Sulfur in the air stream is one of the major contaminants affecting the performance stability of cathodes of solid oxide fuel cells (SOFCs) such as La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) perovskite. Here sulfur deposition and poisoning was investigated on LSCF bar samples in the presence of 20 ppm SO2 and temperature range of 400–900°C, using scanning electron microscopy, confocal laser Raman spectroscopy and electrical conductivity relaxation (ECR) methods. Sulfur (SO2) reacts with LSCF, primarily forming SrSO4 at high temperatures (i.e., ≥ 700°C) and SrS at low temperatures (i.e., < 700°C). Surface segregated SrO plays an important role in the sulfur deposition. The most important observation of this study is that sulfur deposition shows a distinct volcano-type dependency on the heat-treatment temperature and is most pronounced at temperatures around 700°C, indicating that the reaction rate between the segregated SrO and SO2 is highest at ~700°C. The ECR results indicate that the surface exchange coefficient of LSCF after the exposure to 20 ppm SO2 at 700, 800 and 900°C for 48 h is two orders of magnitude lower than that of the sample tested in the absence of SO2, indicating that sulfur poisoning deteriorates significantly the surface exchange and diffusion processes for the O2 reduction reaction on LSCF electrodes.

The cathode materials of SOFCs, such as LSCF, are highly sensitive to sulfur poisoning. Understanding the sulfur deposition and poisoning mechanism is critical to develop contaminant-tolerant and durable cathodes for SOFCs. Xiong et al. studied the polarization behavior of (La0.6Sr0.4)0.5Mn0.5O3 (LSM) and Sm0.5Sr0.5CoO3 (SSC) cathodes after the heat-treatment of the electrodes to 100 ppm SO2 at 800°C and found that the performance of SSC declined rapidly while LSM was more stable in SO2-contained air.15 The significant difference in the polarization performance of SSC and LSM in SO2-contained air for the O2 reduction reaction has been explained by the difference in the activity of SrO in the LSM and SSC perovskites. Liu et al.16 showed that the performance of cells with La0.6Sr0.4Co0.2Fe0.8O3-δ (LSCF) electrode becomes unstable in the presence of 1 ppm SO2 and drops significantly when the SO2 concentration increased to 20 ppm. The performance degradation is most likely due to the poisoning of SO2 and the formation of SrSO4. Sitte et al measured the surface exchange kinetics of a dense La0.6Sr0.4CoO3-δ sample at 700°C and observed the decreases in the surface exchange coefficient, kchem in the presence of a small amount of sulfur (ppb).18 Ishihara’s group19 reported that the degradation of LSCF is accelerated at low partial pressure of O2 in the presence of sulfur and the degradation is considered to be caused by the Sr segregation and the subsequent formation of SrSO4. On the other hand, Wang et al.20 studied the polarization performance behavior of LSCF in the presence of 0.1 ppm SO2 and two-stages of performance degradation were found. A degradation mechanism based on the occupation of SO2 in the oxide ion vacancies and subsequent formation of SO42− and SrSO4 was proposed for the irreversible poisoning effect of SO2. However, there appears no consensus on the mechanism and kinetics of the deposition and poisoning of sulfur on SOFC cathodes such as LSCF.

In this study, the deposition and poisoning of sulfur on the microstructure and surface exchange and diffusion properties of LSCF cathode materials is investigated in the temperature range of 400–900°C on dense bar samples in air using confocal Raman spectroscopy, scanning electron microscopy as well as electrical conductivity relaxation (ECR) methods. Use of dense bar samples will facilitate the observations of microstructure changes and surface property characterizations.21 The results indicate that the deposition of sulfur species on the LSCF surface and formation of S-containing compounds such as SrSO4 and SrS depends strongly on the temperature, and becomes most pronounced at temperatures around 700°C.

**Experimental**

La0.6Sr0.4Co0.2Fe0.8O3-δ powders (LSCF, Fuel Cell Materials) were pressed into rectangular bars at 300 MPa, and then fired at 1350°C for 5 h in air to form dense LSCF bar samples. The dimension of the sintered samples is 25 mm × 6.6 mm × 0.62 mm. Sulfur deposition and poisoning experiments were carried out on dense LSCF bar samples by heat-treatment at temperatures from 900 to 400°C in the presence and absence of 20 ppm SO2 in dry air. The chemical reactivity between La2O3, SrO, Co3O4 and Fe2O3 oxides and sulfur was investigated by calcination of the oxide powders at different temperatures in the presence of 20 ppm SO2 for 2 h.

XRD (DB Advance, Bruker, Germany) and confocal laser Raman spectroscopy (WITec GmbH, Ulm Germany) techniques were used to examine the phase formation and composition of oxides and LSCF bar samples. The morphology and microstructure of the bar samples after the heat-treatment at different temperatures in the presence and absence of 20 ppm SO2 were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy using a Zesis EVO with 20 keV.
The conductivity relaxation profiles of LSCF bar samples were measured by a standard four-probe method using a measurement system consisting of a Digital Multimeter (Keithley 2001) equipped with a computer and a program written using the LABVIEW 8.5 software. Silver wires were used as the leads, which were attached to an Ag electrode using silver paste. The measurements were carried out at temperatures of 700, 800 and 900 °C in the presence and absence of 20 ppm SO₂ with oxygen partial pressure changing from 0.05 bar to 0.21 bar. The electrical conductivity data of the bar samples were recorded as a function of exposed time and the experimental data were fitted to the theoretical equations\textsuperscript{23} to calculate the oxygen surface exchange coefficients, \( k_{\text{chem}} \). However, the samples that were heat treated at temperatures from 600 to 400 °C in the presence of 20 ppm SO₂ were not evaluated by ECR due to the very low conductivity value of the LSCF samples at these temperatures. The experimental setup for the ECR measurement and sulfur poisoning arrangement of LSCF bar samples were similar to that used for the boron deposition and poisoning studies.\textsuperscript{22}

**Results and Discussion**

**Effect of temperature on the phase and microstructure of LSCF.**—

Figure 1 is the XRD patterns of LSCF bar samples after heat-treatment in the presence of 20 ppm SO₂ at different temperatures for 48 h. The as-prepared LSCF shows typical XRD patterns associated with rhombohedral perovskite structure (curve a, Fig. 1). After heat-treatment at 800 and 900 °C in the presence of 20 ppm SO₂, XRD patterns of LSCF remained the same, suggesting that the main phase is the perovskite structure. However, prominent XRD peaks associated with the formation of SrSO₄ phase\textsuperscript{24} were observed for the LSCF bar sample treated at 700 °C in the presence of 20 ppm SO₂ (curve d, Fig. 1). This indicates the significant reaction between the SO₂ and LSCF bar samples, forming SrSO₄ phase. As the heat-treatment temperatures decreased to 600–400 °C, peaks associated with SrSO₄ phase disappear and a distinct peak at 29.5° was detected (curves e,f,g, Fig. 1). The peak at 29.5° has been identified with the formation of SrS phase.\textsuperscript{25} The XRD results indicate that the formation of the SrSO₄ is most favorable at a temperature of \( \sim 700 \) °C, while the formation of SrS occurs at temperatures below 700 °C.

Figure 2 is the SEM micrographs of the surface of the LSCF bar samples after heat-treatment in the absence and presence of 20 ppm SO₂ in air at different temperatures for 48 h. As shown previously, the surface of as-prepared LSCF sample is characterized by the dense LSCF grains with smooth surface and the grain size is in the range of 2–5 µm.\textsuperscript{22} After heat-treatment in the absence of SO₂, there is a clear formation of isolated small particles on the LSCF surface. For LSCF samples treated at 900 °C for 48 h, particles as large as 2 µm are formed (Fig. 2a) and the formation of such particles is most likely due to the segregated cobalt and in particular strontium species.\textsuperscript{26} With the decrease in the temperature, the size and number of the segregated particles are reduced significantly. In the case of the LSCF bar sample heat-treated at 400 °C for 48 h, the surface is very clean (Fig. 2k), similar to that of as-prepared LSCF sample. These results are in accordance with the surface morphological behavior of LSCF samples after heat-treatment from 600 °C to 900 °C as reported by Oh et al.\textsuperscript{27} and Bucher et al.\textsuperscript{28} The significant reduction in the segregated particles indicates that the strontium and/or cobalt segregation on the LSCF electrode is a temperature-activated process.
Very different from that in the absence of SO2, the size and number of particles formed on the LSCF surface varied significantly with the temperature. For the LSCF sample heat-treated at 900 °C in the presence of SO2 for 48 h, there is a formation of large number of small (∼80 nm) and large (∼700 nm) particles and the formation of the particles appears to be random on both the grain boundaries and the surface of LSCF grains (Fig. 2b). Significant deposition and formation of large and small particles were also observed for the LSCF bar sample after heat-treatment at 800 °C (Fig. 2d). However, the most remarkable formation of particles was observed for the LSCF after heat-treatment in the presence of SO2 at 700 °C (Fig. 2f). The surface of LSCF sample is almost completely covered by the particles formed on the surface of LSCF grains. The particles formed on the LSCF surface were most likely strontium sulfate, SrSO4, indicated by the prominent SrSO4 formation as detected by XRD (curve d, Fig. 1). When the temperature decreased to 600 °C, the numbers of the particles formed on the LSCF surface decreased substantially with few isolated large particles (400 nm) and numerous fine particles (35 nm) (Fig. 2b). As the temperature is reduced to 400 °C, the surface of LSCF sample is very clean (Fig. 2i), similar to that in the absence of SO2 (Fig. 2k). This indicates the significantly reduced activity between the SO2 and LSCF at temperatures below 700 °C.

Figure 3 is the additional SEM micrographs of the deposited particles on different LSCF bar samples after heat-treatment in the presence of 20 ppm SO2 at 700 °C. The deposited particles are characterized by smooth surface without clear crystalline facets (Fig. 3b and 3c). The size of these particles is in the range of 0.5 to 5 μm, much larger than the particles formed at 800 and 900 °C. EDX analysis indicates that the deposited particles contain O, Sr and S and the atomic ratio of Sr to S is 1:1 (Fig. 3d), consistent with the SrSO4 phase as identified by XRD.

The phase of the deposited particles on the surface of LSCF bar samples was further investigated using confocal Raman spectroscopy. Figure 4 is the optical microscopy images and Raman spectra of the LSCF surface after heat-treatment at 900 and 800 °C in the presence of 20 ppm SO2 for 48 h. The formation of irregular particles can be clearly observed. SrSO4 has a characteristic Raman adsorption peak at 456, 620 and 1000 cm⁻¹, very close to 460, 620 and 1003 cm⁻¹ reported for celestine SrSO4. For the reaction at 900 °C, there were formations of large number of small particles along the grain boundaries and based on Raman mapping (Fig. 4A), majority of the particles in the optical microscopy images belong to the SrSO4 phase. As the temperature decreased to 800 °C, formation of SrSO4 was also clearly identified (Fig. 4B), similar to that observed for the LSCF bar samples at 900 °C. The Raman mapping results evidently show the formation of SrSO4 on the LSCF surface after the heat-treatment in the presence of 20 ppm SO2 at 800 and 900 °C. The detection of SrSO4 phase by the Raman spectroscopy and not by XRD also indicates the high sensitivity of Raman spectroscopy techniques in the study of sulfur poisoning on LSCF electrode materials, particularly in the cases where the quantities of the contaminant phase are very small.

As the temperature decreased to the range of 600–400 °C, number of particles deposited on the surface of the LSCF bar samples decreased significantly (Fig. 5). The Raman spectra taken on the surface of LSCF samples after heat-treatment at 600, 500 and 400 °C in the presence of 20 ppm SO2 were similar and no characteristic Raman bands at 456, 620 and 1000 cm⁻¹ for SrSO4 were observed (Fig. 5d). No other Raman peaks were observed most likely due to the little Raman activity of near-cubic perovskite phase of LSCF and the face-centered cubic structure of SrS. Both Raman and XRD results indicate that reactivity between the LSCF and SO2 at temperatures below 700 °C to form SrSO4 is very low or negligible. Nevertheless, the detection of SrS by XRD (see Fig. 1) clearly indicates that SrS is the main product of the reaction between LSCF and SO2 at temperatures below 700 °C.

Activity of constituent oxides of LSCF with SO2.— The reactivity between the constituent oxides of LSCF and SO2 was studied by heat-treatment of La2O3, SrO, Co3O4 and Fe2O3 oxide powders at 900 to 400 °C for 2 h in the presence of 20 ppm SO2 and the XRD patterns of oxides after the treatment are shown in Fig. 6. In the case of SrO, the major phase is SrCO3 and Sr(OH)2 particularly in the high temperature range 600 to 900 °C, probably due to the facile reaction of SrO with CO2 and moist in the air (Fig. 6b). Distinctive SrSO4 peaks were detected between 900 to 700 °C and SrSO4 peaks between 600 to 400 °C. However, the amount of SrSO4 and SrS is relatively small as compared to that of SrCO3 and Sr(OH)2. The phases and their relative amount formed for the SrO-SO2 oxide couples are sum-
marized in Table I. According to the literature, La$_2$O$_3$ is reactive with SO$_2$ to form La$_2$(SO$_4$)$_3$ in the temperatures lower than 237°C,\textsuperscript{31} while Fe$_2$O$_3$ can react with SO$_2$ in the temperature range of 100 to 750°C but Fe$_2$(SO$_4$)$_3$ may decompose above 600°C.\textsuperscript{32} Zhao et al.\textsuperscript{33} showed that Co$_3$O$_4$ reacts with SO$_2$ at 300°C. However, under the conditions of this study, except the formation of La(OH)$_3$ at 400°C (Fig. 6a), no additional peaks or new phases were observed for the reaction between La$_2$O$_3$, Co$_3$O$_4$ and Fe$_2$O$_3$ oxides and SO$_2$ (Fig. 6a, 6c, 6d).

The results indicate that SrO is most reactive with SO$_2$, while the activity of La$_2$O$_3$, Co$_3$O$_4$ and Fe$_2$O$_3$ oxides with SO$_2$ is very low.

**Effect of temperature on the oxygen surface exchange coefficient.**—Figure 7 is the electrical conductivity relaxation profiles of LSCF samples measured at 900, 800 and 700°C as a function of exposure time in the absence and presence of 20 ppm SO$_2$. Oxygen partial pressure changes from 0.05 bar to 0.21 bar. In the absence of SO$_2$, oxygen...
the initial relaxation time is \( \sim 400 \), 1,000 and 2,000 s, respectively (Fig. 7a–7c). The initial oxygen exchange coefficients, \( k_{\text{chem}} \), of as-prepared LSCF measured in the absence of \( \text{SO}_2 \) is \( 6 \times 10^{-4}, 5 \times 10^{-4} \) and \( 2 \times 10^{-4} \) cm s\(^{-1} \) at 900, 800 and 700°C, respectively, and decreased slightly with the heat-treatment time. The small decrease in \( k_{\text{chem}} \) may be due to the surface segregation of isolated particles on the LSCF surface as shown by SEM analysis (Fig. 2A). However, the relaxation time increases significantly with the exposure time for LSCF samples in the presence of \( \text{SO}_2 \). For example, the relaxation time increased from 1,500 s to 3,500 s after the heat-treatment in \( \text{SO}_2 \) from 3 h to 48 h at 800°C (Fig. 7d), while the relaxation time increased from 10,000 s to 30,000 s after the heat-treatment in \( \text{SO}_2 \) from 3 h to 48 h at 800°C. Similar trend was also observed for the samples heat-treated at 700°C, the relaxation time increased from 8,000 s to 60,000 s (Fig. 7f).

In the presence of 20 ppm \( \text{SO}_2 \), \( k_{\text{chem}} \) decreased rather quickly. After the exposure to sulfur for 48 h, the \( k_{\text{chem}} \) of LSCF at 900°C, 800°C and 700°C is \( 9 \times 10^{-3}, 8 \times 10^{-3} \) and \( 2 \times 10^{-3} \) cm s\(^{-1} \), respectively, two orders of magnitude lower than that of the as-prepared LSCF. The significant reduction in \( k_{\text{chem}} \) is clearly related to the sulfur poisoning and formation of \( \text{SrSO}_4 \) on the surface of LSCF cathode materials. As compared to the chromium and boron poisoning, sulfur poisoning is also very significant on the surface exchange properties of the LSCF cathodes. For example, at 800°C, \( k_{\text{chem}} \) of LSCF after the heat-treatment in the presence of 20 ppm \( \text{SO}_2 \) for 48 h is \( 8 \times 10^{-6} \) cm s\(^{-1} \), significantly lower than \( 1.0 \times 10^{-4} \) cm s\(^{-1} \) and \( 6 \times 10^{-3} \) cm s\(^{-1} \) measured after the heat-treatment in the presence of \( \text{Cr}_2\text{O}_3 \) and borosilicate glass for 48 h, respectively.

### Discussion

The observation of \( \text{SrSO}_4 \) and \( \text{SrS} \) phases by XRD, SEM and Raman spectroscopy and significant deterioration of \( k_{\text{chem}} \) of LSCF electrode materials after the heat-treatment in the presence of 20 ppm \( \text{SO}_2 \) indicate that the presence of sulfur in air can cause the significant sulfur deposition and poisoning of LSCF electrodes for the \( \text{O}_2 \) reduction reaction, consistent with that reported in the literature.\(^{15,16,18–20,35}\) The interaction between LSCF and \( \text{SO}_2 \) leads to the formation of \( \text{SrSO}_4 \) at temperatures \( \geq 700°C \) and \( \text{SrS} \) at temperatures below 700°C. Madarasz et al. studied the oxidation behavior of \( \text{SrS} \) in air and showed that oxidation of \( \text{SrS} \) starts slowly at 700°C, forming \( \text{SrSO}_4 \).\(^{36}\) XRD data shows the existence of \( \text{SrS} \) instead of \( \text{SrSO}_4 \) on the LSCF bar samples after the heat-treatment at 800°C in the presence of 20 ppm \( \text{SO}_2 \) and the intensity of the \( \text{SrS} \) phase increases with the decrease of the temperature (Fig. 1). The disappearance of \( \text{SrS} \) peaks for the LSCF bar samples heat-treated at temperatures \( \geq 700°C \) indicates that \( \text{SrSO}_4 \) is more stable than \( \text{SrS} \) particularly at high temperatures, consistent with that reported by Madarasz et al.\(^{36}\) In the present study, the sulfur deposition occurs on LSCF dense bar samples under no polarization (i.e., open circuit) conditions. Therefore, the degradation model based on the occupation of \( \text{SO}_2 \) in the oxide ion vacancies and subsequent formation of \( \text{SO}_4^{2–} \) and \( \text{SrSO}_4 \) for the sulfur deposition and poisoning\(^{15,20}\) would not be applicable in this case.

The most significant finding of this study is the unusual behavior of the sulfur deposition on LSCF bar samples as a function of temperature. As shown in Fig. 2A, the \( \text{Sr} \) segregation of the LSCF decreases with the decrease of temperature, consistent with that reported in the literature.\(^{27,28}\) Very different from the significant reduction in the surface segregated \( \text{SrO} \) particles, the sulfur deposition occurred most significantly at temperatures around 700°C (Fig. 2F). The dependency of the \( \text{Sr} \) segregation and sulfur deposition, i.e., the amount of segregated and sulfur-containing particles formed on the LSCF surface can be semi-quantitatively evaluated, as shown in Fig. 8. In the figure, the degree or magnitude of the surface segregation and sulfur deposition was estimated by measuring the occupied areas of the segregated

### Table I. Reaction products and their relative amount of \( \text{SrO} \) oxide after the heat-treatment at different temperatures in the presence of 20 ppm \( \text{SO}_2 \) for 2 h.

<table>
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<tr>
<th>Temperature, °C</th>
<th>( \text{SrSO}_4 )</th>
<th>( \text{SrCO}_3 )</th>
<th>( \text{Sr(OH)}_2 )</th>
<th>( \text{SrSO}_4 )</th>
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<tr>
<td>900</td>
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*H – high; L – low.*
particles and the sulfur-containing particles formed on the surface of LSCF bar samples. The occupied areas of particles on the surface were obtained by counting the individual particles per unit area based on the SEM images (similar to that shown in Fig. 2). The areas of the segregated particles on the LSCF surface decrease with the temperature, as expected, however, the areas of sulfur-containing particles show a distinct volcano-shaped curve against the temperature. The areas of the sulfur-containing particles increase with temperature from 900 to 700 °C and then decrease dramatically when the temperature decreases from 600 to 400 °C. In the study of the chromium deposition on LSCF cathode, it is well known that the deposition of Cr species occurs preferentially on the surface of the LSCF cathode and at the LSCF cathode and metallic interconnect interface rather than at the cathode/electrolyte interface, forming primarily SrCrO4.37–41 The interaction between the SrO and gaseous Cr species would lead to the formation of Sr-Cr-O nuclei on the surface of LSCF and subsequent crystallization and grain growth of SrCrO4 and/or Cr2O3 solid phases.7,38 With the decrease in temperature, both segregated SrO and partial pressure of Cr species decrease significantly, leading to the significant reduction in Cr deposition, as shown recently.34 The predominant formation of SrSO4 at high temperatures of 900–700 °C and SrS at low temperatures of 600–400 °C indicates that the segregated SrO also plays an important role in the sulfur deposition and poisoning, similar to that observed in the chromium deposition in the LSCF cathodes.38 However, the volcano-type dependency of the sulfur deposition as a function of temperature (Fig. 8) implies that kinetically the nucleation and grain growth for the formation of SrSO4 and SrS phases is a complicated function of temperature. In a recent study of the

Figure 7. Electrical conductivity relaxation profiles of LSCF bar samples as a function of exposure time in the (a,b,c) absence and (d,e,f) presence of 20 ppm SO2 at (a,d) 900 °C, (b,e) 800 °C, and (c,f) 700 °C.

Figure 8. Plots of occupied areas of segregated particles in the absence of SO2 and sulfur-containing particles in the presence of 20 ppm SO2, formed on the surface of LSCF bar samples as a function of the heat-treatment temperatures.
effect of $\text{SO}_2$ on the oxygen permeation properties of LSCF hollow fiber membranes, Gao et al also reported that the sulfur content of the LSCF membrane surface layer after the exposure to $\text{SO}_2$ decreased with increase in temperature from 800 °C to 1000 °C. The decrease in sulfur content indicates the reduced sulfur-containing particles (i.e., $\text{SrSO}_4$) with the increase of temperature, consistent with the reduced $\text{SrSO}_4$ phase when the temperature increased from 700 °C to 900 °C in this study. Based on the classical nucleation theory, the nucleation and crystal growth is a competition between the effective diffusion coefficient and energy barrier for the formation and growth of nuclei. For example, in the study of crystal nucleation and growth of NaF in photo-thermo-refractive glass, Dyamant et al. observed the parabolic relationship between the nucleation rates of NaF and temperature with the maximum rate at $\sim 485^\circ$C. $\text{SrSO}_4$ phase exhibits an excellent stability from room temperature to 1400 °C with a structural transformation at 1158.3°C. Thus, once $\text{SrSO}_4$ is formed, the grain growth of the $\text{SrSO}_4$ phase would be determined by the kinetics of the reaction between $\text{SrO}$ and $\text{SO}_2$. The pronounced formation of $\text{SrSO}_4$ at 700°C indicates that the reaction between the $\text{SO}_2$ and segregated $\text{SrO}$ depends strongly on the temperature with the highest activity at temperatures close to $\sim 700$ °C. This seems to be supported by the observation that at high temperatures of 800 and 900 °C the dominant phase formed between $\text{SrO}$ and $\text{SO}_2$ is $\text{SrCO}_3$ and $\text{Sr(OH)}_2$ rather than $\text{SrSO}_4$ and $\text{SrSO}_4$ (see Fig. 6 and Table I). With the further decrease in temperature to 600 °C, the sulfur deposition to form $\text{SrS}$ would be limited by segregated $\text{SrO}$ due to the substantial reduction in the segregated $\text{SrO}$.

The standard Gibbs free energy, $\Delta G$ of possible sulfur compounds of the reaction between LSCF and $\text{SO}_2$ such as $\text{SrSO}_4$, $\text{CoSO}_4$ and $\text{Fe}_2(\text{SO}_4)_3$ can be calculated based on the thermodynamic database. For example, at 700 °C, the $\Delta G$ of $\text{SrSO}_4$, $\text{CoSO}_4$ and $\text{Fe}_2(\text{SO}_4)_3$ is $-561.74$, $-171.88$ and $-57.77$ kJ mol$^{-1}$, respectively. Despite the negative $\Delta G$ values, no $\text{CoSO}_4$ and $\text{Fe}_2(\text{SO}_4)_3$ phases were observed by the XRD as well as Raman spectroscopy analysis of the LSCF bar samples after the heat-treatment in the presence of 20 ppm $\text{SO}_2$ under the conditions of the present study. This indicates that kinetically, the reactivity of cobalt and iron oxides with $\text{SO}_2$ is very low. The low activity of cobalt and iron oxides with sulfur is also confirmed by oxide couple study (see Fig. 6) and the reported observation of $\text{SrSO}_4$ and $\text{CoFe}_2\text{O}_4$ and not $\text{CoSO}_4$ and $\text{Fe}_2(\text{SO}_4)_3$ for the sulfur poisoned LSCF cathodes.

Conclusions

Sulfur deposition and poisoning mechanism were investigated on dense LSCF bar samples after the heat-treatment in the presence of 20 ppm $\text{SO}_2$ and temperature range of 400 to 900°C, using XRD, SEM, confocal Raman and ECR techniques. $\text{SO}_2$ reacts with LSCF, forming $\text{SrSO}_4$ phase at temperatures $\geq 700$ °C and $\text{SrS}$ at temperatures below 700°C. The surface segregation of $\text{Sr}$ and/or $\text{Co}$ species on the LSCF bar samples decreases significantly with the temperature, however, the sulfur deposition on the LSCF surface shows a distinct volcano-type dependency on the temperature. Sulfur reaction and deposition to form sulfate, $\text{SrSO}_4$ is most significant at $700$ °C. The fundamental reason for such volcano-type sulfur deposition behavior as a function of temperature is not completely understood. However, the results appear to indicate that the reaction between the segregated $\text{SrO}$ and $\text{SO}_2$ is most active kinetically at $\sim 700^\circ$C. ECR results indicate that the surface exchange coefficient of LSCF after the exposure to 20 ppm $\text{SO}_2$ at 700, 800 and 900°C for 48 h is $9 \times 10^{-5}$, $8 \times 10^{-4}$ and $2 \times 10^{-6}$ cm s$^{-1}$, respectively, which is much lower than 2.8 $\times 10^{-4}$, 5 $\times 10^{-4}$ and 6 $\times 10^{-5}$ cm s$^{-1}$ of the sample tested in the absence of $\text{SO}_2$. Presence of sulfur in air has a significant detrimental effect on the microstructure and surface exchange coefficient of LSCF electrode materials for the $\text{O}_2$ reduction reaction.