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Enhanced electrochemical response of Sr(Ti_{0.3}Fe_{0.7}Ru_{0.07})O_{3-δ} anodes by exsolved Ru-Fe nanoparticles

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Mixed conducting oxide with nominal composition Sr(Ti_{0.3}Fe_{0.7}Ru_{0.07})O₃₋₆ (STFRu) is studied, in comparison with SrTi_{0.3}Fe_{0.7}O₃₋₆ (STF) oxide, as anodes for solid oxide fuel cells. Exposing STFRu to reducing fuel conditions at 800 °C for 4 h results in the exsolution of essentially all of the Ru and a small fraction of the Fe from the oxide, and the formation of Ru_{1-x}Fe_x nanoparticles on the oxide surfaces. Most of the nanoparticles have the hexagonal structure expected for Ru-rich alloys, and thermogravimetric analysis suggests the composition x ~ 0.2. A small fraction of bcc-structure, presumably Fe-rich, nanoparticles are also detected. Comparison of cells with STFRu and STF anodes shows that the presence of Ru induces a reduced polarization resistance and increase the maximum power density for most cell operating conditions, particularly at lower temperatures and hydrogen partial pressures. For example, at 700 °C and 30% H₂ fuel, the maximum power density is 0.1 W/cm² for STF compared to 0.3 W/cm² for STFRu. There is also a significant change in the shape of the current-voltage curves and the p_{H_2} -dependence of the anode polarization resistances $R_{P,A} \propto (p_{H_2})^{-m}$, from $m \sim 0.5$ -1.0 for STF to $m \sim 0.11$ -0.29 for STFRu; these suggest that Ru_{1-x}Fe_x nanoparticles improve anode performance by promoting hydrogen adsorption.

Introduction

Solid oxide fuel cell (SOFC) anodes composed of electronicallyconducting oxides, e.g. (La,Sr)CrO₃ and (Sr,La)TiO₃, are alternatives to Ni-YSZ anodes that can provide improved tolerance to redox cycling, fuel impurities, and hydrocarbon fuels.¹ While such anodes often yield higher polarization resistance than Ni-based anodes,¹ B-site substitution leads to mixed ionically and electronically conducting (MIEC) character that can improve anode performance. Examples include (La,Sr)(Cr,Fe)O₃,² Sr₂(Mo,Fe)O₆,³ and SrTi_{0.3}Fe_{0.7}O₃ (STF).^{4, 5} The latter material yields polarization resistance as low as 0.13Ω cm² at 800 °C in humidified hydrogen, approaching the values achieved in state-of-the-art Ni-YSZ anodes.⁶

Oxide anode performance can be further improved by a catalytic metal present either in the anode formulation (e.g., Ni-YSZ), introduced via infiltration,⁷⁻¹⁰ or substituted into the oxide and subsequently exsolved to form catalytic nanoparticles on the oxide surfaces.¹¹⁻²⁴The exsolution anodes have the advantages of utilizing

additional processing steps are required. In cases where the anode was characterized before and after nanoparticle exsolution¹⁴⁻¹⁶ or compared with the corresponding nanoparticle-free anode,⁶ the nanoparticles were found to substantially decrease anode polarization resistance. Although there have been a couple of reports of Pd exsolution, from (La,Sr)CrO312 or (La,Sr)(Mn,Fe)O3,21 most reports have featured Ru or Ni exsolution. There have been a number of reports of Ru exsolution from chromites, either (La,Sr)(Cr,Ru)O₃^{11, 14, 16} or (La,Sr)(Cr,Fe,Ru)O₃.²⁵ Many recent reports have focused on Ni or Ni-alloy exsolution from various oxides, (La,Sr)(Cr,Ni)O₃^{15,} 22 (Sr,La)(Ti,Ni)O₃,18-20 including (La_{0.7}Sr_{0.3})(Cr_{0.85}Ni_{0.1125}Fe_{0.0375})O_{3-x},²⁶ Sr₂FeMo_{0.65}Ni_{0.35}O_{6-δ},²⁸ and Sr0.95(Ti0.3Fe0.63Ni0.07)O3-6. Although Ru is more expensive than Ni, it has potential advantages as an exsolved catalyst – Ru provides very good nanoparticle stability as compared to Ni even at sizes of a few nm,¹⁵ and it is less prone to coking in hydrocarbon fuels than Ni. To date, however, Ru has been used only in chromite-based anodes.

a relatively small amount of active catalyst, which is present as highly

active nanoparticles within a well-defined layer, and that no

Here we report a new anode composition, Ru-substituted $SrTi_{0.3}Fe_{0.7}O_3$, where Ru exsolution is expected. The amount of Ru substituted was kept relatively low, 7% of the B-site cations, in order to minimize the cost of Ru. The structure and composition of the oxide and the nanoparticles formed by exsolution is described, along with electrochemical performance of cells operated under typical SOFC conditions. The results are compared directly with the

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corresponding Ru-free STF anodes, showing directly the effect of nanoparticle exsolution.

Experimental

Powders of $SrTi_{0.3}Fe_{0.7}O_3$ (STF) and Ru-substituted composition $Sr(Ti_{0.3}Fe_{0.7}Ru_{0.07})O_{3-\delta}$ (STFRu, alternatively written $Sr_{0.935}(Ti_{0.28}Fe_{0.655}Ru_{0.065})O_{3-\delta})$ were synthesized via solid state reaction from precursor powder combinations of SrCO₃, Fe₂O₃, TiO₂and RuO₂ (Alfa Aesar and Sigma Aldrich). Note that the STFRu was A-site deficient by the amount of the excess Ru added to the B site. The STF and STFRu powders were calcined at 1100°C for 12 hours in air. La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O₃ (LSGM) electrolyte pellets withLa_{0.4}Ce_{0.6}O₂ (LDC) barrier layer were prepared as in our previous reports.⁴Other STFRu compositions with Ru content as low as 1% were also prepared in preliminary work, but the anode performance with a Ru content lower than 7% was relatively poor; thus, only the 7% composition was studied further.

Detailed studies of the characteristics of STFRu and STF powders before, during, and after reduction were carried out by combining thermogravimetric analysis (TGA) with X-ray diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy. The powder reduction process was done by first heating in Ar with $PO_2 =$ $2x10^{-4}$ atm up to 800°C and then switching the atmosphere to a H₂-Ar-H₂O mixture with a corresponding equivalent oxygen partial pressure $PO_2 = 4x10^{-21}$ atm. This PO_2 is chosen because it corresponds to the typical measured open circuit potential of the cells (1.069 V at 800°C) relative to the cathode reference state of $PO_2 = 0.5$ atm. Powders were collected at 0, 1 and 4 h after start the reduction process, for analysis by XRD and TEM.

The mass loss during reduction was measured using a highly sensitive thermogravimetric analysis (TGA) system consisting of a symmetrical thermobalance based on a Cahn 1000 electrobalance coupled to an oxygen sensor.²⁸ The thermobalance allows the determination of sample mass changes within ±10 µg for about 0.6 g powder samples. The oxygen content was determined by taking into account the formation of a plateau in the equilibrium isotherm of mass vs pO₂, as observed previously for the STF composition.²⁹ This plateau corresponds to the complete Fe⁺³ formation, wherein 3- δ = 2.65. In order to show results that are independent of the amount of powder, mass changes were normalized to the initial mass.

Phase characterization of the as-prepared and reduced powders was performed by powder X-ray diffraction (XRD, Scintag). XRD patterns were collected in air, at room temperature, with a PANanalytical Empyrean diffractometer by using CuK(α 1 + α 2) lines, a graphite monochromator and a 3D PIXEL detector. Microstructure and morphology were studied by using TEM, High Resolution TEM (HR-TEM) and High Resolution Scanning TEM (HR-STEM). The samples were studied in a Philips CM 200, a TECNAI F-20 and a TALOS F200X electron transmission electron microscopes, operated at 200 kV. The CM 200 operates with a LaB₆ filament while the TECNAI F 20 and TALOS F200X operate with a FEG. TALOS microscope is equipped with 4 SDD detectors (Super-X EDS System). Powder samples were dispersed in isopropanol and ultrasonicated % 15 Min/Afterwards two drops were deposited over ultrathin carbon support film TEM grids and dried in air. The images were analyzed by using the Digital Micrograph (Gatan) program.

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The STFRu||LDC|LSGM||LSCF-GDC|LSCFbutton cells were prepared as follows. The electrolyte support was an \sim 300-µm-thick dense LSGM pellet. The LSGM powder was ground, mixed with polyvinyl butyral (PVB), benzyl butyl phthalate (BBP) and polyalkylene glycol (PAG), and tape cast. After drying, several layers were hot pressed, laminated, cut to shape, and fired at 1450°C for 10hours to form the \sim 300 μ m thick electrolyte. The LDC layer was applied to the anode side by screen printing and fired at 1350 °C for 4 hours to yield a ~ 3µm-thicklayer of LDC with minimal porosity. ⁴STF and STFRu inks were prepared by grinding the relevant powder and mixing with 150 wt% Heraeus V-737 vehicle in a three-roll mill. The STFRu or STF ink was screen-printed onto the LDC-coated side of the LSGM pellet and fired at 1150°C for 2 hours in air. The resulting anodes were porous \sim 10-µm-thick layers with a particle size of \sim 1-2 µm, slightly smaller compared with prior work on STF-based anodes due to the lower powder synthesis temperature and the shorter electrode calcination time.⁴ A composite cathode layer containing 50 wt% La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ (LSCF) (Praxair) and 50 wt% Ce_{0.9}Gd_{0.1}O₂ (GDC) (NexTech) was screen printed onto the other side of the LSGM pellet, dried at 150°C for 20 minutes in air, followed by another layer of pure LSCF. The cell was then fired at 1100°C for 2 hours. Gold grids were screen printed on both sides for current collection. The functional electrode area was0.5 cm².

For electrochemical testing, the SOFC was mounted on top of an alumina tube using Ag ink as the gas seal and also as an electrical connection to the anode. A second, smaller tube placed inside this assembly was used to supply fuel, with ambient air present at the cathode. At the beginning of each cell test, the cell was heated to 800 °C under Ar. The anode was supplied with humidified H₂ (97% H₂, ~3% H₂O) at a flow rate of 50 sccm and Ar at 50 sccm once the cell reached testing temperature, and maintained for ~ 3 h in order to induce any cation exsolution prior to electrochemical testing. The measured cell open circuit potential suggests that there was slight leakage of air into the fuel, resulting in a slightly higher H₂O content in the fuel and an effective oxygen partial pressure $pO_2 = 4x10^{-21}$ atm. For tests carried out at different cell temperatures, measurements were taken first at 800 °C and then at decreasing temperatures. Tests versus H₂ partial pressure were done by diluting H₂ with Ar and humidifying with \sim 3% H₂O, with a total flow rate of 100 sccm. Cells were kept under 50% humidified hydrogen and 50% Argon initially, and then the partial pressures were varied in sequence from low to high hydrogen partial pressure. Electrochemical impedance spectroscopy (EIS) was carried out using an electrochemical workstation (IM6, Zahner) over the frequency range from 0.1-100 kHz. After testing, the cells were fractured and the cross-sections were examined using scanning electron microscopy (Hitachi 8030).

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Results

Chemical and Structural Characterization

Figure 1a shows ex situ XRD patterns from Sr(Ti_{0.3}Fe_{0.7}Ru_{0.07})O₃₋₆ (STFRu) powder reduced for different times at 800°C and $pO_2 = 4x10^{-1}$ ²¹ atm. Prior to reduction, the STFRu pattern is consistent with the SrTi_{0.3}Fe_{0.7}O₃ XRD diffraction pattern, shown for comparison in the inset in Figure 1b, suggesting that Ru is fully incorporated into the perovskite structure, despite the 7% A-site deficiency. However, after longer reduction time three peaks between 38° and 46° emerge; this can be seen more clearly in the magnified view of this region in Figure 1b. Table 1 gives the lattice parameters for the new phase, which indexes well to hcp-Ru-rich phase (JCPDS 00-001-1253). This change is accompanied by a broadening and shift of the perovskite phase peaks to smaller angle. The peak shift indicates an increase in the lattice parameter (values are given in Table 1), which is similar to that seen for STF and can be explained by the oxygen loss expected for the reducing condition. The broadening, from FWHM = 0.38 to 0.53° for peak at ~46.5°, indicates a change in the crystallinity of the oxide phase. The peak broadening was not observed for STF (see inset Figure 1b), indicating that there was no change of crystallinity in this case.



Figure 1. (a) XRD scans from STFRu reduced for 0 (blue), 1 (red), and 4 h (black). (b) Magnified view of the region of the STFRu XRD scans where the oxide peaks broaden and shift to lower angle and new peaks, associated with Ru–rich hcp phase, appear after reduction. The insert in (b) shows, for comparison, diffraction patterns from STF before and after reduction, where the only change is a peak shift.

Representative TEM images from STFRu powder are shown in Figure 2. No nanoparticles are present prior to reduction (a), whereas a uniform distribution of nanoparticles with sizes typically from 5 - 20 nm can be observed on the oxide surfaces after reduction (b). The nanoparticles are most readily observed at the oxide particle edges (indicated by arrows), but surface particles can also been seen as dark spots over the entire surface. These observations are similar to

prior observations of Ru nanoparticle exsolution from Ru-substituted perovskites.¹⁴⁻¹⁶ Figures 2c and 2d are HRD TEND in ages showing higher magnification views of the post-reduction oxide phase with a single nanoparticle. In Figure 2c, lattice fringes can be seen in the oxide, but are not obvious in the nanoparticle. Nonetheless, the Fast Fourier Transform (FFT) of the nanoparticle, inset in Figure 2c, shows clear spots indicating an interplanar spacing in good agreement with that obtained from the above XRD data (Table 1). These values also agree reasonably well with the interplanar spacing of hexagonal Ru compact (002) planes, with lattice parameter c = 4.28 Å (a = 2.71). However, it is difficult to ascertain the nanoparticle composition from lattice parameter measurements because the Ru-Fe hcp alloy phase exists over a wide range of compositions with little variation in lattice spacing - for example, Ru_{0.25}Fe_{0.75} alloys are reported to have a = 2.68 and c = 4.26 Å.^{30, 31}Furthermore, the present measured lattice parameter values are outside of the range expected for hcp Ru-Fe, possibly due to experimental error and/or strain induced by the oxide-metal hetero-interface. Figure 2d shows an example of a larger nanoparticle, and also shows striations in the oxide phase; this may be a result of the oxide B-site deficiency due to exsolution; note that similar striations were observed in STFNi⁶ after the oxide became B-site deficient due to exsolution. Figure 2e shows a portion of the oxide matrix and the corresponding FFT showing the expected perovskite structure. This region was analyzed by TEM-EDS, yielding the composition SrTi_{0.3}Fe_{0.7}O₃. That is, there was complete Ru depletion but no Fe exsolution, at least within the EDS accuracy of a few % in this region. Note that a few of the nanoparticles show a bccstructure (Figure 2f), and hence are presumably Fe-rich; these are too few (<2% of the anode material) to be observed by XRD. To determine if Fe is present in the exsolved Ru-rich hcp nanoparticles, the samples were analyzed in a TALOS TEM/STEM microscope specially designed for local chemical determination. Figure 3 (a) and (b) show HR-STEM and HR-TEM images of exsolved nanoparticles, respectively. The inserts in the figures show the EDS spectra of specific locations marked with a cross on the images. These spectra confirm that both nanoparticles are actually Ru-Fe alloy.

Table 1. Lattice parameters measured in as-prepared and reduced STFRu powders by XRD and TEM. (STF initial or fresh a = 3.88Å, final or reduced a = 3.91Å).

| Phase | Lattice | initial | Final | |
|-----------------------|---------------|---------|-------|------|
| | parameter (Å) | XRD | XRD | TEM |
| Perovskite (STFRu) | а | 3.89 | 3.92 | 3.86 |
| Ru-phase | а | | 2.64 | |
| (hcp) | С | | 4.35 | 4.23 |

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Figure 2. TEM of STFRu powder (a) before and (b) after the reduction process; (c) and (d) HR-TEM images after reduction with the Fast Fourier Transform (FFT) of selected areas showing typical Ru-rich nanoparticles on the oxide phase; (e) cubic perovskite zone with composition determined by EDS of Sr 50%, Fe 35% and Ti 15% (Ru-free STF); and (f) a bcc Fe-rich cubic nanoparticle.

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Figure 3. (a) HR-STEM and (b) HR-TEM with their corresponding EDS spectra. The peaks of Cu correspond to the grid.

Figure 4 shows the TGA-measured evolution of powder mass *m* normalized to the initial mass m_i at 800°C for STF and STFRu. The initial condition (i) corresponds to Ar with pO₂ = 2x10⁻⁴atm and the final condition (f) to humidified H₂-Ar with an effective pO₂ = 4x10⁻²¹ atm. The STF sample mass decreases due to oxygen loss associated with partial Fe-reduction, reaching a stable mass within ~ 15 min. In the initial condition, there is a mixed Fe^{+3/+4} valence with average oxidation state +3.11. Once reaching a stable mass after reduction, there is a mixed Fe^{+2/+3} valence with average oxidation state +2.93. For STFRu, the initial mass loss is faster, and then the loss continues to longer times and larger values than for the STF case. It appears that the mass has stabilized by the end of the 90-minute reduction.



Figure 4. TGA-measured mass loss versus time for STF and STFRu, initially in Ar with $pO_2 = 2.10^{-4}$ atm, after exposure to a reducing fuel environment with $pO_2 = 4 \ 10^{-21}$ atm.

The greater STFRu mass loss compared to STF can be attributed to the oxygen evolved upon formation of the metallic Ru-rich phase (see Figs. 1 and 2). The expected mass loss can be estimated based on some assumptions. First, we assume that the oxygen loss associated with the change in Fe oxidation state in the oxide is the same for STFRu as in STF. That is, the (i) condition for STFRu corresponds to Ru⁺³ and Fe^{+3/+4} with an average oxidation state of +3.11, whereas the (f) condition has a more reduced Fe-state (+2.93). If we also assume that all of the Ru is exsolved from the oxide (reduction from Ru⁺³ to Ru⁰), as suggested by the oxide EDS analysis, but no Fe is exsolved, the predicted mass loss $m/m_i = 0.986$. This is

less than the measured loss of 0.983; the larger mass loss is explained by reduction of some of the Fe to metal (Fe의여ክ ቹወቶም፤ብዿናሸርፅ፤ዪፖራዩē alloy nanoparticles. (The amount (< 2%) of bcc Fe-rich nanoparticles is too small to affect the mass loss.) Based on the measured mass loss, the average nanoparticle composition is estimated as Fe_{0.2}Ru_{0.8}. The exsolution of a limited amount of Fe to form alloy nanoparticles has been shown previously.⁶ Note that Fe is reduced from the oxide only to the extent that it can form an alloy with the exsolved Ru. Since the amount of Ru is low, the amount of Fe that can exsolve is also limited. Thus, after the Ru and a small amount of Fe has exsolved, the remaining STF is stable, as shown by the stable mass at the end of the the TGA test. While this could alternatively be explained by a greater reduction of Fe in the oxide to +2.85, this would be surprising because the oxide after exsolution would be essentially the same STF composition where a Fe state of +2.93 was measured above. The difference in the stabilization time between STFRu and STF can be explained by the relatively slow kinetics of Ru and Fe diffusion to the STFRu surfaces, as compared to the oxygen diffusion and surface reaction rates responsible for oxygen loss from STF.

The above results, taken together, indicate that the hcp nanoparticles contain some Fe. This is consistent with prior reports indicating that nanoparticles exsolved from Fe-containing oxides can contain substantial amounts of Fe.^{6, 26, 27, 32} It is also expected given that the excess free energy of Ru-Fe alloy formation is negative.³⁰ The observation of bcc nanoparticles along with hcp nanoparticles is consistent with the Ru-Fe phase diagram – there is a two-phase coexistence region where a bcc Fe-rich phase coexists with hcp Ru-Fe with ~ 75% Fe below ~ 700°C.³⁰



Figure 5. Current-voltage curves at different operating temperatures.

Electrochemical Characterization

Current-voltage characteristics of single cells with STFRu anodes are shown at different temperatures in Figure 5, for anode H₂ partial pressures p_{H_2} = 0.97 atm (p_{H_2O} = 0.03 atm) with fuel flow rate of 50 sccm. The cell current density and power density show the expected increases with increasing temperature. The j-V curvature is mostly positive, indicating activated behavior. This is in contrast to results for cells with STF anodes, which show a pronounced negative

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curvature that was explained by an H₂ adsorption limitation.^{4, 6} Figure 6 shows the results at various p_{H_2} at 750 °C with a total flux of 100 sccm. There is relatively little change in the slope or curvature of the *j*-V curves with decreasing p_{H_2} - most of the decrease in cell current arises from the decrease in open-circuit potential – at least until p_{H_2} is decreased to 0.1 atm, where there appears to be a limiting current.



Figure 7 shows EIS response data from STFRu cells, measured at open circuit potential at 750°C at different pH₂ values. The Nyquist plots (Fig. 7 a) show a slight increase in the high-frequency intercept with decreasing pH₂, indicating an increase in cell ohmic resistance; this has been explained previously by an increase in the resistivity of STFbased anodes, which contributes to the ohmic resistance.4, 25 The total polarization resistance increases by ~ 50 % with decreasing pH_2 . The EIS Bode plots (Fig. 7b) show two main responses, at ~ 1 and 20 Hz, along with a small response at higher frequency, very similar to that reported for Ni-substituted STF.⁶ Fits to the EIS data using three RQ elements are shown in Figure 7 to provide a good match with the data. On the other hand, the higher frequency response resistance values from the fits do not measurably change with pH₂, suggesting that this process is related to the cathode. The same two responses are observed at different temperatures, and the ~ 20 Hz response resistance grows more rapidly with decreasing temperature than the ~ 1 Hz response, and becomes the dominant response below 750 °C.

Figure 6. Current-voltage curves at different hydrogen partial pressures at



Figure 7. (a) Nyquist and (b) Bode plots of EIS data from the STFRu anode cells, measured at 750 °Cat various pH₂ values with pH₂O fixed at 0.03 atm. Also shown are fits to the EIS data, obtained using an equivalent circuit with a resistor and three RQ elements.

Figure 8 displays the anode polarization resistance $(R_{P,A})$, taken as the sum of the 1 and 20 Hz responses obtained from the fits, plotted versus pH₂ at various temperatures. The data are fitted reasonably well by power law dependences $R_{P,A} \propto (p_{H_2})^{-m}$ with $m \simeq 0.11$ -0.29 except at 700 °C where the *m* value is lower. This p_{H_2} dependence of $R_{P,A}$ is lower than that previously reported for STF,⁴ where the fitted power law was $m \approx 0.5$ and 1. That is, $R_{P,A}$ for STF increased much more rapidly with decreasing p_{H_2} than in the present STFRu results. For example, the $R_{P,A}$ increased by ~ 400% for STF upon decreasing pH_2 from 1 to 0.1 atm (at 750 °C), much larger than the ~ 50% increase observed for STFRu in Figures 7 and 8. The strong p_{H_2} dependence for STF was attributed to a rate-limiting hydrogen dissociative adsorption process.⁴ The much weaker dependence for STFRu can be explained by the Ru-Fe nanoparticles providing sites for fast hydrogen dissociative adsorption, thereby eliminating the adsorption process as a rate-limiting step; the charge transfer process, with a characteristically weaker p_{H_2} dependence, is then the limiting step.



Figure 8. Anode polarization resistance versus H₂ partial pressure measured at different temperatures.

The effect of Ru substitution is most readily observed by directly comparing the above results for cells with STFRu anodes with those

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for Ru-free STF anodes, as shown in Figure 9. Results are shown at 800 and 700 °C, with p_{H_2} values of 0.97 and 0.3 atm. Both cells show nearly identical open circuit potentials at each measurement condition and also similar values of low-current resistances. The difference arises at high current density, where the STFRu cell shows a *j*-V with slightly positive curvature, whereas the STF cell shows an apparent limiting current behaviour. The increase in current at cell voltages < 0.4V is discussed elsewhere.⁴ Figure 10 shows maximum power density values versus p_{H_2} from the STFRu- and STF-anode cell *j*-V data at various temperatures. At 800 °C and p_{H_2} = 0.97 atm, the

STF and STFRu cells show similar power density. However, ethall other conditions, the STFRu-anode cell yields a substantially higher power density than the STF-anode cell. That is, the STFRu cell has a much slower decrease in power density with decreasing p_{H_2} and temperature than the STF cell. For example, the maximum power density of the STFRu cell for p_{H_2} = 0.29 atm and T = 700 °C was ~ 3 times higher for the STFRu cell (Fig. 9(d)). These increases of power density for the STFRu agree with the change of mechanism proposed from the EIS analysis when nanoparticles are present on the surface.



Figure 9. Comparison of current-voltage results for cells with STFRu-7 and STF anodes at (a) 800 °C 97% H₂, (b) 700 °C 97% H₂, (c) 800 °C 29.1% H₂, and (d) 700 C 29.1% H₂.

Figure 11 shows current-voltage curves taken at various times during a life test carried out on a STFRu anode cell at 700°C with no current. The cell resistance increased and power density decreased gradually with time up to ~ 200 h, after which the cell became more stable. A similar test done at 750°C at a current density of 0.4 A/cm² yielded a similar result, with initial degradation followed by stabilization. Both cases yielded an increase in cell resistance and decrease in power density by ~ 25% over the life of the test. From EIS measurements, the degradation appears to be split approximately equally between the anode and cathode responses. X-ray diffraction after life tests shows only the perovskite oxide phase and the exsolved metal phase. A gradual increase in anode polarization resistance may be related to slight coarsening of the metallic nanoparticles over long times at elevated temperature, as suggested previously for Ru-substituted chromite anodes.^{14, 16} More extensive life testing will clearly be needed to fully assess the long-term stability of these anodes.



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Figure 11. Current-voltage curves at different times during a life test carried out on a STFRu anode cell at 700 °C with no current.

Discussion

The above electrochemical test results show substantially different characteristics for STFRu compared to STF. This includes a more linear dependence of V on j for STFRu, without the pronounced limiting current behavior seen in STF. This also leads to substantially higher j values at normal cell operating voltages, along with higher power densities. There are a number of prior reports showing that exsolution can reduce anode resistance and increase cell power density.^{6, 13-17, 27, 32} The low frequency anode response in Figure 10 is similar to that reported for STF, but the power-law dependence is weaker than that observed for STF, where $m \ge 0.5.^4$ As discussed previously, the hydrogen oxidation reaction in STF is strongly limited by hydrogen dissociative adsorption at lower temperatures and pH₂ values, resulting in limiting current behavior and relatively large m values.⁴ Prior results for (La,Sr)(Cr,Ru)O₃ and Sr(Ti,Fe,Ni)O₃ anodes have shown that exsolved Ru or Ni-Fe nanoparticles, respectively, improve anode performance by accelerating hydrogen adsorption,^{4,} ⁶ such that charge transfer, with a characteristically different *m* value and *j*-V dependence, becomes the rate limiting step. The present results are similar to those observed for Ni-Fe nanoparticles exsolved from Sr(Ti,Fe,Ni)O₃. This, together with the observation of Ru-Fe exsolved nanoparticles (Figure 2), suggests that the same explanation can be applied here. An oxide structure change is also observed after exsolution, perhaps due to the oxide becoming B-site deficient due to the loss of Ru and Fe; this change may also impact anode electrochemical characteristics.

Conclusions

 $Sr(Ti_{0.3}Fe_{0.7}Ru_{0.07})O_3$ (STFRu) was produced by solid state reaction and was shown by both XRD and TEM to exsolve primarily Ru-rich hcp

nanoparticles under the reducing conditions present at a SQFC and the during cell operation. At 800°C and high pH₂, the power density and anode polarization resistance was similar for cells with STFRu and STF anodes. However, at lower temperatures and pH₂ values, the STFRuanode cells yielded substantially higher maximum power density and decreased anode polarization resistance than STF-anode cells. Thus, STFRu anodes should have an advantage over STF anodes in stacks operating with high fuel utilization and reduced temperature. The results support the idea that metallic nanoparticles improve anode performance by providing a fast pathway for hydrogen adsorption.

Conflicts of interest

There are no conflicts to declare.

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