Polarization-Induced Hysteresis in CuCo-Doped Rare Earth Vanadates SOFC Anodes

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Abstract
The physical and electrochemical properties of strontium substituted cerium vanadates in which a portion of the cerium cations have been substituted with transition metals (Ce$_{0.8}$Sr$_{0.1}$Cu$_{0.05}$TM$_{0.05}$VO$_4$$_{-0.5x}$, TM = Ni or Co) were investigated and their suitability for use in solid oxide fuel cell (SOFC) anodes was assessed. Upon reduction at elevated temperature, Cu and Co or Cu and Ni were exsolved from the electronically conductive Ce$_{1-x}$Sr$_x$VO$_4$ lattice to produce Cu-Ni and Cu-Co catalytic nanoparticles. The Ce$_{0.8}$Sr$_{0.1}$Cu$_{0.05}$Co$_{0.05}$VO$_3$ appears to have high activity and relatively high hydrocarbon tolerance, suggesting that intimate contact between the exsolved Cu and Co and that the majority of the Co nanoparticles must be at least partially coated with the Cu. The electrochemical performance when used in anodes operating on hydrogen has been characterized, and the results demonstrate the exsolution of both metals from the host lattice; but observed dynamic changes in the structure of the resulting metal nanoparticles as a function of SOFC operating conditions complicate their use in SOFC anodes.

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Solid oxide fuel cells (SOFCs) are of interest due to their relatively high energy conversion efficiencies and fuel flexibility. The fuel flexibility of SOFCs results from the fact that \(O^2-\) anions, rather than \(H^+\) ions, are transmitted through the electrolyte. Direct utilization of hydrocarbons, however, is still not possible in conventional SOFCs because Ni-YSZ composites, the most commonly used anode composition, catalyze the formation of carbon deposits including fibers that cause deactivation.\(^1,2\) One solution to this problem is to replace the Ni with an electronically conductive material that does not catalyze the formation of carbon from hydrocarbon fuels. Electronically conductive ceramics, including titanates,\(^3,4\) manganates,\(^5,6\) chromates,\(^7,8\) and bronzes\(^9,10\) have been investigated for this application. These materials have been shown to have a low susceptibility to sintering and coking and are more redox stable and tolerant of impurities, like sulfur, than Ni.\(^11-13\) While promising results have been obtained with ceramic-based anodes, these anodes unfortunately have relatively low catalytic activity for oxidant reactions, resulting in high electrode overpotentials unless they are decorated with nanoparticles of a highly catalytic metal (e.g. Ni, Pt, or Pd).\(^14,15,16,17,18,19\) Sintering of the catalytic nanoparticles, however, is still an issue that hinders the long-term stability of the anode.

One approach that has been proposed to enhance the catalytic activity of ceramic-based anodes is to use materials for which the metal nanoparticles catalysts can be generated in situ through their exsolution from a conducting perovskite host.\(^20,21,22,23,24,25\) This concept is similar to that used in self-regenerating automotive emissions catalysts that were first developed by researchers at Daihatsu.\(^26,27,28,29\) So called “intelligent” automotive catalysts use perovskite (\(ABO_3\)) oxides (e.g. \(LaFeO_3\)) in which a catalytic metal, typically the noble metals Pt, Pd, or Rh, is substituted for a small portion of the B-site cations. Under mildly reducing conditions the easily reduced noble metal cations are exsolved from the lattice and precipitate as nanoparticles that decorate the surface of the perovskite. Since the catalytic converter in an automotive emissions control system oscillates between oxidizing and reducing conditions, the noble metals undergo dissolution/exsolution cycles that help maintain the metal surface area and catalytic activity. The Barnett group has recently demonstrated the use of this phenomenon in SOFC anodes.\(^30,31,32,33,34\) They used the electronically conducting perovskite, \(La_{0.5}Sr_{0.5}Cr_1-xM_xO_3\) where \(M = Ni, Pd,\) and \(Ru\), and showed that metal nanoparticles with diameter of \(<5\) nm were produced from the perovskite lattice upon exposure to a reducing environment.\(^35,36,37,38,39,40\) This in turn greatly enhanced the performance of electrodes based on this material. Since redox cycling could also be used in an SOFC to regenerate any metal surface area loss due to sintering, this approach provides a novel strategy for both optimizing the catalytic properties of ceramic anodes for SOFC for specific fuels and for maintaining long-term performance.

While exsolution of catalytic metals can be used to enhance the catalytic activity of an SOFC anode, in order to obtain a high performance anode, the host oxide must also have high electronic conductivity. Recently, we and others have shown that alkaline earth (AE) substituted rare earth (RE) vanadates (\(RE_{1-x}AE VO_4\)), such as \(Ce_{1-x}Sr VO_4\) and \(La_{1-x}Sr VO_4\), have electronic conductivities approaching 1000 S cm\(^{-1}\) under some conditions, and are chemically stable in a variety of fuels including \(H_2\), \(H_2S\), and \(CH_4\).\(^41,42,43,44,45\) These properties make the vanadates ideal candidates for use in SOFC anodes designed to run on hydrocarbon fuels. We have also demonstrated that when doped with catalytic metals, Ni and Co, the metals can be exsolved from the lattice upon exposure to reducing atmospheres.\(^46,47\) While similar to the perovskites discussed above, the vanadates exhibit a somewhat more complex phase behavior. In their fully oxidized form, \(RE_{1-x}AE VO_4\) has a zircon structure. Upon exposure to reducing conditions, however, they undergo a phase change to the perovskite structure.\(^48,49\) Exsolution of a portion of the metals from the lattice accompanies this phase change.\(^50\) 

\[RE_{1-x}AE VO_4\] anodes doped with \(Co \text{ or } Ni\) (used as a composite with YSZ) have been shown to exhibit high electrochemical activity and unusually high redox stability, with the latter property being partially due to the exsolution/dissolution of the catalytic metals. These anodes, however, are not hydrocarbon stable since both Ni and Co catalyze carbon formation.\(^51\) It has previously been shown in studies of anodes with a more conventional design that the propensity for Ni and Co to catalyze coke deposition can be ameliorated by alloying with a less reactive metal, such as Cu, while still maintaining high oxidation activity.\(^52,53\) Particles composed of Ni and Cu, form a solid solution so that both Cu and Ni remain at the surface. Based on previous work, Cu-Ni alloys exposed to dry methane still formed significant amounts of carbon up to alloy compositions of 20% Ni. Unlike Cu-Ni alloys, the Cu and Co in Cu-Co mixtures remain as separate phases, with the surface enriched in Cu due to its lower surface free energy. The low activity for C-C bond breaking and forming on Cu causes these particles to have a lower activity for coke formation, even for compositions with high Co:Cu ratios. Enough of the more active metal remains exposed, however, to allow relatively high catalytic activity for oxidation reactions to be maintained.

In the present study we have explored the possibility of doping \(RE_{1-x}AE VO_4\) with both Cu and Co or Cu and Ni and using the exsolution phenomena described above as an in situ means to synthesize Cu-Ni and Cu-Co catalytic nanoparticles, with the goal of using these materials to produce high-performance, highly robust SOFCs.
anodes that can directly utilize hydrocarbon-based fuels. Specific materials that have been studied include Ce0.8Sr0.1Cu0.05Co0.05VO3 and Ce0.8Sr0.1Cu0.05Ni0.05VO3. The exsolution of the metals from these materials and their electrochemical performance when used in anodes operating on hydrogen have been characterized. Preliminary studies of their hydrocarbon stability are also reported. The results obtained in this study demonstrate the exsolution of both metals from the host lattice, but observed dynamic changes in the structure of the resulting metal nanoparticles as a function of SOFC operating conditions complicate their use in SOFC anodes.

Experimental

Bulk Ce0.8Sr0.1Cu0.05TM0.05VO4−δ powders were used for XRD analysis and (where TM = Ni, Co) were prepared using an aqueous precursor solution containing the appropriate amounts of Ce(NO3)3·6H2O (Alfa Aesar, 99.5%), Sr(NO3)2 (Alfa Aesar, 99.9%), NH4VO3 (Fisher Scientific), and either Ni(NO3)2·6H2O, Co(NO3)2·6H2O, or Cu(NO3)2·3H2O (Alfa Aesar, 99.9%). Citric acid (Fisher Scientific) was also added as a complexing agent to aid in the formation of a more homogeneous mixture. The precursor solution was dried and the resulting powder was calcined at 973 K in air to form the zircon phase. Perovskite Ce0.8Sr0.1Cu0.05TM0.05VO3 materials were produced by reducing the Ce0.8Sr0.1Cu0.05TM0.05VO4−δ in humidified H2 (3% H2O) for 3 hours at 1073 K before exposing them to dry methane at 1073 K for 3 hours and measuring their weight gain resulting from carbon deposition. The morphological structure of the porous composites was determined using scanning electron microscopy (SEM) (FEI Quanta 600 ESEM) and X-ray diffraction (XRD) using Cu Kα radiation. For the XRD measurements, a small amount of YSZ was physically mixed with the oxides to act as a reference.

Solid oxide fuel cells 1-cm in diameter were used in all fuel cell measurements. These cells were fabricated using porous-dense porous tri-layer YSZ wafers that were produced using tape casting methods that have been described in detail previously.5–6 Porous 4 mm × 4 mm × 15 mm YSZ slabs were prepared using methods that have been described in detail previously.5,6,55 The vanadates were added to the porous YSZ slabs by infiltrating the aqueous precursor solution followed by drying and annealing in air at 973 K. Multiple infiltration/annealing cycles were used to obtain the desired 30 wt% loading. The stability of the vanadates in hydrocarbons was assayed by exposing Ce0.8Sr0.1Cu0.05TM0.05VO3/YSZ composites under humidified H2 (3% H2O) for 3 hours at 1073 K before exposing them to dry methane at 1073 K for 3 hours and measuring their weight gain resulting from carbon deposition. The morphological structure of the porous composites was determined using scanning electron microscopy (SEM) (FEI Quanta 600 ESEM) and X-ray diffraction (XRD) using Cu Kα radiation. For the XRD measurements, a small amount of YSZ was physically mixed with the oxides to act as a reference.

Solid oxide fuel cells 1-cm in diameter were used in all fuel cell measurements. These cells were fabricated using porous-dense porous tri-layer YSZ wafers that were produced using tape casting methods that have been described in detail previously.5–6 For each cell, the dense electrolyte layer was 65-μm thick and 1-cm in diameter. The 60% porous YSZ layers on each side of the dense electrolyte layer were 50-μm thick with a BET surface area 0.3 m2g−1, 40 wt% Sr-doped lanthanum ferrite, La0.8Sr0.2FeO3 (LSF), was added to one porous layer to form a cathode using multiple cycles of infiltration of an aqueous solution containing dissolved La(NO3)3·6H2O (Alfa Aesar, 99.9%), Sr(NO3)2 (Alfa Aesar, 99.9%), and Fe(NO3)3·9H2O (Fisher Scientific) in the appropriate molar ratios, followed by calcination in air at 723 K. After the infiltration steps the composite cathode was calcined to 1123 K for 4 h to form the perovskite structure. Previous studies have shown that cathodes of this design have an ASR of ~0.15 Ω cm2 in air at 973 K.16,58 The Ce0.8Sr0.1Cu0.05TM0.05VO3 anode was synthesized in a similar manner except that a 30 wt% loading was used and it was calcined to only 973 K. The anode was reduced in humidified H2 (3% H2O) at 973 K prior to cell testing. Silver paste current collectors were applied to both electrodes and the cells were mounted onto an alumina tube using a ceramic adhesive (Aremco, Ceramicbond 552). All the cell tests were performed with the cathode exposed to ambient air and the anode exposed to humidified H2. Electrochemical impedance spectra were measured between 0.1 Hz and 300 kHz with a 1 mA AC perturbation. Both impedance spectra and V–I polarization curves were measured using a Gamry Instruments potentiostat.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of (A) Ce0.8Sr0.1Cu0.05Co0.05VO3−δ, and (B) Ce0.8Sr0.1Cu0.05Ni0.05VO3−δ oxidized at 973 K in air. The peaks are labeled as follows: (▲) cubic YSZ, (●) zircon Ce0.8Sr0.1Cu0.05VO3, and (□) Ce0.8Sr0.1Cu0.05Ni0.05VO3.

**Results and Discussion**

XRD was used to determine the phase composition of the Cu and Co or Cu and Ni vanadates following various pretreatments. XRD patterns for (A) Ce0.8Sr0.1Cu0.05Co0.05VO3−δ and (B) Ce0.8Sr0.1Cu0.05Ni0.05VO3−δ samples that were calcined in air at 973 K for 2 hrs are presented in Figure 1. The zircon structure of Ce0.8Sr0.1Cu0.05Co0.05VO3−δ and Ce0.8Sr0.1Cu0.05Ni0.05VO3−δ was confirmed by the presence of the expected diffraction peaks near 24.0, 32.4, 34.1, 36.4, 38.9, 43.2, 46.1, and 48.0 degrees 2θ.43,46 The XRD patterns are comprised of peaks that correspond only to Ce0.8Sr0.1Cu0.05Cu0.05VO3−δ and Ce0.8Sr0.1Cu0.05Ni0.05VO3−δ and do not contain any peaks indicative of other oxide phases including TM2V2O7 (where TM = Ni, Co, or Cu), thus demonstrating that the single phase vanadates were formed.

As noted above, the transition metal doped vanadates undergo a phase change from the zinc structure to the perovskite structure upon reduction, with a portion of the metals being exsolved from the lattice.30 This is demonstrated by the XRD patterns in Figure 2 for (A) Ce0.8Sr0.1Cu0.05Co0.05VO3−δ and (B) Ce0.8Sr0.1Cu0.05Ni0.05VO3−δ samples that were reduced in humidified H2 at 973 K. For comparison purposes, XRD patterns for reduced vanadates that contain only one of...
the transition metals (C) Ce₀.₈Sr₀.₁Cu₀.₁VO₃, (D) Ce₀.₈Sr₀.₁Co₀.₁VO₃, and (E) Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃ are also included in the figure. The large peaks at 40.1 and 46.7 degrees 2θ are indicative of the perovskite phase. Peaks corresponding to the bulk transition metals are also apparent between 43 and 45 degrees 2θ for each sample. The positions of the expected peak for each metal are indicated in the figure. Note that the Cu diffraction peak overlaps with one of the minor peaks for the perovskite vanadate. The presence of peaks indicative of the transition metals in each pattern further demonstrates that the phase transition from zircon to perovskite is accompanied by the exsolution of the transition metals from the lattice.

Note that the XRD pattern for Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃ (pattern A) contains peaks indicative of both Cu and Co, thereby demonstrating that both metals have been exsolved from the host oxide lattice upon reduction. Similarly, the pattern for Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃ (pattern B) contains peaks for both Cu and Ni. For this sample an additional peak is also present at 44.2 degrees 2θ. Unlike Cu and Co, Cu and Ni are miscible.⁴⁹,⁵²,⁵³ We therefore assign the peak at 44.2 degrees 2θ to Cu-Ni alloy particles. Although particles with a range of compositions are likely to have been formed, the 44.2 degrees 2θ peak position is consistent with a 50:50 Cu:Ni alloy composition.⁵³

While the exsolved metals would be expected to enhance the catalytic activity of an SOFC anode made with these materials, as discussed in the introduction, intimate contact between the Cu and the Co or Ni will be required to produce catalysts that do not undergo severe coking upon exposure to hydrocarbons. To assess whether this can be achieved for transition metal decorated surfaces produced by reduction of Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃ and Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃, we exposed porous composites of these materials with YSZ to dry methane at 1073 K for 3 hrs. SEM images of these samples after this treatment are displayed in Figure 3. For comparison purposes, images obtained from reduced Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃ and Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃, YSZ composites subjected to the same treatment are also included in the figure. The weight gain for each sample after the hydrocarbon treatment is listed in Table I.

Panel A in Figure 3 corresponds to the CH₄-treated Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃-YSZ composite. Cu is a relatively unreactive metal and does not catalyze carbon fiber formation from hydrocarbons.⁴⁹,⁵⁵ As expected, this image does not contain any evidence for carbon deposition, and this sample exhibited only a negligible weight gain. In contrast, for the reduced Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ sample whose surfaces are decorated with Co nanoparticles, wormlike carbon fibers are readily apparent in the SEM image obtained after exposure to CH₄ (panel B, Fig. 3) and this sample exhibited a 12% weight gain. Unfortunately, similar results were obtained from the Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃-YSZ composite. The SEM image for this sample (panel C, Fig. 3) shows the presence of a high concentration of carbon fibers and the weight of the sample increased by 61%. The high activity of this sample for carbon fiber formation is consistent with previous results for Cu-Ni alloys.⁵⁶ Although one would expect some suppression of the carbon formation in Cu-Ni alloys, carbon formation with a 50:50 Cu-Ni alloy is still significant. More promising results were obtained for the Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃-YSZ composite. The SEM image of this sample after exposure to CH₄ (panel D, Fig. 3) is nearly devoid of carbon fibers and the weight gain for the sample was only 2%. Since Co is highly active for carbon fiber formation, this result indicates that there is intimate contact between the exsolved Cu and Co and that the majority of the Co nanoparticles must be at least partially coated with the Cu.

Based on the hydrocarbon stability tests, the Cu-Co substituted vanadates were considered more promising for use in SOFC anodes and were therefore the focus of electrochemical testing. This was done using SOFC button cells that with a 65-μm thick YSZ electrolyte, an infiltrated 30 wt% Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃-YSZ composite anode, and a 40 wt% LSF-YSZ composite cathode.⁵⁶–⁵⁸ For comparison purposes, cells with Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ, Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ, and Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ composite anodes were also used in some experiments. The fuel-cell measurements reported here focused on characterizing stability of the Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃-YSZ anode while operating with humidified H₂ (3% H₂O) fuel.

Polarization curves for each cell at 973 K using humidified H₂ as fuel are shown in Figure 4. Each curve was measured starting from OCV, followed by ramping the potential to 0 V and back to OCV using a linear scan rate of 0.025 Vs⁻¹ in both directions. The polarization curves for the cells with the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃ (dashed black curve) and Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ (dashed blue curve) and Ce₀.₈Sr₀.₁Cu₀.₁VO₃-YSZ (dotted red curve) were all nearly linear and reversible, showing the same behavior in both scan directions. As will be discussed below, more complex hysteretic behavior was observed for the cell with the

<table>
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<th>Sample</th>
<th>% weight gain</th>
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<tr>
<td>Ce₀.₈Sr₀.₁Cu₀.₁VO₃</td>
<td>&lt; 1</td>
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<tr>
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</tr>
<tr>
<td>Ce₀.₈Sr₀.₁Cu₀.₀₅Ni₀.₀₅VO₃</td>
<td>61</td>
</tr>
</tbody>
</table>

Table I. Percentage weight changes after exposure to dry CH₄ at 1073 K for 3 hrs.
Ce₀.₈Sr₀.₁Cu₀.₀₅Co₀.₀₅VO₃-YSZ anode. Each cell had an open-circuit potential near the theoretical Nernst value of 1.1 V. As reported previously, relatively poor electrochemical performance was obtained from the cell with the CeVO₃-YSZ composite anode (ASR_anode = 2.70 Ω cm²) due to the low catalytic activity of this material.³⁰,⁴⁷ Only slightly better performance was obtained for the cell with the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃-YSZ anode (ASR_anode = 0.65 Ω cm²) which is consistent with the low catalytic activity of both Cu and the vanadate. Excellent performance was obtained from the cell with the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃-YSZ anode which had an ASR_anode of only 0.1 Ω cm² (This assumes that the cathode ASR 0.15 Ω cm², as determined in other work.¹⁰,¹¹). This result is consistent with the surface of the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃ being decorated with highly catalytic Co nanoparticles under reducing conditions as demonstrated above.

Unusually complex behavior was exhibited by the cell with the Ce₀.₃Sr₀.₁Cu₀.₀₅Co₀.₀₅VO₃-YSZ composite anode, including hysteresis in the polarization curve, with abrupt changes in performance occurring at several voltages (Figure 4). The initial portion of the polarization curve for this cell, starting from OCV and ramping to ~0.3 V (solid red curve in Fig. 4), closely follows that of the cell with the Ce₀.₈Sr₀.₁VO₃-YSZ anode. As shown by the impedance spectrum obtained at point A (see figure insert), the anode ASR in this portion of the polarization curve is 0.15 Ω cm² after subtracting off the cathode ASR, 0.15 Ω cm². The hydrocarbon stability tests described above indicated that the Co nanoparticles exsolved from the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃ lattice under reducing conditions are primarily coated with Cu. The similarity in the initial performance of the two anode formulations containing Co, however, demonstrates that, for the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃-YSZ anode, enough Co remains exposed to impart high catalytic activity for H₂ oxidation.

Near 0.3 V, an abrupt change in the electrochemical properties of the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃-YSZ anode takes place, causing a rapid decrease in cell performance as the voltage is ramped from 0.3 to 0 V. As shown by the solid blue curve in Figure 4, the polarization curve for the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃ cell exhibited hysteresis and was not immediately reversible, with low performance persists upon reversal of the sweep direction from 0 to ~0.78 V. In this region of the polarization curve the cell performance was close to that of the cell with the Ce₀.₈Sr₀.₁VO₃-YSZ anode. As shown by the impedance spectrum collected at point B, the anode ASR in this region of the polarization curve was 0.65 Ω cm² (the estimated cathode ASR of 0.15 Ω cm² has again been taken into account here). At 0.78 V on the increasing voltage sweep, another abrupt change occurs, with the cell performance switching from the low-activity state back to the high-activity state exhibited by the fresh cell. This high-activity state then persists up to OCV. The hysteretic behavior exhibited by this cell was stable and occurred for repeated polarization curve measurements at a variety of scan rates. Similar results were obtained with multiple cells and the changes in performance occurred at nearly the same voltages (~0.3 and ~0.8 V) in all cases.

It is important to note that the impedance spectra show that the ohmic contribution remained fixed at 0.3 Ω cm² in both the high- and low-performance regions of the polarization curve. This value is consistent with that expected for the 65 μm thick YSZ electrolyte layer, ruling out the possibility that the change in cell performance is due to a change in the electronic conductivity of the vanadate phase or the formation of an insulting layer at the YSZ-vanadate interface.

In situ characterization of the phase composition and structure of the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃-YSZ composite anode in both the high- and low-activity states, in the region near the electrolyte-anode interface, would be required to provide a definitive explanation for the observed hysteresis in electrochemical properties. However, the results here provide important clues as to its possible origin. It is useful to first consider the structure of the Cu and Co nanoparticles that are exsolved from the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃ lattice under reducing conditions. The hydrocarbon stability tests (Figure 3) demonstrate that the anode has relatively low catalytic activity for the production of carbon fibers from hydrocarbons. Since Co by itself has high activity for this reaction, Co nanoparticles must be in intimate contact with Cu on the reduced electrode. Since Cu and Co are nearly immiscible and do not form bulk alloys, the nanoscale mixtures of these metals that are produced by the exsolution process would be expected to phase separate; furthermore, due to the lower surface free energy of Cu, one would expect this process to produce Cu-coated Co particles.

A previous study of a Cu-CeO₂-YSZ composite electrode (the Cu and CeO₂ were added using wet infiltration) that was coated with a thin layer of Co using electrodeposition demonstrated that Cu does indeed segregate to a Cu surface.²⁴ Under typical SOFC operating conditions, this anode was found to have high hydrocarbon stability and did not catalyze carbon fiber formation. In this study X-ray photoelectron spectroscopy (XPS) was used to characterize a 250-nm Co film that had been electrodeposited onto a Cu foil as a function of temperature in ultra-high vacuum (a reducing environment). It was found that, at temperatures above 800 K, Cu migrated through the Co film, ultimately coating its surface. Furthermore, analysis of the XPS peak intensities during sputter depth-profile measurements indicated that the equilibrium thickness of the Cu coating was only 1-2 monolayers.

While coating of the Cu particles with a thin layer of Cu could explain the low activity of the reduced Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃ anode for carbon deposition, some Co must still be exposed since the catalytic activity of the anode for H₂ oxidation at high cell potentials is essentially the same as that for an electrode that contains only Co nanoparticles. Based on these observations, we propose that, for the Ce₀.₃Sr₀.₁Cu₀.₀₅VO₃ anode, some Co is present in the thin layer of Co using electrodeposition demonstrated that Cu does not catalyze carbon fiber formation. In this study X-ray photoelectron spectroscopy (XPS) was used to characterize a 250-nm Co film that had been electrodeposited onto a Cu foil as a function of temperature in ultra-high vacuum (a reducing environment). It was found that, at temperatures above 800 K, Cu migrated through the Co film, ultimately coating its surface. Furthermore, analysis of the XPS peak intensities during sputter depth-profile measurements indicated that the equilibrium thickness of the Cu coating was only 1-2 monolayers.

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It is interesting to estimate the anode overpotentials corresponding to the critical points in the V-i curve for the cell with the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃ anode. Based on the estimated anode ASR for the high- and low-activity regions of curve (0.15 Ω cm² and 0.65 Ω cm²), the anode overpotentials at the points where the performance jumps occur are 0.165 V (0.15 Ω cm² - 1.1 Acm⁻²) and 0.163 V (0.65 Ω cm² - 0.25 Acm⁻²), respectively. This in turn can be related to an increase in the Po2 in the three-phase boundary (TPB) region relative to the anode compartment gas phase, from 10⁻²⁴ atm in the anode compartment to approximately 10⁻¹⁰ atm at the TPB.

Although the Po2 at the TPB remains well below that needed to oxidize either bulk Co (~10⁻¹⁸ atm⁶²) or Cu (~10⁻¹¹ atm⁶³), we suggest that the switch in catalytic performance of the Ce₀.₈Sr₀.₁Cu₀.₀₅VO₃ anode from that characteristic of a Co catalyst to one characteristic of a Cu catalyst at low cell potentials is due to oxidation of the Co that is exposed in the Cu-coated, Co

![Figure 5. Schematic of the structure of the Cu-Co particles and the effect of polarization.](Image 318x57 to 534x177)
particles on the electrode surface. It would not be surprising if these isolated cobalt atoms have thermodynamic properties that vary somewhat from that of the bulk material. Indeed, it has been suggested that small Co nanoparticles are more easily oxidized than bulk Co and can become oxidized at a significantly lower $P_{O_2}$. Support and promoter effects have also been reported to alter the redox properties of small Co particles. Since CoO does not exhibit the high oxidation activity of metallic Co, when the Co becomes oxidized the catalytic activity would decrease. The observed switching behavior for the Cu-Co system is therefore likely to be due to oxidation/reduction of the surface Co in the Cu-Co particles at the $P_{O_2}$ corresponding to an anode overpotential of $\pm 0.164$ V. Based on this scenario, the exposed Co provides the catalytic activity at low anode overpotentials ($P_{O_2}$) and Cu provides the catalytic activity at high overpotentials as shown schematically in Figure 5.

The performance of the anodes made with Cu-Co mixtures is very intriguing and provides another example of the use of exsolution from Cu-Ni and Cu-Co mixtures with the surface of the mixture enriched with Cu due to its lower surface energy (note that Ni and Cu form an alloy, while Co and Cu form separate phases), which decorate the surface of the oxide. The hydrocarbon stability tests and the electrochemical performance measurement demonstrated that majority of the Co nanoparticles must be at least partially coated with the Cu, with some isolated Co atoms in the surface Cu layer providing the catalytic activity for $H_2$ oxidation. However, an unusually complex behavior was exhibited by the cell anode overpotentials.

References


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