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Effect of anodic polarization on carbon deposition on Ni/YSZ anodes exposed to methane

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ABSTRACT

The formation of carbon is a problem when operating solid-oxide fuel cells (SOFC) containing nickel/yttria-stabilized zirconia (Ni/YSZ) anodes with hydrocarbon fuels directly. Previous studies have examined the carbon formed ex-situ on Ni/YSZ anodes. In this study, we have examined the carbon formed in-situ under operating conditions, and investigated the effects of current density, time, and anode thickness on both the amount and type of carbon formed at 1073 K using temperature programmed oxidation and scanning electron microscopy. The carbon formed under operating conditions was more reactive and contained hydrogen compared to the carbon formed at open circuit potential that did not contain hydrogen. When the current density was increased less carbon was deposited, but the characteristics of the carbon did not change. With increasing time and/or anode thickness, the carbon deposits became more difficult to remove and decreased in hydrogen content.

1. Introduction

Fuel cells are highly efficient devices that directly convert chemical energy into electrical energy. Because there is not an established infrastructure for hydrogen processing and distribution, one of the major obstacles for commercialization of fuel cell technology is the need for hydrogen fuel. Some types of fuel cells, however, can operate with hydrocarbon fuels such that a hydrogen infrastructure is not required. In particular, solid-oxide fuel cells (SOFC) operate at temperatures above 873 K and have been shown to work well on hydrocarbon fuels in the presence of an excess of steam—generally with steam to carbon ratios greater then two [1,2]. Without steam, coking and subsequent deactivation of the fuel cell will occur on the traditional nickel/yttria-stabilized zirconia (Ni/YSZ) anodes [3].

Carbon deposition takes place through the catalytic dissociative adsorption of hydrocarbons on the Ni surface. For example, with methane, solid carbon is formed through reaction (1) [4]. The adsorbed carbon can be removed through the addition of steam as shown in reaction (2). The presence of large quantities of steam in the feed, however, makes the fuel cell system more complex, and reduces the overall process efficiency due to the decrease of the open circuit potential (theoretical maximum potential).

$$CH_4 \rightarrow C + 2H_2 \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 \quad (2)$$

Carbon deposition on Ni has been extensively studied because of the use of Ni catalysts in many industrial applications, such as steam reforming and methanation. The composition of the reacting gas, the temperature, the catalyst support, the Ni particle size, and the presence of different promoters on the catalyst affect the rate of carbon deposition [4]. In addition, carbon can form diverse structures including adsorbed, polymeric, vermicular filaments, carbide, and graphitic, which affects carbon reactivity [4], and the extent of catalyst deactivation [5].

The Ni in a Ni/YSZ anode, however, is not identical to a supported catalyst. Dispersed nickel catalysts used in steam reforming consist of porous supports, nickel contents of 15–20 wt%, and nano-sized nickel particles [6]. In contrast, Ni/YSZ anodes contain 40 wt% or higher Ni, and micron-sized Ni and YSZ particles. Several characterization studies of the carbon deposits formed on Ni/YSZ exposed to methane have been published [7–10]. In general, temperature programmed oxidation (TPO) experiments showed that carbon becomes less reactive with increasing exposure time and temperature. Under certain conditions, the number of deposited carbon atoms can be greater than the number of surface Ni atoms. This fact has led researches to suggest the formation of carbon fibers [7,8]. Our previous work examined the

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types of carbon that form on Ni/YSZ pellets (~1 mm thick) exposed to humidified methane [9]. At lower reaction temperatures (773–873 K) carbon nanofibers were formed, while at higher temperatures (873–1073 K), the deposited carbon dissolved into the nickel particles. In either case, after methane exposure the Ni/YSZ pellets had expanded; within a SOFC, this expansion could result in fracture of the cell.

These ex-situ studies provide a good basis for studying the carbon formation problem, but they only consider methane catalytic decomposition and reforming reactions, and have not included the electrochemical reactions present in a working fuel cell. In a SOFC, oxygen ions are produced at the cathode and are transferred to the anode through the electrolyte; the number of oxygen ions transferred is proportional to the cell current. When there is no current flowing (open circuit conditions), the cell is at electrochemical equilibrium and the cell potential is at its maximum. When the current is flowing (polarized conditions), there is a reduction of the potential from the equilibrium value according to the current drawn. It has been reported that by maintaining a high cell current density, stable operation using hydrocarbons with low or no steam content in the fuel was achieved [3,11]. The current density within a cell, however, is not constant [12,13]. Thus, it may not be feasible to maintain the entire stack at a sufficient current density to prevent coking.

In this paper, we have studied the carbon deposits formed on polarized-Ni/YSZ anodes exposed to methane at 1073 K. The carbon deposits have been characterized using temperature programmed oxidation and scanning electron microscopy (SEM), and compared to the deposits formed at open circuit conditions. The effect of current density, time, and anode thickness on the carbon deposition has also been examined. As expected, less carbon is formed under polarized conditions, i.e., with the presence of oxygen ions in the system, but interestingly, this carbon contains hydrogen compared to the carbon formed at OCP that is completely dehydrogenated.

2. Experimental

2.1. Button cell preparation

In this work, electrolyte supported (button) cells were employed. To prepare the NiO/YSZ slurry, a mixture of 50 wt% NiO powder (Alfa Aesar) and 50 wt% YSZ (Tosoh, TZ-8Y) was ball milled for 48 h with zirconia milling media in ethanol. Terpineol (Alfa Aesar) was added to the NiO/YSZ powder to form a slurry, which was painted onto 0.5 mm thick YSZ (Tosoh, TZ-8Y) electrolyte disks. The anode material was sintered at 1623 K for 4 h in air with a heating and cooling rate of 5 K/min. After sintering, the anodes were ~25 μm-thick. Thicker anodes (50 μm and 75 μm) were also prepared. The geometric area of the anodes was 0.4 cm^2. For the cathode and reference electrodes, platinum paste (Engelhard) was used. Once the cell electrodes were completed, electrical contacts were connected to the cell by applying a loop of silver wire to the electrodes. The wires were attached to the electrodes using silver paste in the case of the Ni/YSZ electrode and platinum paste in the case of the platinum electrodes. Glass paste (ESL 4460, Fuel Cell Store) was used to seal the anode side of the cell onto the cell holder. The cell holder (Fig. 1) consisted of an external alumina tube, 18.5 cm long and 1.4 cm internal diameter and an inlet tube, 0.9 cm internal diameter. Preliminary studies indicated that the amount, but not the nature, of the carbon deposit on the anode increased when Pt current collectors were used instead of Ag current collectors. As a result, Ag current collectors were used with all of the anodes in this study.

All cell tests were performed at 1073 K and at atmospheric pressure. The anodes were reduced with a stream of 10% H_2 in He at 1073 K for 1 h, and then exposed to pure CH_4 (Praxair) with a flow rate of 50 ml/min (STP). The residence time of the feed in the alumina tube was 11.38 s but the conversion was sufficiently small that the change in the gas phase composition was negligible. The cathode side of the cell was open to atmospheric air. The experiments were performed for different periods of time – between 6 h and 72 h – and different current densities—0, 1 mA/cm^2, 10 mA/cm^2 and 50 mA/cm^2. Relatively low current densities were used to accelerate the formation of carbon. After a specific exposure time, the cell was cooled to room temperature in helium before breaking the glass seal to retrieve the cell and characterize the carbon deposits.

2.2. Characterization

Temperature programmed oxidation was used to identify the stability and amount of carbonaceous species formed on the Ni/YSZ button cells exposed to methane. TPO experiments were carried out using 10% O_2 in He with a flow rate of 50 ml/min (STP). The temperature was ramped from room temperature to 1173 K at 10 K/min and the effluent gases were analyzed using a mass spectrometer (Cirrus 200 Quadrupole). Masses 44 (CO_2), 32 (O_2), 28 (CO), 18 (H_2O), and 4 (He) were monitored during TPO, and the CO_2 and H_2O signals were calibrated after each experiment using gas mixtures of known concentration. Scanning electron microscopy (Philips XL30 ESEM) was used to study the morphology of the carbon deposited on the anodes. The samples were broken to expose the interior of the anode, and gold coated before analysis to reduce charging in the SEM.

3. Results and discussion

3.1. Effect of current density

To evaluate the effect of current density on the nature of the carbon deposits, Ni/YSZ anodes were exposed to methane for 6 h at current densities between 0 mA/cm^2 (open circuit conditions) and 50 mA/cm^2. After exposure, TPO was used to determine the amount and reactivity of the deposited carbon as shown in Fig. 2. The TPO profile of the anode exposed to methane at open circuit conditions consisted of one CO_2 peak at ~973 K (Fig. 2a). Comparable results are reported in the literature [7,9,14], where under similar conditions peaks between 823 K and 1073 K are found. The carbon that has formed at open circuit conditions contains no hydrogen as there was essentially no H_2O evolved during the TPO analysis (see enlargement of the H_2O signal in Fig. 2a). The TPO profile for the sample exposed to methane with a current density of 50 mA/cm^2 is shown in Fig. 2b and is substantially different than the profile in Fig. 2a. First, the amount of carbon formed under polarization is approximately 100 times less than at open circuit conditions (compare *y*-axes in Fig. 2a and b). Second, there are multiple CO_2 peaks that evolve at

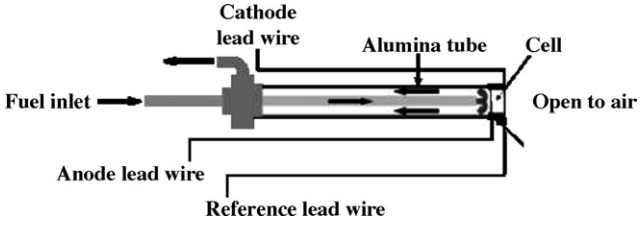

Fig. 1. Schematic of cell holder.