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Abstract

Cu-based, solid oxide fuel cell (SOFC) electrodes were modified by electrodeposition of Co. The addition of only 5-vol% Co by electrodeposition significantly improved the thermal stability compared to either Cu-ceria-YSZ, Cu-Co-ceria-YSZ, or Co-ceria-YSZ electrodes prepared only by impregnation with much higher metal loadings, demonstrating that electrodeposited metal layers form metal films with better connectivity. In the absence of Co, SEM showed structural changes in the impregnated Cu after heating to 1173 K in humidified H₂ and these changes caused large increases in the ohmic resistance of fuel cells, as measured by impedance spectroscopy. In contrast, the ohmic resistance of a cell with 13-vol% Cu, 9-vol% ceria, and 5-vol% Co increased only slightly after 48 h at 1173 K in humidified H₂. While a Co-ceria-YSZ composite was found to form large amounts of carbon upon exposure to dry CH₄ at 1073 K for 3 h, the Co-Cu-ceria-YSZ composites did not form measurable amounts of carbon for the same conditions. XPS results for a Cu foil with a 250-nm Co film demonstrated that Cu migrates to the surface of the Co upon heating above 873 K, forming a stable Cu layer that appears to be approximately one monolayer thick. The implication of these results for the development of practical SOFC electrodes for the direct utilization of hydrocarbons is discussed.

Keywords

solid oxide fuel cells; electrodeposits; thermal stability; methane tolerance; cobalt

Comments

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A Study of Thermal Stability and Methane Tolerance of Cu-Based SOFC Anodes with Electrodeposited Co

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Abstract

Cu-based, solid oxide fuel cell (SOFC) electrodes were modified by electrodeposition of Co. The addition of only 5-vol% Co by electrodeposition significantly improved the thermal stability compared to either Cu-ceria-YSZ, Cu-Co-ceria-YSZ, or Co-ceria-YSZ electrodes prepared only by impregnation with much higher metal loadings, demonstrating that electrodeposited metal layers form metal films with better connectivity. In the absence of Co, SEM showed structural changes in the impregnated Cu after heating to 1173 K in humidified H₂ and these changes caused large increases in the ohmic resistance of fuel cells, as measured by impedance spectroscopy. In contrast, the ohmic resistance of a cell with 13-vol% Cu, 9-vol% ceria, and 5-vol% Co increased only slightly after 48 h at 1173 K in humidified H₂. While a Co-ceria-YSZ composite was found to form large amounts of carbon upon exposure to dry CH₄ at 1073 K for 3 h, the Co-Cu-ceria-YSZ composites did not form measurable amounts of carbon for the same conditions. XPS results for a Cu foil with a 250-nm Co film demonstrated that Cu migrates to the surface of the Co upon heating above 873 K, forming a stable Cu layer that appears to be approximately one monolayer thick. The implication of these results for the development of practical SOFC electrodes for the direct utilization of hydrocarbons is discussed.

Introduction

Direct utilization of hydrocarbons in fuel-cell systems could provide significant advantages. Theoretically, direct utilization is possible in solid oxide fuel cells (SOFC) because the ceramic electrolytes transport oxygen anions rather than protons; in practice, it is usually necessary to reform hydrocarbons before sending them to an SOFC anode because of the problem of carbon deposition [1-3]. While gas-phase pyrolysis reactions can contribute to the carbon-deposition problem [4-5], surface reactions are primarily responsible for anode fouling. The large majority of SOFC use a Ni-based anode and Ni catalyzes the formation of filamentous carbon [6]. Carbon formation can often be avoided by replacing Ni with an electron conductor that does not catalyze carbon formation, such as Cu [7-9]. However, Cu-based anodes exhibit relatively poor thermal stability due to sintering of the interconnected Cu network and resulting in a loss of electrode conductivity [10].

One approach for improving thermal stability is to use bimetallic electrodes in which Cu provides carbon tolerance and a second metal provides thermal stability, and this motivation has led our laboratory to investigate several bimetallic compositions. Anodes based on Cu-Ni mixtures were not found to be very effective at suppressing carbon formation, primarily because Cu and Ni form solutions. When Cu-Ni mixtures were exposed to dry CH_4 at 1073 K to determine their tendency to form carbon, it was found that the mixture needed to contain at least 80% Cu in order to significantly suppress carbon formation [11]. Anodes based on Cu-Co mixtures were found to be effective at suppressing carbon formation. For this system the two metals do not form a solution, but rather exist in the form of two separate phases [11-12]. Because the Cu-rich phase apparently coats the Co, even bimetallic compositions containing small amounts of Cu were found to strongly suppress carbon formation.

More recently, we have investigated Cu-Cr electrodes [13]. In the previous work with Cu-Ni and Cu-Co mixtures, the composite electrodes were prepared by impregnation of the metal salts into porous yttria-stabilized zirconia (YSZ), followed by reduction of the metal ions to their metallic state. Because oxides of Cr cannot be readily reduced, the Cu-Cr electrodes were produced by electrodeposition of Cr onto the Cu-YSZ composite. Electrodeposition introduces Cr metal directly and also produces a layered structure, since deposition occurs only on conductive substrates that are connected to the outside circuit. Results from electrodeposition of Cu onto a Ni-YSZ cermet indicated that this technique was very effective at selectively coating

the Ni component of the composite [14]. Unfortunately, dissolution of Ni into the Cu layer at SOFC operating temperatures will likely make the Cu-Ni electrodes an unstable system for long-term operation. In the Cu-Cr study, it was demonstrated that the Cr significantly enhanced the thermal stability of electrodes in dry H₂. Unfortunately, the addition of H₂O to the H₂ caused oxidation of the Cr films and loss of the enhanced thermal stability.

In the present study, we examined Cu-Co electrodes prepared by electrodeposition of Co onto a reduced Cu. As with Cr, we expected that Cu and Co would remain as separate phases; unlike Cr, Co should remain in a reduced state under the range of P(O₂) expected in the anode compartment. The results of this study demonstrate that the Co layer does improve the thermal stability of Cu-based anodes. Furthermore, the incorporation of an electrodeposited layer of Co onto the Cu provides better thermal stability than co-impregnated Cu-Co electrodes with similar metal loadings, probably due to differences in the structure of the metal films prepared by electrodeposition. While Co catalyzes the formation of carbon fibers in the same way as Ni, it is found that Cu migrates through Co films and coats Co surfaces after heating above approximately 873 K to impart good carbon tolerance.

Experimental

The methods used for fabricating cells were similar to those described elsewhere [8], except that in the present work a thick electrolyte was used for structural support. This allowed for the use of a thin anode layer which simplified the electrodeposition of Co by allowing the plating process to be performed in a few minutes without causing concentration gradients in the plating bath. The first step in synthesizing the cells was to prepare a 1.2-cm diameter, YSZ (8 mol % Y₂O₃-doped Zr₂O₃, Tosoh) wafer, one side of which was dense and one side porous. The wafer was made by laminating together two green tapes, one of which contained graphite (Alfa Aesar, mesh 325) pore formers, then firing the green body to 1823 K for 4 h. The dense side of the wafer was 300-μm thick while the porous side was 35-μm thick and approximately 65% porous. Before adding the anode components to the porous layer of the YSZ wafer, a 50-wt% mixture of YSZ and La_{0.8}Sr_{0.2}MnO₃ (LSM, Praxair Technologies) was mixed with graphite (10 wt %) and applied to the dense side of the YSZ wafer with a glycerol slurry. This cathode layer, 0.18 cm² in area, was then calcined to 1523 K.

The anode was prepared by initially impregnating Ce and Cu salts into the porous side of the YSZ wafer. The anodes in all of the cells in this study contained 9-vol% ceria, which was

added by impregnation of a $\text{Ce}(\text{NO}_3)_3$ aqueous solution, followed by calcination in air at 723 K to decompose the nitrate ions. The ceria in the anode structures was calcined in air at 1173 K for an additional 12 h before adding Cu so as to make the ceria less soluble in acids during electrodeposition. After ceria addition, the anodes were impregnated multiple times with aqueous solutions containing urea together with either $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, or mixtures of $\text{Cu}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$. After each impregnation, the sample was calcined to 723 K in air to form the oxides. Urea was included with the metal salts to produce a more uniform metal distribution in the pore structure [10].

For those cells that had electrodeposited Co, the equivalent of 13-vol% Cu was first added to the porous layer, after which the entire cell was reduced in humidified (3% H_2O) H_2 at 723 K for 2 h. These reducing conditions were sufficient to completely reduce CuO to its metallic state without destroying the LSM cathode layer [15]. The initial Cu loading was chosen to be 13-vol% which was the minimum loading required for complete electrical connectivity of the Cu in the electrode. When smaller amounts of Cu were added, electrodeposition of additional metal was visibly non-uniform due to the fact that plating can only occur on particles that are electrically connected to the external circuit. After reduction of the cell, a Ag wire was attached to the Cu-containing electrode using Ag paste and the LSM cathode layer was sealed with wax to keep it from being exposed to the plating bath.

Co was plated onto the Cu under galvanostatic conditions with a Gamry potentiostat (Model 1286A). In order to achieve uniform plating of the Co inside the porous electrode, it was necessary to avoid both Co(II) concentration gradients and potential gradients in the plating solution within the YSZ pores [14]. Concentration gradients were minimized by using low plating current and a relatively high concentration of Co(II) in the plating solution. Potential gradients in the solution were minimized by increasing the solution conductivity. The Co electrolyte solution contained 100 g/L $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 60 g/L H_3BO_3 , with HCl added until the solution had a pH of 2. The electrodeposition current was maintained at 10 mA and a Co-foil counter electrode was used. The temperature of the electrolyte solution was 323 K; upon completion of the plating process, the electrode was rinsed with deionized water. The Co content was maintained at 5-vol% unless otherwise noted.

The phases present within the anodes, before and after exposure to operating conditions, were determined by x-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation. Scanning electron

microscopy (SEM) was used to analyze the morphology of the metal components both before and after heating to higher temperatures. To characterize the surface composition of the Cu-Co electrodes, model samples were prepared by electrodepositing a 250-nm layer of Co onto a 0.8-mm thick Cu foil. These samples were analyzed by x-ray photoelectron spectroscopy (XPS) in an ultrahigh vacuum (UHV) system with a base pressure of $\sim 2 \times 10^{-10}$ Torr that was equipped with an ion sputter gun.

For fuel cell testing, the electrical contacts were achieved with Au wire and Au paste at the anode and with Ag wire and Ag paste at the cathode. The cells were attached to an alumina tube with a ceramic adhesive (Aremco, Ceramabond 552). Impedance spectra were measured in the galvanostatic mode with a frequency range of 0.1 Hz to 100 KHz and a 1-mA ac perturbation using a Gamry Instruments impedance analyzer. The ohmic resistances of cells were determined from the high frequency intercept with the abscissa on the Cole-Cole plots of the impedance spectra. Because we did not use reference leads, a small ohmic contribution, $\sim 0.2 \Omega \cdot \text{cm}^2$ at 1173 K, was present in all of the spectra. To accelerate sintering processes that would cause cell deactivation, cell testing was performed at 1173 K, a much higher temperature than we expect would be used for operation of direct-utilization anodes.

Results

Phase Structure

The Cu-Co, bimetallic composites that were prepared by electrodeposition were first characterized by XRD to establish the metal phases that were formed. These samples had 9-vol% ceria, 13-vol% Cu, and 5-vol% Co. The XRD patterns in the range from 41 to 53 degrees 2θ obtained immediately after deposition of the Co and following reduction of the composite in humidified H_2 at 1173 K for 5 h are shown in Fig. 1. The as-deposited composite, Fig. 1a), shows peaks for Cu and YSZ in their expected positions. Immediately after deposition, the Co is in the hexagonal HCP form, as indicated by the single peak at 47.5 degrees. Reduction at 1173 K had no effect on the Cu diffraction line, Fig. 1b), demonstrating that alloy formation did not occur. High-temperature reduction caused a significant fraction of the Co to transform to the cubic FFC structure.

Morphological Structure

Fig. 2 shows SEM images of Cu-ceria-YSZ composites with 18-vol% Cu and 9-vol% ceria upon reduction in H_2 at 723 K for 2 h (Fig. 2b)) and 1173 K for 5 h (Fig 2c)). To help

distinguish the metal in these images, a micrograph of a similar sample with only 9-vol% ceria is shown in Fig. 2a). The images show that ceria forms a rough, relatively uniform coating over the YSZ pores. Upon the addition of CuO and reduction at 743 K, well-connected, Cu particles of irregular shape are formed, having characteristic dimensions of less than 0.5 μm . After heating to 1173 K, the Cu forms isolated, essentially spherical particles. On some of the larger particles, crystallographic facets can be observed. For electrode applications, the loss in connectivity of the Cu phase is disastrous in that electrical conductivity is lost.

SEM micrographs for a Cu-Co composite with 9-vol% ceria, 13-vol% Cu, and 5-vol% Co are shown in Fig. 3. Immediately following the deposition of Co (Fig. 3a)), the metal film appears to cover the pores more evenly than the 18-vol% Cu layer in Fig. 2b). The average Cu-Co layer has the appearance of a sintered layer of 0.1- μm particles. This difference in appearance may be due to the electrodeposition process covering over rough edges in the metal layer. After heating the Cu-Co composite to 1173 K in H_2 for 5 h, Fig. 3b) shows that the metal sinters into continuous metal film. The formation of large Cu spheres observed in Fig. 2c) is clearly suppressed, even though the XRD results showed Cu and Co remain in separate phases. For electrode applications, the connectivity of the metal film in Fig. 3b) is clearly desirable.

Electrode Performance and Stability

To determine the effect of film morphology on cell performance, a series of 300- μm thick, electrolyte-supported cells that were identical except for the amount and structure of the metal phase were prepared and then characterized using electrochemical measurements at 1173 K as a function of time. The anodes in each of the cells were 35- μm thick and contained 9-vol% ceria. The V-i curves and corresponding impedance spectra for a cell with 18-vol% Cu and no Co are shown in Figs. 4 and 5 after various operating times. The performance of the cell is already low after 1 h at 1173 K, showing a maximum power density of less than 120 mW/cm^2 , and the performance degraded over time, with a maximum power density of only 60 mW/cm^2 after 48 h. The cause for the low performance is readily apparent in the impedance spectra. Even after 1 h, the ohmic contribution, determined from the high-frequency intercept with the abscissa, was 0.88 Ωcm^2 . Since the electrolyte and leads to the cell contribute a combined resistance of 0.5 Ωcm^2 at 1173 K, a significant portion of the ohmic losses are due to the anode, even after 1 h. After 48 h, the ohmic losses are greater than 2.4 Ωcm^2 . At this point, most of the conductivity in the anode is likely due to the ceria layer. No attempt was made to analyze the non-ohmic

contributions to the spectra, since poorly conducting electrodes also tend to show high polarization losses [10].

Because the increase in ohmic loss as a function of time is a good measure of connectivity in the metal phase of the anode, this property was used to monitor the thermal stability of cells as a function of metal content and preparation method. The results of these studies are shown in Fig. 6. The data for the cell with 18-vol% Cu have already been discussed and are included in the plot. The cell with the best performance was the one with 13-vol% Cu and 5-vol%, electrodeposited Co. The initial ohmic contribution to the impedance spectrum at 1173 K was close to that expected for the electrolyte and leads, $0.55 \Omega \cdot \text{cm}^2$. This increased to $0.72 \Omega \cdot \text{cm}^2$ after 48 h, but the metal phase still exhibited reasonable connectivity. The overall performance of this cell was also reasonably good, exhibiting a total cell resistance of $0.80 \Omega \cdot \text{cm}^2$ and a maximum power density of 375 mW/cm^2 . Decreases in the power density as a function of time scaled with the increased ohmic resistance.

The method by which Co is added to the electrode will affect the structure of the metal phase, which in turn could affect the thermal stability. Therefore, a cell with 13-vol% Cu and 5-vol% Co prepared by co-impregnation of the metal salts was also tested. Surprisingly, the data in Fig. 6 shows that this cell exhibits only slightly better performance than the cell with only Cu in the metal phase. After 1 h at 1173 K, the ohmic losses were above $0.8 \Omega \cdot \text{cm}^2$; this increased to above $2 \Omega \cdot \text{cm}^2$ after 48 h. The structure of the metal phase must play a large role in maintaining connectivity. To determine whether this loss in connectivity is associated with Cu, we also examined cells with 18-vol% Co and 30-vol% Co, prepared by impregnation. Again, the cell with 18-vol% Co was only marginally better than that of the cell with 18-vol% Cu, with the ohmic loss increasing to $1.6 \Omega \cdot \text{cm}^2$ after 48 h. The cell with 30-vol% Co approached the stability of the cell with electrodeposited Co, but the 30-vol% Co cell still showed a slight initial increase in the ohmic losses during the first hour of operation at 1173 K. (It was determined that anode conductivity in the 30-vol% Co cell was lost during the first hour at 1173 K by briefly cooling the cell to 973 K and showing that the ohmic resistance had increased from its initial value, prior to the cell reaching 1173 K.) Based on the observations with impregnated Co, electrodeposition of Co onto Cu forms a more stable metal film at much lower Co contents.

Surface Composition

One of the primary motivations for preparing anodes by addition of metals into a porous YSZ substrate, rather than using conventional Ni-based composites, is that electrodes can be made of metals that will not catalyze carbon formation [7-9]. In this regard, Co is similar to Ni in that it readily catalyzes the formation of carbon fibers upon exposure to dry methane and other hydrocarbons [16]. Because electroplating of Co onto Cu will cause Co to be at the surface of the metal phase, we expected that it would be necessary to plate Cu onto the Co in order to suppress carbon formation when operating cells with hydrocarbons. However, Cu plating was unnecessary due to the migration of Cu onto the Co surface.

Evidence for Cu migration onto the Co film is shown by the photograph in Fig. 7. The picture is of the anode side of two cells that were each heated in dry H₂ to 1073 K, then exposed to dry CH₄ at 1073 K for 3 h, and finally cooled back to 298 K in dry H₂. The cell on the right was made by impregnation of 9-vol% ceria and 18-vol% Co into the porous YSZ, while the cell on the left had 9-vol% ceria, 13-vol% Cu, and 5-vol% electrodeposited Co. In agreement with the literature, large amounts of carbon formed on the Co-only electrode. Visual inspection showed no evidence for any carbon on the Cu-Co cell.

To better understand why the Cu-Co electrode did not form carbon, a 250-nm Co film on a Cu foil was prepared by electrodeposition and the surface composition was measured using XPS as a function of annealing temperature in vacuum. XPS is surface sensitive because the photoelectrons at the detection energies have a mean-free-path of approximately 2 nm. Spectra were collected at 298 K immediately after deposition and after heating in ultra-high vacuum to 473, 673, 873, and 1073 K. Fig. 8 shows the raw data for the 2p regions of the spectra associated with Co (Fig. 8a)) and Cu (Fig. 8b)), while Fig. 9 shows the Cu(2p_{3/2}):Co(2p_{3/2}) peak-intensity ratios determined from this raw data. The data show a dramatic increase in the intensity of the peaks associated with Cu beginning at 873 K, with an additional increase after heating to 1073 K. This increase can be seen more easily from the Cu(2p_{3/2}):Co(2p_{3/2}) intensity ratio in Fig. 9.

Although an increase in the Cu peak intensity could be caused by the Co film coalescing into particles, two additional observations contradict this interpretation. First, the Co peak intensities in Fig. 8a) remained almost constant. The constant Co peak intensity also indicates that the Cu coverage is never more than a few monolayers thick. Second, after annealing to 1073 K, the sample was sputtered with $\sim 10^{16}$ Ar⁺ ions/cm², a flux similar to what would be required to

remove one monolayer. As shown in both Figs. 8b) and Fig. 9, this caused a significant decrease in the Cu peak intensities, suggesting that Cu is present at approximately one monolayer.

Discussion

The most important observation from this study is that high thermal stability can be achieved through electrodeposition of Co films onto impregnated Cu particles. Furthermore, this thermal stability is achieved with much smaller amounts of Co than would be necessary if the metal were added by impregnation. The structure of the Co incorporated by electrodeposition is very different from that incorporated by impregnation. The electrodeposited Co appears to fill the gaps that are present in the impregnated Cu layers, allowing a more continuous, stable metal film to be prepared. Metal layers prepared by the impregnation process appear to be more randomly distributed within the pore structure, so that larger metal amounts are required for connectivity in the metal film. The data indicate that electrodeposition allows the preparation of a film that more uniformly covers the pore structure.

Based on the surface-characterization studies, Cu readily migrates to the Co surface, forming approximately one monolayer over the Co surface after only modest annealing conditions. Based on earlier work with Cu-Co mixtures, the driving force for forming the Cu monolayer involves attractive, Cu-Co interactions and a decrease in the free energy of the Cu-Co system, due to Cu having a lower surface energy than Co [17]. The fact that Cu can migrate through a relatively thick, 250-nm Co film to get to the Co surface by 873 K guarantees that Cu overlayers in Cu-Co electrodes will form spontaneously in Cu-Co bimetallic electrodes.

Given the high mobility of Cu in Cu-Co mixtures at fuel-cell operating temperatures, it is interesting that Cu is so effective in forming a passivating layer over the Co. In the present study, the Cu-Co electrodes were exposed to dry CH₄ for only 3 h, but an earlier study with co-impregnated Cu and Co exhibited negligible carbon formation, even after exposure to CH₄ for 500 h [12]. The opportunity that this presents is obvious. As the present work demonstrates, bimetallic Cu-Co electrodes can provide the thermal stability of Co with the carbon tolerance of Cu.

Finally, it should be noted that the electrodeposition process is very flexible. In principle, it could be applied to producing electrodes with three metals or to produce alloys. The technique can also be applied to produce coatings on conventional, metal-ceramic composites, as was recently demonstrated with Cu deposited onto Ni-YSZ cermets [14]. Given the propensity of Cu

to migrate to Co surfaces, the deposition of Cu onto Co-YSZ cermets would likely result in electrodes that would be highly tolerant towards carbon formation in the presence of methane. The purpose of this study was to demonstrate concepts that could be applied to the development of thermally stable, direct-utilization electrodes. We believe there is still much one can do to further improve these systems.

Conclusion

Electrodeposition of Co onto a Cu-ceria-YSZ composite can dramatically improve the thermal stability of SOFC electrodes. Electrodes prepared by electrodeposition of Co exhibit much better thermal stability than Co-ceria-YSZ electrodes prepared by Co impregnation and having much higher Co loadings, suggesting that the electrodeposited film has a different, more "connected" structure. Because Cu readily diffuses through the Co film and forms a monolayer of Cu on the Co, the Co-Cu-ceria-YSZ electrodes have excellent tolerance to carbon formation in hydrocarbon fuels.

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- Fig. 1 XRD patterns of Co-Cu-ceria-YSZ (5-vol% electrodeposited Co, 13-vol% Cu, 9-vol% ceria) (a) as-deposited and (b) after exposure to humidified H₂ at 1173 K for 5 h. The various phases are marked (▲) Co hexagonal close-packed and (●) Co face-centered cubic.
- Fig. 2 SEM micrographs of (a) a ceria-YSZ composite (9-vol% ceria) and a Cu-ceria-YSZ composite (18-vol% Cu, 9-vol% ceria) following reduction in humidified H₂ at (b) 723 K for 2 h and (c) 1173 K for 5 h.
- Fig. 3 SEM micrographs of a Co-Cu-ceria-YSZ composite (5-vol% electrodeposited Co, 13-vol% Cu, 9-vol% ceria) (a) as-deposited and (b) following reduction at 1173 K for 5 h.
- Fig. 4 Cell performance curves at 1173 K in humidified H₂ for Cu-ceria-YSZ (18-vol% Cu, 9-vol% ceria) following exposure to 1173 K for (○) 1 h, (◇) 6 h, and (Δ) 48 h.
- Fig. 5 Impedance spectra at 1173 K in humidified H₂ for Cu-ceria-YSZ (18-vol% Cu, 9-vol% ceria) following exposure to 1173 K for (○) 1 h, (◇) 6 h, and (Δ) 48 h. The spectra were obtained at the current density corresponding to the maximum power density.
- Fig. 6 Ohmic resistance measurements at 1173 K in humidified H₂ as a function of time for (○) Co-Cu-ceria-YSZ (5-vol% electrodeposited Co, 13-vol% Cu), (◇) Cu-ceria-YSZ (18-vol% Cu), (Δ) Co-Cu-ceria-YSZ (co-impregnation of 5-vol% Co and 13-vol% Cu), (□) Co-ceria-YSZ (18-vol% Co), and (x) Co-ceria-YSZ (30-vol% Co).
- Fig. 7 Photograph of (a) Co-Cu-ceria-YSZ (5-vol% electrodeposited Co, 13-vol% Cu) and (b) Co-ceria-YSZ (18-vol% Co) after reduction in dry H₂ at 1073 K and exposure to dry CH₄ for 3 h at 1073 K.
- Fig. 8 XP spectra of the (a) Co(2p) region (2p_{1/2} left and 2p_{3/2} right) and (b) Cu(2p) region (2p_{1/2} left and 2p_{3/2} right) as a function of temperature and upon sputtering after heating to 1073 K.
- Fig. 9 Cu(2p_{3/2}):Co(2p_{3/2}) peak intensity ratios as a function of temperature and upon sputtering after heating to 1073 K.

Fig. 1

Fig. 2

Fig. 3.

Fig. 4

Fig. 5.

Fig. 6

Fig. 7

Fig. 8

Fig. 9