CO AND CH₄ ELECTROCHEMICAL OXIDATION 
ON Ni PATTERNED ANODES

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ABSTRACT

Single cell SOFCs with Ni patterned anodes sputtered onto single crystal 
YSZ electrolyte discs were used to examine electrochemical oxidation of 
H₂, CO, and CH₄ under dry and wet (~4% H₂O) conditions. High-surface-
area porous YSZ/LSM cathodes provided low cathodic overpotentials for 
isolation of anodic processes. Polarization curves of H₂ and CO from 750-
850°C indicated that for patterns with < 100 μm line widths, power 
densities and impedance spectra more closely scale with Ni surface area 
than with three-phase-boundary lengths. CH₄ electrochemical oxidation 
also suggested a very weak influence of three-phase boundary lengths for 
temperatures ≥ 800°C. Results indicate detrimental effects of H₂O on CO 
oxidation power densities due to drops in open-circuit voltages, although 
polarization resistances did not drop significantly. Similar drops in OCV 
with H₂O addition were observed for CH₄, but steam-reforming rates 
become significant above 800°C such that polarization resistances for CH₄ 
increase to approach those of H₂. Impedance spectra suggest that a low 
frequency process controls CO oxidation for temperatures ≤ 800°C but 
becomes less dominant at higher temperatures. Impedance spectra for 
CH₄ oxidation show the dramatic drop in polarization resistance as steam-
reforming rates become appreciable, indicating the importance of 
temperature in sustaining reliable Ni anode performance.

INTRODUCTION

Numerous efforts to sustain direct utilization of hydrocarbons in SOFCs (1-4) have 
indicated that conventional Ni/YSZ SOFC anodes are prone to uncontrolled carbon 
deposition under conditions for dry hydrocarbon feeds, particularly for species with 
multiple carbon atoms. Some researchers have explored the possibility of using 
alternative operating strategies where either steam (1, 3) or O₂ (5, 6) is added to the anode 
flow stream such that a porous anode matrix will provide catalytic reforming or partial 
oxidation and thereby convert some, if not all, of the hydrocarbon into H₂, CO, and 
perhaps some CH₄ (7, 8). Internal reforming reactions have been shown to work well 
under some conditions at minimizing carbon deposition such that stable operation may be 
achieved even on conventional Ni-based anode structures (1, 3). It is thus important to
understand the electrochemical oxidation of CO and CH$_4$ to ascertain under what if any conditions and fuel compositions, internal reforming can be sustained such that Ni/YSZ can provide a viable anode for carbonaceous fuels.

The current study focuses on the behavior of both CO and CH$_4$ electrochemical oxidation on Ni/YSZ anodes and on the impact of H$_2$O on the electrochemical oxidation process. To avoid the uncertainties of heterogeneous chemistry in non-electrochemically active regions of conventional porous anode structures, patterned anodes with their well-defined three-phase boundary lengths are used to characterize the electrochemical oxidation processes. Other studies have adopted this approach for H$_2$ oxidation on Ni/YSZ anodes (9-11), but to date this approach has not been adopted for carbonaceous fuels on Ni/YSZ. Recent papers (1,7) have indicated that questions remain regarding the mechanisms for electrochemical oxidation of these simple molecules and thus it was hoped that the direct electrochemical oxidation studies on the patterned anodes would provide new insight.

The electrochemical oxidation of dry CO on Ni/YSZ anodes must involve multiple steps, including 1) non-dissociative CO adsorption most likely on the Ni surface, 2) surface diffusion of CO toward the TPB, 3) O$_2^-$ transport to the TPB, and 4) a two-step charge transfer reaction involving O$_2^-$ and CO at the TPB region. In general, CO oxidation has a lower exchange current density (up to an order of magnitude lower (12)) and higher anodic overpotentials than H$_2$ on Ni-based electrodes (3), and most research have postulated that the CO oxidation step is generally the rate-limiting step (13). While there has been some agreement as to the rate-limiting step for CO oxidation under dry atmospheres, there has not been a clear consensus on the impact of H$_2$ and H$_2$O on CO electrochemical oxidation, in particular on Ni/YSZ electrodes. Mechanistic interpretation is complicated in porous electrode studies where it is uncertain to what extent the non-electrochemically active regions provide water-gas shift conversion of CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$. One recent study showed that the addition of more than 10% H$_2$ to a CO fuel stream caused performance of the fuel to approach that of pure H$_2$ vs. pure CO (3), but the study is inconclusive as to whether water-gas shift reactions played a role or whether the H$_2$ played a catalytic role for electrochemical oxidation of CO.

Very few fundamental studies have been carried out for direct CH$_4$ electrochemical oxidation over Ni anodes although numerous studies of CH$_4$ oxidation in porous Ni/YSZ anodes with and without steam addition have been undertaken as summarized elsewhere (1, 7). Thus, there is an opportunity for improving our understanding on the behavior of CH$_4$ and CO electrochemical oxidation over Ni surfaces and its impact on SOFC performance with hydrocarbon feeds. This paper presents experiments with patterned Ni anode deposited onto single crystal YSZ electrolytes with their well-defined three-phase boundary lengths to characterize the electrochemical oxidation of CO and CH$_4$ with and without the presence of H$_2$O. The experimental results, both voltammetric measurements and impedance spectra, provide a departure point for exploring critical processes that control electrochemical oxidation of hydrocarbon species in SOFCs.

**EXPERIMENTAL SET-UP**

A model single cell SOFC was prepared by supporting the membrane electrode assembly (MEA) on a fully dense single-crystal 8% YSZ electrolyte disk (99.99% pure from MTI Corp.), 25.4 mm in diameter and 0.5 mm in thickness. The YSZ electrolyte supported a
high-surface area porous cathode, which was tape-cast as a thin layer, 50 μm thick and 12 mm in diameter. The cathode consisted of a 1:1 mixture of La$_{0.85}$Sr$_{0.15}$MnO$_3$, and YSZ (8% by mole yttria) and was prepared in a similar manner described by Park et al. (2).

To create the anode, a thin layer of Ni (100-150 nm) was sputtered onto the polished side of the YSZ disk. Four patterned anodes were etched out of the Ni layer by means of photolithography. The patterns consisted of 3 mm long parallel strips of varying widths (10, 20, 50, and 100 μm wide) as shown in Figure 1. Profilometry measurements indicated the thickness of the anodes to be between 100-150 nm and the width of the “vertical” walls to be << 1 μm. The parallel strips of the anode were separated by 50 μm of exposed YSZ electrolyte. Gold wire leads were connected with a gold paste to 2 mm pads on the outside edge of the collector bars. The gold paste and collector pads were covered with dense YSZ paste to eliminate their impact on the electro-oxidation measurements.

![Figure 1. Images of patterned Ni anodes with expanded images showing resolution of TPB at Ni/YSZ interface.](image)

Table 1 summarizes the geometric properties of the four patterned anodes (which exclude the covered connecting pads for the leads). The patterns are referred to by the width of the parallel Ni strips (10, 20, 50, and 100 μm respectively). The anodes (including the collector crossbars) were patterned to provide the same total Ni surface area ($a_{\text{anode}} = 0.0364 \pm 0.0005 \text{ cm}^2$) with different TPB lengths ($l_{\text{TPB}}$) per unit of electrolyte area ($a_{\text{mem}}$).

| Pattern line width (μm) | 10  | 20  | 50  | 100 |
|-------------------------|-----|-----|-----|-----|
| $l_{\text{TPB}}$, length of patterned TPB (m) | 0.616 | 0.309 | 0.124 | 0.063 |
| $a_{\text{anode}}$, Ni surface area (cm$^2$) | 0.0369 | 0.0365 | 0.0360 | 0.0359 |
| $a_{\text{mem}}$, electrolyte area (cm$^2$) | 0.206 | 0.129 | 0.083 | 0.068 |
| $l_{\text{TPB}}/a_{\text{mem}}$ (m/cm$^2$) | 2.33 | 1.87 | 1.18 | 0.74 |

The electrolyte area in Table 1 is defined as the area that includes the Ni lines, the 50 μm spacings of exposed YSZ between lines, and a boundary around the outside of the pattern as wide as the electrolyte thickness (500 μm). Careful optical inspection of the patterns at room temperature indicated almost no holes or cracks in the Ni, and this along with the
extremely sharp anode-electrolyte interface achieved with the photolithography suggests that the true effective $l_{TPB}$ is approximated by the geometric value. This is in contrast to earlier studies where corrections to $l_{TPB}$ from the geometric value were used (10).

As seen in Table 1, $l_{TPB}/a_{mem}$ varies by a factor of 3 from 0.74 for the 100 μm patterns to 2.33 for the 10 μm patterns. These values are comparable to tests on Ni patterned anodes in previous studies (9-11). It was anticipated that with the porous cathodes providing minimal resistance in comparison to the pattern anodes, charge transfer impedances might correlate with $l_{TPB}/a_{mem}$ although as shown in the results, such a correlation was not observed. Previous patterned anode studies have attempted to correlate V-I data with $l_{TPB}/a_{mem}$ (9), but significant scatter raised questions as to whether a strong correlation existed.

The patterned anode MEA's tested in this study were instrumented with a K-type thermocouple pasted onto the cathode electrolyte near the disk center. The MEA's were attached to an alumina tube (22.2 mm OD, 15.9 mm ID) with a high temperature zirconia-based ceramic paste. Concentric alumina feed tubes (4.8 mm OD, 3.2 mm ID) were passed into the larger outer tubes to provide the inlet flows to both electrodes. The entire assembly was placed inside a temperature-controlled furnace. The total flow rates to both electrodes were maintained constant for all experiments and provided significant amounts of excess fuel and oxidizer (two times the fuel) over the respective electrodes to minimize gas-phase reactant concentration gradients across the electrode. The cathode feed tube delivered atmospheric dry bottled air at 980 sccm, and the anode feed tube delivered 209 sccm of fuel (H2, CO, or H2/CO mixtures) diluted by 418 sccm of Ar at 1 atm. Excess O2 helped to minimize cathodic overpotentials and was viewed as a preliminary alternative to depositing a reference electrode on the anode side. The contribution to the overpotentials from the cathode in this study are estimated to be < 0.1 V at the maximum current densities (< 0.25 A/cm2) and thus overpotentials measured over the range of current densities presented herein are primarily from bulk electrolyte losses and losses due to anode processes. Subtracting out the bulk losses allowed for a comparison of anodic losses for the different patterned anodes and for different fuel feed compositions and operating temperatures.

Polarization measurements were made with dry fuel feeds initially. After measurements on dry fuel mixtures were made, fuel/argon mixtures were bubbled through a water bath at 25 °C before entering the anode side for measurements on wet fuel feeds. An Autolab PGSTAT30 (Eco Chemie) was employed for the polarization curve measurements and for AC impedance spectroscopy in potentiostatic mode (with 10 mV excitation amplitude) at open circuit over a frequency range from 100 kHz down to 10 mHz. For all fuel compositions in this study, electrochemical measurements were made at $T_{cell}$ ranging from 750 ± 10 °C up to 900 ± 10 °C. Multiple cells were tested for these experiments to test consistency of the results with respect to different coating methods.

RESULTS AND DISCUSSION

With the four pattern anodes in this study, it was hoped to obtain correlations between polarization resistances, $R_{pol}$, and anodic overpotentials, $\eta_a$, and anode geometric properties, principally $l_{TPB}$ and $l_{TPB}/a_{mem}$. As indicated in Table 1, $l_{TPB}$ for the four
different pattern geometries varied by an order of magnitude, and $l_{TPB}/a_{mem}$ varied by a factor of 3. Since all four patterns were tested in reference to the same porous LSM cathode and YSZ electrolyte, differences in V-I curves and impedance spectra for the same conditions should be related to differences in $l_{TPB}$ if charge transfer TPB processes are in any way rate-limiting. However, as indicated in Figure 2 plots of corrected voltage ($V_{cell} - IR_{bulk}$) vs. current density ($i_A$ based on Ni anode surface area) at $T_{cell} = 850 \, ^\circ C$ for dry H$_2$, dry CO, and wet CO and at $T_{cell} = 900 \, ^\circ C$ for dry CH$_4$ reveals that the $\eta_a$ for the different anodes follow surprisingly similar trends with respect to $i_A$. There is a noticeable increase in $\eta_a$ and associated drop in $\omega_A$ for the 100 $\mu$m pattern in comparison to the other patterns. The poorer performance of the 100 $\mu$m pattern, with its relatively low $l_{TPB}$, was not evident for the pure CO results, which, as discussed more fully below, suggests alternative mechanisms may be rate-limiting for CO electrochemical oxidation in comparison to that of H$_2$.

![Figure 2. Voltage (corrected for IR$_{bulk}$ losses) vs. A/cm$^2$ of patterned anodes for dry H$_2$, dry CO, and CO with 4% H$_2$O in Ar at $T_{cell} = 850^\circ C$ and for dry CH$_4$ at $T_{cell} = 900^\circ C$.](image)

The fact that electrochemical oxidation rates and $\eta_a$ do not show a strong trend with respect to either $l_{TP}$ or $l_{TPB}/a_{mem}$, particulary for H$_2$ and CO, suggests that the rate controlling process(es) may not be the three-phase boundary charge transfer reactions as suggested in earlier studies for H$_2$ with patterned anodes (9, 10). Since the electrodes all possess similar $a_{anode}$, the results suggest that processes related to Ni surface area, such as adsorption, may control the H$_2$ and CO electrochemical oxidation rates. This hypothesis is in agreement with some studies which have suggested that above 845 $^\circ C$, adsorption equilibration processes control H$_2$ electrochemical oxidation in porous cermet Ni/YSZ anodes (14). Adsorption rate-limiting processes have not been suggested for CO (12), and yet the different patterned anodes indicate very similar performance despite the order of magnitude variation in $l_{TPB}$. An alternative explanation to the adsorption control is the creation of micro-pores or -cracks at the high $T_{cell}$ due to differences in thermal expansion of the Ni and YSZ. No evidence in post-testing microscopic analysis of patterns has suggested the formation of such cracks, but as of yet this theory remains untested.
The results in Figure 2 also show the importance of OCV in distinguishing the performance of the different fuels. Both wet CO and dry CH₄ polarization curves show a dramatic drop in OCV from their thermodynamic equilibrium voltage. This is particularly dramatic for the wet CO in comparison to the dry CO. Although the slopes of $\eta_a$ at low $i_A$ suggest that the polarization resistance ($R_{pol}$) is not significantly impacted by the presence of H₂O (as borne out in the impedance spectroscopy), the significant drop in OCV suggests that the CO electrochemical oxidation has not reached an equilibrated state even after several hours with the addition of H₂O. This observation can be corroborated with the idea that the addition of H₂O to the fuel stream leads to significant hydroxylation of the YSZ surface (15) thereby inhibiting what is likely to be the principal CO electrochemical oxidation pathway: CO(Ni) + O²⁻(el) ⇌ CO₂(g) + (Ni) + 2e⁻. The drop in OCV for CH₄ from its thermodynamic limit may actually be due to a similar phenomena in that CO on the Ni surface is not provided an adequate pathway to equilibrate with the O²⁻(el) due to hydroxylation of the electrolyte. These results suggest that heterogeneous water gas shift reactions do not occur significantly near the electrochemically active TPB region.

The impact of $T_{cell}$ upon the electrochemical oxidation process of all three fuels was explored and some of the results are plotted for the 50 µm pattern in Figure 3. Results show minimal change in $R_{pol}$ for H₂ with increasing $\eta_a$, indicating minimal activation losses even at 750°C. On the other hand, CO and CH₄ show activation losses with subsequent drops in $R_{pol}$ as $\eta_a$ approaches 0.5 V. The dramatic reduction in $R_{pol}$ for CH₄ at the higher $\eta_a$ results in $R_{pol}$ approaching values very similar to those of H₂ suggesting that steam reforming from produced H₂O is oxidizing the C on the Ni surface and making available H for electrochemical oxidation. A similar drop in $R_{pol}$ is observed for CO only at $T_{cell} \geq 850°C$, but the mechanism for this drop is unclear. Results for wet CH₄ and CO show similar behavior to the dry conditions only with the requisite drop in OCV.

![Figure 3. Voltage (corrected for $IR_{bulk}$ losses) vs. $A/cm^2$ of 50 µm patterned anode for dry H₂, dry CO, and dry CH₄ for a range of $T_{cell}$ values.](image)

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wet CH₄ oxidation actually shows a larger reduction in \( R_{pol} \) when compared to the dry CH₄ and thus provides higher \( i_A \) as \( \eta_a \) increases to 0.5 V.

To more fully appreciate the effects of overpotential on the oxidation kinetics, Tafel plots for CO and CH₄ over the range of conditions studied are shown in Figure 4. Fits to Tafel plots have limited value for reactions where multiple processes influence oxidation rates, as expected for CO here, but fits at large \( \eta_a \) to the equation [1] to derive effective exchange current densities \( i^0 \) and anode exchange coefficients \( \alpha_a \).

\[
i_{A,f} = i^0 \exp \left( \frac{-E_{act}}{RT} \right) \exp \left( \frac{\alpha_a \eta_a F}{RT} \right) \text{ for large positive } \eta_a \quad [1]
\]

Results from the fits to the Tafel plots in Figures 4a and 4b are summarized in Table 2. It is clear from the Tafel plots that the Butler-Volmer equation did not apply universally for both the cathodic and anodic processes as the intercept at \( \eta_a = 0.0 \text{ V} (= i^0 \text{ in [1]) do not agree. Nonetheless, if a single process controls at the high } \eta_a, \text{ then equation [1] provides a basis for evaluating kinetic rates. As documented in Table 2, the } i^0 \text{ increased with temperature for both fuels and approximate } E_{act} \text{ for the } i^0 \text{ are given in Table 2. The approximate value for CO is 0.6 eV but this value is only empirical as there is clearly a transition in the reaction process between 800 and 850°C. On the other hand, CH}_4 \text{ suggests an } E_{act} \text{ of 3.2 eV which is twice as high as 1.6 eV observed for dry H}_2 \text{ in the same temperature range. This difference suggests that the electrochemical oxidation process which may largely be the same for CH}_4 \text{ and H}_2 \text{ at high } \eta_a \text{ is not the rate-limiting process. However, the values for } \alpha_a \text{ in Table 2 indicate that overpotential plays a very strong role in the CH}_4 \text{ oxidation rates and thus its impact on Ni-CH}_4 \text{ surface chemistry should be further explored.}

Figure 4. Tafel plots of (a) CO and (b) CH₄ electrochemical oxidation on selected patterned anodes as a function of \( T_{cell} \) for both dry and wet conditions. Empirical fits based on single-step kinetics at high \( \eta_a \) are shown.
Table 2. Summary of Tafel plot fitting parameters for effective exchange and anodic charge transfer coefficient for CO and CH4 oxidation at large $\eta_a$.

| $P_{\text{fuel}}$ (kPa) | $T_{\text{cell}}$ (°C) | $i^2/|TPB|$ (A/m) | $\alpha_a$ | $E_{\text{act}}$ for $i^2$ (eV) |
|--------------------------|----------------------|------------------|-------------|------------------|
|                          | dry / wet            | dry / wet        |             |                  |
| $P_{CO} = 33.3$          | 746                  | 7.0e-3 / 5.9e-3  | 0.17 / 0.15 | 0.61             |
|                          | 797                  | 9.9e-3           | 0.18        |                  |
|                          | 784                  | 1.3e-2 / 4.7e-3  | 0.26 / 0.24 |                  |
| $P_{CH4} = 33.3$         | 800                  | 2.2e-5 / 4.3e-5  | 0.68 / 0.64 | 3.17             |
|                          | 900                  | 4.0e-4           | 0.74        |                  |

The values for the effective $\alpha_a$ derived for CO at high $\eta_a$ are quite low in comparison to previous half-cell studies on Ni/YSZ for H2 electrochemical oxidation on patterned anodes (9, 10). Thus, the $\alpha_a$ for CO in Table 2 cannot be associated with a fundamental charge transfer step.

To supplement the understanding gained from the polarization studies, impedance spectra, which provide significantly more kinetic information, were taken across the entire cell for all of the anode feeds and individual patterns at $\eta_a = 0.0$ V. The impedance spectra for the 10 $\mu$m pattern with dry feeds of CO and CH4 for dry and wet conditions are shown in Figure 5. Bulk resistances are included in the impedance plots in order to displace the polarization resistance spectra for ease of visualization. The CO spectra are dominated by two processes — one at high frequencies and a second at low frequencies. For CO the low frequency process provided the largest fraction. Approximate relaxation frequencies $\omega^*$ for the low frequency process are between 1 and 2 Hz and not a strong function of temperature. This lack of temperature dependence again suggests that CO

![Figure 5. AC impedance spectra at $\eta_a = 0.0$ V for (a) CO, dry and wet, at $T_{\text{cell}} = 800^\circ$C and 850°C and (b) CH4, dry and wet, at $T_{\text{cell}} = 850^\circ$C and 900°C.](image-url)
oxidation may be controlled by adsorption at the temperature ranges studied herein. This hypothesis remains to be tested with comparison of impedance spectra to kinetic modeling studies. It is surprising that the presence of H2O does not increase $R_{pol}$ at $\eta_a = 0.0$ V. This is in agreement with the polarization plots which suggested that H2O only causes increased $R_{pol}$ only for CO at high $\eta_a > 0.4$ V. As with the dry fuel feed, the impedance spectra can be modeled by a high and low frequency process. The addition of H2O actually does not significantly impact the $a^*$ for the dominant low frequency process in the CO impedance spectra.

The impedance spectra for CH4 show the dramatic increase in $R_{pol}$ at $\eta_a = 0.0$ V for the direct exposure of the Ni surface to CH4. At $T_{cell} = 800^\circ$C, $R_{pol}$ at $\eta_a = 0.0$ V is over an order of magnitude larger than that for CO but the increase in $T_{cell}$ to 900°C resulted in a dramatic decrease in $R_{pol}$ to values of approximately 400 $\Omega$. Fitting the impedance spectra for CH4 remains problematic because of the significant low frequency noise and as such, dominant processes cannot be readily identified as with the CO oxidation. This will be alleviated in future studies with the use of reference electrodes on the anode side.

It should be noted that while the high values for $R_{pol}$ at $\eta_a = 0.0$ V are shown in Figure 5, the $R_{pol}$ for CH4 reduced to $< 100 \Omega$ as $\eta_a$ increased above 0.5 V. As stated earlier, this suggested that steam reforming becomes significant with the production of H2O from the increased production at higher $\eta_a$. This CH4 behavior has significant implications in direct utilization of SOFC, which remains to be explored as the kinetic processes of so-called direct electrochemical oxidation are more fully understood.

CONCLUSIONS

The use of patterned anodes provided a means to investigate the multi-step electrochemical oxidation of CO and CH4 on Ni anodes in both dry and wet environments. The isolation of the electrochemical oxidation processes from non-electrochemical chemistry and gas-phase diffusion allowed for a clearer assessment of the effects of anode geometric parameters such as $a_{anode}$ and $l_{TPB}/a_{mem}$ as well as anode feed H2O content. For the temperature range of this study (750-900°C), the polarization and AC impedance measurements for the Ni/YSZ anode point to Ni surface area-dependent phenomena controlling the reaction rates for $l_{TPB}/a_{mem} > 1.0$ m/cm². This results stands in contrast to other patterned anode half cell studies which suggested that polarization did correlate strongly with $l_{TPB}/a_{mem}$ for H2 oxidation (9, 10). However, the difference in YSZ surface conditions with the half-cell studies and the lower temperatures may have resulted in differences in the rate-controlling step in those studies and the current study. The results of the current study provide a strong indication that adsorption/desorption equilibration may play a decisive role in the oxidation of both CH4 and CO. It will be important to explore this hypothesis further by examining model predictions of impedance spectra and polarization curves using multi-step chemistry (even with uncertain rates) for CH4 and CO electrochemical oxidation on Ni/YSZ anodes. While quantitative mechanisms for such multi-step processes do not exist, the kinetic richness of electrochemical measurements, and in particular AC impedance spectra, provides a basis for exploring the rates of the adsorption/desorption and charge transfer processes that may control the oxidation rates of the fuels.
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