$CeCu_2O_4$ as a functional layer on solid oxide fuel cells for synthetic biogas reforming[*]

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Keywords: SOFC; biogas; reforming, catalytic layer

Abstract: At present Solid Oxide Fuel Cells (SOFC) are one of the most promising electrochemical devices which can convert chemical energy into electrical energy. Their ability to work with different kinds of fuel (eg. biogas) makes them noteworthy. A problem arises when solid carbon starts to be deposited on the anode: this leads to the degradation of the fuel cell. A simple solution is to apply a catalytic functional layer, which is able to reduce carbon deposition by reforming biogas internally. In this paper $CeCu_2O_4$ was chosen as a catalytic layer, due to its high catalytic activity. Two different ways of $CeCu_2O_4$ deposition are investigated – from solution and from paste. The obtained results were compared with an unmodified cell.
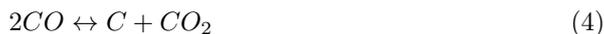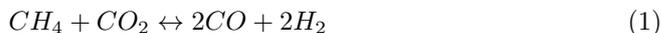
1. Introduction

Fuel cells are electrochemical devices which can convert chemical energy into electrical energy with heat and water as by-products. One of the types of fuel cells are Solid Oxide Fuel Cells (SOFC). They consist of a porous cathode, a porous anode, and a dense solid oxide electrolyte, which conducts only oxide ions. SOFC are called clean energy sources because they emit lower amounts of pollutants than conventional combustion engines, steam or gas turbines ((Haseli et al., 2008; Bavarsad, 2007). SOFC can be powered by many types of fuels (McIntosh and Gorte, 2004; Van Herlea et al., 2004). Hydrogen was first applied by Grove (Balmer, 2011) and it is commonly used these days. Methane (Sfeira et al., 2001), methanol (Laosiripojana and Assabumrungrat, 2007), natural gas (Boder and Dittmeyer, 2006) and biogas (Shiratoria et al., 2008) are also widely used. However, if they are intended to be used for power generation they must be reformed externally (Cocco and Tola, 2009) or internally (Clarke et al., 1997; Peters et al., 2002). In these processes, fuel is converted into hydrogen and carbon monoxide. External reforming processes are costly. Internal reforming is cheaper, and thus more desirable.

Biomass is a source of environmentally friendly biogas (Piroonlerkgul et al., 2008), which usually consists of methane (40 – 65%) and carbon dioxide (30 – 40%). Reforming reactions of biogas are presented by a set of equations (1) – (5) (Asencios et al., 2011; Bereketidoua and Goula, 2012).

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{1}$$

$$CO_2 + H_2 \leftrightarrow H_2O + CO \tag{2}$$

$$CH_4 \leftrightarrow C + 2H_2 \tag{3}$$

$$2CO \leftrightarrow C + CO_2 \tag{4}$$

$$C + H_2O \leftrightarrow CO + H_2 \tag{5}$$

Equation (1) presents CO_2 reforming, while equation (2) describes reverse water gas shift. Reaction (3) shows methane decomposition. A Boudoared reaction is represented by equation (4). Equation (5) presents carbon gasification. The major products of reforming reactions (hydrogen and carbon monoxide) can be used as a direct fuel for solid oxide fuel cells. Currently new catalytic materials are searched for in order to increase biogas reforming reaction efficiency.

An anode is called a fuel electrode. In SOFC it is mainly a composite of nickel oxide and a Yttria-Stabilized Zirconia (YSZ). In such cells, fast SOFC degradation takes place during fuel cell operation with biogas, especially with hydrocarbon (Takahashi et al., 2011). This phenomenon occurs when carbon deposits on the anode as a result of methane cracking on nickel (Macek et al., 2010). Therefore, new materials with better catalytic properties are sought.

The development of effective catalysts for methane and other volatile organic compounds (VOC) is needed. Nowadays the most commonly used catalysts are noble metals like Ir, Pt, Pd, Rh and especially Ru or nickel compounds. Catalysts based on noble materials are characterized by high activity. Unfortunately, high production costs of such systems limit their widespread application in industry. The nickel catalyst, mainly built onto alumina or silica, was studied. The main disadvantage of this system is related to a change of metal oxidation state and carbon deposition during sintering. To minimize these disadvantages the most obvious action would be decreasing working temperature. However, a part of the methane reforming reaction must take place at high temperatures, usually above 700 °C, to achieve significant conversion of methane.

It was proven that compounds from the family $LnCoO_3$ (Ln = La, Pr, Nd, Sm, lub Gd) had high activity and selectivity for synthetic gas reforming (Lago et al., 1997). Oxides with a perovskite structure such as a $LaNiO_3$, $La_{0.8}Ca(or\ Sr)_{0.2}NiO_3$ and $LaNi_{1-X}Co_XO_3$ (X = 0.2-1.0) are resistant to sintering and carbon deposition (Choudhary et al., 1996). Ni/La_2O_3 was investigated as a catalyst for partial oxidation of methane to synthetic gas and it was confirmed that conversion of methane to hydrogen was close to thermodynamic predictions (Tsipouriari and Verykios, 1998).

Cerium oxide abilities to store, release and transport oxygen make it a good catalyst for biogas reforming. It can convert methane directly into synthetic gas at temperatures below 600 °C. Cerium oxide was also used to assist Pt or Ni catalysts in partial oxidation of methane or reforming with carbon dioxide (Otsuka et al., 1993,

1997, 1998). Using cerium oxide as a support for nickel provides the active catalyst. Unfortunately, the deposition of carbon is fast and the catalyst stops to fulfill its task (Tang et al., 1998). In recent years composite catalysts Cu-Ce-O with high catalytic activity received special attention again. In 1995 it was reported that $CuO\text{-}CeO_2$ catalyst was very active for methane oxidation, in the presence of carbon monoxide. Conversion reached up to 95 % (Liu and Flytzanistephanopoulos, 1995).

Other materials based on copper and cerium oxide were widely studied as a catalytic material for biogas. The effects of r preparation were observed by many researchers, since various methods of preparing catalytic material might have a different effect on carbon deposition and degradation of the fuel cell. In this paper the copper-cerium-oxide catalyst was prepared in two different forms. Namely, a thick film layer on the anode, and the catalyst soaked into a thick film deposited on the anode. Fuel cells with an anode modified in this way are going to be investigated.

2. Experimental design

For the investigation presented in this paper three sets of fuel cells were used. The first one served as a reference. It was a commercial 1-inch anode supported button type solid oxide fuel cell (Nimbo Research Institute of Materials, China). The second set included the same cell, but modified. A porous skeleton of YSZ ($Y_{0.16}Zr_{0.84}O_2$) was deposited on the anode. The skeleton was soaked in a cerium-copper precursor. The third set was a commercial cell modified by deposition of cerium-copper-oxide from paste on the anode.
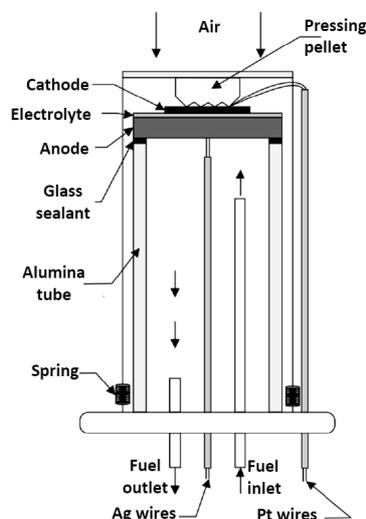

Fig. 1. Measurement cell.

The porous skeleton was prepared by deposing a layer of YSZ from paste (1.6 cm in diameter). The paste was made from YSZ powder (Tosoh) and an ESL 401

vehicle. The ingredients were grinded in a mortar for about one hour. The paste was deposited on the anode and sintered for 2 h at 1100 °C. The skeleton's porosity was 50 %.

The precursor of cerium-copper was made from copper nitrate (II) $Cu(NO_3)_2$ x $3H_2O$ [0,2 M] (Chempur, 99,0 % purity) and cerium nitrate (III) $Ce(NO_3)_3$ x $6H_2O$ [0,1 M] (Aldrich). The nitrates were dissolved in distilled water. The obtained solution was heated to 80 °C and stirred continuously for 3 h. As a result a blue homogeneous solution was obtained.

The YSZ porous skeleton was soaked in the copper-cerium precursor. Under the influence of capillary forces the solution infiltrated the YSZ skeleton. After each soaking the cells were placed on a hot plate heated to 400 °C until the water evaporated and the nitrates decomposed. The cell was weighed in order to determinate the increase of its weight. The infiltration process was repeated to obtain an increase of 2 % of the YSZ skeleton weight. Then the fuel cell was annealed for 2 h at 900 °C.

In order to make the copper-cerium-oxide paste, which was used in the third sample set, a copper-cerium precursor was prepared as described above. The precursor was placed in a dryer for 48 h at 100 °C and then fired at 900 °C for 7 h. A blue powder of copper-cerium-oxide was created after sintering. The powder and the ESL 401 vehicle were grinded in a mortar for about 1 h. The paste was applied on the cell anode creating a 1.6 diameter catalytic layer. The cells with the catalytic layer were sintered for 2 h at 900 °C.
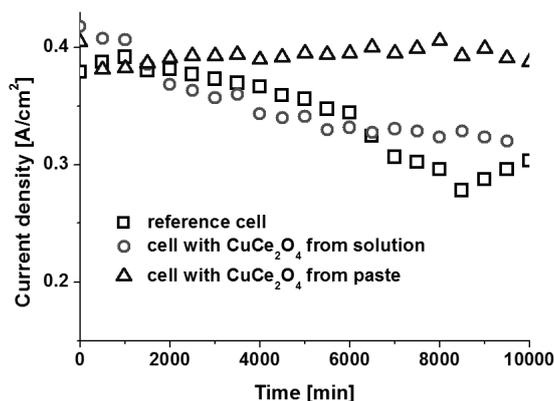

Fig. 2. Current density as a function of time for the reference cell, the cell with $CeCu_2O_4$ from the precursor, and the cell with $CeCu_2O_4$ from paste.

Three sets of fuel cells were measured using a specially constructed measuring cell showed in Fig. 1. It enables a fuel supply from the anode and an air supply from the cathode. The measured cells were spring-loaded and sealed with a glass sealant to the anode compartment in order to prevent gas leaks. The cathodes and anodes were connected to a measuring device (HAMEG 8143) using gold wires. The measuring cell was placed in the furnace. Two types of measurement data were acquired using computer software: current density versus voltage plot, and current density versus
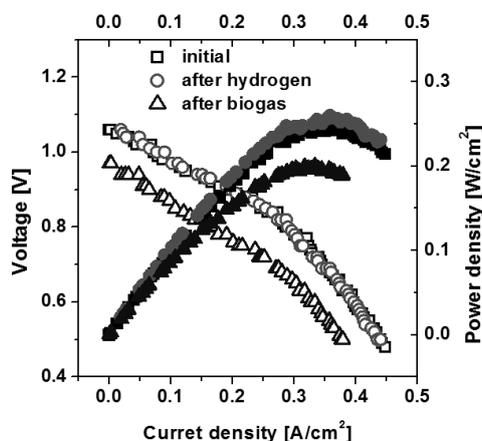
Fig. 3. Current-voltage and current-power plots for the reference cell.

time plot at a loading condition of 0.65 V for over 10000 min. In order to reduce the anode, initially hydrogen was delivered as fuel. Then, after a short time, hydrogen was replaced by dry synthetic biogas consisting of methane and carbon dioxide mixed at a volume ratio of 60/40. The current-voltage measurements were collected every 24 hours. The measurements were performed at 750 °C.

3. Results and discussion

Current density as a function of time for the three sets of fuel cells are presented in Fig. 2. Maximum current density was obtained at the beginning of the measurements during fuel cell operation with hydrogen. The cell without copper-cerium-oxide catalyst is marked on the graph as the 'reference cell'. It undergoes a degradation process, which is manifested by the decrease of current density with time once the cell is fueled by biogas. The fuel cell with the YSZ skeleton soaked in copper-cerium is marked on the graph as the „cell with $CeCu_2O_4$ from solution". It shows similar behavior as the reference cell. Here also current density decreases with time. The fuel cell with a copper-cerium-oxide catalytic layer deposited from paste (Fig. 2 „cell with $CeCu_2O_4$ from paste") acts quite differently. It did not show any degradation in time. Current density was almost constant. The copper-cerium-oxide catalytic layer deposited from paste has better catalytic properties than the catalytic layer formed from the precursor.

The current-voltage plots for the 'reference cell' are shown in Fig. 3. The initial measurement is marked as the 'initial' and was obtained before the current density versus time measurements. The 'after hydrogen' means that the measurement was made in biogas just after measurements in hydrogen were completed. The 'after biogas' means, that measurement was collected in biogas at about of 10000 minutes of fuel cell operation. The measurement after operation in hydrogen does not show current and power density decrease. It can be observed that biogas had a negative
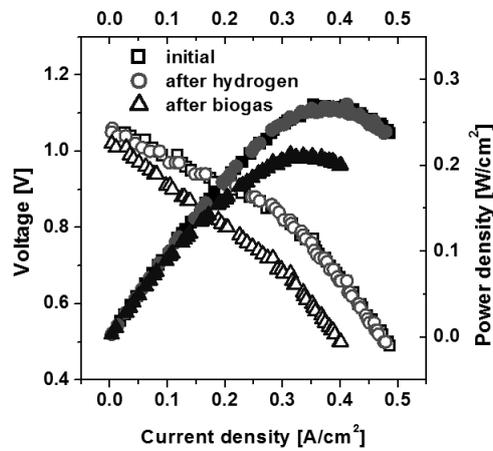
Fig. 4. Current-voltage and current-power plots for the cell with $CeCu_2O_4$ from solution.
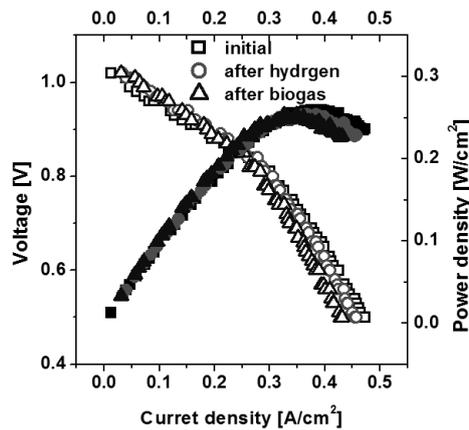

Fig. 5. Current-voltage and current-power plots for cell with $CeCu_2O_4$ from paste.

influence on the fuel cell performance. An open circuit voltage drop was observed, which can suggest that the electrolyte of the fuel cell was cracking due to carbon formation. Current and power density also decreased. The current-voltage plots for the cell with the $CeCu_2O_4$ catalyst from the precursor are shown in Fig. 4. The measurement 'after hydrogen' again was from the same as the 'initial'. In the case of the 'after biogas' an open circuit voltage drop was not observed, but still current and power density decreased. The results for cell with copper-cerium-oxide catalytic layer deposited from paste are shown in Fig. 5. Again, the measurements were similar to the 'initial' and the 'after hydrogen' case. In the case of the 'after biogas' the open circuit voltage did not decrease. Moreover, current density is almost similar to the

initial results. Only a small decrease is observed at high current densities.

4. Conclusions

The CeCu$_2$O$_4$ catalytic layer fulfills its role in fuel cells powered by biogas. However, it must be applied in an appropriate way. Soaking CeCu$_2$O$_4$ into the YSZ skeleton deposited on an anode gave insufficient results. The copper-cerium-oxide layer from paste resulted in stable current and power density in time. The fuel cell with a catalytic layer of CeCu$_2$O$_4$ from paste was affected by a significantly slower degradation process.

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