

# Numerical model for evaluation of the effects of carbon deposition on the performance of 1 kW SOFC stack – a proposal

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**Abstract.** Solid oxide fuel cells are high-temperature electrochemical energy conversion devices which operate at elevated temperature (600-900°C). As a result it possible to internally reform the incoming fuel, thus except hydrogen and carbon monoxide, SOFCs can be fuelled with various hydrocarbonaceous gases. The presence of carbon-containing compounds in the fuel might result in the formation and of carbon in a form of a thin layer on the SOFC anode. The carbon deposition process depends on the thermodynamic conditions, such as temperature and steam to carbon ratio. The higher the temperature, the longer period of time is required for the solid carbon particles to deposit on the porous surface. The correlation used for this study is based on creating the ternary diagrams or Gibb's diagrams. The presented results cover a first stage of the analysis of the carbon deposition processes in SOFCs, focusing mainly on the numerical study of the changes of the fuel cell performance due to degradation of anode performance. A dedicated model of SOFC was proposed. It accounts for the diminution of the active area and/or deactivation by the increase of the resistance of the anode. The article presents the proposed methodology and the numerical approach.

## 1 Introduction

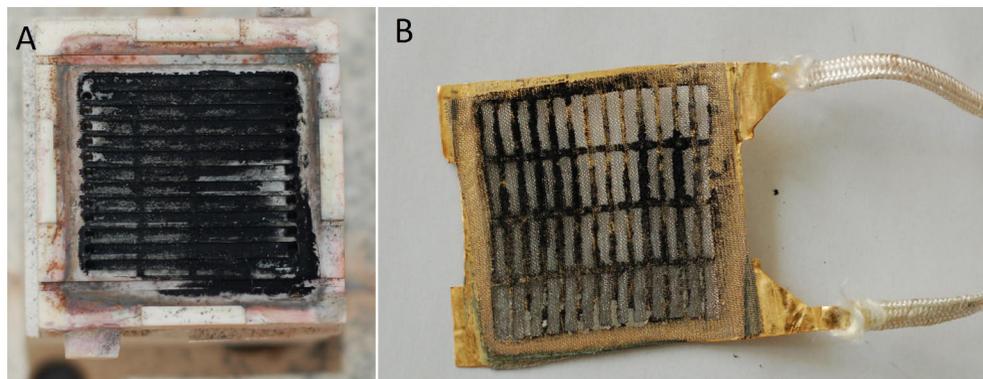
The carbon deposition process is an important issue, which can occur in various chemical and power systems. Fuels or generally gas mixtures containing hydrocarbons such as methane, ethane, propane, etc., and optionally other volatile organic compounds *i.e.* alcohols or ethers such as dimethyl ether (DMR) can be a subject of such a reaction. The iron and steel industry is highly dependent on metallurgical coke, which is produced from high-grade bituminous coal, and has crucial roles as an energy source, reducing agent, and maintaining bed permeability in blast furnace operation. A pyrolysis process is used to convert high-grade coal to coke, tar, and gas in a coke oven unit. The main product, coke, is transported to the top of the blast furnace and used as a reducing agent. Tar vapor and gases are the by-products and contain high amounts of carbon and energy. The tar material is mainly composed of condensable organic materials and may cause operational problems such as pipe plugging, condensation, and tar aerosol formation [1]. For the gasification

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processes it is crucial to achieve a long-life catalyst for biomass conversion. One of the major mechanisms in the deactivation of gasification catalysts is carbon deposition. This process results in a decrease in the active surface area of the catalytic metal particles. The strategy to prepare catalysts with a tolerance for carbon deposition is to use a basic support material, achieve a high dispersion state of metal particles, and introduce promoters to the catalysts [2]. Oxy-fuel IGCC is a concept of new coal fueled power generation with CO<sub>2</sub> capture capability without large penalty on thermal efficiency. An imperative issue to be solved to realize this concept is to reconcile pre-combustion sulfur removal and retaining the inorganic gas composition of the coal derived gas. Although introduction of dry gas sulfur removal is desired to protect gas turbine from corrosion and to preserve the gas composition, the sulfur removal sorbent containing zinc ferrite installed in the process may suffer from the severe side reaction of carbon deposition [3]. The process of carbon solid particles deposition also on the porous surface might result in changing of the flow parameters. The deposit, also called soot, alters the structure which later affects thermal management and flow pattern of channel. Additionally, in reactors and electrochemical systems, the carbon layer affects the geometry of the functional layer and leads to a significant deterioration of the physical-chemical properties of the material and can considerably suppress the ability to withdraw the heat from the process in case of high temperature systems. An example of the porous surface where carbon deposition can lead to severe disorders and deterioration of the parameters are the electrodes of Solid Oxide Fuel Cells (SOFC). The problem can be significant in fuel cell systems which are fed by fuel which composition and flow can fluctuate, for example SOFCs combined with gasifiers [4].

Solid oxide fuel cells are the high-temperature electrochemical energy conversion devices which operate at elevated temperature, typically in range 600-900°C. The high operating temperature allows for internal reforming process of hydrocarbonaceous fuels, thus SOFCs can be fueled with various gases containing hydrocarbons and their mixtures as well alternative energy carriers including dimethyl ether and ammonia [5]. As a result, under proper thermodynamic conditions, the deposition of solid carbon particles on the SOFC anode might occur. An example of the massive carbon deposition on the surface of a planar SOFC is shown in Fig. 1. Consequences of the soot formation are clearly observable on parts, exposed to anodic subspace (A and B). In this case high extent of deposits caused a complete cell disintegration.



**Fig. 1.** Massive carbon deposition on the surface of a planar SOFC, where: A - manifold after removing the SOFC cell, B - golden current collector [6]

The formation and deposition of carbon on the porous surface is a well-known problem, which was studied and analyzed by many research groups. Significant number of articles

were published, approaching the carbon deposition problem in three different yet correlated aspects.

The first aspect concerns studying the influence of anode porous material type on the carbon deposition process [7]. In the field of fuel cells with solid oxide electrolytes, two major problems were identified when fuelling with gases composed of carbon and hydrogen. One problem is high sensitivity to impurities such as sulfide and chloride, which poisons the SOFC anode and leads to the rapid performance degradation [8]. The other problem is carbon deposition which can be accelerated by catalysts present in the materials making the SOFCs. Nickel/yttrium-stabilized zirconia (Ni/YSZ) cermet is the most commonly used SOFC anode material due to its catalytic effect on the electrochemical oxidation of fuel. At the same time, nickel is an excellent catalyst for the carbon deposition reactions, such as methane cracking (Eq. (1)), reduction of carbon monoxide (Eq. (2)) and disproportionation of monoxide (Eq. (3)) [7, 9-11].



The deposited carbon can deactivate and eventually passivate the Ni-catalyst and can cause rapid degradation of the cell's performance and its mechanical stability through worsening of the thermal management and the distribution of reagents. Because of these, several research groups proposed alternative dopants to the anodic materials, which hinder the carbon deposition process, without compromising the fuel cell performance [12-14].

The second area of research is oriented at studying the effects of various SOFC operation parameters, such as the temperature, fuel type or the steam-to-carbon ratio (S/C) which describes the ratio of molar amount of water steam to molar amount of carbon elements in the anode gas and SOFC current load. Subotic et al. [10] analysed the SOFC behavior under various operating conditions as well as the carbon formation process in regimes of different fuel compositions. They have prepared a set of experimental data showing the correlations between specific fuel parameters, affecting the carbon deposition mechanisms. Koh et al. [15] found that carbon deposited with humidified methane on Ni/YSZ porous surface is reversible when it is oxidized at a current load of thermodynamically carbon-free condition. This reversible carbon deposition does not affect the performance of a cell. The results published by Chen et al. [9] show that the morphology of the deposits and the degradation of the cell performance were significantly influenced by the operating temperature of the SOFC. They stated that for the fuel cell with Ni/YSZ anode fueled with syngas, the cell degraded faster once the carbon was formed and deposited. The damages at the microstructural level in the proximity of anode surface induced a cell's conductivity decrease. Alzate-Restrepo et al. [16] studied the electrolyte-supported cell with Ni/YSZ anodes exposed to CO/H<sub>2</sub> mixtures at the temperature of 1073 K operating at the current density of 10 mA/cm<sup>2</sup>. During the tests the carbon formation occurred after a longer period of time (in the worst case after 6 h of operation) and led to deactivation of the anode by increasing the polarization resistance, reducing the porosity and blocking the active sites. Singh et al. [17] investigated the rate and speed of carbon deposition process in a SOFC fueled by tar biogas and operating in wide range of parameters. The thermodynamic analysis indicated that the amount of carbon decreased as the steam content of the fuel stream was increased. Carbon deposition found to be negligible as the operating conditions were varied to achieve the fuel mixture with higher water content (from 5% to 15% of H<sub>2</sub>O in feed gas).

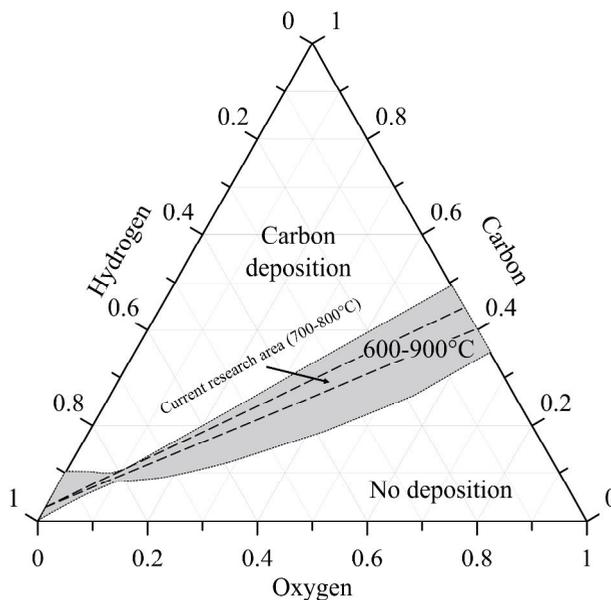
Kupecki et al. [18] discussed the effects of flow parameters on the stack performance in different flow configurations which can affect the thermodynamic parameters in the anodic compartments for different fuels. The problem of carbon deposition in micro-cogenerative power systems was discussed with respect to serially connected fuel cell stacks [19].

In such a configuration the role of a fuel processor is played by the first stack, therefore the threat of carbon formation inside the anodic compartments of the second or third stacks in series is eliminated. Depending of the fuel type and the expected system functionality, the fuel processing unit has to be adjusted to enable high electrical and overall efficiency as well eliminate the potentially dangerous issues, such as the discussed carbon formation [20].

The third aspect is the usage of the different mathematical models for describing and simulating the mechanisms and conditions required for the carbon formation and deposition process to take place. The common method to simulate the coke formation and deposition process is the Gibbs Free Energy Minimization (GFEM) method, which allows to compute the field of thermodynamic parameters which favor the formation of solid carbon particles [21-23]. The key parameter affecting the carbon formation reaction is the ratio between the steam and carbon (S/C) which is defined according to Eq. 4.

$$S/C = \text{molar flow of steam} / \text{molar flow of carbon-containing gases (except CO}_2\text{)} \quad (4)$$

Additionally, the temperature of the cell and the gases affects the process. The higher is the temperature, the longer period of time is required for the solid carbon particles to deposit on the porous surface. The correlation used for this study is based on creating ternary diagrams, commonly called the Gibb's diagrams (see Fig. 2).



**Fig. 2.** Gibb's diagram at 1 atm. (data based on [24]). Gray area is a domain where carbon deposits may have transient morphology, from fine soot at lower boundary to graphite on upper.

The theoretical boundaries of the carbon deposition process are defined by the carbon formation isotherms, which depict the equilibrium composition for different gas mixtures, which contain carbon, hydrogen and oxygen atoms. The Gibb's diagrams aid in estimating

the regions of parameters and compositions which should be generally avoided [24]. However, considered model are targeted on boundary region, where carbon formation is expected, its morphology is not settled (Fig. 2).

Despite the existence of numerous publications reporting the studies of the influence of SOFC operation parameters on the coke deposition process, authors clearly point the need for *in situ* analysis combined with numerical modeling. The two combined methods can enable detailed multi-variant study of selected parameters and their effect on carbon formation and deposition. Additionally, in the current literature lacks the reports on the verisimilar impact of the anode gas velocity and degree of flow turbulence (Reynolds number) on the speed and rate of coke concretion. For that reason a new modeling approach was proposed.

## 2 Methodology

The proposed model of a solid oxide fuel cell is based on zero-dimensional approach, which is a commonly used method. Solid Oxide Fuel Cell voltage is defined by the following function [25,26]:

$$E_{SOFC} = (\mathcal{E} - i_{max} \cdot r_1 \cdot \eta_f) / (r_1(1 - \eta_f)/r_2 + 1) \quad (5)$$

where:

$\mathcal{E}$  – e.m.f, the maximum voltage defined by the work of an isothermal process;  $\eta_f$  – fuel utilization factor defined by the current working conditions of the cell;  $i_{max}$  – the maximum current density limited by amount of delivered fuel or oxidant;  $r_1$  – the area specific resistance defined by ionic conductivity of the solid electrolyte and  $r_2$  – the area specific resistance defined by electronic conductance [27].

The fuel cell generates power in processes at constant temperature, i.e. isothermal process. Thus, the maximum voltage is defined by the maximum work of the isothermal process. Mixtures of various components occur in the case of the analyzed fuels. Given these circumstances, the general form of Nernst's equation is used to estimate the e.m.f. of the integral electrochemical process in SOFC:

$$\mathcal{E} = R \cdot T \cdot \ln(p_{O_2, cathode} / p_{O_2, anode}) / 4F \quad (6)$$

where:  $T$  – the absolute temperature;  $R$  – the universal gas constant;  $F$  – the Faraday constant;  $p_{O_2, cathode}$  – oxygen partial pressure at the cathode outlet;  $p_{O_2, anode}$  – oxygen partial pressure at the anode outlet. Taking in account negligible electronic transference numbers of YSZ in conditions, typical for SOFC (see, for example [28,29]), voltage losses associated with electrolytic permeability of the solid electrolyte membrane may be ignored. The open circuit voltage  $E_{OCV}$  formula was written as follows:

$$E_{OCV} = \mathcal{E} / (r_1/r_2 + 1) \quad (7)$$

The maximum cell current presented in Equation 5 depends on the fuel flow and Faraday constant:

$$I_{max} = 2F \cdot n_{H_2, eq} \quad (8)$$

Factor  $n_{H_2, eq}$  was introduced to account for variable composition of incoming fuel. Under assumption that fuel undergoes complete external or internal reforming reaction, the hydrogen equivalent molar flow to the anode compartments of a cell writes:

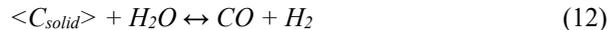
$$n_{H_2, eq} = n_{H_2} + n_{CO} + 3n_{CH_3OH} + 4n_{CH_4} + 6n_{C_2H_5OH} + 7n_{C_2H_6} + 10n_{C_3H_8} \quad (9)$$

Hydrogen equivalent can be calculated for gases containing different hydrocarbons and for other hydrogen carriers. By this mean different fuels can be compared on the same basis. Hydrogen equivalent becomes of high attention when performance of SOFC fed by different fuels is evaluated. Electric current in a fuel cell depends on a gas flow, therefore fuel utilization factor  $\eta_f$  was introduced to correlate these. The factor is basically defined as a ratio of fuel consumed by the cell to generate electrical current  $I$ , to the maximal current  $I_{max}$  dependent on total amount of fuel supplied to a cell:

$$\eta_f = I_{SOFC} / I_{max} \quad (10)$$

Model was implemented in Aspen HYSYS 8.0 modeling software. Full description of the methodology was presented in [18]. The numerical model was also preliminary validated, simulating SOFC stack operation, fueled by the gas mixture of hydrogen and nitrogen [18]. For the current study, the presented SOFC mathematical model is combined with the model which computes the equations of carbon formation isotherms [23]. Theoretical boundary between non-deposition and deposition can be defined by finding equilibrium composition for different gas mixtures, based on three elements: carbon, hydrogen and oxygen. The set of mathematical equations refers to water, carbon monoxide, carbon dioxide, methane and hydrogen. Boundaries can be found for different temperatures as so-called carbon formation isotherms. Gases with different compositions can be located on the Gibb ternary diagram (see Fig. 2) and evaluation of the possible threat of solid carbon formation and deposition can be performed.

The equilibrium can be described by the following reactions:



The following equilibrium constants correspond to reactions 11-14 respectively:  $K_1$ ,  $K_2$ ,  $K_3$   $K_4$ . The equilibrium in the system can be then excepted after simple rearrangement as four equations [30].

$$K_3 = n_{CO} \cdot n_{H_2O} / n_{CO_2} \cdot n_{H_2} \quad (15)$$

$$K_1 \cdot K_2 = p^2 \cdot n_{H_2}^3 \cdot n_{CO} / n_{CH_4} \cdot n_{H_2O} \quad (16)$$

$$4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} - n_H \cdot S = 0 \quad (17)$$

$$n_{H_2} = const \quad (18)$$

with the normalization condition:

$$n_{CH_4} + n_{CO} + n_{CO_2} + n_{H_2} + n_{H_2O} = 1 \quad (19)$$

where factor S of equation 17:

$$S = 5n_{CH_4} + 2n_{CO} + 3n_{CO_2} + 2n_{H_2} + 3n_{H_2O} \quad (20)$$

Equation for the content of water in the system can be found by putting  $n_{H_2}=A$  and  $n_H$  as a parameter, and eliminating variables from the above equations:

$$b_1 n_{3H_2O} + b_2 \cdot 2n_{2H_2O} + b_3 \cdot n_{H_2O} + b_4 = 0 \quad (21)$$

where:

$$b_1 = 2g_2 \cdot (1 + g_3)$$

$$b_2 = g_1 \cdot (2 + g_3) - 3g_2 \cdot g_3 + Ag_2 \cdot (2 + 3g_3)$$

$$b_3 = 2Ag_1 \cdot (1 + g_3) - 2(1 + g_1 \cdot g_3)$$

$$b_4 = A \cdot (g_3 - 2) + 4 - g_3$$

$$g_1 = K_1 \cdot K_2 / p^2 \cdot A^3$$

$$g_2 = K_1 \cdot K_2 / p^4 \cdot A^4 \cdot K_3$$

$$g_3 = n_H / (1 - n_H)$$

The content of methane, carbon mono- and dioxide in the system can be found using equations 22-24, respectively.

$$n_{CH_4} = (1 - n_{H_2O} - A) / (1 + g_1 \cdot n_{H_2O} + g_2 \cdot n_{H_2O}^2) \quad (22)$$

$$n_{CO} = g_1 \cdot n_{CH_4} \cdot n_{H_2O} \quad (23)$$

$$n_{CO_2} = g_2 \cdot n_{CH_4} \cdot n_{H_2O}^2 \quad (24)$$

Amount of oxygen in the system is found as:

$$n_{O_2} = n_{H_2O}^2 / n_{H_2}^2 \cdot K_{pw} \quad (25)$$

where  $K_{pw}$  is the equilibrium constant of water formation reaction. The positions of the equilibrium concentrations in the Gibbs triangle (corresponding to different content of carbon, hydrogen and oxygen) can be found using reactions 17, 26 and the normalization condition 27.

$$n_{CH_4} + n_{CO} + n_{CO_2} - n_C S = 0 \quad (26)$$

$$n_H + n_C + n_O = 1 \quad (27)$$

The algebraic method can be used for determining the equilibrium compositions of the gas mixture, however parameters  $n_{H_2}$  and  $n_H$  have to be manipulated to do so. It was previously reported [31] that these methods are especially precise in the regions of a Gibbs triangle where equilibrium is highly sensitive to changes of  $n_C$ ,  $n_H$  and  $n_O$ .

According to the calculation scheme, calculations can be performed for different temperatures in order to define carbon formation isotherms. Precise definition of the carbon formation boundary allows taking countermeasures to prevent this dangerous process from occurring.

For this study, complex experiments will be performed in order to analyze the formation and deposition of coke process on the SOFCs anode for different operating points of the fuel cell. Based on the realized experiments, a proper numerical model will be made, describing this process, and taking into consideration SOFCs operation temperature, fuel cell current load, steam-to-carbon ratio, including the process kinetics, which influence anode gas flow turbulence rate. Modeling of an SOFC using zero-dimensional dynamic models as well as modeling of static fuel cells on fixed operating point are presented in [23,25,27,32]. The prepared numerical method will be adopted and extended to enable use of mathematical tools for describing the carbon deposition mechanisms and later to allow the validation and tuning of the models using experimental data. The proposed

methodology targets the determination of the operating parameters of SOFC which eliminate the risk of formation of the carbon layer on the porous surface of the anode. In addition, the consideration of flow parameters on the process kinetics allows to uniquely figure out impact of the flow turbulence on secretion and deposition of carbon on the surface of the surface of dense ceramic and on a porous layers. The usage of dedicated mathematical model will allow to generalize the mechanisms description in a parametric way, allowing the determination of process boundaries in units and processes using gases composed of hydrogen and carbon elements.

### 3 Conclusion

The proposed numerical tool combines the electrochemical model which is based on the electric circuit equivalent, and the calculation algorithm which serves as a computational model for determination of the carbon formation isotherms under given working conditions. The concept for correlating the coke formation and deposition in the anodic compartments relies on the foreseen reduction of the active area of the SOFC and/or deterioration of the ionic transport due to pore clogging. This can be included in the dynamic model by correlation of the area specific internal ionic and electronic resistances of the cell. In order to identify the process, correlate the rate of formation, thickness of the deposit layer and the cell's performance electrochemical degradation, the series of experimental investigations is needed. Further work will be related to the experimental analysis of the process in order to provide data for the model calibration and validation. The objective is to qualitatively and quantitatively analyze selected factors and their influence on the electrochemical fuel oxidation in regimes in which the soot formation can be expected. This will be achieved using a test bench which is currently under construction

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