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Ni–YSZ SOFC anodes—Minimization of carbon deposition

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Abstract

An advantage of solid oxide fuel cells (SOFC) over some other types of fuel cells is the extended range of fuels they can use. Besides hydrogen, hydrocarbons are often used. A problem that may arise on a prolonged operation of cells using hydrocarbons is the formation of carbon deposits on the anodes. These deposits deteriorate the cell performance by blocking the access of reactants to the anode surface and into its pores, thus changing the micromorphology of the anode. The behavior of anodic material during the extended contact with such fuels must be tested and if needed modifications must be made in its composition in order to reduce the rate of carbon deposition.

Ni–YSZ cermet materials prepared by different processes (sol–gel and combustion synthesis) with variations in composition and presence of dopants were tested by exposing these materials to methane at elevated temperatures. The thermal dissociation of methane, which leads to carbon deposits on the cermet surface, was studied by the analysis of the gas phase using mass spectrometry and gas chromatography. The influence of anode composition and its microstructure on carbon deposition was studied as well as the influence of some dopants. The amount of the deposited carbon was determined by temperature programmed oxidation.

Keyword: Powders-chemical preparation; Composites; Fuel cells; SOFC

1. Introduction

Solid oxide fuel cells (SOFCs) are an attractive energy conversion systems because of their high efficiency and low pollution. The high operating temperature of SOFCs cells gives rise to excellent fuel flexibility. Besides hydrogen various hydrocarbons, which transform in the anode to hydrogen and carbon monoxide by an internal steam reforming process, can also be used as fuels. The internal reforming operation results in simplification and lower costs of the whole power generation system owing to the exclusion of the pre-reformer. Natural gas is a relatively cheap and commonly available fuel. Its main component is methane. The Ni/Y_2O_3-stabilized zirconia (Ni–YSZ) anode material catalyzes the internal reforming reactions of methane[1,2]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (1)$$

or

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (2)$$

Carbon deposition on steam reforming catalysts is a problem known to petrochemical industry for a long time. The catalysts surface, pores and voids may be fouled by carbon or coke deposits produced by cracking/condensation reactions of hydrocarbons, intermediates and/or products. Deposits can be in various forms such as graphite or higher molecular weight hydrocarbons. The reactivity of the deposits depends on the conditions of their formation and ageing.

The formation of carbon proceeds either via methane dissociation or according to the Boudouard reaction:

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

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

The Ni–YSZ anodic materials for SOFCs are similar to catalysts used for reforming methane and other hydrocarbons, so similar problems with carbon deposition can be expected.[3] It has been found out that the quantity of deposited carbon during methane reforming is strongly affected by the operating temperature and the methane/steam ratio. Operating at high temperatures or at steam to hydrocarbon ratios below a critical value can cause

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formation of carbon deposits which plug the electrode pores and voids, and can also pulverize the anode surface. The deposition problems will become even more pronounced if biogas is used as a fuel in the future. Namely the presence of tars from the biogas can enhance carbon deposition.[4]

The carbon deposition rate can be partially decreased by using a proper steam-to-methane (hydrocarbon) ratio, by changing the micromorphological characteristics of anode and by the addition of some dopants. The presence of certain dopants such as precious metals,[5] CaO and molibdenum[6,7] lowers the carbon deposition rate.

In the properly operated fuel cells the deposition of carbon is not expected to occur. However as progressively more long-term tests of SOFC cells are being carried out such problems obviously do arise and gain on importance. Testing of SOFC membranes with respect to the carbon deposition is a complex and lengthy task. The whole process of preparing single cell components, joining them into an operating cell membrane and testing is very time consuming. Gas analysis and ac impedance analysis have been used to determine the rate of carbon deposition.[8–10] In the development phase of new anode materials a fast method for discriminating between the susceptibility for carbon deposition of different anode compositions is essential.

Testing of anode materials without going through the whole cell membrane preparation is a very tempting option. A system was set-up for testing carbon deposition rates on powdered anode materials via a gas phase analysis by measuring the evolution of hydrogen which is the result of methane dissociation (reaction (3)).

The system consists of a furnace with temperature controller where the anode sample is brought to a proper temperature and a gas analysis part. The system is connected to a gas supply with constant flow of carrier gas/methane mixture. The gases are led from the furnace to the gas sampling valve of a mass spectrometer and gas chromatograph. Furnace and gas analysis apparatuses are coupled via a heated capillary in order to prevent condensation of less volatile components.

2. Experimental

2.1. Sample preparation

Samples of anode materials were prepared by two methods which enable a good dispersion of nickel oxide and nickel obtained after the reduction in the YSZ phase.

2.2. Sol–gel process in methanol (SGM)

Ni–YSZ anode cermet material was prepared by the gel precipitation method in methanol. Into a methanol solution of analytical grade metal chlorides ($NiCl_2 \cdot 6H_2O$, $ZrCl_4$, yttrium was introduced by dissolving Y_2O_3 in zirconium tetrachloride solution) gaseous ammonia was bubbled up to a pH value of 8.0. The precipitate was washed, until a negative reaction on chloride ions was obtained ($AgNO_3$ test). Then it was dried for 6 h at 120 °C, milled in a planetary ball mill and calcined for 2 h at 900 °C.[11]

2.3. Combustion synthesis (CS)

NiO/YSZ composite powders were prepared by a modified combustion synthesis. The combustion system was based on the citrate–nitrate reaction system. The starting substances for a reactive gel preparation were $ZrO(NO_3)_2 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, citric and nitric acid. All precursors were mixed together to prepare a solution which was kept over a water bath at 60 °C under vacuum (30 mbar) for 6 h until it transformed into a solid green gel. The dried gel was pressed into pellets and ignited at the top to start a self-sustaining combustion reaction producing fine NiO/YSZ powders. The mixtures of NiO/YSZ were ball-milled in ethanol for 3 h and subsequently dried in air for few hours and dry milled for 1 h. After that the product was calcined at 900 °C for 1 h. Doped samples were prepared with the addition of 1% $AgNO_3$, $Cu(NO_3)_2$ or $Co(NO_3)_3$ into the starting solution.[12]

2.3.1. Testing system set-up

Thirty to 33.00 mg samples were put into a quartz tube (diameter = 6 mm, length = 400 mm) as a plug of a height of 3–4 mm. Two thermocouples for temperature measurement and programming of the furnace were mounted beneath the sample. The quartz tube was put into an electrical furnace and connected via 1/8 in. stainless steel capillaries on one end with a gas supply and on the other with gas sampling valves of mass spectrometer and gas chromatograph as shown in Fig. 1. The gas mixture was fed on the lower end of the quartz tube (the flow rate was 4 L/h). An overpressure in the system was 10–30 mbar. Samples were exposed to gas mixtures in the temperature interval from 20 to 930 °C with a heating rate of 10 K/min and cooled down with 20 K/min.

The samples were first heated up in an atmosphere of Ar–H_2 (96–4 vol.%) mixture up to the temperature 930 °C and than isothermally heated for 50 min to complete the reduction of nickel oxide. After cooling down to room temperature they were exposed under the same temperature program (except that the isothermal part was omitted) to Ar–CH_4 (96–4 vol.%) mixture to test the carbon deposition on the samples. After cooling the sample for the second time a temperature programmed oxidation of the deposited carbon in Ar–O_2 (80–20 vol.%) mixture was performed.

2.3.2. Analysis of gas streams

Output gases were simultaneously analyzed by a mass spectrometer Inficon Quadrex 200 (input pressure 1 mbar, head pressure 2.5×10^{-6} Torr, gain 6×10^{-11} A, scan time 2703 ms, scanning borders 0–50 amu) and gas chromatograph Agilent Micro GC 3000A (carrier gas helium, analytical columns: plotU, plotQ with timed inputs and molecular sieve with backflush input, detector type: TDC, inlet temperature 140 °C, injector temperature 100 °C, column temperatures 70 °C, column pressure 2.068 bar, analysis run time 180 s).

Electron micrographs of calcined, pelleted and subsequently sintered (1350 °C) and reduced (1000 °C) samples were taken

Table 1
Composition of tested anode materials

Sample[a]	Nickel content (vol. %)	YSZ content (vol. %)	Dopant (%)	Process
SGM-40	40	60	–	Sol–gel in methanol
CS–40 (B1)	40	60	–	Combustion synthesis
CS–50 (B3)	50	50	–	Combustion synthesis
CS–50	50	50	–	Combustion synthesis
CS–50–Co	50	49	1	Combustion synthesis
CS–50–Ag–Cu	50	49	0.5–0.5	Combustion synthesis

[a] Number 40 or 50 designates the nickel content (vol.%) in final composite.

by a Zeiss Supra 35 VP SEM with an EDS analyzer instrument.

3. Results and discussion

The composition of samples prepared by the sol–gel and the combustion synthesis is listed in Table 1.

Electron microscopy of thermally treated samples shows that nickel particles having a typical size from 1 to several micrometers are homogenously distributed within a continuous ceramic phase (Fig. 2). Uniform distribution of dopants within the samples can be seen from EDS mapping in all cases except for the CS–50–Ag–Cu sample where some silver-rich areas were found.

The testing procedure for carbon deposition consisted of three phases:

- TPR (temperature programmed reduction) of a given NiO/YSZ composite by H_2/Ar gas mixture.
- TP deposition of carbon from dry methane/Ar gas mixture onto the surface of the anode material under isothermal or dynamic conditions.
- TPO (temperature programmed oxidation) of the deposited carbon.

By TPR with an Ar/H_2 mixture it was assured that all nickel oxide was reduced to metal. The gas phase analysis of the Ar/H_2 carrier gas that flowed through the furnace enabled also the determination of the reduction temperature interval and the amount of hydrogen used for this process.

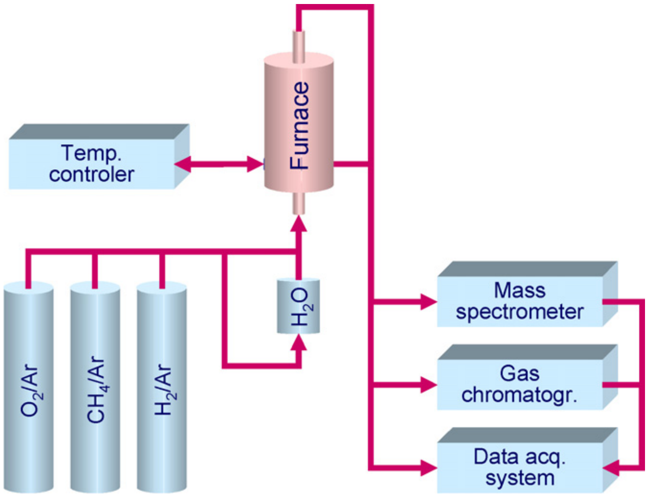

Fig. 1. Test system for TPR, TP deposition and TPO.

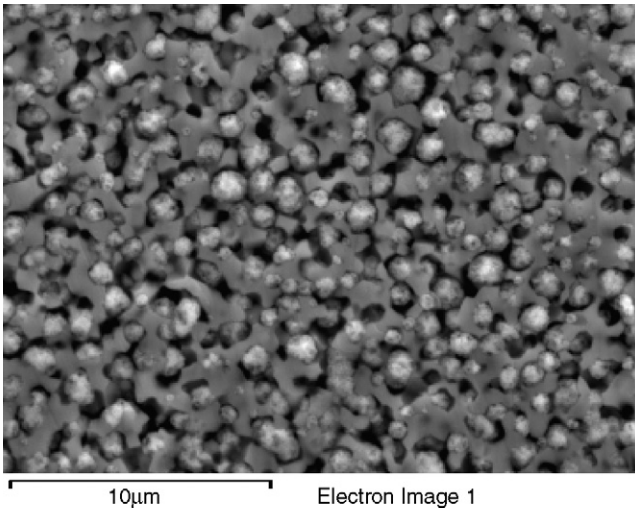

Fig. 2. SEM micrograph of thermally treated sample CS–40–B1.

In the second phase, which proceeded under a temperature programmed conditions a methane/argon mixture was blown through the anode sample which resulted in the deposition of carbon onto the sample surface (Fig. 3). The deposition of carbon could be followed up indirectly by measuring the concentration of hydrogen in the carrier gas that evolved during the thermal dissociation of methane in contact with the anode material (reaction (3)).

Third phase, TPO of the deposited carbon coupled with the determination of the amount of evolved carbon dioxide (carbon

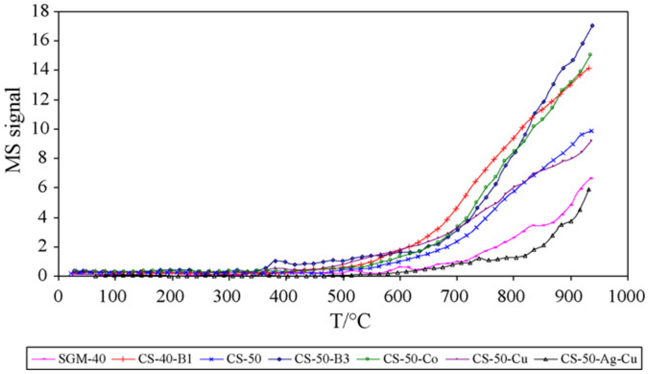

Fig. 3. Hydrogen evolution during TP deposition of carbon.

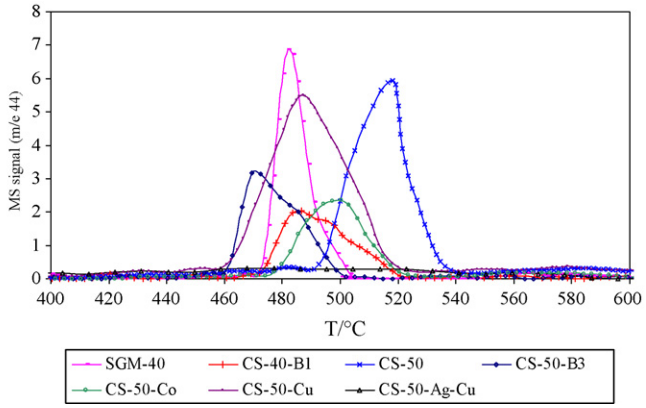

Fig. 4. TPO of carbon deposits on anode materials.

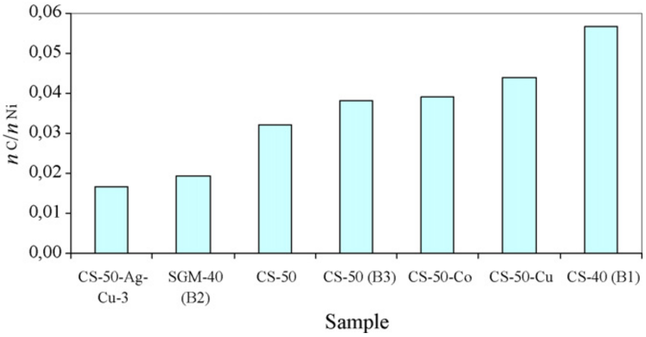

Fig. 5. Amount of carbon deposited on anode materials.

monoxide was present in very low concentrations) served for the determination of the amount of carbon deposited on the anode material. Besides that, the reactivity of carbon toward oxidation was also obtained in this way (Fig. 4).

The results of testing of different materials are given in Fig. 3. The results obtained under the dynamic heating program of 10 K/min using dry methane mixture showed that hydrogen evolution begins in a temperature interval from 350 to 610 °C. After the initial temperature of hydrogen occurrence the rate of hydrogen evolution increases with temperature but at different rates for different samples.

Results show, that the lowest hydrogen concentration in gas exiting the furnace was observed for the CS–50–Ag–Cu sample. In the first part up to 710 °C the samples CS–50–Ag–Cu and SGM-40 behave similarly but after this temperature interval the hydrogen concentration rises more steeply for the latter sample. For samples CS–40–B1, CS–50–Co and CS–50–B3 the highest concentrations of hydrogen in the carrier gas were obtained. From these results it can be concluded that the lowest amount of carbon deposit was formed in the case of CS–50–Ag–Cu. The curves for hydrogen evolution were affected by the synthesis method used for their preparation, presence or absence of dopant, amount of nickel and also other conditions of sample preparation.

The amount of deposited carbon was alternatively determined in the third run of the testing procedure, after cooling down the furnace. The methane flow was exchanged for synthetic air (80 vol.% Ar and 20 vol.% oxygen) and then the temperature program was run again. This lead to TPO of the previously formed carbon deposit which manifests as a peak of an increased concentration of carbon dioxide (mainly) and carbon monoxide in the carrier gas. From these peaks the actual amount of the deposited carbon was calculated (Fig. 4). As expected from TP deposition experiments the lowest carbon deposit was found in the case of CS–50–Ag–Cu sample.

Besides the data on the amount of the deposited carbon, TPO also provides some data on its reactivity. Namely, the temperature at which the carbon dioxide peak has a maximum value depends also on the form and reactivity of the deposit—the higher the peak temperature, the lower the carbon reactivity toward oxidation. These data may provide a useful means for differentiating between various forms of the deposits especially in the first phases of deposition when there is not enough material to be detected by other methods. Under the same conditions, TPO of carbon nanotubes, char (soot) and graphite give temperature maxima at 276, 564 and 826 °C, respectively. A longer temperature interval for oxidation or a bimodal curve also indicated the formation of different types of carbon species. It can be seen from the figure that for sample CS–50–Ag–Cu very low curve extending over a broad temperature range was observed. Other samples showed more pronounced peaks that differed in height and shape. Maxima of TPO curves can be found from 477 to 520 °C. The amount of carbon deposited on anode materials in moles per mole of nickel in the anode material is presented in Fig. 5.

Testing of carbon deposition rates by the gas phase analysis of dry methane or other hydrocarbons in contact with anode material does not entirely correspond to the conditions in a fuel cell since in the later case high ratios of water vapor to methane are also present. Beside that in a fuel cell the deposited carbon can be oxidized also by the oxygen ions coming from the cathode side through the electrolyte to the anode side. Nevertheless, this method enables a fast screening of the behavior of anode materials in contact with methane and a quick assessment of different formulations and dopants that could give materials more resistant to carbon deposition. The sensitivity of the method is very high so that the early phases of carbon deposition can be observed.

4. Conclusion

The synthesis path, the composition as well as the microstructure of anode materials affect carbon deposition on anode surface. From the obtained results it can be seen that the sample CS–50–Ag–Cu doped with silver and copper and prepared by the combustion synthesis, gives less carbon deposits than other tested samples. This sample is closely followed by that prepared by the sol gel process in a methanol medium with 40% of nickel. During the deposition run they behave similarly up to a temperature of 710 °C but at higher temperatures less hydrogen evolution was observed for the sample marked as CS–50–Ag–Cu sample. This was confirmed also by TP oxidation of the deposited carbon.

Testing of the gas phase composition (methane) in contact with anode materials is a fast screening method that can indicate which material will be more prone to form carbon deposits but it cannot replace the conventional testing involving formation of SOFC membrane and carrying out tests out under electrical load.

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