EVALUATION OF THE THERMODYNAMICS AND KINETICS OF CATALYTIC STEAM REFORMING OVER SOFC ANODE MATERIALS

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ABSTRACT

The purpose of this investigation is to study the catalytic effect of SOFC anode material on steam reforming of methane and coking. The thermodynamics and kinetics of various reactions taking place at the anode of the solid oxide fuel cell when methane is used as fuel have been investigated at various steam/methane ratios at 1000°C. An analysis of the residual gas from the SOFC under open circuit condition showed the extent of steam reforming in the presence and absence of the anode. The carbon deposition, when different steam/methane ratios were used, has been studied after running the cell under open circuit conditions. The structure of the cermet after exposure to different conditions has also been analyzed using optical microscope and AES.

1. INTRODUCTION

The high temperature operation of solid oxide fuel cells (SOFC) allows internal reforming of methane and hence provides an efficient way to utilize the world's natural gas reserves. High operating temperatures (1000°C-1200°C) however raise the cost of heat exchangers, pipes and other auxiliary parts in addition to lowering the cell life. Lowering the operating temperature to 800°C-900°C would require an increase in the steam/methane ratio in order to avoid carbon deposition on the anodes. Carbon deposition at the anode is known to cause degradation of the cell performance through polarization and rapid losses of reforming (1,2). If a suitable catalyst could be found that promotes the steam reforming without causing carbon deposition, the operating temperature could be lowered. It is the scope of the current work to understand the catalytic effects of the Ni-ZrO₂ cermet and identify the parameters that influence the catalytic process. These findings are useful for developing and processing new and better catalytic materials to be used as anodes in the SOFC.
Hydrogen generation through catalytic steam reforming primarily occurs through the following reaction.

$$\text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{anode}} \text{CO} + 3\text{H}_2$$  \[1\]

To a certain extent, the water-gas-shift reaction is catalyzed as well at the anode (3).

$$\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{anode}} \text{CO}_2 + \text{H}_2$$  \[2\]

The coking, which results in carbon deposition is represented by the following reactions.

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$$  \[3\]

$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$$  \[4\]

A perfect anode should catalyze reactions [1] and [2], and inhibit reactions [3] and [4]. The role of Ni as a catalyst for reaction [3] has been observed in the literature (3). Reaction [4] is simply the reverse Boudouard reaction and due to its sluggish kinetics not expected to contribute significantly to coking at the anode (4). In addition to reactions [1]-[4], a number of other reactions involving higher hydrocarbons may also occur, but under our operating conditions these were found to be insignificant. Note that reactions [1]-[4] may contain a number of intermediate steps such as adsorption, dissociation, surface diffusion etc. and either one or more of these can be rate limiting. Recognizing the rate limiting step is a good starting point for developing a better catalyst. The present work investigates the extent to which the various reactions at the anode proceed under the SOFC operating conditions by analyzing the residual exit gas. Ni-ZrO$_2$ anodes have been structurally and chemically analyzed after exposure to different gas compositions. The evaluations in the present work have mostly been made under open circuit condition. Since the oxygen partial pressure over the anode is lowest under this condition, the risk of having carbon deposition is maximal. In order to ensure that there was no oxygen migration through the electrolyte the thickness of the same was kept at 1.5 mm.

2. EXPERIMENTAL SETUP AND PROCEDURE

The schematic of the cell arrangement is shown in Fig. 1. The electrolyte consisted of a fully dense YSZ disc, 16 mm diameter and 1.5 mm thick. The anode was prepared by dip coating the YSZ disc in a Ni-ZrO$_2$ slurry and then subjecting it to a sintering procedure. The slurry was prepared by mixing 54 weight% Ni powder (INCO type 287) with 6 weight% YSZ powder (TOSOH TZ-8Y) and 40 weight% PVA solution. Varying the YSZ content in the slurry had a great influence on the final adherence of the
cermet to the electrolyte substrate. A minimum of 5-6 weight% YSZ was necessary to obtain a well bonded electrode. The PVA solution consisted of 6% Polyvinyl Alcohol (Dupont Elvanol Grade 75-15) and de ionized water. The coated substrate was heated for 17 hours at 1100°C in an atmosphere of 5% H₂ and 95% N₂. After cooling the substrate it was infiltrated with a solution containing 30 vol% ZrO₂ powder and 70 vol% of a mixture of de ionized water and nitric acid. Finally the substrate was sintered a second time for 7 hours at 1200°C in a atmosphere of 5%H₂ and 95%N₂. The typical composition of the final cermet was 75 weight%Ni and 25 weight%ZrO₂, with an average porosity between 20-30%. A more detailed description of the various steps and method for determining porosity has been published (5). The thickness of the anode was maintained at around 65 μm. Pt paste (Englehard 6926 which contains no flux) was painted on the other side of the electrolyte substrate to be used as cathode. The electrode coated electrolyte substrate was then mounted at the end of a alumina tube. A high temperature ceramic adhesive (Ultra-Temp 516, Aremco products, INC) was applied at the joint between tube and substrate with the purpose of bonding and sealing the substrate to the tube. After drying the adhesive, the system was heated and maintained for 5 hours at 90°C. A nickel wire connected to a gauze was pressed with a alumina tube on the cermet-anode. Similarly a platinum gauze connected to a Pt wire was pressed onto the cathode using an alumina tube. The length of the furnace was 60cm with a constant temperature zone of 35cm. CH₄(g) and H₂O(l) were introduced into a mixer that was maintained at 180 °C. The liquid water was injected by using a micro-pump (115 VAC 50/60 HZ model, Manostat). The rate at which water was introduced into the system was maintained at a constant level (0.014 moles/min) and the ratio of CH₄/H₂O was varied by changing the CH₄ input to the system. A fine stainless steel tube (ID = 0.4mm) was used to introduce the gas mixture into the hot zone of the furnace. The tube was kept small so that the gas would quickly reach the hot zone unreacted and thus maintain the desired CH₄/H₂O ratio. The outer furnace tube was kept large enough so that the gas mixture had sufficient time to reach 1000°C before contacting the anode. When smaller tubes were used, no reaction whatsoever was detected and the inlet gas composition was exactly the same as that of the outlet. Even when pure CH₄ was passed through the tube no carbon deposit was detected. Calculations based on convective heat transfer showed that the gas in this case did not have enough time to get heated. Lowering the total flow rate to increase the gas residence time in the hot zone would mean lowering the water flow rate. This was not desirable since this would result in longer time periods between subsequent drops pumped from the micro pump which would lead to an uneven gas composition. After analyzing the data from these experiments, future experiments with lower gas flow rates will be performed with a micro-pump having better resolution. The gaseous reaction products were led out through an alumina tube that pressed the nickel gauze onto the cermet. Thus the gases in the system were forced to contact the cermet before exiting. The exit gases were quenched and analyzed by a residual gas analyzer (M200 Quadropole Gas Analyzer, Dycor/AMETEK). The gas analyzer was pre calibrated for
the CH₄-H₂-CO-CO₂ system. The theoretical calculations of various equilibrated conditions were carried out using the SOLGASMIX code that is based on a free-energy minimization algorithm.

3. RESULTS AND DISCUSSION

Catalytic effect and reaction kinetics

The catalytic performance of the Ni-ZrO₂, for steam reforming of methane, was studied by analyzing the product gases. Since the steam in the outlet gas was collected in a condenser as liquid water, the gas analyzer gave the fractions of the species CH₄, H₂, CO and CO₂. The fraction of a specie fᵢ in the outlet gas can be expressed as:

\[ fᵢ = \frac{Nᵢ}{\sum Nᵢ} \]  \[\text{[5]}\]

Where \(Nᵢ\) is number of moles of H₂, CH₄, CO, or CO₂ in the outlet product gas per unit time. The term \(\sum N_{\text{species}}\) is the total number of moles of dry outlet gas per unit time and can be expressed as \(N_{H₂} + N_{C\text{inlet}} - N_{C\text{dep}}\). \(N_{C\text{inlet}}\) is the number of moles of carbon in the inlet gas which is equal to the moles of carbon in the outlet gas \(N_{CH₄} + N_{CO} + N_{CO₂}\). Using equation [5], \(N_{H₂}\) can now be expressed as \(f_{H₂}(N_{CH₄\text{inlet}} - N_{C\text{dep}})/(1-f_{H₂})\). By using this expression for \(N_{H₂}\) in the denominator of equation [5] it can be found that the number of moles of species i in the outlet gas can then be written as:

\[ Nᵢ = fᵢ \cdot \left(\frac{N_{CH₄\text{inlet}} - N_{C\text{dep}}}{1-f_{H₂}}\right) \]  \[\text{[6]}\]

The mass balance for hydrogen gives the number of moles of steam in the product gas:

\[ N_{H₂O} = 2 \cdot N_{CH₄\text{inlet}} + \frac{N_{CH₄\text{inlet}} \cdot (2 \cdot f_{CH₄\text{inlet}} + f_{H₂\text{inlet}})}{1-f_{H₂}} \]  \[\text{[7]}\]

By applying a mass balance for oxygen and assuming that the oxygen leaking into the system was insignificant (based on the open circuit voltage reading), the rate of carbon deposition can be expressed as:

\[ N_{C\text{dep}} = N_{CH₄\text{inlet}} - \frac{(1-f_{H₂}) \cdot 2N_{CH₄\text{inlet}}}{2f_{CH₄\text{inlet}} + f_{H₂\text{inlet}} - f_{CO} - 2f_{CO₂}} \]  \[\text{[8]}\]

Figures 2 and 3 show the theoretically calculated (using SOLGASMIX algorithm) thermodynamic equilibrium values at 1000°C for H₂, CO₂ as well as those obtained
from real experimental conditions with and without the Ni-ZrO₂ cermet at CH₄/H₂O ratios of 1/9, 1/6, 1/4 and 1/2. The strong deviation from equilibrium for the experimental values is due to most of the methane and steam remaining unreacted. Apparently reactions [1] and [2] are extremely sluggish and therefore the efficiency of reforming is nearly zero when no cermet is used. When no cermet was used some carbon was observed in the hot zone of the furnace when CH₄/H₂O ratio was greater than 1/4. According to theoretical calculations (SOLGAS MIX) carbon should not form under equilibrium conditions if sufficient reforming takes place and at 1000°C this should be the case when CH₄/H₂O < 1. Evidently the fact that carbon does form shows that the kinetics of the reforming reaction [1] is indeed slow whereas reaction [3] is taking place. Figure 2 and 3 also show the effect of the Ni-ZrO₂ cermet under open circuit conditions compared to the blank run. Clearly both reactions [1] and [2] are catalyzed by the cermet as the rates of H₂ and CO₂ are increased by nearly an order of magnitude. The results seem to suggest that CH₄ and CO are preferentially adsorbed on the cermet and converted to H₂, CO and CO₂. The product gas analysis when the cermet was used is shown in fig. 4 together with the carbon deposition calculated from equation 8. From mass balance considerations and using equations [1] and [2], if no carbon was deposited the rate of H₂ evolution, N₇H₂, should follow the equation given below.

\[ N₇H₂ = 3 \cdot N_{CO} + 4 \cdot N_{CO₂} \]  \[9\]

The positive deviation of the actual N₇H₂ from equation [9] is due to additional H₂ formation from reaction [3]. This seems to be supported by the N₇dep line which is increasing along with the increasing N₇H₂ deviation in fig. 4. Fig. 5 shows effectivity of reforming and is expressed in terms of the fraction of CH₄ and H₂O converted as a function of fraction of CH₄ in the inlet gas, the amount of water vapor being constant. The fraction of converted steam seems to be continuously increasing as methane input is increased. The methane conversion on the other hand seems to go through a maximum at XₗCH₄inlet = 0.2. The reason for this is not clear but may be explained by considering that CH₄ and CO molecules compete for the adsorption sites on the cermet. This phenomenon has also been suggested in literature (6). Once all the available adsorption sites for CH₄ are filled, apparently when XₗCH₄inlet = 0.2, a further increase in the inlet methane does not result in an increase in its conversion. A possible increase in the anode surface area or increasing the Ni dispersion could at this stage shift the apparent CH₄ conversion maximum to higher XₗCH₄inlet.

Sintering and Carbon deposition on the anode

A cross section of an anode exposed to CH₄/H₂O =1/4 for 10 hours is shown in figure 6. It can be seen here that the Ni particles may have slightly sintered. The open circuit voltage (OCV) of the cell under these conditions was around 0.85 V. The anode shown
in Fig. 7 was exposed to CH\textsubscript{4}/H\textsubscript{2}O = 1/2 (with an OCV of 0.9 V) for 10 hours and subsequently large white agglomerates were seen filling the porous areas and in the experimental set-up some carbon flakes were also found underneath the cell assembly. Cells that were run for over 10 hours at CH\textsubscript{4}/H\textsubscript{2}O = 1/2 had significant amount of cracks on the surface and the cermet seemed to be bulging. A similar phenomenon has been reported earlier by Mogensen et. al. (7). In experiments where the CH\textsubscript{4}/H\textsubscript{2}O ratio was increased above 1/2 the cermet completely peeled off from the electrolyte. The surface of the anode shown in figure 7 was also analyzed using AES (Auger Electron Spectroscopy). Three 1\mu m (diameter) areas were scanned as shown in figure 8. Area 1 is the white phase filling up the pores, area 2 is the three phase contact region (Ni-ZrO\textsubscript{2}-pore) and area 3 is the pore. Due to high background disturbances the Auger electron spectrum for area 3 was hard to interpret. Both areas 1 and 2 showed characteristic Auger electron energy peaks for oxygen and carbon but area 1 also showed peaks for Zr. No Ni was found at the outer surface of the anode. It is possible that most of the Ni is covered by deposited carbon. Table 1 shows the relative composition based on the respective peaks for areas 1 and 2. It should be noted that the values in table 1 are based on the number of counts from peak to peak and the sensitivity factor of the scan and therefore are relative values that should not be taken as exact composition analysis.

| Area 1 | Element | Peak-to-peak | Sensitivity Factor | Concentration(%) |
|--------|---------|--------------|-------------------|-----------------|
|        | C       | 197800       | 0.140             | 18.21           |
|        | O       | 2200400      | 0.400             | 70.92           |
|        | Zr      | 134900       | 0.160             | 10.97           |
| Area 2 | Element | Peak-to-peak | Sensitivity Factor | Concentration(%) |
|        | C       | 138600       | 0.140             | 16.53           |
|        | O       | 1574000      | 0.400             | 65.69           |
|        | Zr      | 1705000      | 0.160             | 17.79           |

In order to examine the depth of the carbon layer, the surface was sputtered with Argon for approximately 10 minutes. After sputtering in area 2, Ni was detected in addition to O, C and Zr. Area 1 still showed characteristic spectra for Zr and O but no carbon was found. The white phase seems to be predominantly zirconia that has sintered into a larger particle. Based on the above mentioned observations, the probable reason for the cracks on the anode and its peeling when CH\textsubscript{4}/H\textsubscript{2}O > 1/2, is stated below:

The carbon preferentially deposits around the nickel and probably separates the nickel from the fine zirconia particles. The zirconia particles without the intermediate nickel particles begin to agglomerate and sinter to the substrate. The entire process pushes the
carbon covered nickel particles towards the surface creating cracks and preventing the nickel particles from further sintering.

SUMMARY

An experimental arrangement equipped with a gas analyzer has been designed and built to evaluate the effectiveness of SOFC anode materials towards internal steam reforming of methane. The present study was conducted at 1000 °C with Ni-ZrO₂ cermet anodes. In the absence of cermet, no reforming of methane was noticed, but when CH₄/H₂O ratio was greater than 1/4, carbon deposition was noticed. Reforming of methane occurred in the presence of the cermet and the critical CH₄/H₂O ratio for carbon deposition also increased. As the methane input to the system was increased keeping the water at the same level, a maxima in methane conversion was noticed although the water conversion increased continuously. Carbon was seen to preferentially deposit around the nickel particles causing them to separate from the zirconia. This facilitated the zirconia to sinter and agglomerate into larger particles and causing the nickel portions to finally peel from the electrolyte substrate.

FUTURE WORK

The results reported in this paper forms a base line for evaluating internal reforming characteristics of other anode materials as a function of temperature. The role of ionic and electronic defects in the cermet will be elucidated. New experimental techniques will include measuring exchange current densities of the anode and evaluating anode polarization as a result of carbon deposition.

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835
Ni wire
METHANE
STEAM
outlet for gaseous reaction products
Ni Gauze
anode (Ni-Zr cermet), thickness 0.05 mm

Pt gauze
Pt wire
electrolyte (YSZ), thickness 1.5mm, cathode (Pt paste)

AIR inlet

Figure 1. Configuration of the cell

![Graph showing the outlet rate of H₂ as a function of inlet CH₄ feed or inlet gas ratio of (CH₄/H₂O); - equilibrium, ♦ no cermet, 0 Ni-ZrO₂]

Figure 2. Outlet rate of H₂ as a function of inlet CH₄ feed or inlet gas ratio of (CH₄/H₂O); - equilibrium, ♦ no cermet, 0 Ni-ZrO₂

![Graph showing the outlet rate of CO₂ as a function of inlet CH₄ feed or inlet gas ratio of (CH₄/H₂O); □ equilibrium, ♦ no cermet, 0 Ni-ZrO₂]

Figure 3. Outlet rate of CO₂ as a function of inlet CH₄ feed or inlet gas ratio of (CH₄/H₂O); □ equilibrium, ♦ no cermet, 0 Ni-ZrO₂
Figure 4. Outlet rate of H₂, CO, CO₂ and carbon deposition C_{dep} as a function of inlet CH₄ feed or inlet gas ratio of (CH₄/H₂O); □ H₂, +CO₂, ◦CO, △ 3NCO+4NCO₂; -Δ-N_{dep}

Figure 5. Effectivity of reforming expressed as fraction of converted CH₄ and H₂O as a function of fraction CH₄ in inlet feed gas, □ H₂O, ■ CH₄

Figure 6. Cross section of an anode that was exposed for 10 hours to CH₄/H₂O ratio of 1/4
Figure 7. Cross section of an anode that was exposed for 10 hours to CH₄/H₂O ratio 1/2

Figure 8. AES image of the surface of the cermet shown in figure 9. The numbers 1, 2 and 3 refer to the areas that were examined by Auger Electron Spectroscopy (AES)