LC-coated SUS444 substrate consists of perovskite LaCrO_3 and small amounts of chromium (III) oxide (Cr_2O_3) phases. On the other hand, the LSC-coated SUS444 surface consists

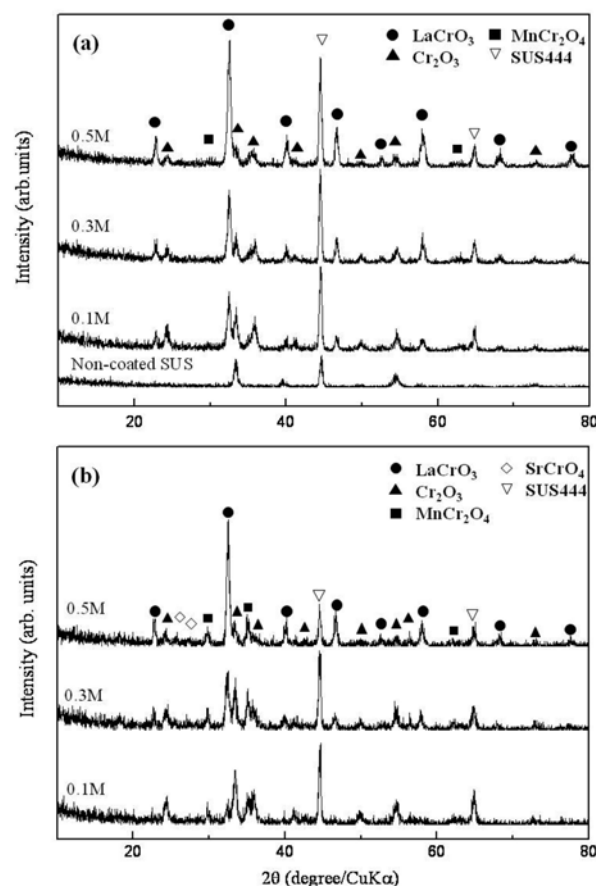


Fig. 1. X-ray diffraction patterns of LC (a) and LSC (b) thin films on SUS444 substrates (heat-treated at 700°C for 1 h).

of perovskite, chrome-manganese spinel (MnCr_2O_4) and Cr_2O_3 while trivial amounts of strontium chromite (SrCrO_4) phases are detected in 0.5 M LSC-coated SUS444. Irrespective of strontium doping in the thin film, the relative intensity of the perovskite phase is increased and the Cr_2O_3 is decreased with increasing concentration of the precursor solution. The relative intensity of the Cr_2O_3 scale, meanwhile, becomes negligibly small in the 0.5 M LC thin film. This result indicates that as the concentration of the precursor solution is increased, the thickness of the thin film is also increased. If so, oxygen ion transport may be more hindered in a thin film from a precursor solution with a high concentration, which

would result in slow growth of the Cr_2O_3 scale.

Higher relative intensity of the MnCr_2O_4 phase in the LSC than the LC thin film might be due to the slower diffusion rate through the LC thin film. During oxidation, the Cr_2O_3 scale reacts with manganese from the stainless steel substrate and the MnCr_2O_4 spinel was formed on the top of the surface, because of very fast diffusion of manganese, as reported by other researchers [16, 17]. In the case of the LC-coated SUS444, the diffusion of manganese is more effectively depressed by the LC thin film because the LC thin film has a denser microstructure than the LSC, as will be described later.

The SrCrO_4 phase that is formed in the LSC thin film (Fig. 1 (b)) might be associated with a reaction between strontium in the La-Sr-Cr gel film and the Cr_2O_3 scale during heat-treatment at an intermediate temperature. This phase remains even at temperatures higher than 700 °C (results not shown here) [12]. The thermal expansion coefficients of LaCrO_3 and SrCrO_4 are $8.6 \times 10^{-6}/\text{K}$ and $17.5 \times 10^{-6}/\text{K}$, respectively [18], and the formation of the SrCrO_4 phase in the intermediate temperature range, therefore, obstructs sintering of the LSC thin film.

The cross-section of the LC thin films on the SUS444 substrate is shown in Figure 2. The LC thin films are well adhered to the substrate. As is apparent from Fig. 2, the thickness of the LC thin film depends strongly on the concentration of the precursor solution, and the film thickness is gradually increased with an increase in the concentration of the precursor solution. The film thickness is estimated to be approximately 0.8, 1.4 and 2 μm for the LC thin film prepared from 0.1, 0.3 and 0.5 M precursor solutions, respectively. A higher concentration of the precursor solution results in a much more viscous solution. The viscosity of the 0.1 and 0.5 M precursor solutions is increased from 23.1 to 135.5 cp, respectively. Leonormand et al. have reported that the concentration of the precursor solution, i.e., solid content of the gel film, is the most important factor in determining the thickness of a crystallized LC thin film [19].

Figures 3 and 4 show the surface microstructures of LC and LSC thin films on the SUS444 substrates after heat-treatment at 700 °C for 1 h. The coating layer is continuous and uniform in microstructure. As is evident from Fig. 3, the 0.1 M LC thin film has a denser microstructure than does the 0.3 and 0.5 M films. On the other hand, the grain size of the LC is increased with an increase in the concentration of the precursor solution. The microstructure of the thin film is considered to be significantly related to the gel film thickness. The film thickness is increased as the concentration of the precursor solution is increased. When a coating layer becomes thick, gelation in a viscous film occurs more rapidly than evaporation before it dries. A large amount of remaining solvent is then removed from the gelled structure, and finally the coating layer takes on a porous microstructure [20]. In the case of the LSC thin films (Fig. 4), the microstructure is relatively porous and SrCrO_4

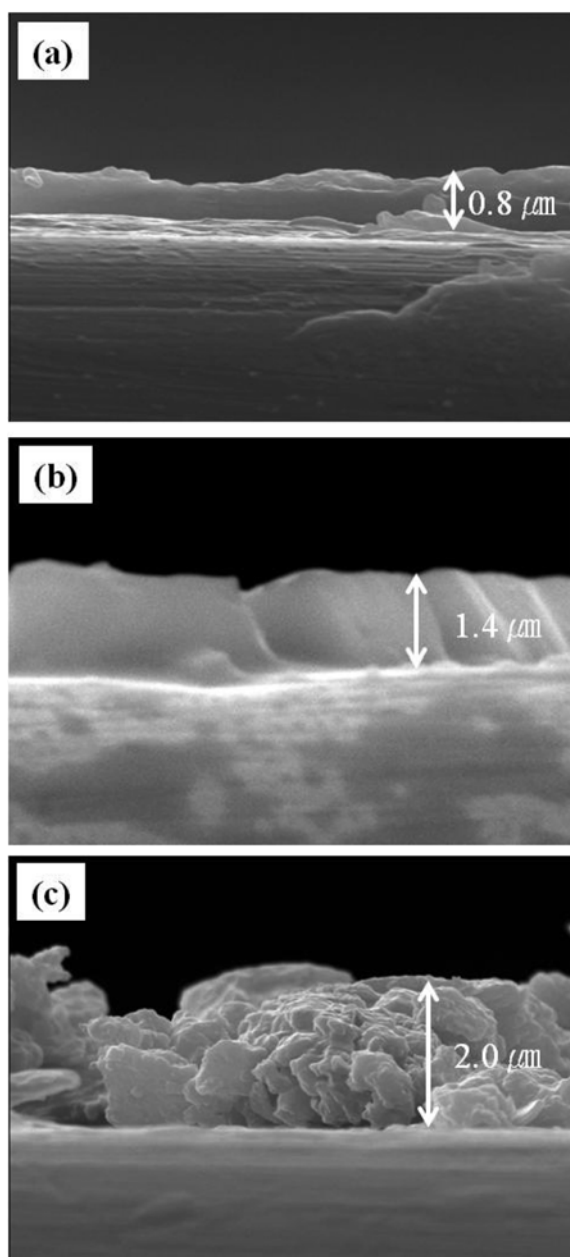


Fig. 2. Cross-section scanning electron micrographs of 0.1 M (a), 0.3 M (b) and 0.5 M LC thin films coated on SUS444 substrates (heat-treated at 700 °C for 1 h).

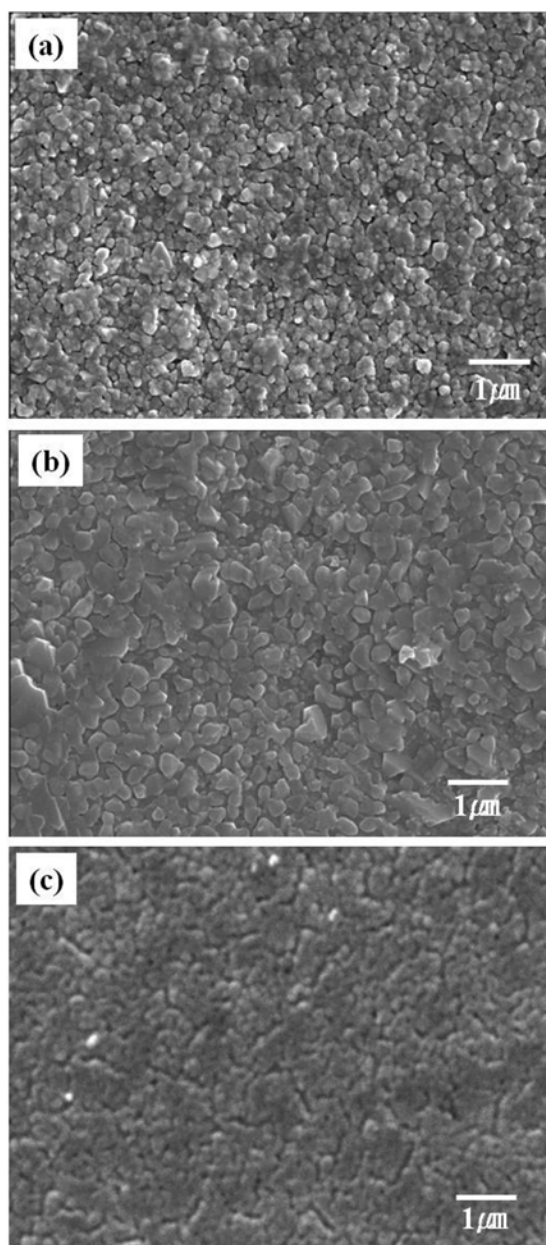


Fig. 3. Scanning electron micrographs of 0.1 M (a), 0.3 M (b) and 0.5 M LC thin films coated on SUS444 substrates (heat-treated at 700 °C for 1 h).

grains, which are indicated by arrows, are observed, especially in the 0.5 M LSC thin film. Formation of the SrCrO_4 phase may be responsible for the porous microstructure, as noted previously [18].

X-ray diffraction patterns of LC and LSC thin films oxidized at 700 °C for 100 h are presented in Fig. 5. For comparison, non-coated SUS444 substrates oxidized under the same conditions are also given in Figure 5. Comparing 0.5 M LC or LSC-coated SUS444 with the non-coated SUS444, the effect of the protective coating is clear. The relative intensity of the Cr_2O_3 and $(\text{Mn,Cr})_3\text{O}_4$ spinel is significantly reduced in the LC and LSC-coated SUS444. In addition, the protective coating effect is greater in the 0.5 M LC or LSC-coated thin film. The relative intensity

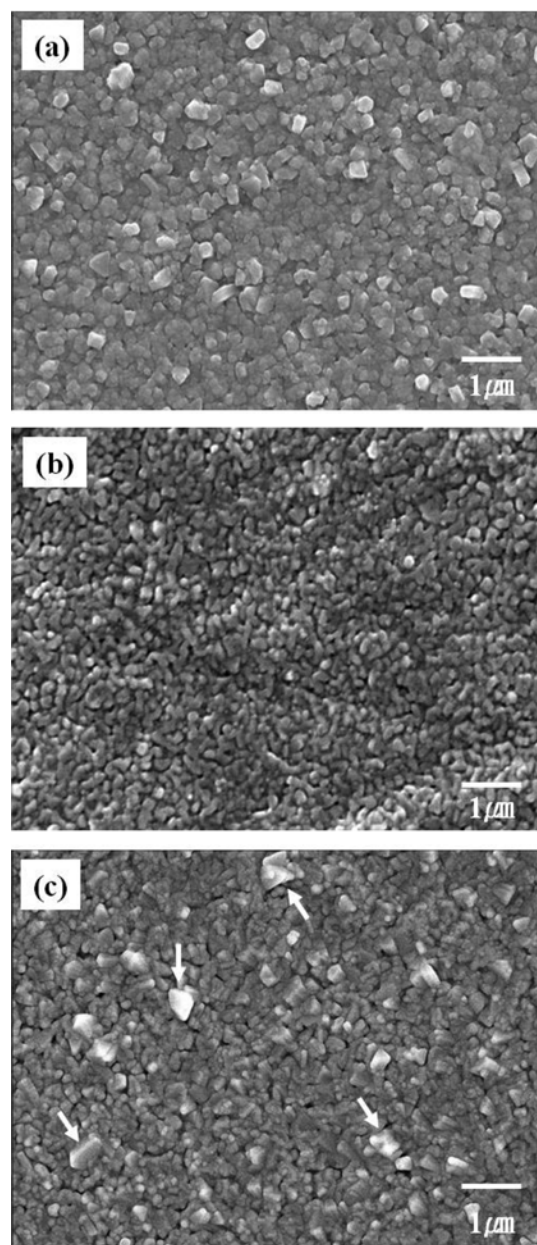


Fig. 4. Scanning electron micrographs of 0.1 M (a), 0.3 M (b) and 0.5 M LSC thin films coated on SUS444 substrates (heat-treated at 700 °C for 1 h).

of the Cr_2O_3 and MnCr_2O_4 phases is increased after 100 h oxidation. This result suggests that although the 0.1 M LC or LSC-coated thin film has a dense microstructure, its thickness is not sufficient to effectively hinder the oxidation of the SUS444 substrate. As the oxidation proceeded, there was no increase in the relative intensity of the Cr_2O_3 phase in the case of the 0.3 M and 0.5 M LC films.

The presence of the spinel phase alleviates the electrical resistance in the oxide scale, and also is effective in reducing Cr-poisoning at the interfaces of the cathode and YSZ electrolyte [13, 15, 21]. However, it is possible that the formation of $(\text{Mn,Cr})_3\text{O}_4$ spinel can lead to a porous structure, owing to the difference in the diffusion rates of the various species and volume changes in the film [13].

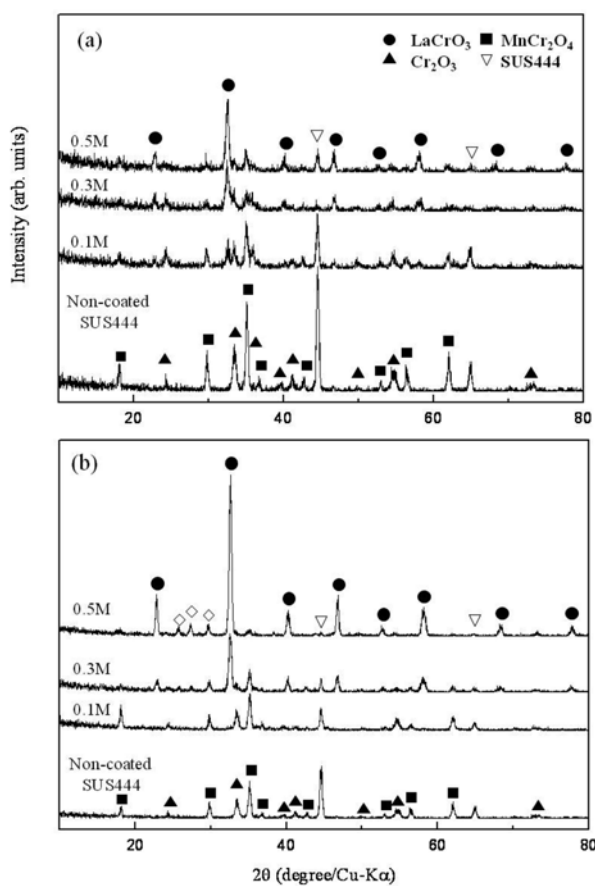


Fig. 5. X-ray diffraction patterns of LC (a) and LSC (b) thin films on SUS444 substrates (heat-treated at 700 °C for 100 h).

Comparing Fig. 1(b) with Fig. 5(b), it is found that the intensity of the LaSrO_4 phase in the LSC-coated SUS444 sample after 100 h oxidation is greater than that before oxidation. It is considered that the Cr_2O_3 scale formed during oxidation reacts with the strontium remaining in the surface of the thin film.

The area specific resistance (ASR) of the oxidized samples is shown in Fig. 6. The samples were oxidized

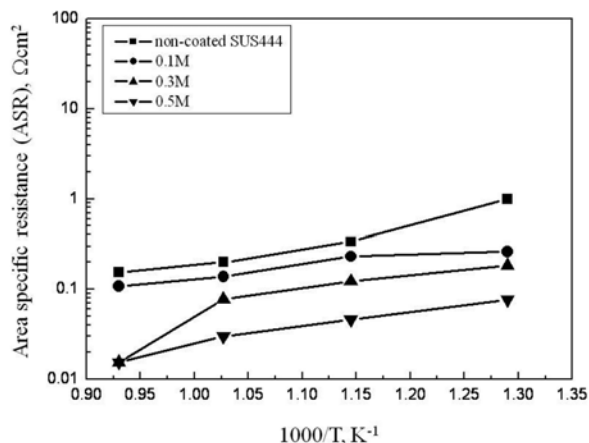


Fig. 6. Area specific resistance of LC thin film coated SUS444 substrates as a function of temperature (at 700 °C for 100 h).

at 700 °C for 100 h in air. The ASR value of the 0.5 M LC-coated SUS444 substrates differs by one order of magnitude, compared with the non-coated SUS444 sample. The value decreases with an increase in the concentration of the precursor solution; in other words, the thickness of the coating layer. The ASR values are estimated to be approximately 0.140, 0.046, 0.03 and 0.2 $\Omega \cdot \text{cm}^2$ for the 0.1, 0.3 and 0.5 M LC-coated SUS 444 and non-coated SUS444 samples, respectively, at 700 °C. It can be considered that LC-coated SUS444 is suitable for application as an interconnector in an IT-SOFC.

Conclusions

LaCrO_3 (LC) and $(\text{La}_{0.8}\text{Sr}_{0.2})\text{CrO}_3$ (LSC) thin films were uniformly coated on a SUS444 substrate by a sol-gel technique. From XRD analyses, the perovskite LaCrO_3 phase was confirmed in all samples. In the LSC-coated SUS444, the LaCrO_4 phase might result in a more porous microstructure. For LC and LSC thin films, increasing the concentration of the precursor solution resulted in an increase of film thickness. A thicker gel film could be obtained from a more viscous precursor solution. However, the microstructure of the thin film become more porous as the concentration of the precursor solution was increased. Sophisticated control of the precursor solution for the thin film was required to control both the microstructure and the thickness of the film. It appears that the presence of LC and LSC thin films effectively inhibited oxidation of the SUS444 substrates. The LaCrO_3 -coated SUS444, which was prepared from a 0.5 M/L precursor solution, showed the best ASR. The ASR values were estimated to be 0.03 and 0.34 $\Omega \cdot \text{cm}^2$ for LaCrO_3 -coated and non-coated SUS444, respectively.

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