Performance Degradation of Lanthanum Strontium Cobaltite after Surface Modification

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In the present study, the surface of La0.6Sr0.4CoO3 (LSC) was modified via atomic layer deposition (ALD) using CoOx as the modification material. The effect of the ALD CoOx treatment on the LSC-based anode-supported solid oxide fuel cell was analyzed and the ALD CoOx-treated cell was found to exhibit lower power density than that of the bare cell. Based on the electrochemical impedance spectroscopy measurements, it was concluded that this degradation stems mainly from the increased polarization loss, which results from the deterioration of the oxygen surface exchange property. Similarly, examining the bode plot revealed that the impedance at frequencies lower than 1 kHz increased mainly after the CoOx treatment; this increased impedance is believed to be associated with the limitation of O2 adsorption and dissociation.

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Conventional solid oxide fuel cells (SOFCs) are operated at high temperatures (≥800 °C) in order to ensure rapid kinetics and fast ion transport.1 However, lower operating temperatures are required to decrease the thermal budget and guarantee long time stability.2 For this reason, thin film electrolyte SOFC systems such as μ-SOFCs, were proposed and reported to have high power density owing to low ohmic loss.3, 4 The performance of SOFCs at low temperatures (<650 °C) is hindered by the sluggish kinetics of the cathode.5, 6, 7 Therefore, developing a cathode which exhibits low polarization loss is essential to further improving this performance. Various mixed ionic electronic conducting (MIEC) ceramics such as La1-xSrxCoO3-y (LSC), La1-xSrFeO3 (LSF), and La1-xSrCo1-yFe2O3 (LSF) have been proposed as cathode materials for low-temperature operation of the SOFC.8–10 The charge transport at the MIEC cathode consists of five steps: (1) oxygen adsorption and dissociation; (2) oxygen ionization; (3) oxygen ion incorporation; (4) bulk diffusion; (5) oxygen ion transfer at the cathode/electrolyte interface. Among these processes, the surface kinetics, which includes steps (1) to (3), is typically considered as the rate-determining step rather than a stage involving bulk oxygen ion conduction.11–14

Composite cathodes, which are fabricated by mechanically mixing different materials, can lead to improved cathode performance. Although electrolyte materials such as yttria-stabilized zirconia (YSZ) have been widely used as additives in forming the composite cathodes, transition metal oxides such as cobalt oxide can also be added. For example, Chen et al. reported that a composite of Ba0.5Sr0.5Co0.8Fe0.2O3-δ and 10 wt% of CoOx exhibited better total conductivity and fuel cell performance compared to that of pure Ba0.5Sr0.5Co0.8Fe0.2O3-δ.15

A surface modification technique has recently been introduced as an alternative method of increasing the catalytic activity of SOFC cathodes. In contrast to the composite cathode strategy, surface modification ensures adhesion between the cathode and electrolyte without the use of high sintering temperatures.18 Surface modification of the backbone cathode with a nanoparticle or thin film has been suggested as one means of enhancing the surface kinetics. Furthermore, the addition of ceramic nanoparticles or a thin film to the SOFC cathode, via infiltration, can decrease the polarization loss and enhance the stability.19 Both mixed conducting oxides, and even binary oxides with low ionic conductivity and negligible catalytic activity, have been reported to increase the performance of cathodes.20 However, the reported results regarding cathode surface modification are somewhat contradictory. For example, Yamahara et al. reported that the power density of a Sr-doped LaMnO3 (LSM) cathode-supported SOFC doubled after infiltration by Co2O3 nanoparticles.21, 22 In contrast, Huang et al. reported that CoOx infiltration did not improve the performance of an LSM-based cathode.23 However, Bidrawn et al. reported that even inert additives such as K2O and CaO promote the non-ohmic impedance of LSF and LSM.24 In addition, although strontium oxide (SrO) is considered to be detrimental to the SOFC cathode owing to Sr segregation phenomena,25 modification with SrO was reported to lead to a decrease in the polarization resistance.26 The aforementioned discrepancies can be attributed to infiltration-induced changes in the cathode morphology and inhomogeneous infiltration layers owing to the complex structure of the cathode.14, 23, 24 Therefore, it is difficult to determine whether the enhanced cathode performance truly results from the additive.

Atomic layer deposition (ALD) can be used to study the effect of the surface modification of the SOFC cathode on the performance. ALD is a thin film deposition tool, which is based on chemical vapor deposition. In the ALD process, a vaporized precursor adsorbs on the substrate and the unreacted precursor is purged by an inert gas. A supplied oxidant then reacts with the adsorbed precursor and the by-product is purged by an inert gas. The precursor/purge/oxidant/purge step is defined as one cycle of ALD; this cycle-by-cycle process enables precise control of the film thickness. ALD can be performed at lower deposition temperatures than that of other techniques, and can thus prevent structural change of the backbone electrode during modification.27 In addition, the self-limiting nature of the ALD ensures that the modification material is uniformly formed on the porous substrate.28 Yu et al. concluded that ALD-added CeO2 and SrO had a detrimental effect on the performance of various cathodes.27 In other studies, ALD Al2O3 was intentionally applied to cathodes in order to examine the relationship between geometric blocking and the performance.29, 30 Another study suggested that conformal coatings of ALD ZrO2 film could significantly enhance the stability of LSC cathodes.31

Although studies of CoOx-treated LSM- and LSCF-based cathodes have been well documented, there is no consensus regarding the performance of LSC cathodes surface treated with CoOx.21–23, 31 As such, in this work, we studied the effect of ALD cobalt oxide (CoOx) treatment on an LSC cathode based on an anode-supported SOFC cell. The low deposition temperature used in this study (200 °C) results in minimal 3-dimensional change in the cathode structure during modification. We compared the power performance and electrochemical impedance of the bare and CoOx-treated cells at various temperatures. One of the main findings of this study is that the ALD CoOx treatment results in a decrease in the cell performance owing to the degradation of the cathode surface; this degradation is related to the surface exchange, especially to the limitation of O2 adsorption and dissociation.
A 1 cm × 1 cm anode-supported cell was used for this study. The NiO/stabilized yttria-zirconia (NiO-YSZ) substrate was fabricated by a conventional powder process. The 8 μm-thick NiO-YSZ anode functional layer and 6.5 μm-thick YSZ electrolyte were fabricated by screen-printing. In addition, pulsed layer deposition (PLD) was used to insert a 300-nm-thick gadolinia-doped ceria (GDC) buffer layer between the YSZ and LSC in order to prevent undesirable cathode/electrolyte reactions. The 2.5-μm-thick LSC (La₂₀.₅Sr₇.₅O₃₋ₓ/CoOₓ, x = 0.₃) thin film cathode was deposited by PLD, as described in a previous study. Figure 1 shows the microstructure of the cell used in this study.

The ALD treatment with CoOₓ was performed using bis(1,4-diisopropyl-1,4-diazabutadiene)cobalt [C₁₆H₃₂N₄Co, Co(dpdab)] (UP Chemical Co.) as a precursor and ozone as an oxidant. Nitrogen gas (purity ≫ 99.999%) flowing at a rate of 2.5 sccm was used to purge the unreacted precursor and by-product. Therefore, one cycle of ALD consisted of N₂ purge/Co(dpdab)₂ pulse/N₂ purge/O₃ pulse and Co(dpdab)₂ pulse for durations of 30 seconds and 4 seconds, respectively. The ALD process was performed with a thermal ALD system (ICOT Inc.) that is composed of a stainless steel tube type chamber whose vacuum is maintained by using a rotary pump; details of the configuration of the system are provided elsewhere. The pressure during deposition was maintained at 0.1 Torr and deposition was performed at 200 °C. In addition, Co(dpdab)₂ was heated to 95 °C and the gas line for ozone supply was maintained at room temperature. Bare and 30-μm-thick YSZ electrolyte cathode/electrolyte reactions. The 2.5-μm-thick LSC (La₂₀.₅Sr₇.₅O₃₋ₓ/CoOₓ, x = 0.₃) thin film cathode was deposited by PLD, as described in a previous study. Figure 1 shows the microstructure of the cell used in this study.

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The ASRpol of the 30-cycle ALD CoOx-treated sample is higher than those of the former, indicating that modification using ALD CoOx is detrimental to the power performance of the cell. However, almost no change in the ASRohm, irrespective of the operating temperature, can be inferred from the distance between the high- and low-frequency intercept and includes contributions from both the cathode and anode. The ASRpol of the 30-cycle ALD CoOx-treated sample is higher than that of its bare counterpart. This suggests, as was reflected in the I-V results, that the increased polarization loss stems mainly from the degradation of the electrode with the ALD treatment. Specifically, the increased ASRpol owing to the ALD treatment, is believed to result from the degradation of the cathode that has more sluggish reaction kinetics than the anode. The Nyquist plots in Figure 6a, 6b, and 6c were fitted with an equivalent circuit, which consists of one resistance associated with the non-charge transfer process, which includes gas transport, adsorption-desorption of oxygen, and surface diffusion of adsorbed oxygen species. In contrast, the transport of oxygen ions through the electrolyte is affected by the ALD CoOx modification, although the microstructure remains unchanged. Therefore, the impedance-modified surface property of the cathode depends mainly on the differing properties of the cathodes can differ from each other.

Figure 7 shows an Arrhenius plot of the fitted data of the polarization resistance of both samples. By using the temperature dependence of the polarization resistance, we can calculate the activation energy in terms of the ASRpol. As the figure shows, the ALD CoOx-treated cell has a higher (1.21 eV vs. 0.92 eV) activation energy of ASRpol than that of the bare sample. This implies that the former is less suitable for low-temperature operation than the latter. In addition, the difference in activation energy results mainly from the differing properties of the bare and CoOx-treated cathodes and as such, the rate determining step of the cathodes can differ from each other.

Bode plots (Figure 8) were used in order to identify the rate determining step for both samples. We confirmed that the surface chemistry is affected by the ALD CoOx modification, although the microstructure remains unchanged. Therefore, the impedance-modified frequency regime shown in the bode plot should be related to changes in the surface property of the cathode. This surface property is associated with the non-charge transfer process, which includes gas transport, adsorption-desorption of oxygen, and surface diffusion of adsorbed oxygen species.
across the electrode/electrolyte interface is considered a charge transfer process. Figure 8 shows that the bare and CoOx-treated samples have the same impedance in the high frequency region \( f \geq 10 \text{ kHz} \); therefore, it can be concluded that this frequency domain is not associated with the oxygen surface exchange. This is plausible since the high-frequency domain is associated with oxygen ion transport at the cathode/electrolyte interface; this ion transport is referred to as the charge transfer process. In this study, the CoOx treatment results in changes in the impedance at frequencies lower than 1 kHz; the modification should therefore, degrade the surface exchange property of the cathode including the non-charge transfer process. The higher activation energy of the ASRpol of the CoOx-treated cell, compared to that of the bare cell (Figure 7), can be attributed to the degradation of surface exchange characteristics owing to modification.

Mechanisms of cathode degradation owing to ALD treatment have been proposed in previous studies. Kungas et al., concluded that an ALD Al2O3 layer can block the oxygen vacancy site on LSF and the consequent decreased vacancy concentration results in limited O2 dissociative adsorption. Yu et al. reported a similar mechanism in the case of ALD-deposited SrO, which deactivated the cathode surface by forming blocking layers; however, CeOx prevented the O2 dissociation process. CoOx treatment via ALD is believed to limit the O2 adsorption and/or dissociation process. This limitation of adsorption and dissociation is associated with the low-frequency regime \( f \leq 100 \text{ Hz} \). In this study, the CoOx-treated sample exhibits a higher impedance in the low-frequency domain than that of its bare counterpart; this implies that the CoOx-treated cell exhibits limitation of adsorption and/or dissociation.

The activation energy of the imaginary impedance at various frequencies was analyzed (Figure 9) in order to further understand this
limitation. As previously stated, the high- and low-frequency regimes are associated with the charge transfer and non-charge transfer processes, respectively. For frequencies higher than 100 Hz, the activation energy remained above 0.52 eV in both cases indicating that the bare and the CoOx-treated samples exhibit thermally activated charge transfer processes. In addition, for frequencies ranging from 100–0.2 Hz, the activation energy of the latter remains relatively high (with a maximum value of 1.61 eV) while that of the former decreases gradually. Since the general activation energy of the limiting process including both adsorption and dissociation is high (1.5–1.6 eV), then with a maximum activation energy of 1.61 eV, it can be concluded that the increased impedance owing to the CoOx treatment results from both the adsorption and dissociation limiting step.

Conclusions

Atomic layer deposition was used to determine the effect of CoOx treatment on LSC. XPS and XRD analyses revealed that as-deposited ALD CoOx has a valence a state of Co2+. C converted the CoO to Co3O4, which implies that the increased impedance owing to the CoOx treatment results from both the adsorption and dissociation limiting step.

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