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Keywords
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Comparison of the Performance of Cu-CeO$_2$-YSZ and Ni-YSZ Composite SOFC Anodes with H$_2$, CO, and Syngas

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Abstract

In this study the performance of a solid oxide fuel cell (SOFC) with Cu-CeO$_2$-yttria-stabilized zirconia (YSZ) was compared to an SOFC with Ni-YSZ anode while operating on H$_2$, CO, and syngas fuels. Cells with Cu-CeO$_2$-YSZ anodes exhibited similar performance when operating on H$_2$ or CO fuels, while cells with Ni-YSZ anodes exhibited substantially lower performance when operating on CO compared to H$_2$. Enhancing the catalytic activity of the Cu-CeO$_2$-YSZ anodes by adding Co was shown to produce cells that exhibited higher performance when operating on CO compared to H$_2$ at 973 K. The effect of fuel concentration and dilution on cell performance was also investigated and it was found that the kinetics of the oxidation of H$_2$ are positive order in P$_{H_2}$ for Cu-CeO$_2$-YSZ anodes and nearly zero order in P$_{H_2}$ for Ni-YSZ anodes. The oxidation of CO on Cu-CeO$_2$-YSZ anodes was also found to exhibit positive order in P$_{CO}$. It was also demonstrated that dilution of H$_2$ by H$_2$O had little effect on the kinetics of H$_2$ oxidation on both the Cu-CeO$_2$-YSZ and Ni-YSZ anodes.

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1. Introduction:

In many of the proposed applications for solid oxide fuel cells (SOFCs) the system will be powered using syngas (i.e. a mixture of H\textsubscript{2}, CO, and N\textsubscript{2}) produced via reforming of hydrocarbons. It is, therefore, important to understand how fuel composition and the presence of diluents such as N\textsubscript{2} and reaction products such as CO\textsubscript{2} and H\textsubscript{2}O affect SOFC performance. While most studies of SOFCs in the literature report performance characteristics for operation on humidified H\textsubscript{2}, there have been some studies that have looked at the effect of fuel composition [1-4]. For example, it has been reported that for SOFCs with conventional Ni-YSZ cermet anodes, the rate of the electrochemical oxidation of H\textsubscript{2} is 2-3 times greater than that of CO [1,2]. Jiang & Virkar found that for a cell with a Ni-YSZ anode that exhibited a maximum current density of 1.7 W cm\textsuperscript{-2} at 1073 K while operating on H\textsubscript{2}, had a maximum current density of only 0.3 W cm\textsuperscript{-2} when the fuel was switched to a 45%/55% CO/CO\textsubscript{2} mixture.

While CO by itself is a poor fuel for Ni-based anodes it can be used to produce more H\textsubscript{2} via the water gas shift reaction (WGS),

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2,
\]

which is also catalyzed by Ni. For fuels that have high CO contents, for example syngas produced from coal, H\textsubscript{2}O may need to be added to the fuel in order to effectively utilize the CO. Of course for cells that operate at high conversion the fuel will become diluted in both CO\textsubscript{2} and H\textsubscript{2}O. Thus, it is important to understand how the partial pressure of these species in the fuel affects the kinetics of the anode reactions. In the case of water, there have been several reports in the literature that suggest that it has a promoting effect on the rate of electrochemical oxidation of H\textsubscript{2} [5-9].
While much is already known about how syngas composition and the presence of reaction products and other diluents affects the performance of SOFCs with Ni-YSZ anodes, relatively little is known about how these factors affect the performance of anodes with other formulations. We have developed SOFC anodes that are composites of Cu, CeO$_2$ and yttria-stabilized zirconia (YSZ). In this anode formulation the CeO$_2$ acts primarily as an oxidation catalyst, while the Cu provides electronic conductivity [10,11]. Although these anodes were initially developed for the direct utilization of hydrocarbons without the need for reforming [12-15], they can also operate on syngas and may have some advantages, such as sulfur tolerance, compared to Ni-based anodes for this fuel [16]. The goal of this study was, therefore, to compare the performance of SOFCs with Ni-YSZ and Cu-CeO$_2$-YSZ anodes while operating on H$_2$, CO and syngas and to evaluate how the presence of diluents and reaction products affects their performance.

2. Experimental

The anode and cathode supported cells used in this study and their characteristics are summarized in Table 1. Cathode supported cells were used in studies comparing the performance of Cu-CeO$_2$-YSZ and Ni-YSZ anodes. These cells were supported on a LSF-YSZ composite cathode, used YSZ as the electrolyte, and had either Cu-CeO$_2$-YSZ (cell 1) or Ni-YSZ (cell 2) composite anodes. The cells were 1 cm in diameter and produced via tape casting using methods that have been previously described in detail [10]. A porous YSZ cathode and a dense electrolyte layer for each cell were formed by casting a tape containing yttria-stabilized zirconia (YSZ) with graphite and polymethylmethacrylate (PMMA) pore formers over a pure YSZ green tape. A porous YSZ anode layer was then
added by painting a YSZ slurry containing the pore formers onto the exposed side of the electrolyte tape. The three-layer green tape was then calcined at 1823 K, producing a 60 µm thick, dense YSZ layer between 600 and 200 µm thick porous YSZ layers. LSF was added to the 600 µm thick porous YSZ layer in order to form the cathode. This was accomplished using sequential impregnations of a solution containing La, Sr and Fe nitrates (La(NO$_3$)$_3$·6H$_2$O, Alfa Aesar, ACS 99.9%; Sr(NO$_3$)$_2$ Alfa Aesar, ACS 99.0%; Fe(NO$_3$)$_3$·9H$_2$O Alfa Aesar, ACS 98+%)) in a 0.8:0.2:1 molar ratio. LSF-YSZ composite cathodes with a 40:60 molar composition were obtained after calcination at 1123 K. A more detailed description of the fabrication of LSF-YSZ cathodes using this approach can be found elsewhere [17].

The anode composites used in this study had an area of 0.35 cm$^2$. The Cu-CeO$_2$-YSZ anodes (15 wt% Cu and 11 wt % CeO$_2$) were prepared by impregnating the 200 µm thick porous YSZ layer with aqueous solutions of Ce(NO$_3$)$_3$ and Cu(NO$_3$)$_2$ followed by calcination at 723 K to form the oxides. The copper oxide was reduced to Cu metal during cell activation in H$_2$. Ni-YSZ anodes (38 wt % Ni) were produced in a similar manner using impregnation with aqueous Ni(NO$_3$)$_2$. Since the Cu-CeO$_2$-YSZ and Ni-YSZ anodes were fabricated using identical porous YSZ layers and impregnation procedures they have similar porosities and microstructures. Ag paste and an Ag mesh were used to make electrical contact with the cathode and Au paste and an Au mesh were used for the anode. For performance testing each cell was sealed onto a 1.0 cm diameter alumina tube using a zirconia-based adhesive (Aremco, Ultra-Temp 516) and then the entire cell was placed
inside a furnace and heated 2 Kmin$^{-1}$ to 973 K while exposing the cathode to air and the anode to H$_2$.

Two additional anode supported cells with anode thicknesses of 300 µm and 3 mm were also used in this study. These cells were prepared using procedures similar to those described above, except for the fact that thick porous YSZ layer was used as the anode, and thin layer as the cathode. The cell with the 3 mm anode (cell 4) was used to study diffusional limitations, while the cell with the 300 µm anode was used to study the effect of the addition of a cobalt co-catalyst (cell 3). For this latter cell, cobalt was added by impregnation using a solution containing Cu and Co nitrates in a 1:1 molar ratio.

During testing each fuel cell was operated at atmospheric pressure and mass flow controllers were used to adjust the flow rates and composition of the various gasses (i.e. H$_2$, CO, CO$_2$, He, and N$_2$) sent to the anode. The cathode was left exposed to the atmosphere. The syngas used in this study contained 25% H$_2$, 25% CO and 50% N$_2$. The total flow rate of fuel to the anode was held constant at 200 mLmin$^{-1}$. For this flow rate the fuel conversion within the cell was less than 5% for all fuel compositions and current densities studied. A temperature controlled water bubbler was used to introduce water into the fuel. All impedance data were recorded in the galvanostatic mode using a Gamry Instruments impedance spectrometer.

3. Results & Discussion:

3.1. Cell Performance in Syngas: Comparison Between Cu-Ceria and Ni
Voltage versus current (V-I) curves for the cathode-supported cells with Cu-CeO$_2$-YSZ (A) and Ni-YSZ (B) anodes at 973 K while operating with H$_2$, CO, and syngas are presented in Figure 1. Impedance spectra while operating at a current density of 150 mA cm$^{-2}$ are also displayed for each cell in this figure. The Cu-Ceria-YSZ cell (cell 1) exhibited an open circuit voltage (OCV) of 1.2 V for all fuels tested. This value is due to the fact that non-humidified fuels were used for this cell. The maximum power density for this cell when running on H$_2$ was 305 mW cm$^{-2}$ and the cathode-to-anode impedance spectrum contains two arcs centered at approximately 1 kHz and 4 Hz. In a previous study of LSF-YSZ cathodes of the same structure as that used here it was shown that they have an area specific resistance (ASR) of ~0.1 ohm-cm$^2$ and a characteristic frequency of 1 kHz in impedance spectrum [17]. Thus, the 1 kHz arc in the impedance spectrum for the cell 1 can be assigned to the cathode. The large arc centered at 4 Hz is, therefore, due primarily to processes occurring on the anode.

The OCV for cell 2 with the Ni-YSZ anode operating on humidified H$_2$ ($P_{H_2O} = 0.03$ atm) was 1.1 V which is in agreement with the Nernst equation. The maximum current density for this cell with H$_2$ was 136 mW cm$^2$ which is significantly less than that obtained for the Cu-CeO$_2$-YSZ cell. The impedance spectrum shows that this lower performance is due primarily to a high ohmic loss in this cell of 1.1 ohm-cm$^2$. This can be attributed to the microstructure of the anode. In a previous study of Cu-CeO$_2$ anodes it was shown that the impregnated ceria forms an even coating on the surface of the porous YSZ [10] which in addition to providing catalytic activity enhances the electrical conduction path throughout the anode. In cells without ceria the contact between the YSZ and the metal is not as good
because the metal tends not to wet the surface of the YSZ. Thus for the Ni-YSZ cell, the high ohmic loss can be attributed to an increase in the effective thickness of the electrolyte due to poor distribution of the impregnated Ni layer.

The data in Figure 1 for operation on the various fuels illustrate several important points. For the Cu-CeO$_2$-YSZ cell, the performance when using either H$_2$ or CO is nearly identical. Only slightly lower performance was obtained when running on syngas which can be attributed to dilution of the combustible portion of the fuel in N$_2$. This is in contrast to the reactivity trends observed for the Ni-YSZ cell for which the performance when running on CO was substantially less than that for H$_2$. The maximum power densities for this cell were 136, 120 and 73 mW cm$^{-2}$ for H$_2$, syngas and CO, respectively. Thus for the Ni-YSZ cell, the maximum power density when operating on CO was only 50% of that when operating on H$_2$. The poor performance on CO for this cell is also reflected by the large increase in the anode arc in the impedance spectrum upon switching from H$_2$ to CO. This result is consistent with that reported previously by Jiang and Virkar [4] who also observed poor performance for cells with Ni-YSZ cermet anodes when running on CO. Also note that the performance of the Ni-YSZ cell on syngas is only slightly less than that when using H$_2$ and the impedance spectra for operation on these two fuels are similar. This demonstrates that when running on dry syngas only the H$_2$ component of the fuel is being oxidized.

Since Ni by itself is a good CO oxidation catalyst, the low performance of the Ni-YSZ cell for this fuel cannot be ascribed to poor catalytic activity within the anode. One possible explanation for the poor performance on CO is that the combustion reactions involve fuel molecules adsorbed on the oxide surface at or near the three-phase boundary.
Hydrogen adsorbs dissociatively on Ni and it is possible that the H atoms “spillover” onto the YSZ where oxidation takes place. This type of spillover process for H atoms on metals supported on oxides is well documented in the catalysis literature [19]. In contrast to H atoms, spillover of CO adsorbed on a metal to an oxide support generally does not occur. One would not expect to observe these effects for a Cu-CeO$_2$-YSZ anode, since in this case the metal is largely inert as evidenced by the fact that substitution of Cu with Au gives identical electrode performance [20]. Thus for the Cu-CeO$_2$-YSZ anode, the reactions appear to take place on the ceria which is active for both H$_2$ and CO oxidation.

It is known that the redox properties of ceria can be enhanced by the addition of a catalytic metal and indeed we have observed enhanced anode performance by the addition of precious metals to the ceria [21] and by adding Co to the Cu phase [22]. In the case of the Cu-Co bimetallic anodes, the surface of the metallic phase appears to be primarily Cu, as demonstrated by a low susceptibility for carbon formation when running on hydrocarbons, but with some Co dissolved within the Cu, as evidenced by improved performance for H$_2$ and CH$_4$ [22]. In order to determine whether the enhancements associated with Co might extend to CO, the performance of a cell in which Co, in addition to Cu and CeO$_2$, was impregnated into the anode (cell 3) was measured. Current voltage curves and impedance spectra obtained from this cell as a function of fuel composition are displayed in Figure 2. The addition of Co did produce an increase in performance and the maximum power densities for this cell were approximately 20% higher than those obtained from the Cu-CeO$_2$ cell. For operation on humidified H$_2$, syngas, and CO the maximum power densities were 310, 360, and 370 mW cm$^{-2}$, respectively at 973 K. Thus, cell 3 exhibited higher performance when operating on CO compared to H$_2$. It is noteworthy that
the performance of the cell with the Cu-Co-CeO$_2$-YSZ anode, even with a relatively thick electrolyte and operating at lower temperatures, exhibits a performance in CO that rivals that of some of the best Ni-YSZ cells operating on H$_2$ at 1073 K reported in the literature [4].

The impedance spectrum in Figure 2 also shows that cell 3 has an ohmic loss of 0.35 ohm cm$^2$. Assuming a conductance of 0.02 S cm$^{-1}$ for YSZ at 973 K [18], the ASR of the 60 µm electrolyte layer should be ~0.3 ohm cm$^2$, which is close to the experimental value obtained here. The higher value of 0.6 ohm-cm$^2$ ohmic loss measured for cell 1 (Figure 1 panel (A)) can be attributed difference in metal content between cells 1 and 3, which were 15 and 30 wt %, respectively. This variation could have lowered the electronic conductivity in the case of cell 1 resulting in a higher ohmic resistance.

When considering how fuel composition affects cell performance one must recognize that in addition to CO, H$_2$ and N$_2$, reformed hydrocarbon fuels are likely to contain small amounts of hydrocarbon impurities. It is therefore important to evaluate the propensity for these impurities to foul the anode via carbon deposition and their effect on the kinetics of the oxidation of CO and H$_2$. The stability of Cu-CeO$_2$-YSZ anodes in the presence of hydrocarbons and their ability to directly utilize hydrocarbon fuels has previously been demonstrated [12-15]. Thus, carbon fouling due to hydrocarbon impurities should not be an issue for this anode formulation. The effect of hydrocarbon impurities on the performance of these anodes when operating on syngas, however, has yet to be evaluated. We therefore carried out a set of experiments with cell 1 using H$_2$ and CO fuels containing 10% n-C$_4$H$_{10}$. The results of this study are shown in Figure 3. For comparison
purposes, I-V curves for cell 1 running on pure H$_2$, CO, and n-C$_4$H$_{10}$ are also included in the figure. Due to the slower kinetics for the oxidation of the n-C$_4$H$_{10}$ the cell performance is significantly lower when running with this fuel compared to H$_2$ or CO. This result is consistent with that reported in previous studies [23]. For CO and H$_2$ fuels the addition of 10% n-C$_4$H$_{10}$ resulted in only a modest decrease in cell performance suggesting that the primary effect of adding butane was to dilute the CO and H$_2$.

3.2. Influence of Fuel Concentration

Concentration is another variable that will affect the kinetics of the electrochemical oxidation of the fuel. Since in a large cell or a stack that operates at high fuel utilization the fuel will be diluted by the oxidation products, CO$_2$ and H$_2$O, it is important to understand how this will affect performance. To investigate this, the performance of cells with Ni-YSZ (cell 2) and Cu-CeO$_2$-YSZ (cell 1) anodes were measured as a function of fuel composition at 973 K. In this study the cell performance was measured for a fuel consisting of H$_2$ diluted in both He and H$_2$O. For the Cu-CeO$_2$-YSZ cell, the effect of diluting CO in an inert gas and CO$_2$ was also studied.

Figure 4 displays V-I curves for the Cu-CeO$_2$-YSZ (panel A) and Ni-YSZ (panel B) cells as a function of H$_2$ partial pressure at 973 K. In this set of experiments the partial pressure of H$_2$O in the fuel was held constant at 0.03 atm and the flow rates of H$_2$ and He were adjusted to give H$_2$ partial pressures of 0.1, 0.5, and 0.97 atm. The corresponding Nernst potentials for these fuel compositions are 1.1, 1.07, and 1.0 V, respectively, which agree well with the measured OCVs for both cells. The cathode and electrolyte losses for these cells can be approximated using the previously measured value of the ASR of the
LSF-YSZ cathode (0.1 ohm-cm$^2$) [17] and estimates of the effective ASR of the electrolyte obtained from the impedance spectra in Figure 1. The anode overpotentials as a function of current density for each fuel were estimated from the difference in the OCV, the operating potential, and the voltage losses associated with the cathode and electrolyte. These estimates are also displayed in Figure 4.

For the Cu-CeO$_2$-YSZ cell, the anode performance depends on the H$_2$ partial pressure. This kinetics of the anode reaction for this cell is positive order in P$_{H_2}$ as reflected by the decrease in the anode overpotential with increasing P$_{H_2}$. With the Ni-YSZ anode, the effect is much less pronounced. For current densities less than 190 mA cm$^{-2}$, there is a negligible change in the anode overpotential as P$_{H_2}$ is increased from 0.1 to 0.97 atm, indicating that the reaction is essentially zero order in P$_{H_2}$. From 190 to 500 mA cm$^{-2}$, changing the pressure from 0.97 to 0.5 atm still had no effect on the anode overpotential; however, there was a precipitous drop in the overpotential at lower partial pressures. We currently do not completely understand the reason for this drop; however, it cannot be attributed to diffusional limitations since the overall cell conversion was less than 5% and a similar drop was not observed at higher temperatures where the performance levels were much higher. One possible explanation for this feature is that the oxidation of H$_2$ on the Ni-based anode exhibits complex kinetics and there is a change in the rate limiting step at low H$_2$ concentrations.

Figure 5 displays V-I curves as a function of the partial pressure of the fuel at 973 K for the Cu-CeO$_2$-YSZ cell (cell 1) while operating on dry CO or CO diluted in either N$_2$ or CO$_2$ (panel A). Plots of the anode overpotentials are also included in the figure. Dilution
of the CO in N$_2$ had no appreciably effect on the OCV of 1.1 V. At current densities lower than 100 mA cm$^{-2}$ dilution also had little effect on the anode overpotential, while at higher current densities it caused a significant increase in the overpotential. Although this dependence on current density may indicate complex kinetics, overall these results show that the anode reaction is positive order in P$_{CO}$.

Diluting the CO in 50% CO$_2$ caused the OCV to decrease to 0.97 V as predicted by the Nernst equation. Dilution in CO$_2$ also resulted ~0.1 V smaller anode overpotentials compared to dilution in N$_2$. Since the V-I curves for these two fuel compositions are parallel to each other, this difference appears to be due primarily to a reduction in the OCV rather than inhibition of the rate of reaction on the anode due to the presence of CO$_2$. It is useful to compare this result to that reported previously by Jiang & Virkar who also studied how dilution of CO in CO$_2$ affects the performance of an SOFC with a Ni-YSZ anode [4]. For operation at 1073 K they found that as P$_{CO}$ was decreased from 1 to 0.44 atm by diluting in CO$_2$ the maximum power density decreased by 60%. In the present study decreasing P$_{CO}$ from 1 to 0.5 atm by diluting in CO$_2$ produced only a 27% decrease in the maximum current density at 973 K. These results again serve to illustrate the differences in the kinetics of the oxidation of CO on Cu-CeO$_2$-YSZ compared to Ni-YSZ and the superiority of the former for this reaction.

For hydrocarbon fuel, dilution has relatively little effect on the performance as has been reported previously for the Cu-CeO$_2$-YSZ cell running in n-butane [23]. In this earlier study, it was also shown that the oxidation products acted primarily as diluents, so that the presence of H$_2$O and CO$_2$ did not significantly affect the power density. Additionally it
should be noted that thermodynamics predicts that $P_{O_2}$ should not change significantly with conversion when hydrocarbons are used as fuels; however, in the case of $H_2$ this change is more substantial.

The influence of $P_{H_2O}$ on the kinetics of the $H_2$ oxidation reaction on the anode was also investigated. Figure 6 displays V-I curves obtained from the Cu-CeO$_2$-YSZ (cell 1) and Ni-YSZ (cell 2) cells at 973 K as a function of $P_{H_2O}$. In this series of experiments $P_{H_2}$ was held constant at 0.1 atm and the $N_2$ and $H_2O$ flow rates were adjusted to give $P_{H_2O}$ values of 0, 0.03, and 0.5 atm (only data for 0.03 and 0.5 atm were collected for the Ni-YSZ cell). Panel A in the figure shows that for the Cu-CeO$_2$-YSZ cell increasing $P_{H_2O}$ lowered the OCV as predicted by the Nernst equation. At low current densities this caused a decrease in the cell performance with increasing $P_{H_2O}$. At high current densities, however, the V-I curves were largely independent of $P_{H_2O}$ indicating that water had little effect on the kinetics of the oxidation reaction for this anode composition. Examination of the anode overpotentials rather than just the cell V-I curves leads to a similar conclusion. For example, at a current density of 400 mA cm$^{-2}$ the anode overpotential (calculated in a manner similar to that described above and taking into account the water produced in the cell) was 0.4 volts for $P_{H_2O} = 0$ and 0.03 and 0.5 atm. This result is in contrast to that obtained for the Ni-YSZ cell at 973 K where the addition of 0.5 atm of $H_2O$ produced a noticeable decrease in current density for current densities greater than 175 mA cm$^{-2}$. Again note the pronounced change in slope at intermediate current densities suggesting complex kinetics for the $H_2$ oxidation reaction. This result indicates that at 973 K the oxidation of $H_2$ on Ni-YSZ anodes is slightly negative order in the water concentration.
Data for the effect of $P_{H_2O}$ on the performance of the Ni-YSZ cell while operating on $H_2$ at 1073 K is also presented in Figure 6. At this temperature the addition of 0.5 atm of water had little effect on the cell performance except for a slight lowering of the OCV. Also note that at this temperature the V-I curve is almost linear and does not contain the pronounced change in slope at intermediate current densities. Since the diffusivity of a gas is only a weak function of temperature, this result further demonstrates that the change in slope in the V-I curve observed at 973 K is not due to diffusional limitations. The results obtained at 1073 K are in agreement with those reported previously for Jiang and Virkar who also found that other than lowering the OCV, the addition of water to $H_2$ fuel had little effect on the kinetics of the anode reaction for an SOFC with a Ni-YSZ anode [4]. Both of these studies, therefore, demonstrate that for operation on $H_2$ the addition of water has a relatively small effect on the kinetics of the oxidation reaction on the anode. These results do not agree with previous reports that addition of $H_2O$ increases the rate of $H_2$ oxidation on the anode [5-9] and indicate that the rate expression for this reaction is nearly zero order in $P_{H_2O}$ at 1073 K and slightly negative order in $P_{H_2O}$ at 973 K.

3.3. Diffusional Limitations.

In assessing the effect of fuel concentration and the addition of diluents on the performance of the fuel cells it is important to be able to distinguish between effects caused by changes in the kinetics of the anode oxidation reactions and those resulting from diffusional limitations in the porous anode. In the preceding analysis we have argued that the changes were due exclusively to the anode kinetics and not diffusional limitations. This
assumption can be justified using a simple Fick’s Law analysis. Diffusional limitations will become important when the fuel concentration at or near the three phase boundary, $C_{TPB}$, deviates significantly from that at the surface of the anode, $C_{\text{surface}}$. If one assumes a homogenous anode structure and that electrochemical oxidation at the TPB is the sole reaction, the deviation of $C_{TPB}$ from $C_{\text{surface}}$ can be estimated using the following equation

$$i = nF \ast \left[ \left( \frac{D_{\text{FUEL, EFF}}}{\delta} \right) \ast \left( C_{\text{surface}} - C_{TPB} \right) \right]$$

(1)

where $i$ is the current density, $n$ is the number of electrons produced by the oxidation of each fuel molecule, $F$ is Faraday’s constant, $D_{\text{FUEL, EFF}}$ is the effective diffusivity for the fuel in the porous anode, and $\delta$ is the thickness of the anode. The effective diffusivity for H$_2$ can be approximated using the Chapman-Enskog equation [24] along with values for the anode porosity and tortuosity which are estimated to be 0.35 and 3, respectively [23]. This gives an estimated value of $D_{\text{H}_2, \text{EFF}}$ of 1.2 cm$^2$ s$^{-1}$.

Equation 1 predicts that for the cells with 200 µm thick anodes, operating with a P$_{\text{H}_2}$ at the surface of the anode of 0.1 atm (the lowest P$_{\text{H}_2}$ used for these cells) at 973 K, a current density of $\sim$1500 mA cm$^{-2}$ is required for $C_{TPB}$ to be only 10 % less than $C_{\text{surface}}$. Since this current density is significantly greater than the maximum current densities obtained from the Cu-CeO$_2$-YSZ and Ni-YSZ cells, this analysis shows that diffusional limitations did not affect performance. In order to demonstrate the validity of this analysis, experiments were conducted with a Cu-CeO$_2$-YSZ cell that was similar to the other Cu-ceria cell used in this study except that the anode was 3 mm in thickness (cell 4). With this
much thicker anode it was easier to operate under conditions for which diffusional limitations should occur. Figure 7 displays V-I curves and impedance spectra for cell 4 at 973 K as a function of \( P_{\text{H}_2} \). For operation on humidified \( \text{H}_2 \) (3% \( \text{H}_2\text{O} \)) at 1 atm, the V-I curve is nearly linear with a maximum current of \( \sim 600 \) mA cm\(^{-2} \). At this current density, equation 1 predicts that \( C_{\text{TPB}} \) is only 6% less than \( C_{\text{surface}} \). Thus, as is observed experimentally, for this fuel concentration diffusional limitations would not be expected to have a significant affect on cell performance. When \( P_{\text{H}_2} \) is lowered to 0.05 atm by diluting in He, however, the V-I curve exhibits a large change in slope at \( \sim 200 \) mA cm\(^{-2} \) at which point the current density rapidly approaches a limiting value of 260 mA cm\(^{-2} \). At this current density equation 1 predicts that \( C_{\text{TPB}} \) will be \( \sim 50 \% \) less than \( C_{\text{surface}} \). Since, as discussed earlier, the kinetics of the \( \text{H}_2 \) oxidation reaction on this anode are positive order in \( P_{\text{H}_2} \), it is not surprising that a 50 % reduction in the fuel concentration at the TPB has a significant affect on cell performance. The data in Figure 7 also shows that changing the diluent from He to \( \text{N}_2 \) causes the switch to diffusional control to occur at a lower current density of 150 mA cm\(^{-2} \). This is the expected result, since the higher mass of \( \text{N}_2 \) relative to \( \text{H}_2 \) would produce a slight decrease in the effective diffusivity.

The data in Figure 7 for operation of the cell on pure and diluted n-C\(_4\)H\(_{10}\) are also consistent with estimates of diffusional limitations based on equation 1. For n-butane, \( D_{\text{eff}} \) is estimated to be 0.1 cm\(^2\) s\(^{-1}\) which is an order of magnitude lower than that for \( \text{H}_2 \). This decrease in \( D_{\text{eff}} \) relative to that for \( \text{H}_2 \), however, is roughly offset by the fact that for n-C\(_4\)H\(_{10}\) 26 electrons are produced per reaction compared to only 2 for \( \text{H}_2 \). Thus, for the same fuel partial pressure one would expect diffusional limitations for n-C\(_4\)H\(_{10}\) to become
apparent at nearly the same current densities as that for H$_2$. As shown in Figure 7 this is indeed the case.

4. Summary

In this study it was demonstrated that there are dramatic differences in the performance of Cu-CeO$_2$-YSZ and Ni-YSZ anodes when running on CO and syngas fuels. The Cu-CeO$_2$-YSZ composite anodes exhibited high activity for the electrochemical oxidation of H$_2$ and CO and similar performance was obtained for both of these fuels. It was even possible via the addition of a cobalt co-catalyst to produce Cu-CeO$_2$-based anodes that exhibited higher performance on CO compared to H$_2$. For example, a cell with a Cu-Co-CeO$_2$-YSZ anode and a relatively thick 60 µm YSZ electrolyte had maximum power densities of 310 and 370 mW cm$^{-2}$ at 973 K when operating on H$_2$ and CO, respectively. The high activity of the Cu-CeO$_2$-based anodes for CO oxidation was in sharp contrast to that obtained for Ni-YSZ anodes. In agreement with previous reports it was found that while Ni-YSZ anodes have high activity for H$_2$ oxidation, they do not effectively catalyze the oxidation of CO and therefore exhibit poor performance when operating on this fuel. Thus, when operating Ni-YSZ anodes on dry syngas, only the H$_2$ component of the fuel is utilized.

Studies of the dependence of fuel concentration on cell performance also showed that the kinetics of the electrocatalytic oxidation of H$_2$ are positive order in P$_{H_2}$ for Cu-CeO$_2$-YSZ anodes and nearly zero order for Ni-YSZ anodes. In contrast to previous
studies, dilution of H$_2$ by H$_2$O was found to have little effect of the anode kinetics for both Cu-CeO$_2$-YSZ and Ni-YSZ anodes.

Acknowledgments

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References:


Figure Captions:

Figure 1. V-I curves and impedance spectra measured at 150 mA cm$^{-2}$ for cells 1 and 2 operating at 973 K on the following pure fuels: (■) H$_2$, (●) CO, and (♦) syngas. Panel (A) is for cell 1 with the Cu-CeO$_2$-YSZ anode and panel (B) is for cell 2 with the Ni-YSZ anode.

Figure 2. V-I curves and impedance spectra measured at 150 mA cm$^{-2}$ for cell 3 with a Cu-Co-CeO$_2$-YSZ anode operating at 973 K on (■) H$_2$, (●) CO, and (♦) syngas fuels.

Figure 3. V-I curves for cell 1 with a Cu-CeO$_2$-YSZ anode operating at 973 K on the following dry fuels: (■) H$_2$, (●) CO, and (▲) n-C$_4$H$_{10}$, and fuel mixtures: (■) 90% H$_2$/10% n-C$_4$H$_{10}$ and (■) 90% CO/10% n-C$_4$H$_{10}$.

Figure 4. Plots of voltage and anode overpotential versus current for the Cu-CeO$_2$-YSZ (cell 1) (A) and Ni-YSZ (cell 2) (B) anode cells as a function of P$_{H_2}$ at 973 K. The P$_{H_2O}$ in the fuel was held constant at 0.03 atm and the flow rates of H$_2$ and He were adjusted to give P$_{H_2}$ values of (■) 0.97, (●) 0.5, and (▲) 0.1 atm.

Figure 5. Plots of voltage and anode overpotential versus current for a Cu-ceria-YSZ anode cell (cell 1) operating at 973 K in (●) pure CO, (●) 50% CO diluted in N$_2$, and (♦) 50% CO diluted in CO$_2$.
**Figure 6.** V-I curves for cells with (A) Cu-CeO$_2$-YSZ (cell 1) (B) Ni-YSZ (cell 2) anodes operating at 1 atm and 973 K with a fuel containing 0.1 atm of H$_2$, (▲) 0, (▲) 0.03, and (Δ) 0.5 atm of H$_2$O, and the balance He. V-I curves obtained at 1073K are also shown for the Ni-YSZ cell for fuels containing 0.1 atm of H$_2$, (■) 0.03, (□) 0.5 atm of H$_2$O, and the balance He.

**Figure 7.** V-I curves for cell 4 with a 3 mm thick Cu-CeO$_2$-YSZ anode operating at 973 K in the following fuels: panel A, (■) humidified H$_2$ (3 % H$_2$O), (□) 5% humidified H$_2$ in He, and (■) 5% humidified H$_2$ in N$_2$, and panel B, (●) n-C$_4$H$_{10}$, (ο) 5% n- C$_4$H$_{10}$ in He, and (●) 5% n- C$_4$H$_{10}$ in N$_2$. 
### Table 1 – Summary of the cells used in this study

<table>
<thead>
<tr>
<th>Cell</th>
<th>Support</th>
<th>Anode Composition (wt % of cermet)</th>
<th>Thickness (µm)/Area (cm²)</th>
<th>Cathode Composition</th>
<th>Thickness (µm)/Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cathode</td>
<td>Cu (15) - CeO₂ (11)</td>
<td>200 / 0.35</td>
<td></td>
<td>600 / 0.785</td>
</tr>
<tr>
<td>2</td>
<td>Cathode</td>
<td>Ni (38)</td>
<td>200 / 0.35</td>
<td></td>
<td>600 / 0.785</td>
</tr>
<tr>
<td>3</td>
<td>Anode</td>
<td>Cu-Co (30) - CeO₂ (15)</td>
<td>300 / 0.785</td>
<td></td>
<td>60 / 0.35</td>
</tr>
<tr>
<td>4</td>
<td>Anode</td>
<td>Cu (30) - CeO₂ (15)</td>
<td>3000 / 0.785</td>
<td></td>
<td>60 / 0.35</td>
</tr>
</tbody>
</table>

1. All cells had a 60 µm YSZ electrolyte.
2. All cells had a LSF-YSZ composite cathode.
Figure 1.
Figure 2.
Current Density (mA/cm²)

Voltage (v)

Figure 3.
Figure 4.
Figure 5.
Figure 6
Figure 7.