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Enhanced hydrogen oxidation activity and H_2S tolerance of Ni-infiltrated ceria solid oxide fuel cell anodes

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HIGHLIGHTS

- Catalytic amounts (≤3 wt.%) of Ni were infiltrated into porous GDC anodes.
- Ni-infiltration significantly enhanced the rate of the H_2 oxidation reaction.
- Far less S poisoning was observed for Ni-infiltrated GDC anodes in 10 ppm H_2S.
- Ni-infiltrated GDC anodes exhibit improved long-term stability in 10 ppm H_2S.

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ABSTRACT

The effect of Ni infiltration into porous Gd-doped ceria (GDC) anodes on their H_2 oxidation performance, with and without added 10 ppm H_2S, is reported here. Porous GDC anodes (ca. 10 μm thick) were deposited on yttria stabilized zirconia (YSZ) supports and then infiltrated with catalytic amounts of a Ni nitrate solution, followed by electrochemical testing in a 3-electrode half-cell setup at 500–800 °C. Infiltration of 3 wt.% Ni into the porous GDC anode lowered the polarization resistance by up to 85%, affecting mainly the low frequency impedance arc. When exposed to 10 ppm H_2S, the Ni-infiltrated anodes exhibited a ca. 5 times higher tolerance toward sulfur poisoning compared to GDC anodes alone, also showing excellent long-term stability in 10 ppm H_2S. In the presence of H_2S, it is proposed that Ni, likely distributed as a nanophase, helps to maintain a clean GDC surface at the Ni/GDC interface at which the H_2 oxidation reaction takes place. In turn, the GDC will readily supply oxygen anions to the adjacent Ni surfaces, thus helping to remove adsorbed sulfur.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that efficiently and cleanly convert the chemical energy of fuels directly to electricity and heat. High efficiency, fuel flexibility, low emissions, and modularity are the key advantages of combined heat and power SOFC systems that are helping to drive this technology forward [1]. Owing to their high working temperature (600–800 °C), SOFCs are capable of using natural gas, diesel, etc. as a fuel. However, common SOFC anode materials, such as nickel–yttria-stabilized zirconia (Ni–YSZ), suffer from several disadvantages, such as coking in hydrocarbon fuels [2], poisoning even at low levels of H_2S [3,4], and redox instability with accidental air exposure [5].

To overcome these problems, ceria and doped-ceria mixed ion and electron conductors (MIECs) have been extensively studied as anodes, due to their high catalytic activity and their ability to use hydrocarbon fuels without coking [6–9]. As recently proposed by Shishkin and Ziegler [10] and experimentally proven by Chueh et al. [11] and Nakamura et al. [12], ceria alone is catalytically active for H_2 oxidation. The use of ceria-based MIEC anodes increases the number of active sites without the need for a three phase boundary, as in the case of metal–oxide composites, thus helping to lower the polarization resistance (R_p). For example, it has been shown that increasing the ceria layer thickness from 7 to 45 μm linearly decreased the R_p value due to the associated higher catalytic surface area [12].

However, it has also been reported that Gd-doped ceria suffers from sulfur poisoning when exposed to 10 ppm H_2S [13] and several studies have been carried out to understand and overcome this problem [14–20]. Ni–GDC composite anodes (with a Ni content above the electron conduction percolation limit) have shown

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particularly promising performance [21–23], illustrating better hydrogen oxidation reaction (HOR, reaction (1)) kinetics and H_2S tolerance compared to conventional Ni–YSZ anodes [24].

$$H_2\ (g) + O^{2-}_{(GDC)} \rightarrow H_2O\ (g) + 2e^-_{(GDC)} \quad (1)$$

Another issue is redox instability, caused by the extensive expansion of Ni when it is converted to NiO [25], which can degrade the Ni–GDC anode. This can be minimized by using only catalytic amounts of Ni (below the percolation limit of conductivity). Primdahl et al. have demonstrated that a catalytic amount (0.8 wt.%) of Ni infiltrated into a porous GDC structure significantly decreased R_p [26,27]. Liu et al. have also shown a positive effect of the addition of 4 wt.% Ni to a $La_{0.8}Sr_{0.2}Cr_{0.8}Mn_{0.2}O_{3-\delta}$–GDC composite anode when operated in either H_2 or C_3H_8 [28]. However, the effect of catalytic amounts of Ni on the sulfur tolerance of GDC anodes has not been investigated as yet.

In the present study, the effect of Ni infiltration into a porous GDC anode layer on both its HOR activity and sulfur tolerance has been studied using a 3-electrode half-cell set-up at between 500 and 800 °C. It is shown that Ni infiltration significantly improves the HOR activity, affecting mainly the low frequency arc in open circuit impedance measurements. Ni infiltration ($\leq$3%) into ceria also significantly decreases the extent of H_2S poisoning, showing only a ca. 5% increase in R_p at 800 °C, compared to a ca. 40% activity loss for GDC alone, while also greatly improving the anode stability over longer time periods.

2. Experimental procedure

2.1. Cell fabrication

A thin film of $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC, $d_{50} = 0.3$–0.5 μm, Fuel Cell Materials Ltd.), mixed with a terpinol-based carrier, was applied to one side of a dense 1 cm × 1 cm × 0.5 mm Ceraflex YSZ (8 mol.% yttria stabilized zirconia) sheet to form circular (either 0.33 or 0.50 cm^2) working electrodes (WE). A symmetrical counter electrode (CE) and a small reference electrode (RE) were painted on the other side of the YSZ sheet using a similar terpinol-based paste. After drying at 120 °C, the cell was calcined at 1200 or 1250 °C for 4 h to form a porous, 10–20 μm thick GDC electrode. The cells that were fired at 1250 °C reached a stable baseline more rapidly in constant voltage or current experiments than those fired at 1200 °C, while the other properties of these cells remained the same. A microliter pipette was used to infiltrate 0.1 M $Ni(NO_3)_2.6H_2O$ in ethanol into the porous GDC layer, with the solution being seen to fully absorb into the anode structure. As the Ni map (EDX, Fig. 1c) also showed a uniform distribution of Ni throughout the anode microstructure, it was concluded that the Ni content of the anode was indeed 3 wt.%.

Au paste (C 5729, Heraeus Inc., Germany) normally served as the WE, CE and RE current collectors, with Pt paste (LP A88-11S, Heraeus Inc., Germany) sometime used for comparison. Au mesh was then attached to the WE, while Pt mesh was used to contact the RE and CE. The entire cell was then heated to 800 °C at 3 °C min^{-1} in 5 ml min^{-1} N_2 + 20 ml min^{-1} H_2 (3% H_2O), followed by cell testing.

2.2. Electrochemical studies

Electrochemical experiments were carried out in a half-cell set-up at 100 °C intervals between 500 and 800 °C using a mass flow controller adjusted gas mixture of 20 ml min^{-1} H_2 (3% H_2O) and 5 ml min^{-1} of either N_2 or 52 ppm H_2S in N_2 (to generate 10 ppm H_2S). Electrochemical impedance spectroscopy (EIS), constant current (galvanostatic), constant potential (potentiostatic), and open circuit potential (OCP) measurements were carried out using a Solartron 1287/1255 potentiostat/galvanostat/impedance analyzer. OCP EIS analyses (0 V bias, ±10 mV rms, 10^{-2} to 10^5 Hz) were first carried out from high to low frequency and then low to high to verify that the cell was stable and that the EIS data were reproducible. Constant potential experiments were carried out at a 100 mV anodic overpotential, while the applied currents were selected so that the measured anode overpotential was also roughly 100 mV. To confirm that the results obtained from constant potential and constant current experiments were in agreement, especially in the case of H_2S exposure, some samples were tested using both methods back to back.

2.3. Structural characterization

The microstructure and composition of both the as-prepared and long-term tested samples were determined using a Philips XL 30 scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) capabilities (Microscopy and Imaging Facility, University of Calgary). Fractured samples were used to determine the porosity, inter-particle connectivity, and the overall microstructure of the working electrode film. The distribution of Ni in the GDC porous structure was established during cross-sectional analysis by wavelength dispersive spectrometry (WDS), using a JEOL JXA-8200 electron microprobe (University of Calgary, Laboratory for Electron Microprobe Analysis).

3. Results and discussion

3.1. Anode microstructure

A highly porous SOFC anode structure is desired in order to facilitate the transport of fuel to electrochemically active sites and to remove the products from the anode pores. Good connectivity between the anode particles is also necessary in order to provide ionic and electronic conductivity across the electrode layer, which, in turn, enhances the anode activity and decreases its polarization resistance (R_p). To achieve this type of microstructure for porous GDC electrodes, often with varying Gd dopant contents, sintering temperatures of 1100–1350 °C have typically been used in the literature [12,19,27]. It is known that, as the sintering temperature increases, the active surface area decreases, resulting in a higher Rp value. Primdahl and Liu [27] reported a low Rp for a 40 mol.% Gd-doped ceria that was sintered at 1100 °C. In the present study, sintering temperatures of 1200 and 1250 °C were used to enhance the cell stability and to establish a stable baseline for the H_2S poisoning studies.

Fig. 1a shows the microstructure of a typical screen-printed, porous GDC electrode, fired at 1250 °C for 4 h and then infiltrated using 40 μl of a 0.1 M Ni nitrate solution, giving about 3 wt.% Ni after reduction. Fig. 1b shows the structure of a similar electrode, but after more than 60 days of electrochemical testing at 500–800 °C (mainly at 700 and 800 °C) in a reducing atmosphere. Both SEM images show that the GDC particles have good inter-particle connectivity and that the GDC layer has sufficient porosity for unimpeded gas transport. The Ni infiltrate could not be resolved in these SEM images, indicating that Ni is present in the form of nanoparticles, similar to what was observed by Tucker et al. after Ni nitrate infiltration into porous YSZ [29]. However, WDS elemental mapping of Ni, using an electron microprobe (Fig. 1c), shows a uniform distribution of Ni within the porous GDC structure.

After long term (ca. 60 days) testing (Fig. 1b, inset), the GDC particles have sharper edges and appear to be somewhat more sintered as compared to the as-prepared sample (Fig. 1a, inset).