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$La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_{3-\delta}-Gd_{0.1}Ce_{0.9}O_{1.95}$ solid oxide fuel cell anodes: Ru precipitation and electrochemical performance

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ABSTRACT

Composites containing $La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_{3-\delta}$ (LSCrRu) with x=0-0.25 and Gd_{0.1}Ce_{0.9}O_{1.95} (GDC) were studied as anodes in solid oxide fuel cells (SOFCs) with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolytes. Electrode polarization resistance R_P decreased during initial SOFC operation before reaching a minimum. The decrease was more rapid, and the ultimate $R_{\rm P}$ value reached was generally lower, with increasing temperature and Ru content x. R_P was stable at longer times except for x=0.25 where it increased slightly. SOFCs with x=0.18 anodes at 800 °C vielded power densities as high as 0.53 W/cm² with an R_P value. including the (La,Sr)(Co,Fe)O₃–GDC cathode, of $< 0.15 \Omega$ cm². Transmission electron microscopy revealed Ru nano-particles on LSCrRu surfaces; their size increased and their density decreased with increasing temperature. Increasing the Ru content increased the density of Ru surface particles at a given time and temperature. Measured early-stage Ru surface coverage values were consistent with a model where Ru supply to the LSCrRu surface was limited by Ru bulk out-diffusion, but the coverage saturated at longer times. There was surprisingly little Ru particle coarsening over times up to 1000 h at 800 °C, with Ru particles sizes remaining <10 nm. The cell R_P values generally decreased with increasing Ru nano-particle surface area.

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1. Introduction

Oxide anodes for solid oxide fuel cells (SOFCs) often yield higher polarization resistances than the more conventional Ni-based anodes [1]. This is probably due, at least in part, to the lack of an "electrocatalytic" phase such as Ni that promotes a key rate-limiting step in the anode reaction. Evidence for this comes from studies of (La,Sr) CrO₃-based anodes where the addition of relatively small amounts of nano-scale Ni led to reduced polarization resistance [2,3]. It was recently shown that electro-catalytic nano-particles can be produced in oxide anodes by incorporating either Ni or Ru into a perovskite oxide phase: these species remain in the oxide during electrode firing in air, but precipitate onto the surface as metallic nano-particles when the anode is exposed to hydrogen fuel [4.5]. This approach has the advantage of providing very small, <5 nm, Ru nano-particles after electrode high-temperature firing, and has yielded substantial improvements in oxide anode performance. Furthermore, Ru particle size appeared to be stable up to 300 h, and a 300 h SOFC test showed fairly stable performance after the Ru particles formed [5]. Ni nanoparticles were found to be much larger, >10 nm, and yielded only minor reductions in polarization resistance [4].

Here we present more detailed results on the LSCrRu-GDC anodes. Transmission electron microscopy (TEM) was used to observe Ru nano-particle size and surface density as a function of Ru content, nucleation temperature, and time. A simple model, based on Ru outdiffusion from the chromite particles, was used to help explain the results. SOFC life tests were used to observe the anode resistance versus time up to ~300 h. The TEM and electrical test results are compared in order to develop an understanding of how the Ru nanoparticles impact anode performance.

2. Experimental procedure

Powders of La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_{3- δ} (LSCrRu; x=0.05, 0.08, 0.18, 0.25) and $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ (LSCr) were synthesized by solid-state reaction at 1200 °C for 3 h. In the text below, we will abbreviate the oxides as LSCrRu18, for example, for the x=0.18 composition. The average particle diameter was $\sim 1-2 \,\mu m$, as determined by scanning electron microscopy (SEM); a typical SEM image from a typical anode prior to testing is shown in Fig. 1. All powders had X-ray diffraction (XRD) patterns similar to $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, with no RuO_2 phase detected.

Transmission electron microscope measurements were done on LSCrRu powders that were annealed at various temperatures and times in a tube furnace with a gas flow of H₂ humidified with 3% H₂O, the same as that used during SOFC testing. The powder samples were prepared using the ultrasonic method without pulverization. The powders were dispersed in water/acetone by ultrasonic agitations and



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Fig. 1. SEM image of a typical LSCrRu18-GDC anode prior to testing.

the suspension was dropped onto a lacey carbon film, which covered a TEM Cu grid (Ted Pella). The samples were allowed to dry in air prior to TEM observations. Special care was taken to fully remove the water/ acetone and any other possible contaminants, to avoid deterioration of the vacuum and the presence of artifacts during TEM studies.

SOFCs were made with anodes composed of 50 wt.% (La_{0.8}Sr_{0.2}) (Cr_{1-x}Ru_x)O_{3-δ} (LSCrRu) and 50 wt.% Gd_{0.1}Ce_{0.9}O_{1.95} (GDC) (Fuel Cell Materials). A few SOFCs with Ru-free anodes, LSCr-GDC, and anodes with a separate RuO₂ phase, LSCr-GDC-RuO₂, were prepared and tested for comparison. In some cases, a layer of pure LSCr was applied over the anode to improve current collection. All SOFCs utilized La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃₋₆ (LSGM) electrolytes, ~400 µm thick, fabricated via solid-state reaction at 1250 °C followed by uniaxial pressing and sintering for 6 h at 1450 °C. The cathodes were $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)-GDC with a layer of pure LSCF as a cathode current collector. The anodes and cathodes (0.5 cm^2 active area. ~50 um thick) were screen printed on the LSGM electrolytes and fired for 3 h at 1200 °C and 1000 °C, respectively. Note that a La-doped ceria barrier layer is normally needed between Ni-YSZ anodes and LSGM electrolytes to prevent Ni-LSGM reactions and possible La out-diffusion from the LSGM electrolyte [6]; no barrier layers were needed with the present LSCrRu anodes.

For cell testing, Au current collector grids were screen printed over the electrodes and contacted using Ag wires. The square grid array consisted of 0.3-mm-wide Au lines separated by 0.7 mm. Single cell tests were performed as described previously [7] using a four wire setup for current-voltage and electrochemical impedance spectroscopy (EIS, BAS-Zahner IM-6) measurements. In life tests, the cells were first stabilized at temperature with Ar at the anode before starting humidified H₂ flow; times given are after the start of H₂ flow. The fuel flow rate was 50 sccm; stagnant air was present at the cathode. Measurements on other SOFCs indicated that the Ar was entirely purged from the anode compartment before the first electrical measurements were performed (15 min).

3. Experimental results

3.1. Typical LSCrRu-GDC anodes

A >300 h cell test was run at 800 °C at a constant current of 300 mA/cm² for a LSCrRu18–GDC anode. Fig. 2 shows the voltage versus time (a), current–voltage characteristics (b), and EIS plots taken at selected times during the test (c). The voltage increased significantly over time (Fig. 2a), especially during the initial 3 h. A stable voltage was reached between 100 and 125 h that remained relatively constant until the end of the test, at 312 h. Based on the

current–voltage characteristics of the cell (Fig. 2b), the maximum power density increased by 65%, from 194 to 320 mW/cm², during the first 3 h. The power density reached 458 mW/cm² at 120 h, and decreased only slightly to 451 mW/cm² at 312 h. Note that these results are for an average cell of this type. The maximum power density obtained from a large number of cells with LSCrRu–GDC anodes ranged from ~400 to 535 mW/cm².

Fig. 2c shows the impedance spectra measured at various times at a cell voltage of 0.5 V. During the first 3 h of testing, the polarization



Fig. 2. Results from long-term stability testing of a cell with $La_{0.8}Sr_{0.2}Cr_{0.82}Ru_{0.18}O_3$ -GDC anode. The time dependence of the voltage at fixed current density is shown in (a), current-voltage characteristics at selected times are shown in (b) and the impedance spectra measured at 500 mV in (c).



Fig. 3. TEM images from as-prepared LSCrRu powder (a) and powders reduced in H₂ at 800 °C for 1 h (b), 311 h (c) and 1000 h (d).

resistance R_P decreased from 0.90 Ω cm² to 0.60 Ω cm². The impedance spectra showed a minimum R_P =0.23 Ω cm² measured at 96 h that increased up to 0.31 Ω cm² at 312 h. Impedance spectra were also measured at open circuit voltage (OCV), but are not shown here; in this case, R_P decreased to a minimum of 0.32 Ω cm² at 96 h and remained approximately constant up to 312 h. The minimum R_P obtained from a large number of cells with LSCrRu–GDC anodes ranged from 0.13 to 0.34 Ω cm².

TEM images obtained from an as-prepared LSCrRu powder and powders reduced at 800 °C for 1 h, 311 h and 1000 h are shown in Fig. 3. The as-prepared powder shows a smooth chromite surface, with no nano-particles present. After 1 h of reduction, approximately hemispherical Ru nano-particles with a little faceting were observed, each with an average diameter of <5 nm. There was no obvious change in the particle size and density at 300 h. However, after 1000 h of reduction, the average particle diameter grew to \approx 5–8 nm. The relatively stable size of the Ru particles over 300 h is consistent with the stable SOFC performance over this time period shown in Fig. 2.

3.2. (La,Sr)CrO₃-GDC and (La,Sr)CrO₃-GDC-RuO₂ anodes

As a baseline for comparison with the LSCrRu–GDC anodes, data for $(La,Sr)CrO_3$ –GDC anodes and $(La,Sr)CrO_3$ –GDC–RuO₂ anodes was also taken. In the latter case, Ru was present in the as-prepared anode as a separate oxide phase, rather than being present in the chromite phase.

3.2.1. (La,Sr)CrO₃–GDC anode

For cells with LSCr–GDC anodes, the voltage measured at fixed current initially increased gradually. However, the magnitude of the

increase was much less than for the LSCrRu–GDC anodes shown in Fig. 2a. As seen in the current–voltage curves in Fig. 4, the cell reached a power density of only 200 mW/cm² after 312 h. Given the very slow rate of increase of power output of ~1 mW/cm² per 24 h, this cell was not expected to reach the power densities >400 mW/ cm² observed in the LSCrRu–GDC cells. EIS results from a few different cells showed R_P values of 0.68 to 1.85 Ω cm², significantly higher than for the LSCrRu–GDC anode cells (≈0.2 Ω cm²). It can be



Fig. 4. Current–voltage curves obtained from a cell with LSCr–GDC anode tested at 800 $^\circ\text{C}.$



Fig. 5. TEM images obtained from as prepared LSCr powder (a) and powder that had been reduced in H₂/3% H₂O at 800 °C for 45 h (b).

concluded that the majority of the cell performance improvement in Fig. 2 was directly related to the Ru nano-particles. The small performance improvement of the LSCr–GDC anode may be due to a gradual reduction of LSCr upon exposure to the H_2 fuel, which has been shown to increase oxygen ion diffusivity [8,9].

Fig. 5 shows TEM images obtained from LSCr anode powder in the as-prepared form (Fig. 5a) and after 45 h of reduction at 800 $^{\circ}$ C (Fig. 5b). No change in the LSCr microstructure was observed, and no nano-scale surface features were present.

3.2.2. (La,Sr)CrO₃-GDC-RuO₂ anodes

An LSCr–GDC–RuO₂ anode with 5 wt.% RuO₂ was prepared. The RuO₂ particles had an average diameter ~0.5–1 µm based on SEM-EDS images (not shown here). This RuO₂ content was chosen because it matched the calculated weight percentage of RuO₂ in LSCrRu18–GDC. The LSCr-to-GDC weight ratio was kept at 1:1 as in the LSCrRu–GDC anodes. Fig. 6 shows the current–voltage characteristics obtained from a representative cell with this anode. The cell showed an initial improvement in performance, in this case over ~60 h. The improvement was probably due, at least in part, to a similar mechanism as for the LSCr–GDC anodes (Fig. 5). In addition, the RuO₂ particles should have had some beneficial electro-catalytic effect. The electrochemical performance of the LSCr–GDC–RuO₂ anode cells was slightly better (260 mW/cm², R_P =0.32 to 0.66 Ω cm²) than that of the LSCr–GDC anode cells, but worse than the LSCrRu18–GDC anode cells. This is consistent with the idea that the Ru particles enhanced electro-



Fig. 6. Cell current-voltage curves measured at selected times obtained from a cell with LSCr-GDC-RuO₂ anode tested at 800 $^{\circ}$ C.

0.20 OCV No CC 0.15 With CC 40 Hz 0.10 (Ωcm^{2}) 0.05 0.00N. 0.35 0.40 0.45 0.50 0.55 0.60 0.65 -0.05 $Z'(\Omega cm^2)$ -0.10 -0.15-0.20

Fig. 7. Comparison of the impedance spectra at open circuit voltage attained at 96 h for LSCrRu–GDC anode cells with and without an LSCr anode current collection layer. The solid lines show fits to the data obtained by using the EQUIVCRT software [17].

chemistry, but the effect of the micron-scale particles was less than that of nano-scale Ru particles (Fig. 3).

3.3. Effect of anode current collector

In prior studies of LSCrRu–GDC anodes, no current collectors were used other than the Au grid (a square mesh with repeat period of 1 mm and Au mesh width of 0.3 mm) [5]. This raises a potential issue with current collection because the LSCrRu-GDC composite is expected to have rather limited conductivity. The conductivity of LSCrRu is expected to be similar to that of LSCr (≈6 S/cm in H₂ atmosphere at 800 °C [10]), and mixing with 50 vol.% GDC (conductivity ≈0.26 S/cm [11,12]) presumably yields a substantial further decrease in conductivity. To test this, some cells were fabricated with an additional LSCr anode current collection layer. For cells with LSCrRu18-GDC anodes after 95 h at 800 °C, the maximum power density was increased from 400 to 460 mW/cm² by the LSCr current collector, slightly larger than typical cell-to-cell variations. A comparison of impedance spectra measured at 95 h and 800 °C (Fig. 7) showed that the current collection layer reduced the ohmic resistance (high-frequency intercept) by $\geq 0.1 \ \Omega \ cm^2$, but the size of the polarization arc was little changed. This may indicate that a part of the cell area (furthest from the Au collector grid) was inactive due to poor current collection without the LSCr layer. These results suggest that current collector layers are likely useful for achieving maximum power density in cells with these low-conductivity anodes.



Fig. 8. Total resistance versus time for cells with LSCrRu18–GDC anodes maintained at different temperatures.

3.4. Effect of precipitation temperature

In prior reports [4,5], Ru precipitation and the performance of SOFCs with LSCrRu–GDC anodes were observed for anodes maintained at 750 or 800 °C. Here we describe results for LSCrRu–GDC anodes maintained at a wider range of temperatures, 600–800 °C. The time-dependence of the total cell resistance $R_{\rm T}$ measured from the average slope of the current–voltage curves, for the cells maintained at 600, 700, and 800 °C is shown in Fig. 8. The $R_{\rm T}$ values were larger at the lower measurement temperatures, as expected for SOFCs. Note that periodic breaks in the data occurred where the continuous cell testing was interrupted for current–voltage and EIS measurements. The changes in cell performance at these interruptions are not understood at present, but they did not appear to significantly change the overall trend of decreasing $R_{\rm T}$. At each temperature, $R_{\rm T}$ decreased with time, but the decrease occurred later and more gradually as the temperature decreased.

Fig. 9 shows TEM images of LSCrRu after annealing in H_2 for 15 min at 600, 700 and 800 °C. The average diameter of the Ru nano-particles increased from ~1 nm at 600 °C to ~3–4 nm at 800 °C. The particle density decreased with increasing annealing temperature.

3.5. Effect of Ru content

Fig. 10 shows the time-dependence of the total cell resistance $R_{\rm T}$ for representative cells with different amounts of Ru in the anode chromite phase: x=0.05, 0.08, 0.18 and 0.25. The initial R_T value was larger for smaller x, but the decrease in $R_{\rm T}$ was more pronounced and more time was required to reach a saturation $R_{\rm T}$ value. Indeed, for x=0.05 and 0.08, $R_{\rm T}$ continued to decrease through most of the test. The minimum $R_{\rm T}$ values at ~100 h were similar for the x=0.08, 0.18 and 0.25 anodes, 0.70–0.75 Ω cm². The cells with 5 mol% Ru in the LSCrRu decreased to $R_{\rm T} \approx 0.9 \ \Omega \ {\rm cm}^2$ over 80 h; it did not appear these cells would reach the same $R_{\rm T}$ as the higher x anodes over longer times. For x=0.18 and 0.25, R_T quickly reached a minimum and then increased slightly. The inset in Fig. 10 shows more clearly the variation in $R_{\rm T}$ for three different cells with 25 mol% Ru-doped anodes. The three cells showed similar trends, where a minimum $R_{\rm T}$ was reached in a relatively short time, followed by an increase in R_T, although there was considerable cell-to-cell variation. For cells with x=0.18, it appeared that the $R_{\rm T}$ increase began after longer times than for x=0.25; two cells showed slow increases in $R_{\rm T}$ beginning after 20– 96 h, and in one case $R_{\rm T}$ did not increase.

Representative impedance spectra for cells with 5–25 mol% Ru obtained at ~96 h and 500 mV bias are shown in Fig. 11. R_P decreased with increasing Ru content: 0.50 for x=0.05, 0.43 for x=0.08, 0.24 for x=0.18, and 0.21 Ω cm² for x=0.25. However, it is likely that the variation would be smaller if the EIS data were taken at longer times, given that the lower-x cells were improving gradually and the higher-x cells were degrading slowly. The ohmic resistance for the cells with x=0.08–0.25 varied considerably with Ru content, but there was no clear trend. This may be due to cell-to-cell variations in the electrolyte thickness.

TEM images obtained from LSCrRu powders with x=0.05, 0.18 and 0.25 reduced in H₂ at 800 °C for 1000 h (Fig. 12) showed that the surface density of Ru particles increased but particle sizes did not vary



Fig. 9. TEM images of LSCrRu powders that were reduced in H_2 at 600 $^\circ$ C (a), 700 $^\circ$ C (b) and 800 $^\circ$ C (c) for 15 min.



Fig. 10. Total area specific resistance values at 800 °C versus time for cells with LSCrRu–GDC anodes containing different amounts of Ru. The inset shows the variation between cells for a 25 mol% Ru doped anode ($La_{0.8}Sr_{0.2}Cr_{0.75}Ru_{0.25}O_3$ –GDC).

significantly with increasing *x*. The estimated total amount of surface Ru increased by a factor of ~3 times, from ~6.5 atoms/nm² for *x*=0.05 to ~20 atoms/nm² for *x*=0.25. For comparison, R_P values for these anodes decreased by a factor of ~2.5, going from 0.5 Ω cm² for *x*=0.05 to 0.21 Ω cm² for *x*=0.25. This apparent correlation between polarization resistance and surface Ru is discussed in Section 4. The gradually increasing R_T with time for *x*=0.25 (Fig. 10 inset) can potentially be explained by decreasing Ru surface area due to coalescence of the Ru nano-particles. However, the similar particle sizes after 1000 h at 800 °C with much-different cluster densities (Fig. 12) suggests that there was little coalescence; this is rather surprising, especially given the close packing of nano-particles in the *x*=0.25 case.

4. Discussion

A mechanism for Ru nano-particle formation on chromite surfaces has been proposed previously [4,5]. Ru precipitation is driven by the free energy decrease associated with reduction of oxidized Ru (in the chromite phase) to Ru metal, upon exposure to a reducing environment. The reduced metallic phase nucleates on the chromite particle surfaces, and three-dimensional (3D) Ru particles nucleate because of poor wetting with the chromite surface. It was suggested that bulk Ru out-diffusion from within the chromite limited the Ru supply to the



Fig. 11. Impedance spectra measured at 96 h and 500 mV bias from cells with LSCrRu–GDC anodes containing 5, 8, 18 and 25 mol% Ru in LSCrRu. The log frequency (Hz) at select frequencies are labeled for each curve.

surface. A Ru diffusion coefficient was estimated using $D \sim L^2/t$, where the diffusion length *L* at a given *t* was estimated by calculating the *L* value needed to supply a measured amount N_S of surface Ru. Based on this idea, a simple expression for the N_S versus time and Ru content can be obtained:

$$N_{\rm S} \sim x N_{\rm B} L \sim x N_{\rm B} D^{1/2} t \tag{1}$$

where $N_{\rm B}$ is the bulk Ru concentration for x = 1.0, *i.e.*, $({\rm La}_{0.8}{\rm Sr}_{0.2}){\rm RuO}_3$ but assuming the same structure as observed for $({\rm La}_{0.8}{\rm Sr}_{0.2})({\rm Cr}_{1-x}{\rm Ru}_x){\rm O}_3$.

Fig. 13a shows $N_{\rm S}$ values, estimated from TEM images on LSCrRu18 surfaces maintained at three different temperatures, versus *t*. For short times, $N_{\rm S}$ increased with increasing *t*, and the data was consistent with the $t^{1/2}$ dependence given in Eq. (1). The $N_{\rm S}$ values



Fig. 12. TEM images obtained from LSCrRu powders with x=0.05 (a), 0.18 (b) and 0.25 (c) annealed at 800 °C in H₂ for 1000 h.



Fig. 13. Estimated Ru surface coverage N_S (a) and Ru surface area (b) versus time for LSCrRu18 maintained at 600, 700, and 800 °C. A solid line with slope corresponding to $N_S \sim t^{1/2}$ is drawn in (a), for comparison.

tended to be smaller at lower temperature, as expected due to the lower diffusion coefficient D in Eq. (1). For longer times, the Ru amount appeared to saturate or even decrease slightly. This may indicate a limitation on the amount of Ru that can precipitate at the surface. One possible explanation is the limited single-phase field range of LSCrRu; that is, removing too much Ru may be thermodynamically unfavorable because it yields a highly non-stoichiometric (La and Sr rich) chromite [13]. The single-phase field of lanthanum chromite is expected to extend at most to a few percent A-to-B site non-stoichiometry. Furthermore, small changes in lattice spacing with removal of Ru will lead to lattice coherency strains between the depleted near-surface layer and the core of the chromite particle, which would also suppress metal out-diffusion. One possible way of compensating for the Ru loss would be the formation of La- or Sr-rich phases, but TEM and X-ray diffraction observations have not shown any evidence of such phases.

The size and density of Ru nano-particles varied with time, temperature and *x*-value. The present surface nucleation process can be likened to the Volmer-Weber (3D island) nucleation mechanism often observed in vapor-deposited thin films [14]; the main difference was that the source of metal atoms was from within the material rather than from the vapor. In vapor deposition the flux arriving at the surface is normally constant, whereas in the present case the flux declined with time as the chromite particle becomes depleted of Ru. Nonetheless, the basic features should be similar. One of the trends commonly observed for 3D island nucleation is increasing nucleation rate and decreasing nucleus size with decreasing temperature [15], in agreement with the images taken at different temperatures in Fig. 9.

Fig. 13b shows a plot of the Ru surface area versus time estimated from the TEM images. The surface area shows the same general trend as $N_{\rm S}$ – an initial increase in area followed by saturation. One interesting feature in Fig. 13b is that the surface areas are often higher for the lower temperatures, despite the lower Ru amount (Fig. 13a). This is a direct result of the smaller Ru particle size and higher nucleation density at the lower temperatures. A surprising feature of the present results is the relative lack of coalescence even for long times, high temperature (800 °C), and relatively high particle densities. This is illustrated by the images shown in Figs. 3 and 12, and also in Fig. 13b where substantial particle coalescence would decrease the particle surface area. The only indication of decreased surface area is at the longest time, 1000 h, and highest temperature, 800 °C. In thin-film nucleation theory, 3D islands coalesce due to overlap of growing particles or due to particle mobility [16]. The present observation of slow particle coalescence is probably due in part to the cessation of Ru diffusion to the surface (Fig. 13a), which limits particle overlap. The data also suggest that Ru particle mobility must be very low at these SOFC operating temperatures.

The TEM data was used to test the idea that R_P is linked to the amount of Ru on the surface. For example, one can postulate that the electro-catalytic effect of Ru, *i.e.*, the inverse of the polarization resistance R_P , is proportional to the total surface area of Ru nanoparticles. This connection seems plausible given the present data — Fig. 13b shows rapid increase followed by a saturation in surface area that has the same form as the voltage versus time data shown in Fig. 2a. In order to make this connection more quantitative, Fig. 14 shows a plot of R_P for cells maintained at 600, 700, or 800 °C, versus estimated Ru surface areas. The R_P values decreased with decreasing measurement temperature, as normally observed for SOFCs. The data at each temperature showed the expected correlation — R_P decreased with increasing surface area.

The slower decrease in R_P at lower temperature (Fig. 8) is readily understood based on the above arguments: the slower diffusion rate yields a slower accumulation of Ru on the surface, and hence a slower enhancement of electrochemical kinetics. On the other hand, the TEM observations (Fig. 9) indicate higher densities of smaller particles (*i.e.*, higher surface area) at lower *T* at saturation, suggesting that anodes maintained for a long enough time at a lower temperature will ultimately perform better. A few experiments were carried out comparing anodes measured at 800 °C, but with Ru precipitated at 700 °C rather than at 800 °C; the lower precipitation temperature yielded ~10% higher power density.

The higher Ru content anodes required less time to reach a relatively low R_P value (Fig. 11), and ultimately yielded lower R_P values at longer times (Figs. 10 and 11). This was presumably due to a larger



Fig. 14. *R*_P values measured from SOFCs at 600, 700, or 800 °C plotted versus the corresponding Ru surface areas measured on LSCrRu particles. The solid lines are simple linear fits to the data for each temperature.

 $N_{\rm S}$ and hence a higher Ru surface area at a given time, as predicted by Eq. (1), which shows that $N_{\rm S}(t) \propto x$. This trend was also demonstrated experimentally in Fig. 12; $N_{\rm S}$ values estimated from this data varied approximately linearly with x.

The observed increase in R_P at long times for x=0.25 (Fig. 10 inset) can be explained by particle coalescence and hence decreased surface area. This suggests that there is an optimal initial Ru content in the perovskite phase — high enough to reach low R_P in reasonable times, but not so large that coalescence begins to decrease the Ru surface area. It appears that the x=0.08 case might be a reasonable choice, although longer-term studies are needed to determine if the particles begin to coalesce at long times. Alternatively, it may be possible to carry out a preliminary Ru nucleation step to reach an ideal particle size and density in a reasonable time, and then to operate the SOFCs at a lower temperature where further Ru out-diffusion and coarsening is relatively slow.

5. Summary and conclusions

SOFCs with LSCrRu-GDC anodes performed significantly better than those without Ru (LSCr-GDC) or with Ru as a separate phase (LSCr-GDC-RuO₂). TEM studies of LSCrRu-GDC anodes indicated that the improvement was due to Ru nano-particles on the LSCrRu surfaces, and revealed a strong correlation between the nano-particles and cell polarization resistance. Electrode polarization resistance $R_{\rm P}$ decreased during initial SOFC operation before reaching a minimum. The decrease was more rapid, and the ultimate $R_{\rm P}$ value reached was generally lower, with increasing temperature and Ru content x. R_P was stable at longer times except for x=0.25 where it increased slightly. TEM images revealed that early-stage Ru surface coverages increased with increasing temperature and Ru content, consistent with a model where Ru supply to the LSCrRu surface was limited by Ru bulk outdiffusion. The coverage saturated at longer times, perhaps explaining why there was surprisingly little Ru particle coarsening over times up to 1000 h at 800 °C, along with fairly stable polarization resistance. The saturation polarization resistance was lower for higher Ru content, consistent with TEM observations showing higher Ru nanoparticle surface area. The Ru particles were smaller and had a higher surface density when the temperature was decreased. Overall, the cell $R_{\rm P}$ values generally decreased with increasing Ru nano-particle surface area. The mechanism for the improved anode performance is not known, but the Ru nano-particles presumably promote an otherwise slow reaction step, such as H₂ dissociation.

The best-performing cell yielded a maximum power density of 534 mW/cm² and minimum R_P =0.13 Ω cm². These results demonstrate the potential of this material as a high-performance anode active layer.

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