

# Long-Term Cr Poisoning Effect on LSCF-GDC Composite Cathodes Sintered at Different Temperatures

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The impact of sintering temperature on Cr-poisoning of solid oxide fuel cell (SOFC) cathodes was systematically studied. La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3- $\delta$ </sub> - Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub> symmetric cells were aged at 750°C in synthetic air with the presence of Crofer 22 APU, a common high temperature interconnect, over 200 hours and electrochemical impedance spectroscopy (EIS) was used to determine the degradation process. Both the ohmic resistance (R<sub>Ω</sub>) and polarization resistance (R<sub>P</sub>) of LSCF-GDC cells, extracted from EIS spectra, for different sintering temperatures increase as a function of aging time. Furthermore, the Cr-related degradation rate increases with decreased cathode sintering temperature. The polarization resistance of cathode sintered at lower temperature (950°C) increases dramatically while aging with the presence of Cr and also significantly decreases the oxygen partial pressure dependence after aging. The degradation rate shows a positive correlation to the concentration of Cr. The results indicate that decreased sintering temperature increases the total surface area, leading to more available sites for Sr-Cr-O nucleation and thus greater Cr degradation.

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The growing demand for robust, inexpensive, clean, secure, and sustainable energy have stimulated great interest in fuel cells. Among all types, solid oxide fuel cells (SOFCs) are one of the most promising candidates due to high efficiency and fuel flexibility.<sup>1–4</sup> Recently, significant effort has been devoted to the development of intermediate to low temperature (400-800°C) SOFCs. Lowing operating temperature not only decreases the degradation rates but also broadens the selections of materials. The mixed ionic and electronic conducting (MIEC) perovskite  $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$  (LSCF) and its composite with  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  (GDC) is a promising cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs) because of its high intrinsic electrocatalytic activity to the oxygen reduction reaction (ORR) and acceptable thermal expansion coefficient. However, one of the challenges for the commercialization is the durability during long-term operation.<sup>5–9</sup> One of the most severe issues for cathode degradation is Cr-poisoning from Cr-containing stainless steel interconnects at high temperatures. Significant efforts have been given to understand the Cr-degradation mechanisms on SOFC cathodes. Jiang et al.<sup>10–12</sup> shows that gaseous Cr species can be chemically reduced and deposited at triple phase boundaries (TPB) as well as two-phase boundaries, blocking sites active toward the ORR.<sup>10-12</sup> The activity of the ORR on cathodes is governed by several factors, such as the atomic structure, surface composition<sup>13–15</sup> and bulk microstructure.<sup>16</sup> One of the important factors is the availability of active sites on the cathode surface for the ORR to occur. However, the formation of Cr-containing secondary phase, such as SrCrO<sub>4</sub>, could potentially poison the performance. Complete coverage of the passive and insulating SrCrO<sub>4</sub> layer over the cathode surface would easily block the ORR-active sites for effective charge-transfer and oxygen surface dissociation and diffusion. Matsuzaki et al. found that Cr prefers to deposit on the top surface of the LSCF cathode, which is very different from Cr deposition observed on LSM cathodes.<sup>17</sup> Also, Simner et al. found segregated Sr from the LSCF bulk could significantly enhance the deposition of Cr species on the LSCF surface.<sup>18</sup> Despite significant research into Cr based cathode degradation, there has been little

emphasis placed on the effect of cathode sintering temperature on Cr-poisoning.

In this research, sintering effect on Cr-degradation on LSCF-GDC was studied. Small changes in cathode sintering temperature leads to distinct differences in degradation rates for LSCF-GDC composite cathodes exposed to Cr-containing interconnect materials. Elevated cathode sintering temperature will enhance the bonding between cathode and electrolyte, increasing the particle connection of the cathode, promoting the crystalline structure of cathode.<sup>19</sup> Decreased sintering temperature of cathode may lead to smaller cathode particle size, less density,<sup>20</sup> and an increase in total surface area, making the cathode more vulnerable for the nucleation of Cr containing species. Therefore, controlling sintering temperature can provide insight to understand Cr related degradation process. Our results show that the difference in degradation rates reflects a direct impact of the cathode sintering temperature.

#### Experimental

The configuration of the symmetric cell and the test set-up are shown in Fig. 1. GDC Electrolytes were prepared by uni-axial pressing the Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2-8</sub> powder (Fuel Cells Materials) into pellets and subsequently sintering the pellets at 1450°C for 6 h. The pellets were then polished on both side to obtain parallel surfaces with final dimensions of 8 mm diameter and 5 mm thickness. A La<sub>0.60</sub>Sr<sub>0.40</sub>Co<sub>0.20</sub>Fe<sub>0.80</sub>O<sub>3-x</sub>-Ce<sub>0.90</sub>Gd<sub>0.10</sub>O<sub>1.95</sub> paste (1:1 by weight percent, Fuel Cell Materials) was screen printed on both sides of the GDC pellets with a specific area of 0.316 cm<sup>2</sup> that served as the working electrode and counter electrode. In addition, a narrow groove was cut in the middle of the pellet and Pt wire was wound along the groove to act as a reference electrode. The symmetric cells were then sintered at temperatures of 950°C, 990°C, 1040°C, 1080°C for 3 hours in air with a heating rate of 3°C/min and a cooling rate of 5°C/min, and will be referred to as cell 950, cell 990, cell 1040, cell 1080, respectively.

To evaluate the effect of cathode sintering temperature on Cr-induced poisoning, electrochemical impedance spectroscopy (EIS) measurements were carried out using a Solartron 1470E/1400A cell

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Figure 1. Cell configuration and schematic drawing of the experimental setup for the measurement of electrochemical performance for cathode in presence of metallic interconnect.

test system. A three-electrode set-up was used with the one side of the pellet as working electrode, the opposite side as the counter electrode and the Pt wire as the reference electrode. The frequency range was  $10^{-2}$  Hz to  $10^5$  Hz with an amplitude of 10 mV.

A piece of Crofer 22 APU, a common interconnect material, was placed directly between the working electrode contact and the working electrode itself, to best simulate an SOFC stack environment. The compositions of Crofer 22 APU is 22% Cr, 0.5% Mn and 77% Fe. Measurements were taken at 750°C with synthetic air (158 sccm N<sub>2</sub> and 42 sccm O<sub>2</sub>) every 30 min for 200 hours at open circuit potential. To eliminate the effect of self-degradation for La<sub>0.60</sub>Sr<sub>0.40</sub>Co<sub>0.20</sub>Fe<sub>0.80</sub>O<sub>3-x</sub>-Ce<sub>0.90</sub>Gd<sub>0.10</sub>O<sub>1.95</sub> cathode material, the same measurements were taken at cell 950 in the same environment in the absence of Crofer 22 APU, and the results were set as the baseline for cells with Crofer 22 APU to compare with. After 200 hours of aging, temperature and PO<sub>2</sub> dependencies were measured for each sample. Impedance fitting was carried out using ZSimpWin (EChem Software).

X-ray diffraction was performed using a Bruker D8 diffractomoeter with Cu K $\alpha$  radiation in the 2 $\theta$  range of 20–80°. A scanning electron microscope (SEM, Hitachi SU-70 FEG SEM) is used to observe surface microstructural differences between samples. To gain more insight regarding the three-dimensional distribution of Cr-poisoning products, focused ion beam (FIB) nanotomography (FIB-*nt*)<sup>21</sup> was performed on the samples sintered at the highest and lowest temperatures (1080°C and 950°C, respectively). In this technique, a stack of serial images is acquired while milling consecutive slices with an ion beam, revealing three-dimensional microstructural



**Figure 2.** XRD patterns of four cells sintered at different temperatures aged at  $750^{\circ}$ C for 200 hours in the presence of Crofer 22 APU, and the cell aged at  $750^{\circ}$ C for 200 hours without the presence of Crofer 22 APU.

information. In this work, a Tescan *Gaia* immersion-lens FIB/SEM (Tescan, Brno, Czech Republic) system was used to reconstruct large volumes  $(50 - 70,000 \,\mu\text{m}^3)$  at  $\sim 35$  nm isotropic voxel resolution. The acquired images were collected with a low-loss backscatter electron detector ("In-beam BE" detector), which measures primarily phase contrast, such that the intensity of the image can be used to determine sample composition, after corroboration with another elemental analysis technique, such as EDS or electron energy loss spectroscopy (EELS).

## Results

*Phase purity.*—Fig. 2 shows XRD patterns of LSCF-GDC composite cathodes before and after long-term aging at 750°C with the presence of Crofer 22 APU. There is no observable secondary phase on XRD pattern of cathode aged in the absence of Crofer 22 APU (baseline). For cells aged with the presence of Crofer 22 APU, based on the characteristic diffraction peaks around 25°, a secondary phase can be identified as SrCrO<sub>4</sub>.<sup>22</sup> The XRD results imply that there is Cr contamination in all four cells.

*Electrochemical performance.*—EIS measurements were performed on cells with different sintering temperatures to determine Cr effect. Fig. 3 shows the increase of  $R_{\Omega}$  and  $R_{P}$  as a function of aging time in the synthetic air under open circuit potential conditions, at 750°C with the presence of Crofer 22 APU for 200 hours. A baseline sample, sintered at 950°C, was aged without the presence of Crofer 22 APU at 750°C for 200 hours, as shown in green line. Fig. 3a presents



Figure 3. The degradation of  $R_{\Omega}$  (a) and  $R_P$  (b) of cells sintered at different temperatures as a function of aging time in the synthetic air, under open circuit potential conditions at 750°C with or without the presence of Crofer 22 APU for 200 hours.

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**Figure 4.** Impedance spectra of LSCF-GDC cathode sintered at  $950^{\circ}$ C (a),  $990^{\circ}$ C (b),  $1040^{\circ}$ C (c) and  $1080^{\circ}$ C (d) at open circuit potential conditions. Cells were aged at  $750^{\circ}$ C for 200 hours with the presence of Crofer 22 APU, and an equivalent circuit used to fit the impedance spectroscopy data (e). Symbols and solid lines represent experimental data and the best fits, respectively.

the degradation rates of the ohmic resistance  $(R_{\Omega})$  for the cells sintered at different temperatures. The initial resistance for  $R_{\Omega}$  is omitted, as the GDC electrolyte is the major contribution. Cell 950, one sintered at 950°C, shows the fastest degradation rates of all four samples. The ohmic resistance of cell 950 increases by nearly 7  $\Omega$  cm<sup>2</sup>. The degradation rate of cell 1080 is the smallest among all cells, increasing by only about 1  $\Omega$  cm<sup>2</sup> after 200 hours. As for cell 990 and cell 1040, the degradation rate of the  $R_{\Omega}$  is similar; the increases in  $R_{\Omega}$  were 2.5 and 3  $\Omega$ cm<sup>2</sup>, respectively. For cell 990, cell 1040, and cell 1080,  $R_{\Omega}$  increases over the first 70 hours and then remained stable from 70 hours to 200 hours. However, for cell 950,  $R_{\Omega}$  increased throughout all 200 hours of testing.  $R_{\Omega}$  is composed of the electrolyte resistance and the interfacial resistance between LSCF and GDC. We may consider then that all changes in  $R_{\Omega}$  are changes in the interfacial resistance between LSCF and GDC due to Cr contamination as the GDC substrate is inactive to Cr.

Fig. 3b presents the degradation rates for the polarization resistance ( $R_P$ ) as a function of aging time. The initial values of  $R_P$  were close to each other but higher than the  $R_P$  in the absence of Crofer 22 APU, which is likely due to the volatilization and deposition of Cr during the heating process. The  $R_P$  increased dramatically from the initial values, of around 0.5  $\Omega$  cm<sup>2</sup>, by 681%, 613%, 432%, 128% for cell 950, cell 990, cell 1040, and cell 1080, respectively.

Based on EIS results, no detectable degradation was observed for the cell without the presence of Crofer 22 APU during long-term aging (baseline sample). Compared with the ones in the presence of Cr, both  $R_{\Omega}$  and  $R_P$  showed a much greater degradation rate. Therefore, subtracting the degradation rate of baseline, Cr-poisoning clearly shows a direct impact on the degradation.

The cathode sintering temperature is well known to affect the microstructure of cathode by influencing the surface area, porosity, particle connection and contact between electrode and electrolyte.<sup>19,20</sup> The particle connection and bonding between electrode and electrolyte with increasing sintering temperature would be better, leading to the decrease of  $R_{\Omega}$ . On the other hand, lower sintering temperatures would also create a cathode microstructure with larger pores, smaller particle sizes, and more surface area, leading to a decrease of  $R_P$  as well. Therefore, there are multiple factors controlling the actual total  $R_P$  values. Based on EIS results, no detectable degradation was observed

for the cell without the presence of Crofer 22 APU during long-term aging (baseline sample). Compared with the ones in the presence of Cr, both  $R_{\Omega}$  and  $R_P$  showed a much greater degradation rate. Therefore, subtracting the degradation rate of baseline, Cr-poisoning clearly shows a direct impact on the degradation.

Figs. 4a–4d presents the EIS spectra of LSCF-GDC cells at  $750^{\circ}C$ as a function of aging time. Three separated arcs can be characterized. An equivalent circuit of  $LR_{\Omega}(R_HQ_H)(R_MQ_M)(R_LQ_L)$ , as shown in Fig. 4e, was used to deconvolute the impedance spectra and identify the electrode process corresponding to each individual arc. In the equivalent circuit, L is the inductance arising from the test-apparatus,  $R_{\Omega}$  is the series resistance, mainly attributed to the electrolyte, lead wires and part of the interface between the cathode and electrolyte. Q is a constant phase element with admittance  $Q = Y_0(jw)^n$ , where w is the angular frequency, and n is an exponent. The subscripts H, M, L refer to the high, medium, and low frequency arcs, respectively. As shown in Figs. 4a–4d, a good agreement is obtained between the fitting data (solid line) and the experimental data (dotted line). Wang and Jiang<sup>23</sup> proposed that based on impedance spectra, the ORR can be divided into three elementary steps, and each arc can be assigned as follows:

- The low frequency arc represents the oxygen surface exchange reaction consisting of dissociative absorption of oxygen at the electrode surface, reduction of absorbed oxygen to O<sup>2-</sup> ions and oxygen incorporation into the MIEC electrode.
- 2. The medium frequency arc can be ascribed to surface diffusion of oxygen species along the electrode to the TPB areas.
- The high frequency arc can be assigned to charge transfer processes associated with oxygen ion incorporation into the electrolyte lattice.

Therefore, based on the proposed model, we can further determine the Cr effect on each reaction step. The percentage changes of  $R_H$ ,  $R_M$  and  $R_L$  as a function of aging time are plotted in Figs. 5a–5d. The majority of the polarization loss results from the contribution of  $R_L$ . With the increase of sintering temperature, the degradation rate of  $R_H$  becomes much slower. The increase in  $R_L$  suggests that gas-surface interface contributes to the major degradation because



Figure 5. The degradation percentage of  $R_H$  and  $R_M$ ,  $R_L$  of cell 950 (a), cell 990 (b), cell 1040 (c) and cell 1080 (d) as a function of aging time in the synthetic air, under open circuit potential conditions at 750°C with the presence of Crofer 22 APU for 200 hours.

Cr deposition occupies the surface active sites and further limits the oxygen surface exchange reaction. For cathodes sintered at higher temperatures, the changes in  $R_H$  decrease, indicating that the increase in sintering temperature could reduce the effect of Cr-induced degradation on the charge transfer at the interface of cathode and electrolyte.

oxygen partial pressure dependence, and follows the power law:

$$R_i = kPO_2^{-n}$$

where *i* represents different reaction steps. k is an oxygen partial pressure independent constant and *m* is the reaction order for  $PO_2$  dependence. Different reaction steps have different reaction order and theoretical reaction orders for a specific rate-determining reaction step are summarized in the Table L<sup>23–26</sup>

The oxygen partial pressure dependence of each cell is shown in Fig. 6. The ORR on the cathode involves several steps with a different



Figure 6. Dependence of  $R_H(a)$ ,  $R_M(b)$ ,  $R_L(c)$  and  $R_P(d)$  for cells with cathode sintered at different temperatures on oxygen partial pressure after aging under the open circuit potential in the presence of Crofer 22 APU and 750°C at for 200 hours.

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 Table I. Reaction order for each specific rate-determining reaction step.

Reaction step	Reaction order	Description
$\begin{array}{l} O_2(g) {\leftrightarrow} 2O_{ad} \\ O_{TPB} + V^{\cdot \cdot} _{O, electrolyte} \\ {\rightarrow} ~ O^x_{O, electrolyte} \\ O_{ad} {\rightarrow} ~ O_{TPB} \end{array}$	1 0 1/2	Dissociative adsorption Ion incorporation from TPB to the electrolyte Surface diffusion

Fig. 6a shows the values of m for high frequency resistance for four cells. The reaction order m is around 0.35 except for the cell 950, which shows almost no PO<sub>2</sub> dependence ( $m \approx 0$ ). Based on the corresponding reaction order, the high frequency arc can be correlated to the charge transfer process for cell 990, cell 1040 and cell 1080.<sup>24,25</sup> However, the independence of PO<sub>2</sub> for cell 950 may due to Cr particles deposited at the interface that inhibit the charge transfer process. Fig. 6b shows the PO<sub>2</sub> dependence on medium frequency process. This process is characterized by a reaction order of 0.04 for cell 950, 1.13 for 990, 0.45 for cell 1040 and cell 1080, respectively. When the reaction order is near 1/2, such as the case for cell 1040 and cell 1080, the medium frequency process can be attributed to surface diffusion.<sup>26</sup> Cell 950 and cell 990 shows a different rate-limiting step probably due to the influence of Cr-poisoning on the surface diffusion process. Fig. 6c shows the PO<sub>2</sub> dependence of low frequency process for all four cells, the reaction orders are  $\sim$ 0 for cell 950, 0.19 for cell 990, 0.42 for cell 1040, and 0.25 for cell 1080, respectively, the n for  $R_L$  of cell 1080 complies with characteristics of gas diffusion.<sup>24,25</sup> The changes in  $PO_2$ dependence for different cells indicate that the apparent rate limiting steps are a function of sintering temperature, and the cell sintered at the lowest temperature shows the most serious Cr poisoning effect. The changes in sintering temperature can affect the microstructure, the bonding between grains, and surface chemistry of cathodes, leading to a different Cr-poisoning effect.

Fig. 7 shows Arrhenius plots of  $R_{\Omega}$  (Fig. 7a) and  $R_P$  (Fig. 7b). The activation energy of  $R_{\Omega}$  is independent of sintering temperature with values from 0.59 eV to 0.65 eV, which is in good agreement with literature values for the activation energy of GDC ionic conductivity.<sup>27,28</sup> No observable change in the activation energy of GDC electrolyte. On the other hand, the apparent activation energy for  $R_P$  after aging varies significantly with the sintering temperature, the values decreased from 1.40 to 1.10 eV with the increase of sintering temperature. The activation energy for cell 1080, 1.40 eV matches values reported by Leng et al.<sup>29</sup> The difference in apparent activation energies of  $R_P$  also confirms that Cr-induced degradation is a function of sintering temperature, and different sintering temperatures result in different rate limiting steps.



**Figure 8.** SEM micrographs of the cathode surface before and after test under the open circuit potential in the presence of Crofer 22 APU and 750°C for 200 hours with the cathode sintering temperature of 950°C (a and b), 990°C (c and d), 1040°C (e and f), 1080°C (g and h). Inserted is the corresponding micrographs with higher magnification.

*Composition and microstructure analysis.*—SEM images of LSCF-GDC composite electrode surface exposed to the presence of Crofer 22 APU (Figs. 8b, 8d, 8f, 8h) at 750°C for 200 h are shown in Fig. 8. For comparison, SEM micrographs of baseline cell are also shown in Figs. 8a, 8c, 8e, 8g. Inserted pictures shows the microstructure with higher magnification for baseline samples. The cathode microstructure is a function of sintering temperature. As shown in Fig. 8a, for LSCF-GDC composite electrode sintered at 950°C, a



Figure 7. Arrhenius of  $R_{\Omega}$  (a) and  $R_P(b)$  for different sintered temperature after aging with Crofer 22 APU under the open circuit potential and 750°C at for 200 hours.

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large area with macro and micro-pores can be observed. Although the increase of sintering temperature from 990°C to 1080°C (from Figs. 8e to 8g) increases the average particle size and decreases the number of micropores, the cathode still has fine, uniform particles and sufficient macropores for gas diffusion. Overall, The similar initial impedance R<sub>P</sub> for the four cells indicates that the cathode sintering temperature in the investigated range has no significant effect on cathode performance. However, the distinct morphologies of the cathode surface in the absence and presence of Crofer 22 APU, clarify the significant effect of cathode microstructure on Cr poisoning of LSCF-GDC. On the surface of cell 950, there was significant deposition of particles with a distinct crystal facet with size of  $4-5 \ \mu m$  (Fig. 8b), significantly larger than the grain size of the cathode particles. The surface of cell 950 was almost covered by these particles. There are smaller areas of deposition on the cathode surface of cell 990 (Fig. 8d), and smaller particle sizes as compared to those on the surface of cell 950. On the cathode surface of cell 1040, the deposited Cr particles were not continuous and the fine cathode particles are clearly visible (Fig. 8f). Cr deposition on the surface of cell 1080 was significantly lower than the other three (Fig. 8h), the morphology of cell 1080 was almost the same as the baseline cell in the absence of Crofer 22 APU (Fig. 8g). The different Cr deposition effects for different cathode sintering temperatures may be caused by the relatively small differences in microstructure for the four cells. As the cathode sintering temperature decreases, the average particle surface area increases allowing for more activate sites for Cr reaction to occur. The number of micro/macropores increases in the cathode sintered at lower temperature, more Cr compounds to could pass through to the cathode bulk.30

Fig. 9 presents the corresponding EDS patterns of the Cr deposition area for the four cells. Figs. 9a, 9b, 9c, 9d are magnifications of the depositional Cr particles for cell 950, cell 990, cell 1040 and cell 1080 tested with Crofer 22 APU for 200 hours. The particles formed on the surface appear to be composed of Cr, Sr, and O due to the overlapping of Sr and Cr map. This indicates that the particles are likely SrCrO4. A similar composition can be found in all four cells, but as the sintering temperature is reduced, larger particles and a larger coverage area is observed.

Backscatter electron FIB/SEM cross-sectional micrographs of the composite cathode and the corresponding 3D-constructed images for cell 950 and cell 1080 are shown in Fig. 10. In both samples, the cathode was sliced in a direction parallel to the cathode/electrolyte interface, such that the entire thickness of the cathode layer was visible in every image, ensuring the full distribution of phases throughout the cathode is captured. Five distinct intensity levels were present in the images, corresponding to five phases resolvable in SEM. The chemical identity of these phases was confirmed using a combination of EDS and EELS. The images revealed, in order of increasing intensity, the pore phase (which had been back-filled with an epoxy resin for microscopic analysis), a Co/Fe-rich oxide phase, a Cr-rich contamination phase, LSCF, and GDC (see Figs. 10a, 10d). With the phases identified, the images were segmented using the Avizo Fire software (FEI Company, Hillsboro, OR) using a markerbased watershed algorithm (Figs. 10b, 10e). The labeled volume enables a wide range of microstructural quantifications, such as an analysis of each phase's volume fraction distribution through the cathode.

The overall phase fractions were quantified by summing the volume enclosed by each label. The results of this calculation are reported in Table II. On average, the cathode porosity changed slightly, indicating the 130° difference in sintering temperature slightly reduced the total pore volume. Similarly, the LSCF and GDC volume fractions were fairly similar, although a slight decrease in GDC was observed for the 950°C sample. As the Cr is not expected (or observed) to interact strongly with the GDC, this difference can be attributed to an artifact of the measurement, arising from the smaller size of GDC particles in the 950°C data (making them more difficult to resolve in the segmentation than in the 1080°C sample). The most significant variation between the two samples is in the volume of Cr-containing

poisoning products. The  $950^{\circ}$ C sample contained over 3 times the volume of Cr phases as the  $1080^{\circ}$ C cathode, indicating a much stronger poisoning effect in the lower temperature sample, which conforms to the electrochemical results shown in Fig. 3 to Fig. 7.

By averaging the phase fraction data on planes parallel to the electrolyte/cathode interface, a profile of phase fractions was measured normal to the interface, extending fully to the cell surface (Figs. 10c, 10f). For all phases, the profile value oscillates around the global average, with some slight variation due to the presence of larger particles within the volume. No gradient or preferential ordering of the phases was observed with respect to the electrolyte interface or surface. All phases (including the Cr contamination) were observed to be evenly distributed throughout the extent of the cathode thickness, suggesting the formation of Cr-rich deposits is not limited by the kinetics of transfer from the surface into the cathode.

As the primary phase fractions between sintering temperatures are relatively constant, the microstructure is expected to be the catalyst for the difference in Cr-rich phase content between the two samples. To examine the impacts of the phases' surface area and volumes, an analysis of individual pore sizes was performed. The total pore network was separated into individual particles by applying a distance map transform to the phase, and using a watershed algorithm on the result to find the particle boundaries. With the pore phase separated into discrete particles, the surface area and volume of each individual label was calculated. The BET formula can be applied to find the spherical equivalent particle diameter of the particles,<sup>31</sup> and the distribution of these diameters can be visualized in a histogram (Fig. 11). This calculation revealed that while both samples had a similar distribution of the smallest pores (0 to 400 nm), the primary distributions of pore diameters (from 400 to 1300 nm) have quite dissimilar natures. The 950°C sintered sample has a narrower distribution, with a smaller average particle size than the 1080°C sample. These smaller particles lead to a larger surface area to volume area, meaning there are significantly more active sites available for reaction in the 950°C sample. The even distribution of Cr-rich phases throughout the cathode, together with the increased volume fraction in the sample with more active sites is strongly indicative of a gaseous diffusion mechanism in the Cr-poisoning process.

#### Discussion

The Cr deposition on the surface of LSCF cathode is essentially a chemical reaction and is initiated by the nucleation reaction between the Cr species via vaporization or fast solid-state diffusion and the segregated Sr species which act as a nucleation agent.<sup>32</sup> The mechanism for the deposition on the surface of LSCF cathode cannot be explained by the electrochemical reduction mechanism of high valence Cr species in competition with the ORR as proposed for deposition at LSM cathode.<sup>33,34</sup> The present study shows a relationship between the cathode sintering temperature and Cr poisoning of LSCF cathodes and indicates an increase in cathode sintering temperature will decrease the Cr poisoning effect.

There is a well-established relationship between sintering temperature and microstructure of SOFC cathodes. Chen et al. showed that with increasing sintering temperature of  $PrBaCo_2O_{5+\delta}$  cathodes, a decrease in porosity and surface area, and an improved particle connection was observed.<sup>19</sup> Similarly, Zhang et al. revealed for LSM-SDC composite cathode, high firing temperature may result in partial loss of porosity and specific surface area, low sintering temperature would bring about poor bonding between matrix and electrolyte.35 Mogensen et al. also reported that with decreasing temperature, in the range from 1300-1150°C, the electrode was found to be less dense with longer triple phase boundaries.<sup>20</sup> By using SEM, Hunsom et al. found that in the firing temperature between 975°C-1050°C, LSC cathode showed no difference between each other in phase purity and microstructure, however, EIS results show the effect of firing temperature on the cathode performance.<sup>36</sup> Therefore, emphasis was placed on optimization of cathode sintering temperature to achieve



**Figure 9.** Magnifications of the images in Figs. 7b, 7d, 7f, 7h and corresponding corresponding EDS patterns of the Cr deposition area for cell 950 (a), cell 990 (b), cell 1040 (c), and cell 1080 (d) after test under the open circuit potential in the presence of Crofer 22 APU and  $750^{\circ}$ C for 200 hours.

high electrode performance. Leng studied the effect of cathode sintering temperature on the microstructure and performance of LSCF-GDC composite cathodes, and found with decreasing sintering temperature from 1100–995°C, the cathode became more porous with more reaction areas, but weaker connection between agglomerated particles, as showed previously<sup>16</sup>. Therefore, the sintering temperature should be high enough to enable connectivity between the electrode and the electrolyte, low enough to obtain high porosity and reaction surface area. From our study, as-prepared cell 950, cell 990, cell 1040, cell 1080 showed similar initial polarization resistance (Fig. 3). The electrochemical performance is in accordance with the microstructure of the four cells- the fine grain size, sufficient porosity, and good



**Figure 10.** Backscatter electron FIB/SEM cross-sectional micrographs of the composite cathode, smoothed using an edge-preserving non-local means filter. Images were acquired after testing under open circuit potential in the presence of Crofer 22 APU at 750°C for 200 hours with a cathode sintering temperature of 950°C (a) and 1080°C (d) Each image is a representative example taken from a stack of over 1000 images acquired through FIB-nt. (b and e) Segmented images used for phase quantification, obtained by assigning each phase to an image intensity level through the use of a watershed algorithm. (c and f) Profiles of the average volume fraction as a function of distance perpendicular to the cathode/electrolyte interface. The entire thickness of the cathode is included in these profiles (from the electrolyte interface to cell surface), with neither sample showing significant changes in phase distribution throughout the cathode. The average profiles are calculated from reconstructed volumes of  $50,354 \,\mu\text{m}^3$  ( $950^\circ\text{C}$ ) and  $70,280 \,\mu\text{m}^3$  ( $1080^\circ\text{C}$ ).

Table II. Quantification of volume phase fractions calculated from the entire cathode volume (excluding the bulk electrolyte). Reported errors are the 95% confidence intervals for the mean value, obtained by subsampling the existing data 500 times with  $5 \times 5 \times 5 \mu m$  randomly positioned subvolumes.

Sample	Porosity	LSCF	GDC	Co/Fe-Rich phases	Cr-rich phases
950°C 1080°C	$\begin{array}{c} 42.0 \pm 0.4\% \\ 40.8 \pm 0.4\% \end{array}$	$\begin{array}{c} 30.9 \pm 0.6\% \\ 32.2 \pm 0.7\% \end{array}$	$\begin{array}{c} 20.2 \pm 0.8\% \\ 24.9 \pm 0.8\% \end{array}$	$\begin{array}{c} 0.5 \pm 0.1\% \\ 0.2 \pm 0.1\% \end{array}$	$\begin{array}{c} 6.4 \pm 0.3\% \\ 1.9 \pm 0.1\% \end{array}$

connectivity between grains, were an optimized sintering temperature range of 1040–950°C for LSCF-GDC cathodes. Higher sintering temperature has been shown to enhance connectivity between cathode and electrolyte,<sup>19,20</sup> however, the connection is strong enough even for the cell sintered at 950°C which is stable at 750°C for 200 h.

Decreased cathode sintering temperature could allow LSCF to have a smaller grain size, with a larger surface area not only for the ORR but also for the deposition of Cr, as shown in Figs. 10 and 11. The fundamental mechanism of Cr deposition is the nuclei reaction between the Cr vapor and the segregated SrO from LSCF.<sup>32</sup> Previous research has shown that the presence of Cr has detrimental effects on the surface exchange coefficient for the ORR.<sup>37–39</sup> Finsterbusch et al. found that the surface exchange coefficient of LSCF at 800°C decreases by an order of magnitude after coating a 7 nm  $Cr_2O_3$  thin layer.<sup>38</sup> The deposition of Cr on the LSCF cathode surface not only blocks electrochemical sites for ORR, but also inhibits the surface diffusion reaction for oxygen. A larger reaction surface area provides more reaction sites for Cr deposition and leads to severe electrochemical degradation, which is supported by our observed EIS electrochemical results and the morphology of cathode after aging with Cr for 200 h. On the other hand, the segregated SrO may be larger in particle size due to the larger cathode particle size sintered at higher temperature, this in turn would decrease the reaction activity with Cr vapor, while at low temperature, the segregated SrO may be in much smaller in size and is more active for nucleation reaction with Cr. It can be derived from Fig. 11, in which the grain size of cathode increased dramatically with the increase of sintering temperature.



**Figure 11.** Histograms of the pore phase spherical equivalent particle size (calculated from each particle's surface area and volume), for the cathodes sintered at  $950^{\circ}$ C and  $1080^{\circ}$ C. The mean particle size of each sample's primary distribution is indicated in the plot. The higher temperature sintering condition results in a wider distribution of pore sizes, with a significantly larger average size, as expected. Particle size distributions for LSCF and GDC exhibited the same trend. This corresponds to a smaller average surface area for the phases in the  $1080^{\circ}$ C cathode, leading to fewer available sites for Cr reactions to occur.

#### Conclusions

Cr-related degradation is one of the major challenges for the development of SOFCs. In this study, we focus on the understanding of the Cr degradation on LSCF-GDC by controlling cathode sintering temperature. Our results show that Cr induced degradation is dependent on sintering temperature. Increasing sintering temperature of LSCF-GDC composite cathode decreases the total surface area of LSCF, allowing less surface sites for Cr deposition. Gaseous diffusion, rather than solid-state diffusion, of Cr-containing species to the cathode surface is the main pathway for Cr deposition. The results suggest that the microstructure of cathode and the surface configuration of LSCF are the keys to control Cr-degradation.

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