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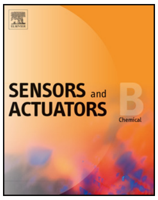

An impedance-based coke sensor for methane reforming systems

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A R T I C L E I N F O

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A B S T R A C T

A coke sensor designed to detect the early stages of catalyst coking in methane reforming systems has been developed. The sensor is made up of catalytic, non-percolating cermet resistive elements printed using an inkjet printer. As carbon is deposited on the catalytic surface, the electrical conductivity of the catalytic material increases, which results in a change in the continuously monitored bridge output voltage. The sensor has been designed to reduce unwanted gas-phase response and increase coking response in methane reforming environments. Voltage change due to gas-phase composition was reduced by a factor of ten from an SLT (strontium-doped lanthanum titanate)-based sensor by using YSZ (yttria-stabilized zirconia) to print all bridge elements. Steam and dry reforming tests were conducted at 600 °C with low steam-to-carbon and CO_2-to-carbon feed ratios to promote coking. The sensor showed strong response (on the order of several hundred millivolts) to carbon formation on the surface under both reforming environments studied. Field-emission scanning electron microscope (FESEM) imaging showed surface catalyst (Ni) particles encapsulated in films of carbon. Impedance spectroscopy of Ni-YSZ revealed resistive and capacitive behavior, both decreasing with the progression of coking. Sensors were regenerated using steam and then demonstrated similar, but smaller, responses to the same coking conditions. Investigation of regenerated sensor surfaces showed the presence of fewer catalyst sites compared to fresh sensors, indicating that the loss of nickel particles leads to a degradation in the sensor response.

1. Introduction

Steam reforming of methane is a mature industry and continues to be the primary and most economical source of hydrogen and syngas, both needed in a variety of chemical and petrochemical processes [1–4]. While several other techniques for hydrogen and/or syngas production (photochemical and photobiological processes, etc.) exist, they are still in the early stages of development and implementation; therefore steam reforming will continue to be an important industry for quite some time [5]. Nickel is the most commonly used catalyst in methane reforming, and catalyst deactivation due to coking is a major concern [6–9]. Coking refers to the formation of (usually unwanted) carbonaceous deposits by a side reaction in petrochemical processes [10]. Coking of the catalyst pellets decreases the active surface area of the catalyst, thereby decreasing the efficiency of the reforming process. While studies have been devoted to developing novel catalysts that are more resistant to coking, their widespread implementation in the industry remains largely absent due to cost, performance, and availability [6,11–14]. The dominant industry practice to avoid coking of the nickel catalyst in the steam methane reforming process is to operate under excess steam at the expense of reforming efficiency [6]. A sensor that can detect the early stages of catalyst coking will be helpful in saving the catalyst material from deactivation, and provide better control of the feed ratios to improve efficiency. Internally reforming solid oxide fuel cells may also benefit from a working sensor [15].

There have been several studies dedicated to the development of a coke sensor. Millichamp et al. used a gallium orthophosphate crystal microbalance to measure the mass change when carbon formed on the catalyst surface attached to the microbalance [16,17]. Müller et al. used impedance spectroscopy to measure changes in the electrical impedance of a catalyst pellet as carbon formed on its surface [18,19]. Wheeler et al. developed an impedance-based sensor that successfully detected trace amounts (<10 μg) of carbon deposits formed on an active nickel surface exposed to coking conditions in a reducing environment by reacting ethylene and hydrogen [20]. The sensor, manufactured using SLT (strontium-doped lanthanum titanate), YSZ (yttria-stabilized zirconia) and NiO (nickel (II) oxide) powders, utilized the fact that the formation of carbon deposits, usually in the form of nanowires, significantly changed the electrical conductivity of a non-percolating layer of catalytic nickel (where the metal particles are dispersed such that there are no connected pathways through the metal phase for

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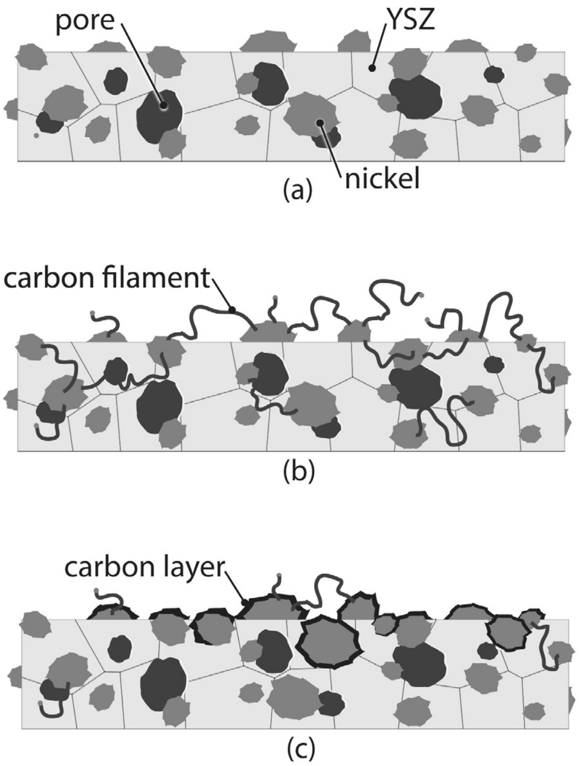


Fig. 1. Schematic of a non-percolating nickel catalyst layer. (a) In the absence of carbon, conduction paths are scarce and the electrical resistance is high. (b and c) Conduction paths open up when carbon deposits appear on the surface. Carbon filaments are abundant as in (b) in ethylene-hydrogen environments. Films of carbon on the nickel surface are more prevalent as in (c) in methane reforming environments and filamentous carbon is rare.

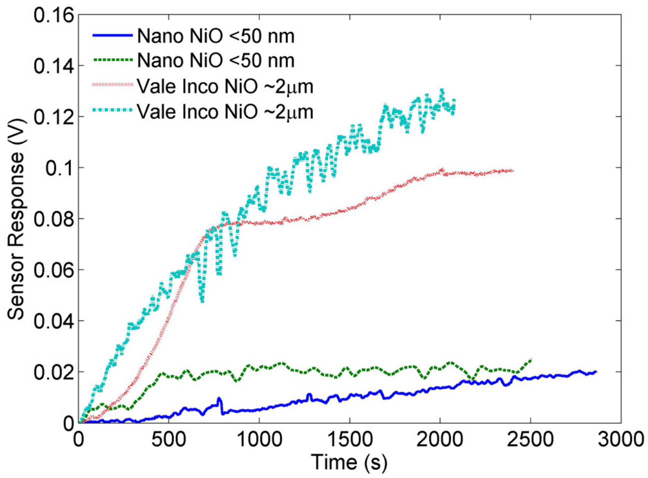
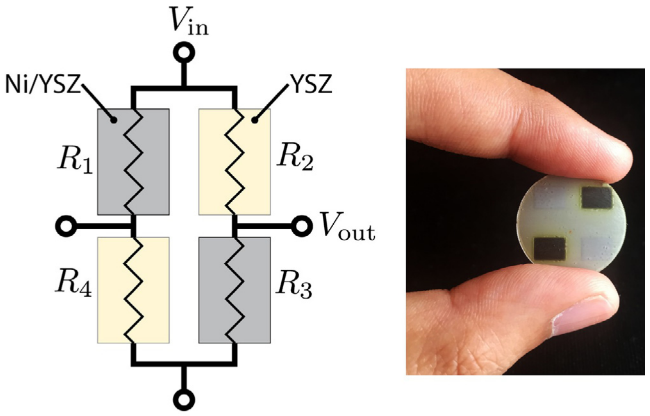


Fig. 2. Effect of nickel particle size on sensor response. Sensors were tested in dry-methane reforming coking conditions.



$$V_{\text{out}} = \frac{R_1R_3 - R_2R_4}{(R_1+R_2)(R_3+R_4)}V_{\text{in}}$$

Fig. 3. The half-bridge circuit that serves as the fundamental working mechanism of the sensor. All four elements of the Wheatstone bridge contain YSZ. Inset: A typical sensor has a diameter 21.5 mm and is 2.8 mm thick.

continuous electrical conduction) [21]. Fig. 1 illustrates the proposed mechanism. Initially, the sensor has a high electrical resistance due the scarcity of conduction paths in the non-percolating layer. As coking begins, carbon is deposited on the sensor surface. Carbon deposits open up conduction pathways between nickel particles, which increases the electrical conductivity of the sensor. The change in the electrical conductivity was monitored using a Wheatstone bridge circuit consisting of Ni-YSZ and SLT elements to detect the early stages of the coking of the catalyst in real time.

The morphology of the coke deposits depends on the coke precursor used. We discovered that the previous generation of sensors were not fully capable of detecting carbon formation in a methane reforming environment. Here, we report a sensor architecture capable of functioning under conditions typical in the steam-methane and dry-methane reforming processes.

2. Sensor architecture and ink formulation

A Fujifilm Dimatix DMP-2800 printer was used to print the Wheatstone bridge pattern onto a cold pressed (green) partially stabilized zirconia disc using inks containing ceramic powders in suspension. The sensor consisted of two elements made up of YSZ and two others made up of a non-percolating mix of NiO-YSZ. Vale Inco Grade F Black Nickel Oxide powder was used. The NiO powder had a mesh size of approximately 2 μm. Sensors made with smaller nickel oxide particles (Sigma–Aldrich <50 nm powder) did not yield strong responses to coking conditions. Fig. 2 compares the signals from sensors made with the two different NiO powders. When tested in a dry-methane reforming environment (0.05 SLPM flow of CH_4 reacted with 0.05 SLPM flow of CO_2 at 600 °C), it was found that the sensors made with the Vale Inco NiO powder had, at least, a 5-times better response to coking than the Sigma–Aldrich nanopowder. The results are consistent with findings in literature: the size of the active nickel particles plays an important role in the rate of coke formation, with smaller particles generally less susceptible to coking [22–26]. The Vale Inco NiO powder used was near the upper limit for the allowable particle size of the Fujifilm Dimatix printer. The printhead has an effective nozzle diameter of 10 μm, and particles larger than 1–2 μm have a large probability of forming aggregates larger than the nozzle diameter. Fig. 3 illustrates the Wheatstone bridge circuit used by the sensor. A printed and sintered sensor is also shown. Sensors are about 21.5 mm in diameter and 2.8 mm thick.

The work of Faino et al. [27] was used to develop the NiO-YSZ and YSZ ceramic suspension inks. Details of the ink formulation are in Table 1. Esprix MX-150 1.5 μm polymethyl methacrylate (PMMA) particles were used as a pore former in the NiO-YSZ ink to promote gas transport in the active catalytic elements. Solsperse 13940 was used as a dispersant. A ball mill was utilized to create and maintain a uniform suspension of powders in the inks.

The dominant form of carbon deposits in the oxidizing environments prevalent in methane reforming systems is different from the reducing environment under which the sensors were