

Role of Hydrocarbon Deposits in the Enhanced Performance of Direct-Oxidation SOFCs

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We have examined the changes that occur in the performance of solid oxide fuel cells (SOFCs) with Cu-ceria-yttria-stabilized zirconia anodes at 973 K following exposure to various hydrocarbon fuels, including methane, propane, n-butane, n-decane, and toluene. For cells with Cu contents of 20 wt % or less, large increases were observed in the power densities for operation in H_2 after the anode had been exposed to any of the hydrocarbons except methane. The increased performance is completely reversible upon oxidation of the anode and subsequent reduction in H_2 . The enhancement decreases with increasing Cu content, implying that the deposits improve the connectivity of the metallic phase in the anode. Impedance spectra taken on cells before and after exposure to hydrocarbon fuels confirm that the conductivity of the anode improves after exposure. Temperature-programmed oxidation and weight changes were used to show that the deposits that enhance performance correspond to ~ 1 wt % of the anode and are probably not graphitic. Measurements of the open-circuit voltages in hydrocarbon fuels change upon current flow. Finally, the implications of these results for operation of SOFC on hydrocarbons without added steam and with low copper contents are discussed.

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The materials used to make anodes in solid oxide fuel cells (SOFCs) must meet several demanding requirements.¹ First, the anode must be electronically conductive at high temperatures, in reducing environments, to remove electrons produced by electrochemical oxidation of the fuel. Second, the thermal coefficient of expansion TCE for the anode must match that of the electrolyte so as to prevent delamination upon heating and temperature cycling. Third, the anode material must catalyze the electrochemical oxidation of the fuel. The material most commonly used for SOFC anodes is a composite of Ni and yttria-stabilized zirconia (YSZ). The YSZ phase of this ceramic-metallic (cermet) composite provides a TCE match to the YSZ electrolyte, supports the Ni particles, and inhibits coarsening of the Ni at the operating temperature. The Ni phase of the anode provides electronic conductivity and some hydrocarbon catalytic-reforming activity. The Ni content is usually above 30 vol % so as to maintain the required level of electronic conductivity.²

A major limitation to Ni cermet anodes is that Ni catalyzes graphite formation in the presence of hydrocarbons unless there is sufficient steam to simultaneously remove carbon as it forms.^{3,4} Therefore, it is not feasible to expose a Ni-based anode to dry hydrocarbons. Based on the catalytic properties of various electronic conductors that could be used in the anode, we focused our attention on developing Cu-based anodes for SOFCs.⁵⁻⁹ Compared to Ni, Cu is not catalytically active for the formation of C—C bonds. Its melting temperature, 1083°C, is low compared to that of Ni, 1453°C; however, for low temperature operation, <800°C, Cu is likely to be sufficiently stable.

Because Cu₂O and CuO melt at 1235 and 1326°C, respectively, temperatures below those that are necessary for densification of YSZ electrolytes, it is not possible to prepare Cu-YSZ cermets by high temperature calcination of mixed powders of CuO and YSZ, a method analogous to that usually used as the first step to produce Ni-YSZ cermets. Therefore, an alternative method for preparation of Cu-YSZ cermets was developed in which a porous YSZ matrix was prepared first, followed by addition of Cu and an oxidation catalyst in subsequent processing steps.^{6,8} Because the Cu phase in the final cermet must be highly connected, high metal loadings are necessary; and, even then, connectivity between all Cu particles in the anode structure is not assured.

In this paper, we will demonstrate that metallic connectivity can limit the performance of the Cu cermet anodes. Fortunately, it ap-

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pears that carbonaceous compounds are formed by larger hydrocarbons in the anodes and that these compounds help to provide connectivity and increase performance. Even at open circuit, the carbonaceous layer appears to reach a steady-state coverage and does not lead to deactivation of the cell.

Experimental

The methods we have used for preparing and testing fuel cells with Cu cermet anodes have been discussed in other papers.^{6,8} Because oxides of Cu melt at temperatures lower than that required for sintering of the oxide components, the fabrication procedure involved preparing a porous matrix of YSZ, impregnating this porous matrix with Cu salt, and finally reducing the salt to metallic Cu.

In the first step, the dense electrolyte layer and the porous YSZ matrix were prepared simultaneously by tape-casting methods. A two-layer, green tape of YSZ, (Tosoh, 8 mol % Y₂O₃, TZ-84) was made by casting a tape with graphite and poly-methyl methacrylate (PMMA) pore formers over a green tape without pore formers. Firing the two-layer tape to 1800 K resulted in a YSZ wafer having a dense side, 60 µm thick, supported by a porous layer, 600 µm thick. The porosity of the porous layer was determined to be \sim 70% by water uptake measurements.9 Next, a 50:50 mixture of YSZ and La_{0.8}Sr_{0.2}MnO₃ (LSM, Praxair Surface Technologies) powders was applied as a paste onto the dense side of the wafer, then calcined to 1400 K to form the cathode. Third, the porous YSZ layer was impregnated with an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ and calcined to 723 K to decompose the nitrate ions and form CeO₂. The porous layer was then impregnated with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and again heated to 723 K in air to decompose the nitrates. All of the cells used in this study were 10 wt % CeO₂, but the Cu content was varied between 5 and 30 wt %.

Electronic contacts were formed using Pt mesh and Pt paste at the cathode and Au mesh and Au paste at the anode. Each cell, having a cathode area of 0.45 cm^2 , was sealed onto 1.0 cm alumina tubes using Au paste and a zirconia-based adhesive (Aremco, Ultra-Temp 516). The entire cell was then placed inside a furnace and heated to 973 K at 2 K/min in flowing H₂. H₂, CH₄, propane, and n-butane were fed to the cell undiluted, while toluene and decane were fed as 75 mol % mixtures with N₂. All hydrocarbons, including those that are liquids at room temperature, were fed directly to the anode without reforming, as discussed elsewhere.¹⁰

The performance at 973 K for each cell was measured by its voltage-current (V-I) curves with n-butane and H_2 fuels, with impedance spectra providing additional information on selected

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Figure 1. Power density as a function of time at 973 K. The cell potential was maintained at 0.5 V while the fuel was switched from H_2 , to n-butane, and back to H_2 . The anode consisted of 10% CeO₂ and 20% Cu.

samples. Since the cathodes and electrolytes were prepared in a similar manner in all cases, changes in the fuel cell performance and in the impedance spectra can be attributed to changes in the anode. Since the fuel flow rates were always greater than $1 \text{ cm}^3/\text{s}$ at room temperature, the conversion of the hydrocarbon fuels was always less than 1%, so that water produced by the electrochemical oxidation reactions was negligible. The impedance spectra were obtained in galvanostatic mode at close to the open-circuit voltage (OCV), using a Gamry Instruments, model EIS300.

The amount of carbon present in the SOFC anode after treatment in n-butane was also measured. To accomplish this, anode cermet samples were exposed to flowing n-butane in a quartz flow reactor at 973 K for various periods of time. We then measured either the sample weight or the amount of CO and CO₂ that formed upon exposure to flowing O₂. In the weight measurements, the sample temperature was ramped to 973 K in flowing He, exposed to flowing n-butane for a limited period, and then cooled in flowing He. Following longer exposures, the samples were flushed in flowing He at 973 K for 24 h before cooling.

In the second method for measuring carbon contents in the anode, samples were exposed to n-butane in the flow reactor at 973 K and flushed with He. Then the sample was exposed to a flowing gas consisting of a 15% O2-85% He mixture and the reactor effluent was monitored with a mass spectrometer. The amount of carbon in the sample was determined from the amounts of CO and CO₂ leaving the reactor. The type of carbon formed was also characterized by TPO in a similar manner. In these measurements, a cermet sample was exposed to flowing n-butane at 973 K for 30 min. The reactor was cooled to 298 K in flowing He and again ramped to 973 K at a rate of 10 K/min in a flowing gas mixture of 15% O2-85% He. In principle, TPO experiments carried out with a mass spectrometer would enable the calculation of carbon-to-hydrogen ratios because the detector should be able to determine the amount of hydrogen in the deposits; however, the background signal for water in our vacuum system was too high to allow accurate measurement of this quantity. A sample of 0.03 g of graphite powder (Alpha Aesar, conducting grade 99.995%) was placed in an identical reactor and heated in a 15% O₂-85% He stream at 10 K/min for comparison. Scanning electron microscope (SEM) measurements of the graphite sample suggested that the particles were shaped as platelets, less than 10 µm in thickness.

Results

The effect of treating the Cu cermet anodes in a hydrocarbon fuel at 973 K is demonstrated by the results in Fig. 1. In this experiment,



Figure 2. Performance curves in H_2 for a cell with an anode consisting of 10% CeO₂ and 15% Cu at 973 K. Results are shown (\blacklozenge) following the initial heating in H_2 (\triangle) followed by 1 h in n-butane fuel, (\diamondsuit) subsequent exposure to 10% O₂ in He, and (\triangle) after exposure to n-butane.

the power density at 0.5 V is shown for a cell with 20 wt % Cu as a function of time while changing the fuel from H_2 , to n-butane, and back to H_2 . The anode had initially been exposed to H_2 for a period of several hours and the cell exhibited a power density of only 0.065 W/cm². Upon changing the feed to pure n-butane, the power density increased to a value of 0.135 W/cm² following a brief transient period. After operating the cell in n-butane for 20 min, the feed was switched to pure H_2 and the power density increased to 0.21 W/cm², a factor of 3.2 greater than the power density that had been observed prior to exposing the anode to n-butane.

This enhancement of cell performance after exposure to n-butane was found to be fully reversible upon reoxidation of the anode. In Fig. 2 and 3, V-I curves and impedance spectra at 973 K are shown after various pretreatments for a cell operating in pure H_2 , with an anode consisting of 10 wt % CeO₂ and 15 wt % Cu. Data are shown for the cell after the initial reduction of the anode in H_2 , after exposing the anode to pure n-butane for 60 min then after exposing it to 15% O₂ in He for 30 min and, finally, after a further 60 min exposure to n-butane. (Following the oxidation cycle, the anode was held in H_2 for 30 min before recording the data.) Initially, Fig. 2 shows that the maximum power density in H_2 was 0.045 W/cm². This increased to 0.16 W/cm² after a 1 h exposure to n-butane.



Figure 3. OCV impedance spectra in H₂ from a cell with an anode consisting of 10% CeO₂ and 15% Cu at 973 K. Results are shown (\blacklozenge) following the initial heating in H₂, (\blacktriangle) followed by 1 h in n-butane fuel, (\diamondsuit) subsequent exposure to 10% O₂ in He, and (\bigtriangleup) after exposure to n-butane.



Figure 4. V-I (closed symbols) and power/density (open symbols) curves for a cell with an anode consisting of 10% CeO₂ with various Cu loadings. The measurements used H₂ as the fuel at 973 K. The data are shown (\blacklozenge) before and (\blacktriangle) after 30 min exposure to n-butane.

Following oxidation in 15% O_2 and reduction in H_2 , the performance curve returned to its initial value. Finally, exposing the cell to n-butane once again increased the performance curve to its higher value.

Figure 3 shows the impedance curves, measured in H₂ at OCV, associated with the V-I curves in Fig. 2. The enhanced performance upon exposure to n-butane and the reversibility upon re-oxidation are evident from the total cell resistances, which are approximately $6 \Omega \text{ cm}^2$ before treatment in n-butane and $1.4 \Omega \text{ cm}^2$ after treatment in n-butane. Of additional interest, the ohmic resistance of the cell, R_{Ω} , measured by the high frequency intercept with the real axis, decreased from ~2.9 $\Omega \text{ cm}^2$ to ~0.6 $\Omega \text{ cm}^2$ after n-butane treatment. Normally, R_{Ω} is associated with the conductivity of the electrolyte. Migration of charged species in mixed-conducting anodes and cathodes gives rise to an interfacial resistance, $R_{\rm I}$, taken to be the difference between the high and low frequency intercepts with the real axis. $R_{\rm I}$, too, decreases from more than $3 \Omega \text{ cm}^2$ to ~1 $\Omega \text{ cm}^2$ after treatment in n-butane.

Similar increases in performance and changes in impedance spectra were reported for an SOFC made with Cu-Ni alloy cermets after long exposures to methane.¹¹ In that paper, it was suggested that there was initially poor connectivity between the metal particles in the cermet anode and that carbon fibers formed by reaction of

methane on Ni allowed conduction of electrons between metal particles. We suggest that similar arguments must be used to explain the results in Fig. 1 to 3. Indeed, one must conclude that there is initially poor connectivity between metal particles in the anode based on the high initial ohmic resistance in Fig. 3. R_{Ω} should be less than 1 Ω cm² for our cell based on literature values for the conductivity of YSZ at 973 K and the thickness of our electrolyte. The fact that R_{Ω} is initially much larger than this implies that part of the ohmic resistance must be in the anode.

An obvious implication of the above conclusion is that increased Cu contents should improve the initial performance and possibly reduce the enhancement observed with treatment in hydrocarbon fuels. This is indeed the case, as shown in Fig. 4 and 5. In Fig. 4a through 4d, V-I curves, with pure H₂ at 973 K, are reported for cells containing 5, 10, 20, and 30% copper, before and after exposure to n-butane for 30 min. The ceria content and YSZ structure were identical in all of the cells. Fig. 4a and b indicate that the initial performance for cells with a low Cu content is poor, but increases dramatically upon exposure to n-butane. The maximum power density increased by a factor of 3.5 for these two cases. The data for the cell with 20% copper, Fig. 4c, showed a more modest improvement, with the maximum power density increasing by a factor of only 2.5 after treatment with n-butane. Finally, data for the cell with 30%



Figure 5. OCV impedance spectra in H₂ for cells having anodes with different copper loadings at 973 K: (\blacksquare) 5% Cu, (\blacktriangle) 10% Cu, (\blacklozenge) 20% Cu, (\blacklozenge) 30% Cu, (a) before and (b) after n-butane exposure.

copper showed only small changes in the performance curves after exposure to n-butane.

Impedance spectra measured at OCV in H_2 on the same cells are shown in Fig. 5, with results before n-butane treatment given in Fig. 5a, and 5b shows the results after treatment. Prior to n-butane, there is a steady decrease in both R_{Ω} and R_{I} as the Cu content increased. The changes in these values are particularly large in going from 10 wt % Cu to 20 wt % Cu. Even after treatment with n-butane, R_{Ω} decreases steadily, going from ~1.0 to ~0.5 Ω cm². The changes in R_{Ω} would suggest that connectivity of the electronic conductors in the anode increase with both the addition of Cu and with n-butane treatment, but that addition of Cu is more effective. However, it is interesting to notice that R_{I} in the 30 wt % Cu cell remains relatively large after treatment in n-butane. Indeed, after treatment in n-butane, the 30 wt % Cu cell had the largest R_{I} of all the four cells investigated.

Assuming that the enhanced anode conductivity is due to deposition of hydrocarbons in the anode, we next examined the increase in the mass of various samples after they had been heated in flowing n-butane at 973 K in a tubular reactor. First, we observed no significant differences in the mass changes for a pure YSZ matrix and for a YSZ matrix having 20 wt % Cu and 10 wt % CeO₂ added. For the Cu cermet, the weight changes were 1.3% after 10 min, 2.1% after



Figure 6. Temperature-programmed oxidation data for a sample consisting of 10% CeO₂ and 20% Cu in a YSZ matrix after exposure to n-butane for 30 min at 973 K. The dashed line is O₂ (m/e = 32) and the solid line is CO₂ (m/e = 44).

30 min, and 4.5% after 24 h. The carbon content based on the production of CO and CO₂ formed by reaction with the 15% O₂-85% He mixture was 2.1% after 10 min and 4.0% after 20 min, but this number also includes any carbon formed on the reactor walls. Since the performance increase following treatment in n-butane occurs in much less than 10 min and is not lost upon exposure to flowing H₂, the small carbon contents observed in these measurements suggest that small amounts of hydrocarbon are needed to increase the connectivity in the anode. This is particularly interesting given that relatively large amounts of Cu need to be added to achieve the same connectivity.

To determine how hydrocarbons other than n-butane would affect the anode, we looked for enhanced performance of a cell made with 20 wt % Cu and 10 wt % CeO2 in H2 at 973 K after exposing it to methane, propane, n-decane, and toluene. Between measurements, the cell was exposed to a 10% O₂-90% N₂ stream to reverse any enhancements caused by the previous fuel. With n-decane and toluene, enhanced performance was observed almost instantly after exposing the fuel to the anode; and the performance enhancements for n-butane, n-decane, and toluene were also indistinguishable. For propane, we again observed a similar enhancement but the enhancement occurred much more gradually. It was necessary to expose the cell to propane for more than 10 min to achieve the maximum power density. With methane, we observed no enhancement, even after several hours. Because methane exhibits a much lower tendency to undergo free radical reactions compared to the other hydrocarbons examined, with propane the next least reactive, we interpret these results as indicating that any fuel which causes hydrocarbons to form in the anode will lead to similar performance enhancements.

We investigated the nature of the anode deposits using TPO carried out in a He-O₂ mixture. Figure 6 shows CO₂ (m/e = 44) and O₂ (m/e = 32) signals from the TPO curves for a YSZ cermet impregnated with 20% Cu and 10% CeO₂ that was exposed to n-butane for 30 min at 973 K before being cooled to room temperature in flowing He. The results show that CO₂ is formed and O₂ consumed in a narrow range of temperatures, between 623 and 723 K. An additional O₂ consumption peak is observed at 773 K that we assign as being due to reoxidation of bulk Cu, although some of the O₂ consumed in the lower peak must also correspond to Cu oxidation. We were unable to observe water formation, but more O₂ is consumed than can be accounted for by CO₂ production and Cu oxidation. The additional O₂ consumption is probably due to water formation but is difficult to quantify. The likely formation of water,



Figure 7. Temperature-programmed oxidation results for 0.03 g of graphite powder. The dashed line is O_2 (m/e = 32) and the solid line is CO_2 (m/e = 44).

together with the fact that the deposits react at low temperatures, strongly suggests that the deposits are not graphitic. In Fig. 7, a TPO curve is shown for the graphite powder sample using the same experimental conditions. CO_2 production does not occur until above 973 K, a value similar to that reported by others.¹² Some of the difference between the graphite and the anode deposits could be due to surface area effects and the presence of ceria in the anode; however, neither the presence of a catalyst¹³ nor the increased surface area would be expected to give a temperature increase of more than 300 degrees.

Finally, to determine whether the oxygen-ion flux through the electrolyte might potentially "clean" the anode, we examined the cell under OCV conditions at 973 K in the presence of 100% flowing n-butane. In Fig. 8, the V-I curves are shown for a cell with 20 wt % Cu using n-butane as the fuel. The results are shown at the beginning of the experiment and after the cell had been held at open circuit for 24 h. There appears to be a slight decrease in the maximum power density after the 24 h exposure but the differences are not significant.

During the course of this experiment, the OCV measurements showed interesting trends, as shown in Fig. 9. Initially, the OCV in n-butane was greater than 1.0 V but it fell quickly to a value of 0.85 V. After \sim 4 h, we briefly shorted the cell, then measured the OCV. Again, the OCV started at more than 1.0 V and decreased rapidly to



Figure 8. V-I (closed symbols) and power density (open symbols) curves for a cell with an anode consisting of 10% CeO₂ and 20% Cu using n-butane as fuel at 973 K. The data were taken on (\blacklozenge) a fresh sample and (\blacktriangle) after holding that sample for 24 h in flowing n-butane at OCV.



Figure 9. A plot of the OCV as a function of time for a cell with an anode consisting of 10% CeO₂ and 20% Cu with n-butane. The cell was short-circuited for 1 min at 4.45 h.

0.85 V. The inset plot shows the transient performance in more detail. Figure 10 shows the results for a similar experiment, except that this time the cell potential was held at 0.5 V for 48 h before measuring the OCV measurement. As shown in the inset, the OCV started at greater than 1.0 V and fell to 0.85 V over a period of less than 1 h. Similar behavior is evident in the transient behavior reported in previous papers⁶ and was observed also for cells in which ceria was not added.

Although we do not have a definitive explanation for the data in Fig. 9 and 10, the data are consistent with the concept that there is a hydrocarbon layer at the three-phase boundary (TPB) in the directoxidation experiments. Since the OCV for these cells with H₂ as the fuel was 1.1 V, it seems unlikely that leaks can account for the low OCV in n-butane at steady state. Also, the theoretical OCV for complete combustion of n-butane to CO₂ and H₂O is 1.12 V at standard conditions and 973 K. While the oxidation of carbon and most hydrocarbons should give an OCV of greater than 1 V, partial oxidation reactions would result in lower standard potentials. For example, the standard potential for oxidation of n-butane to n-butanal is 0.87 V at 973 K. Other redox couples, such as oxidation of Ce₂O₃, cannot account for an OCV of 0.85 V. Therefore, the most likely explanation for the OCV data shown here is that equilibrium is established with partial oxidation reactions. The transients in the OCV are probably due to slow changes in the chemical structure of the hydrocarbon layer within the anode.



Figure 10. Data showing the transient response for a cell consisting of 10% CeO₂ and 20% Cu after maintaining a cell potential of 0.5 V for 48 h.

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Figure 11. Schematic to describe the changes in the three-phase boundary (a) before and (b) after operation with n-butane.

Discussion

Fuel cells that oxidize complex hydrocarbons directly, without first reforming them to hydrogen and CO, are a relatively new discovery. Although a number of groups have accomplished this with methane, ¹⁴⁻¹⁶ there is very little information in the literature on direct oxidation of hydrocarbons with higher molecular weights. Because the oxidation of higher hydrocarbons must involve complex, multistep reactions, it should not be surprising that complex intermediates must exist on the anode surface. There are likely a wide variety of intermediates formed at the anode/electrolyte interface; hydrocarbon deposits are probable and should be expected to affect performance. That these changes should be favorable was unexpected.

The performance enhancements observed here upon exposure of the anodes to hydrocarbon fuels must be due to improved connectivity in the electron-conducting phase based on the fact that the addition of more Cu leads to similar enhancements. Figure 11 is a schematic drawing of what we believe occurs in the region near the TPB upon exposure of the Cu-based anodes to hydrocarbons. For lower Cu contents, some of the Cu particles are initially not connected to the outside circuit and are therefore unable to conduct electrons away from the TPB. The addition of hydrocarbon "residues" likely fills the gaps between the metal particles and provides sufficient conductivity to allow the flow of electrons.

What is surprising is that small amounts of hydrocarbon residue are apparently sufficient to increase the conductivity substantially. Although we do not know the chemical form of the residue, the quantity necessary to significantly enhance performance appears to correspond to no more than 2 wt %. If we assume a density for the residue of 1 g/cm³, a value typical for hydrocarbons, the volume fraction of this residue is less than 5%. If one assumes the density for the residue is more similar to that of graphite, the volume occupied by the residue would be lower. By comparison, the minimum metal content for cermet anodes is reported to be 30 vol %.² Obviously, the Cu contents in our samples were always much less than this. Even the sample with 30 wt % Cu has a volume fraction of Cu that is only 19%. The addition of an extra 5 vol % carbon would not seem to be sufficient to increase the fraction of the electronconductive phase enough to make such a large difference in performance. A partial explanation for the unexpected behavior may lie in the structure of the sample anodes. Since Cu is added to the porous YSZ matrix after the pore structure has been established, the anode structure is likely to be much less random than cermets prepared by more conventional methods. Therefore, the deposits may simply coat the walls of the pores and enhance conductivity much more effectively than would the random addition of an electronconductive phase.

We believe the anode deposits are tar-like, rather than graphitic. Since we observed no noticeable difference in the amounts deposited on pure YSZ and YSZ with Cu and ceria added, it would appear that these deposits form through free radical decomposition, rather than by any surface-catalyzed processes. Based on the TPO results, the deposits are too reactive to be graphitic. Finally, because the enhancements were similar for various hydrocarbon fuels, even though the enhancements occurred rapidly, it would appear that the detailed chemical structure of the deposits is not crucial. However, since hydrocarbons are only electronic conductors when they contain highly conjugated olefinic or aromatic groups, some dehydrogenation of the tars must take place.

The low OCVs observed for n-butane at steady state appear to provide indirect information on the mechanism for hydrocarbon oxidation. Since the complete oxidation of n-butane to CO_2 and H_2O involves 26 electrons, this reaction cannot occur in a single step. As discussed earlier, the standard potential for the partial oxidation of n-butane to n-butanal is 0.85 V, in good agreement with the observed value at steady state, suggesting that the oxygen chemical potential at the anode is established by partial oxidation reactions. The fact that the OCV changes when current flows through the cell would indicate that the species that are present on the surface near the TPB can change depending on how the cell is treated.

One important implication of the results in this paper is that it may be possible to operate a direct-oxidation fuel cell with low metal contents and still get reasonable performance. At low metal contents, reoxidation of the Cu does not destroy the cell, as we have demonstrated in this study. Also, it should be possible to counter the effects of Cu sintering, which is likely to be a problem for operation at higher temperatures due to the low melting temperature of Cu. Therefore, the results of this study could prove to be useful, in addition to scientifically interesting.

There could be significant advantages to fuel cells that can oxidize hydrocarbons directly, without the need for reforming, both for increasing the efficiencies and for simplifying the fuel cell system. This area of investigation is still new, and there is a great deal that needs to be done to prove the commercial viability of this concept. The present study demonstrates that there is much we do not understand about how direct oxidation works and what needs to be done to optimize the performance of SOFCs that oxidize hydrocarbons directly. This area remains a fertile topic for investigation and we expect to see significant advances in the years to come.

Conclusions

Deposits formed in Cu-ceria-YSZ anodes of a SOFC operated with various hydrocarbon fuels can lead to significant enhancements in the performance of the fuel cells due to improved connectivity of the electron-conductive phase. The deposits do not appear to be graphitic and provide significant conductivity even when present at a level of order 1 wt %. Open-circuit voltages suggest that the deposits likely contain partial oxidation products.

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