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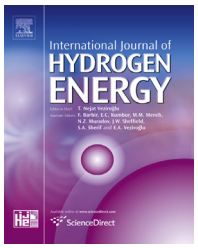

Nickel/gadolinium-doped ceria anode for direct ethanol solid oxide fuel cell

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ABSTRACT

This report investigates the properties of nickel/gadolinium-doped ceria (Ni/GDC) as anode material for bio-ethanol fueled SOFC. The Ni/GDC cermets with 18 and 44 wt.% Ni were prepared by a hydrothermal method. Ethanol decomposition, steam reforming, and partial oxidation of ethanol were studied using a fixed-bed reactor at 1123 K. Carbon was formed only under dry ethanol for both catalysts. The addition of water or oxygen to the feed inhibited the formation of carbon. Ni/GDC was used as the anode current collector layer and as a catalytic layer in single cells tests. No deposits of carbon were detected in single cells with Ni/GDC catalytic layer after 50 h of continuous operation under direct (dry) ethanol. This result was attributed to the catalytic properties of the Ni/GDC layer and the operation mechanism of gradual internal reforming, in which the oxidation of hydrogen provides the steam for ethanol reforming, thus avoiding carbon deposition.

Introduction

Solid oxide fuel cell (SOFC) technology is considered a promising alternative to provide clean electric power. Advantages include high efficiency, relatively low sensitivity to impurities, and the possibility of operating with an internal reformer [1–3]. In the case of direct internal reforming solid oxide fuel cells (DIR-SOFC), the complexity and costs of the fuel cell system are reduced, since the available fuels (hydrocarbons or alcohols) can be fed straight to the anode and reformed to H_2 and CO without the need of an external reformer. In addition, the conversion of these fuels at the anode side can be promoted due to H_2 consumption by the electrochemical reaction, leading to higher conversions and higher efficiencies [1,4,5]. Bio-ethanol is an attractive alternative renewable fuel that can be produced from a variety of biomass sources (e.g., fermentation of sugar cane, fermentation of corn grains, agricultural wastes, and forestry residues) and does not contribute to net CO_2 emissions. Furthermore, in countries like Brazil and the USA, the ethanol production and distribution infrastructures are already established.

Thus, ethanol is an efficient and available fuel that can play an important role as a carbon neutral fuel for SOFC. Nonetheless, relatively few studies have reported on bio-ethanol fueled SOFC. In fact, most of the reported results concern

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ethanol-water mixtures as fuel [6–11], while a limited number of studies have investigated the direct use of pure (dry) ethanol [12–17]. Moreover, data on the stability of such single cells over reasonable periods of time are seldom found [7,16,17].

Different materials have been used as anodes for ethanol fueled SOFC systems. Ni/yttria-stabilized zirconia (Ni/YSZ) cermets are the standard anodes of SOFC systems [18–20]. Ni provides electronic conductivity, while YSZ provides ionic conductivity and thermal stability. However, in order to exceed the percolation threshold for electronic conductivity, a high Ni content (>30 vol. %) is necessary. Since Ni is very active to reforming as well as cracking reactions, such a high volumetric fraction favors carbon formation when hydrocarbons or bio-ethanol are fed directly in SOFCs. The carbon deposits on metal sites located on the anode resulting in rapid degradation of the fuel cell [18,19]. Significant carbon deposition has been detected on Ni/YSZ anodes of SOFC containing high Ni loading and operating directly on pure ethanol [1]. Therefore, the development of anodes for direct ethanol SOFCs that exhibit high catalytic activity to ethanol conversion, high stability and adequate ionic and electronic conductivity at working conditions is still a challenge.

Some strategies have been proposed for suppressing carbon deposition over SOFC anodes such as: (i) the addition of water and/or O_2 to the feed, (ii) the development of alternative anodes, or (iii) the use of catalytic (barrier) layers.

Augusto et al. [21] reported that the addition of water or oxygen to the feed decreases carbon formation during ethanol reforming over Ni/GDC catalysts. Results were explained by a mechanism proposed for the reactions of ethanol conversion over cerium based catalysts [22]. According to this mechanism, carbon formation during ethanol reforming is due to the dehydrogenation of CH_x species, forming C and H. These highly reactive carbon species were formed by the decomposition of dehydrogenated species (e.g., ethoxy, acetaldehyde, acetyl) and acetate species. The oxygen and/or water in the feed can react with these carbon species, producing CO_x species, which avoids catalyst deactivation. Laosiripojana et al. [23] investigated the effect of H_2O/ethanol molar ratio on the amount of carbon formed during steam reforming (SR) of ethanol over Ni/CeO_2 catalysts. Increasing the H_2O/ethanol molar ratio decreased the amount of carbon deposited on the catalysts. However, some researchers [6,11] showed that the use of high steam/ethanol ratios leads to a decrease in the electrical efficiency of the SOFC system.

Alternative materials have been proposed as anodes for SOFC running directly on ethanol such as Cu supported on ceria-based oxides [6,9,12,14,24]. Ceria exhibits a mixed ionic and electronic conductivity under reducing atmosphere with good compatibility with standard SOFC components [25]. In addition, higher conductivities were obtained when ceria was doped with trivalent cations, such as Gd^{3+} [26]. Furthermore, the high oxygen storage capacity of ceria provides a high resistance to carbon deposition during ethanol reforming [27,28]. However, only few studies reported the use of Ni supported on ceria based oxides as anodes of SOFC running on ethanol [13]. Muccillo et al. [13] reported the current–voltage and impedance spectroscopy measurements for SOFC running directly on ethanol, using a commercial Ni/GDC anode (45 vol. %). The results obtained showed a strong deactivation of these anodes at high temperatures (>1073 K), which was attributed to the carbon formation. Nonetheless, the characterization of the tested anodes was not shown.

Another possibility for reducing carbon deposition is the use of anodes with low Ni content. Decreasing the metal content leads to the formation of smaller crystallite sizes. Since the initiation step for carbon formation is more difficult for smaller particles, controlling the number of atoms in an ensemble will most likely suppress the rate of coke formation [29]. In addition, the high metal dispersion obtained for metal nanoparticles increases the number of active sites at Ni based anodes, improving the performance of the SOFC [30]. However, cermets with metal contents below 30 vol. % and prepared by conventional methods did not exhibit an appropriate conductivity for SOFC applications [31].

Therefore, some authors [30,31] have proposed the use of alternative methods to prepare Ni-based anodes with high activity, high stability, high conductivity, and low metal content. Jasinski et al. [31] prepared Ni/samarium-doped ceria cermets with low Ni contents (7.5, 11 and 14 vol. %) by a net-shape procedure. They investigated the effect of Ni content on the electrical conductivity of the anodes under air or using a mixture containing 10% of hydrogen. The conductivity of the cermet with 14 vol. % Ni was close to the conductivity of the cermet with 35 vol. % Ni prepared by a conventional technique. In addition, the anode with 14 vol. % Ni was stable under hydrogen during a period of several hours. According to them, the Ni anode prepared by the alternative method exhibited unique properties and does not follow percolation theory. Recently, a hydrothermal method has been used to prepare anodes for SOFC with high resistance to carbon formation. Ni-based anodes with low metal content (5 wt.% Ni and 5 wt.% Ru) prepared by the hydrothermal method did not exhibit carbon formation during oxidative steam reforming (OSR) of propane under SOFC operating conditions [30]. Augusto et al. [21] investigated the performance of Ni/GDC anodes with low Ni content (18 wt.% Ni) prepared by a hydrothermal method for ethanol conversion reactions. The reaction conditions significantly affected the activity and stability of the catalysts. Ethanol decomposition (ED), SR and partial oxidation (POX) of ethanol reactions at 773 and 1073 K were performed. All samples deactivated during reaction under pure ethanol at 773 K. The addition of water or oxygen to the feed and the increase of reaction temperature improved catalyst stability. Scanning electron microscopy (SEM) and thermogravimetric analysis (TG) showed that the deactivation was due to carbon formation. In the presence of oxygen or water, the mechanism of carbon removal was favored. Moreover, carbon formation was not favored at high reaction temperature due to the reverse of the Boudouard reaction as well as the promoting effect of the support on the carbon gasification reaction. However, Modafferi et al. [30] and Augusto et al. [21] did not study the electrochemical properties of fuel cells operating on ethanol.

Alternatively, instead of changing the standard Ni/YSZ anode some studies reported promising results using a catalytic layer. Such an approach avoids the challenges of finding alternative anodes with superior properties than the ones of Ni/YSZ cermets. The main idea is to separate the