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Investigation of catalytic layers on anode for solid oxide fuel cells operating with synthetic biogas ☆

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ABSTRACT

In this paper solid oxide fuel cells operating with dry synthetic biogas have been examined. In order to increase their stability the layers of CuO-CeO_2, $Cu_{1.3}Mn_{1.7}O_4$ and $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ have been deposited on the Ni-YSZ anode site. These layers should catalyze the internal biogas reforming and prevent the carbon deposition on the anode site. It has been found that CuO-CeO_2 and $Cu_{1.3}Mn_{1.7}O_4$ catalysts led to an increase of the stability (at least 7 days) of the fabricated fuel cells powered by biogas, whereas the unmodified fuel cell, as well as the fuel cell with $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ catalyst degraded gradually with time. A significant amount of carbon nanofibers has been formed on the catalyst surface after fuel cell test. However, they have not formed in the anode area. The use of CuO-CeO_2 and $Cu_{1.3}Mn_{1.7}O_4$ catalysts prevented the carbon deposition on the anode site, and thus the fuel cell degradation was slower when operating with biogas fuel.

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1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device, which can directly convert chemical energy to the electrical energy with by-products in a form of heat and water. It is environmentally friendly because it emits lower amount of pollutants than conventional combustion engines, steam and gas turbines [1,2]. Various types of fuel can be applied to SOFCs [3,4]. Hydrogen was firstly used by Grove [5], and it is commonly applied these days. Methane [6], methanol [7], natural gas [8] or biogas [9] is also widely used. However, if they are intended to be used for power generation they must be reformed externally [10] or internally [11,12]. In these processes, the fuel is converted to hydrogen and carbon monoxide. According to the fact that an external reforming requires additional expensive system, a more desirable solution is an internal reforming. In this work, a particular attention will be paid to the internal reforming of biogas, which naturally comes from biomass [13] and usually consists of methane (40–65%) and carbon dioxide (30–40%). Reactions of dry biogas reforming are presented by set of Eqs. (1)–(5) [14,15].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (1)$$

$$CO_2 + H_2 \leftrightarrow H_2O + CO \quad (2)$$

$$CH_4 \leftrightarrow C + 2H_2 \quad (3)$$

$$2CO \leftrightarrow C + CO_2 \quad (4)$$

$$C + H_2O \leftrightarrow CO + H_2 \quad (5)$$

Eq. (1) presents CO_2 reforming, while Eq. (2) describes reverse water gas shift. The reaction (3) shows methane decomposition. The Boudouard reaction is represented by Eq. (4), while Eq. (5) corresponds to carbon gasification. The major products of reforming reactions (hydrogen and carbon monoxide) can be used as a direct fuel for the solid oxide fuel cells.

Every fuel cell consists of electrolyte and two electrodes: anode and cathode. The anode is called a fuel electrode. The most commonly used material in SOFC technology is a nickel cermet which is a composite of nickel oxide and yttria-stabilized zirconia (YSZ). During fuel cell operation with biogas a fast degradation of the fuel cell with the Ni-YSZ anode occurs [16]. It results from carbon deposition in the anode due to the methane cracking on nickel [17]. The process of carbon deposition is the fastest in the case of dry reforming of methane [18]. However, in real systems operating on natural gas or biogas the fuel is pre-mixed with steam, carbon dioxide, hydrogen, oxygen, or a mixture of them

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by recirculating a fraction of the anode exhaust. Essentially, an external oxidant is thus provided in order to promote the internal reforming and reduce the risk of carbon deposition on Ni electrode [19–21]. A solid carbon formation in the anode reduces mass transport of gas reactants to the triple phase boundary and deactivates the catalytic activity of Ni contained in the anode. As a result the performances of the electrochemical as well as the direct reforming reactions are decreased [19–22]. Moreover, the pipelines can be blocked [19]. Thus, to avoid carbon deposition inside reactors, steam and oxygen levels, catalyst types and operational conditions have to be carefully selected.

Therefore, new materials with better catalytic properties for biogas reforming are sought. Nowadays the most commonly used catalysts are noble metals like Ir, Pt, Pd, Rh and especially Ru or nickel compounds. In spite of their high activity, the catalysts based on noble materials are not widely used in industrial applications due to their high price. The nickel catalyst is much more popular; however, it suffers from undesired sintering of Ni grains as well as from high sensitivity to carbon deposition during operation with biogas. Although a decrease of working temperature can minimize the nickel sintering process, it should not be lower than 700 °C to achieve significant conversion of methane with the use of pure Ni catalyst [23].

The other catalysts are compounds from the $LnCoO_3$ family (Ln = La, Pr, Nd, Sm or Gd). They were characterized by high activity and selectivity for synthetic gas reforming [24]. Also oxides with perovskite structure such as $LaNiO_3$, $La_{0.8}Ca(\text{or Sr})_{0.2}NiO_3$ and $LaNi_{1-X}Co_XO_3$ (X = 0.2–1.0) are resistant to sintering and carbon deposition [25]. In the case of Ni/La_2O_3 catalysts, it was confirmed that the conversion of methane to hydrogen was close to thermodynamic predictions [26].

Another catalytic material is cerium oxide, which is able to store, release and transport oxygen, and thus it is known to be a good catalyst for biogas reforming. The conversion of methane to the synthetic gas takes place at temperatures below 600 °C. Cerium oxide was also used to assist Pt or Ni catalysts in methane partial oxidation or methane reforming with carbon dioxide [27–29]. However, it has been reported [30] that when cerium oxide is used as a support for nickel, the deposition of carbon is fast and the catalyst stops to fulfill its task [30]. In recent years composite catalysts $CuO\text{-}CeO_2$ with high catalytic activity received a special attention again [31,32]. In 1995 it was reported that $CuO\text{-}CeO_2$ was a very active catalyst for methane oxidation in presence of carbon monoxide. The conversion was up to 95% [31].

Also CuM_2O_4 (M = Fe, Al, etc.) spinel oxide can be used as a catalytic layer for synthetic gas internal reforming [33,34]. For instance, $CuMn_2O_4$ may present higher activity than $CuO\text{-}CeO_2$ catalyst [35]. Moreover, Cu-based spinel catalysts have thermal expansion coefficients (TEC) similar to this of the YSZ electrolyte [36], which is often used as a part of nickel anode composite. It has been found [37] that when $Cu_{1.3}Mn_{1.7}O_4$ was mixed with scandia-doped ceria (SDC) and screen printed on the anode site, the fuel cell performance reached 304 mW/cm^2 at 650 °C and carbon deposition was significantly reduced.

Another possible catalytic material is Y- and Fe-doped strontium titanate. In general, perovskite materials show stable performance both in H_2 and hydrocarbon fuels [38]. Among them $SrTiO_3$ substituted in strontium sublattice with a donor-type element, e.g. La, Y, Gd, Nb, shows high electronic conductivity [39]. On the other hand, titanium-site doping modifies the electrochemical and electrical properties of the resulting material, increasing also the thermodynamic stability in both oxidizing and reducing atmospheres. For example, $SrTiO_3$ acceptor doping with Co, Mn or Fe leads to an increase of oxygen vacancies concentration [40], which may provide active sites for fuel oxidation in anodes. Thus, simultaneously strontium and titanium-site substituted $SrTiO_3$ can act as a catalytic material for SOFC anodes [41,42].

Typically, the catalyst materials are deposited by infiltration into the anode skeleton. The alternative approach is to form a catalytic layer on the anode surface. This solution may prevent carbon deposition in the anode material. Moreover, since an internal reforming of H_2-containing fuels can take place in the catalytic layer, the anode will be fed with pure H_2 fuel. On the other hand, this approach requires a suitable design of the fuel cell: either the catalyst should be electronically conductive or the current should be collected from the anode, not from the catalytic layer.

It is obvious that the quality and efficiency of the catalytic layer will strongly depend on the fabrication method. Various methods of catalytic material preparation might have different effects on carbon deposition and degradation of the fuel cell. The aim of this paper is to present the influence of $Cu_{1.3}Mn_{1.7}O_4$, $CuO\text{-}CeO_2$ and $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ (YSTF) catalysts deposited on anode on the properties of modified fuel cells. The comparison of various materials should allow selecting the best candidate for SOFC operating with biogas. In order to make the fuel cell degradation faster and more intensive the experiments have been performed with dry biogas. Although the catalytic properties of the applied compounds towards biogas reforming have been analyzed in our previous paper [43], it is necessary to determine their structural and electrical properties in the fuel cell operating conditions. This approach complements and systematizes the current knowledge about these three potential catalysts for effective biogas reforming, which can operate with commercial Ni-YSZ anode.

2. Experimental

Four types of solid oxide fuel cells were investigated in this paper. The first one was a commercial 1-inch anode supported button type solid oxide fuel cell (Ningbo Research Institute of Materials, China), which operated as a reference cell. The fuel cell consisted of Ni-YSZ anode support (400 μm in thickness, 25 mm in diameter), YSZ electrolyte (10 μm in thickness, 25 mm in diameter) and LSM-YSZ cathode (40 μm in thickness, 11 mm in diameter). The following three were modified reference cells by deposition of cerium-copper-oxide ($CuO\text{-}CeO_2$), $Cu_{1.3}Mn_{1.7}O_4$ and $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ (YSTF) in the form of layers on the anode. An average thickness of the fabricated layers was ~150 μm.

In order to prepare the $CuO\text{-}CeO_2$ powder, copper nitrate (II) $Cu(NO_3)_2 \times 3H_2O$ [0.2 M] (Chempur, 99.0% purity) and cerium nitrate (III) $Ce(NO_3)_3 \times 6H_2O$ [0.1 M] (Aldrich) were dissolved in distilled water. Then the solution was heated up to 80 °C and stirred continuously for 3 h. As a result a blue homogeneous solution was obtained. Next, the precursor was placed in the dryer for 48 hours at 100 °C and then fired at 900 °C for 7 hours. A blue powder of CuO and CeO_2 mixture with molar ratio 2:1 was formed after sintering.

The $Cu_{1.3}Mn_{1.7}O_4$ powder was prepared similarly as $CuO\text{-}CeO_2$. Firstly, copper nitrate (II) $Cu(NO_3)_2 \times 3H_2O$ [0.26 M] (Chempur, 99.0% purity) and manganese (II) nitrate $Mn(NO_3)_2 \times 4H_2O$ [0.34 M] (Panreac) were dissolved in distilled water and ethylene glycol. For complexation and oxidation during decomposition, citric acid was added to this solution. The obtained solution was heated up to 70 °C and stirred continuously for 24 hours, and then sintered for 1 hour at 400 °C in order to receive a powder. Next, the powder was pressed to form a pellet, and in that form it was sintered for 10 hours at 800 °C. The pellet was ground in a mortar to obtain a powder again.

The $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ compound was synthesized by the Pechini method from the following substrates: yttrium nitrate hexahydrate (99.9%, Sigma Aldrich), strontium nitrate (99%, Fluka) and titanium (IV) butoxide (97%, Sigma Aldrich) mixed with citric acid (CA) and ethylene glycol (GE). Titanium butoxide was dissolved in a mixture of CA and GE (in 2:8 molar ratio). Next, the solution was heated up to 70 °C for 3 h. Then the nitrates were added and heated up to 120 °C to induce estrification process of ethylene glycol. The obtained viscous solution was dried at 250 °C yielding a sponge-like polymeric resin. The cleared resin was calcined in air at 1400 °C for 10 h to form the $Y_{0.08}Sr_{0.92}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ powder.

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