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Effects of gas velocity on formation of carbon deposits on AS-SOFC fuel electrodes

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Abstract

The elevated operating temperatures of solid oxide fuel cells (SOFC) create favorable kinetics for the oxidation of carbon-containing gas mixtures, which may include carbon monoxide and light organic compounds. The presence of carbon-based components in the fuel might result in the formation and deposition of soot on the surface of the anode in a fuel cell. This process depends on and is driven by the prevailing thermodynamic, kinetic and electrochemical conditions. The present study was premised on the following: in addition to the aforementioned parameters providing for the operating conditions, gas velocity also affects the formation of deposits on the anode. The role of fuel gas velocity in the process was studied experimentally using 5 cm x 5 cm anode supported solid oxide fuel cells (AS-SOFC) at 750 °C at velocities in the range 0.1 to 0.9 m/s. It was found that carbon deposition was clearly observable approximately 24 hours after the necessary conditions were attained. An intense stage of performance degradation typically lasts for a period of up to 60 hours. An increase in fuel flow velocity leads to an acceleration in the carbon deposition process. The correlation between velocity and cell degradation due to this phenomenon was determined and the corresponding function was proposed.

Keywords: Boudouard Reaction; Carbon Deposition; SOFC; Soot Formation

1. Introduction

Carbon formation and deposition is an important issue that can arise in various systems [1] in which hydrocarbonaceous fuels such as methane, ethane and propane are present. Similar issues might occur when gases like methanol, dimethyl-ether (DME) and others are processed. Formation of solid carbon particles on the porous surface might result in changed flow parameters. Carbon deposits affect the geometry of the functional layer and lead to a significant deterioration in the physical and chemical properties of the material. Additionally, they can adversely affect heat exchange to a significant degree in the case of high temperature processes. Moreover, the thin layer of deposit leads to a reduction in the active area that takes part in high temperature electrochemical processes. The electrodes of a solid oxide fuel cell (SOFC) are a classic example of a porous surface whose functional properties are impacted by deposition.

SOFCs operate in the temperature range of 600–900 °C. The high operating temperature enables internal steam reforming of the incoming fuel, promotes rapid kinetics with non-precious materials and generates high-grade usable by-product heat. This heat can be used to produce hot water in cogenerative systems or to drive bottoming cycles. SOFCs can be a viable option for generating electricity at considerably higher efficiencies than conventional systems. The other advantage includes substantial reduction of emissions due to the direct electrochemical oxidation of fuel instead of combustion. SOFC-based power plants can achieve electric efficiency of 45–65%, which is in excess of the 37–45% reported for conventional systems [2, 3, 4] and up to 60% for natural gas combined cycles (NGCC). The operating principles of solid oxide fuel cells are based on electrochemical oxidation of the fuel in the anodic compartments in the presence of oxygen anions, which migrate through dense electrolyte – an ionic conductor. The electrons that are generated in the process are collected and consumed by the external load (see Fig. 1).

The open circuit voltage of a single SOFC cell (OCV) may be described by the Nernst equation and depends on the difference between oxygen partial pressures at the anode and cathode. Typical values of the SOFC OCV depend on the fuel and are ca.1 V [5].

It is well-known that carbon deposition on a porous surface (for example the anode in an SOFC) is driven by ther-

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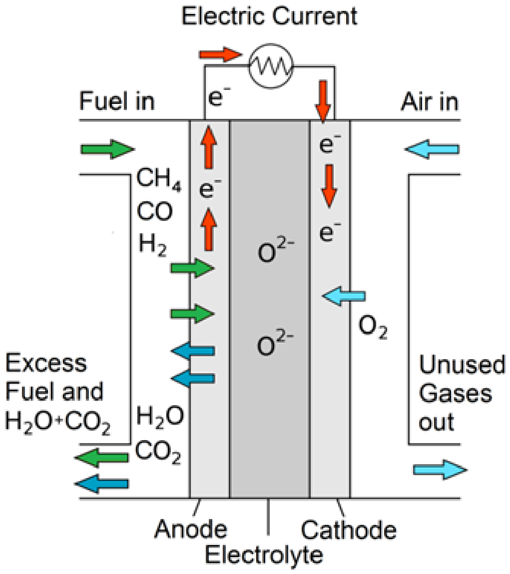


Figure 1: Working principles of SOFC

modynamics. In the case of an SOFC, the steam-to-carbon ratio (S/C), defined as the ratio of the molar concentration of steam to the atomic concentration of carbon in the fuel stream, should be high enough to inhibit the formation and deposition of solid carbon. The effect of the S/C ratio on the process is related to the operating temperature of the cell. However, due to the design and modus operandi of an SOFC, the whole process of formation and precipitation of carbon also depends on other parameters, including current density and the catalytic activity of the materials from which the interior surfaces of the SOFC unit are made, i.e., the anode and interconnect [5, 6].

The flow parameters often affect the kinetics of the multiphase electrochemical reaction, especially on porous surfaces. In the current study, it is claimed that another flow parameter – anodic gas velocity – affects the rate of carbon deposition. During experiments, the process of carbon deposition was studied for various velocities of anodic gas, while the following were maintained constant: gas composition, operating temperature and electric load of the cell.

2. Carbon deposition process

The formation and deposition of carbon on porous surfaces is a well-known phenomenon and has been described in a large number of articles. Typically, the issue is approached in three different but related ways. The first aspect concerns studies into the influence of anode porous material type on the carbon deposition process [7]. Nickel/yttrium-stabilized zirconia (Ni/YSZ) cermet is the most commonly used material for SOFC anodes due to its catalytic effect on the electrochemical oxidation of fuel. For this kind of fuel cell, there are two major problems when fuelled by gases composed of carbon and hydrogen elements. The first is the high sensitivity to impurities such as sulphides and chlorides, which poison the SOFC anode and lead to rapid degradation [8]. The other problem is the formation of soot [7, 9, 10, 11]. Nickel is an excellent catalyst for carbon deposition reactions, such as methane cracking:

$$CH_4 \rightarrow C + 2H_2 \tag{1}$$

reduction of carbon monoxide:

$$CO + H_2 \rightarrow C + H_2O \tag{2}$$

and disproportionation of monoxide:

$$2CO \rightarrow C + CO_2 \tag{3}$$

all of which have solid carbon as one of their products.

Deposited carbon can deactivate the Ni catalyst and cause rapid cell degradation, in terms of structural damage and worsening of electrochemical performance. Consequently, several research groups have proposed different types of dopants to reduce the rate of the carbon deposition process without harming fuel cell performance [12, 13, 14, 15].

The second area of research includes the effects of various SOFC operation parameters, such as operating temperature, fuel type, steam-to-carbon ratio (S/C) and SOFC current load on the process. Subotic V. et al. [10] examined and presented the behavior of the SOFC under various operating conditions and the carbon formation process in terms of different fuel compositions. The authors stated that the use of methane increases open-circuit-voltage, but long-term operation increases carbon formation on the cell more than other gases and thus decreases cell voltage. The higher the concentration of methane, the faster the carbon formation process progresses. Koh J. et al. [16] determined that carbon deposited with humidified methane on Ni/YSZ porous surface is reversible when it is oxidized in a current load of thermo-dynamically carbon-free condition. This reversible carbon deposition does not affect the electrochemical performance. The rate of carbon deposition and oxidation occurred after several hours. The results generated by Chen T. et al. [9] show that the morphology of carbon and the degradation were significantly influenced by the cell operating temperature. They stated that for a fuel cell with an Ni/YSZ anode fuelled with syngas, the cell degraded quickly after carbon was deposited. The microstructure damage close to the anode surface led to a decrease in conductivity. Alzate-Restrepo and Hill [17] described the behavior of an electrolyte-supported solid oxide cell (ES-SOFC) with Ni/YSZ anodes exposed to CO/H_2 mixtures at 1073 K operated at current density of 10 mA/cm^2. During measurements carbon formation occurred over time (in the worst case after 6 h of operation) and deactivated the anodes by increasing the polarization resistance and blocking active sites. Singh D. et al. [18] tested the rate and speed of the carbon deposition process in an SOFC system fuelled by biogas. The thermo-dynamic analysis demonstrated that the amount of carbon decreased as the steam content of the fuel stream increased. Carbon deposition was inhibited when the operating conditions were adjusted to achieve a fuel mixture with higher water content (15%). The maximum rate of carbon deposition was measured at OCV and the value of 0.104 mg/s was reported.

The third aspect is the application of different mathematical models to describe and simulate the mechanisms and conditions required for the carbon deposition process to occur. The most commonly used methodology to simulate soot formation and the deposition process is the Gibbs Free Energy Minimization (GFEM) method, which is used to determine the field of parameters with favorable thermo-dynamic conditions for the formation of solid deposits [19, 20]. Despite the existence of a selection of publications analyzing the influence of SOFC operating parameters and describing alternative mathematical models of carbon deposition, the authors clearly demonstrated the need for in situ analysis supported by thorough laboratory experiments. Experimental data are crucial to verify the hypothesis and validate the mathematical tool [21, 22, 23, 24]. Additionally, in the current literature there is a lack of research addressing the potential impact of the velocity of fuel supplied to the anodic compartments of the SOFC and the degree of turbulence on the speed and rate of carbon formation and deposition.

3. Experimental methodology

In the current study experiments were performed using a batch of planar 5 cm x 5 cm anode supported solid oxide fuel cell (AS-SOFC) based on an Ni-YSZ anode with the effective area of the cathode being approximately 16 cm^2. The cells were fabricated in the Ceramic Branch CEREL of the Institute of Power Engineering. The structure of the cell is shown in Fig. 2 which features a cross-section.

The cell was placed inside ceramic housing made of alumina, between two current collectors made of gold. The operating temperature for each experiment was kept at 750±1 °C inside the furnace.

In order to prevent carbon formation and deposition on the SOFC anode, steam was delivered to the feeding stream. In typical power generation systems, the S/C ratio value is 2.2 [26, 27, 28]. One of the ways to determine this safe value is through the use of ternary diagrams with isotherms of carbon formation or Gibb's diagrams (Fig. 3).

The theoretical boundary between non-deposition and deposition can be defined by determining the equilibrium composition for different gas mixtures, containing carbon, hydrogen and oxygen atoms. Boundaries can be found for different temperatures and are presented in the diagram as isotherms of carbon formation.

When internal reforming (IR) takes place inside the anodic compartments of SOFCs, two chemical reactions occur over the anode: (i) endothermic steam reforming, and (ii) exothermic electrochemical oxidation of fuel, written according to reactions (4) and (5), respectively.

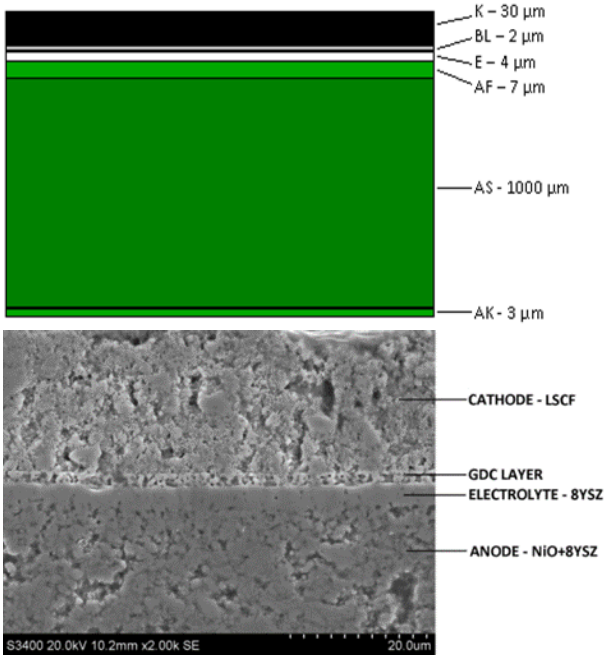


Figure 2: Thickness of the interlayers of the analyzed AS-SOFC (top) and its microstructure (bottom) [25]

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad dH = 165.2\ kJ/mol \tag{4}$$

$$H_2 + O_2 \rightarrow H_2O\,(g) \quad dH = -242\ kJ/mol \tag{5}$$

In order to analyze the carbon deposition during IR reaction which proceeds with insufficient amount of steam, 50 Nml/min of CH_4 was applied as fuel for the fuel cell. Before entering the SOFC, the methane was humidified at 88 °C (Cellkraft P-10). The S/C ratio was adjusted to the desired values in the range 2.0 to 0.15. Throughout the 1000 hour long test a constant current load of 2 A was supplied by the galvanostat (Zahner PP240) to the cell. The electrochemical impedance spectroscopy technique (EIS) was used to monitor the cell parameters and degradation. Throughout the entire duration of the test, the step change of the S/C ratio was approximately 0.1. For each level several EIS measurements were performed. The post mortem analysis of the cell was completed using SEM-EDS (JEOL JSM-6010PLUS/LA).

In the parallel study, the specific composition of the feed gas was chosen and maintained in order to simulate a situation in which the reformate is delivered directly to the fuel cell, allowing carbon formation according to reactions (2) and (3). The dry mixture of 12.5% H_2, 37.5% CO and 50% N_2 (S/C = 0) was used. Taking into account the dimensions of the gas channels in the cell housing, it was possible to compute the velocity of gas for different values of the flow of fuel. The determined velocities range was from 0.1 to 0.7 m/s for fuel flow increasing from 120 Nml/min to 640 Nml/min, respectively. Six separate experiments were

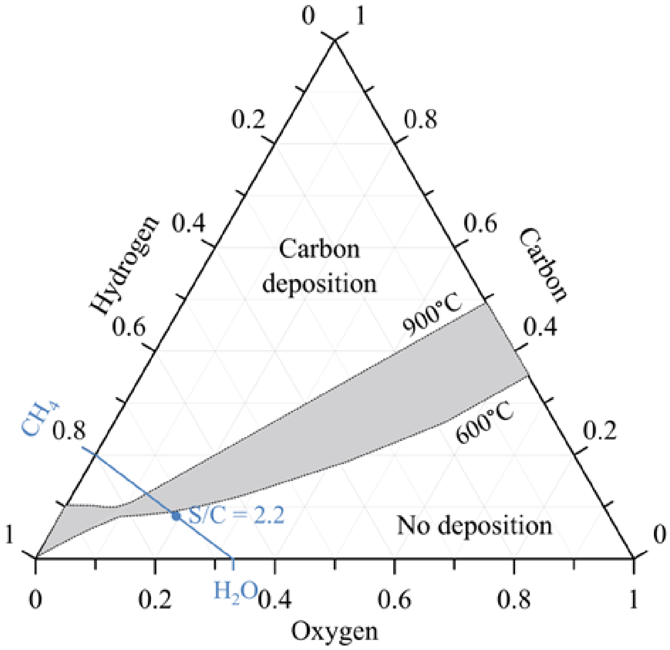


Figure 3: Gibb's diagram for CH4 steam reforming with S/C = 2.2. The gray area is based on [29]

performed under two alternative conditions: open circuit operation (three test runs) and at constant current load 3 A (three more test runs). At constant load, fuel flow varied in the aforementioned range. These values correspond to fuel utilization in the range 38–7%. The duration of every run was seven hours excluding heat-up, cell reduction and cool-down phases. In order to compare the influence of carbon deposition on fuel cell operation and short time degradation, the EIS measurements were performed at a constant electric load of the SOFC of 3 A.

Additionally, after completion of the latter test, it was decided to perform an additional experiment in which a longer exposure of a cell to carbon deposition was investigated. Flow of 640 Nml/min was applied during 200 hours of experiment, at constant, given electric load. During the experiment, multiple EIS scans where done and discussed further, together with the observed fuel cell degradation over time.

4. Results and discussion

Post-mortem analysis of the long-tested cells, fed with steam-methane mixtures, revealed cracks on the edges of the cells (Fig. 4), initially related to an endothermic steam conversion zone. After soot formation, these cracks led to a distributed leakage of air to the anode and oxidation of the solid deposits. It was concluded that further tests with humidified methane (and other hydrocarbonaceous fuels) are inappropriate for determining the influence of anodic gas velocity on carbon formation and deposition.

Results obtained during operation with simulated reformate (S/C = 0) are presented in Fig. 5.

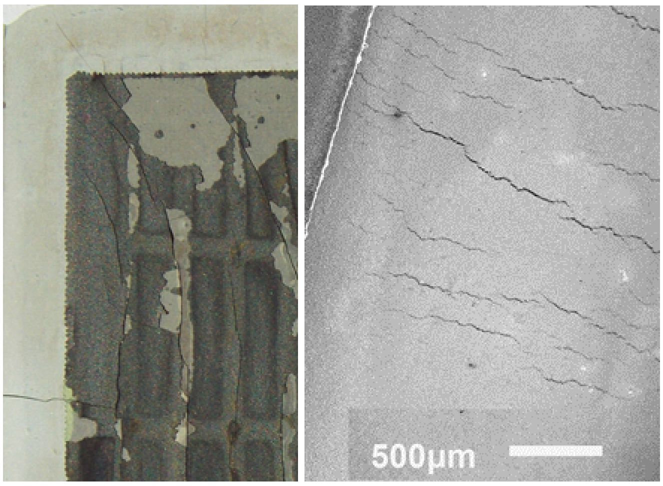


Figure 4: Cracks near the fuel inlet: left—cathode, right—SEM of the anode

The post-mortem analysis of the samples showed that the carbon deposition process is strongly correlated with gas velocity. The rate of formation of carbon deposits is higher in OCV conditions when CO and H_2 do not undergo electrochemical oxidation. This results in a high concentration of carbon monoxide and a low concentration of steam. In this case, the absence of CO and H_2 oxidation forces the Water Gas Shift reaction to proceed according to the reaction scheme (6):

$$H_2O + CO \longleftrightarrow H_2 + CO_2 \tag{6}$$

and hence support the decomposition of carbon monoxide in the Boudouard process (3).

The results of a 200 hour test are shown in Fig. 6. The impact of degradation on the electrochemical performance of the cell in carbon deposition conditions can be observed. Degradation is minor during the first 24 hours of operation after the switch of fuel from H_2-N_2 to CO-H_2-N_2 mixture and can be observed only by some evolution of EIS spectra and minor decrease in voltage, which amounts to 4.3 mV. In the consecutive phase, the transition process occurs and leads to a drop in voltage. The transition lasts approximately 48 hours. The resistances which may be attributed to the electrochemical processes increase (including cathodic) while ohmic resistant decreases slightly. In the following phase, the phenomena may be explained as a result of enhanced contact between the anode and the current collector due to the deposition of carbon particles which exhibit good conductivity. The rise in cathodic polarization may be explained as a result of the soot-covered area of the cell being excluded from transport of electric current. Slow degradation is observable even after 162 hours of operation (Fig. 6).

The complexity of the observable phenomena (anode degradation, blocking of the cell surface from charge transportation, etc.) made it problematic to create a tolerable model for equivalent circuits to describe the evolution of the impedance spectra.

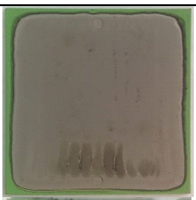
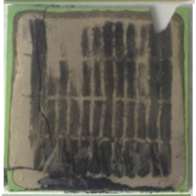
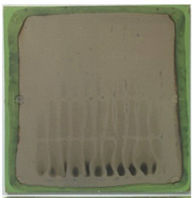
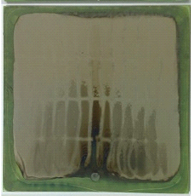
Velocity	OCV	3 A
0.1 m/s		Test not performed
0.3 m/s		
0.5 m/s		
0.7 m/s	Test not performed	

Figure 5: Carbon deposition for various anode gas velocities at 750 ℃ and S/C = 0

The degradation of the fuel cell caused by carbon deposition can be divided into three characteristic zones, which are presented in Fig. 7.

Degradation of ca. 180 mV/1000 h was observed in Zone 1 after approximately 23-24 hours. A transition region (Zone 2) in which the voltage dropped by ca. 120 mV within less than 48 is where the most aggressive degradation appeared. The degradation rate of Zone 3 is similar to Zone 1, with a low degradation rate of ca. 170 mV/1000 h. It can be concluded that carbon formation and processes start at the beginning of Zone 2. After solid carbon particles block the pores of the anode, no further impact of soot deposition on fuel cell performance is observed, thus slow degradation remains (Zone 3).

The same analysis were performed for other values of fuel velocity, i.e., 0.5 m/s and 0.9 m/s. Both values of OCV and cell voltage at 3 A load are different for each anode gas velocity case, thus in order to compare the results, a different approach was proposed. In Fig. 8 voltage drops were shown with reference to the initial value of each experiment. Dots in the chart represent the actual voltage drop measurements, while thin lines are approximations for visualization purposes only.

Analysis of the results leads one to conclude that a similar degradation rate was observed during each of the experiments. Taking into account the measurements, the time after rapid fuel cell degradation begins (transition from Zone 1 to 2) can be correlated with anode gas velocity according to (7):

$$t_{cd} = -37.5v^2 + 90v - 20.625 \tag{7}$$

where: t_{cd} is elapsed time after which the rapid fuel cell degradation caused by carbon deposition starts, and v is the anodic gas velocity.

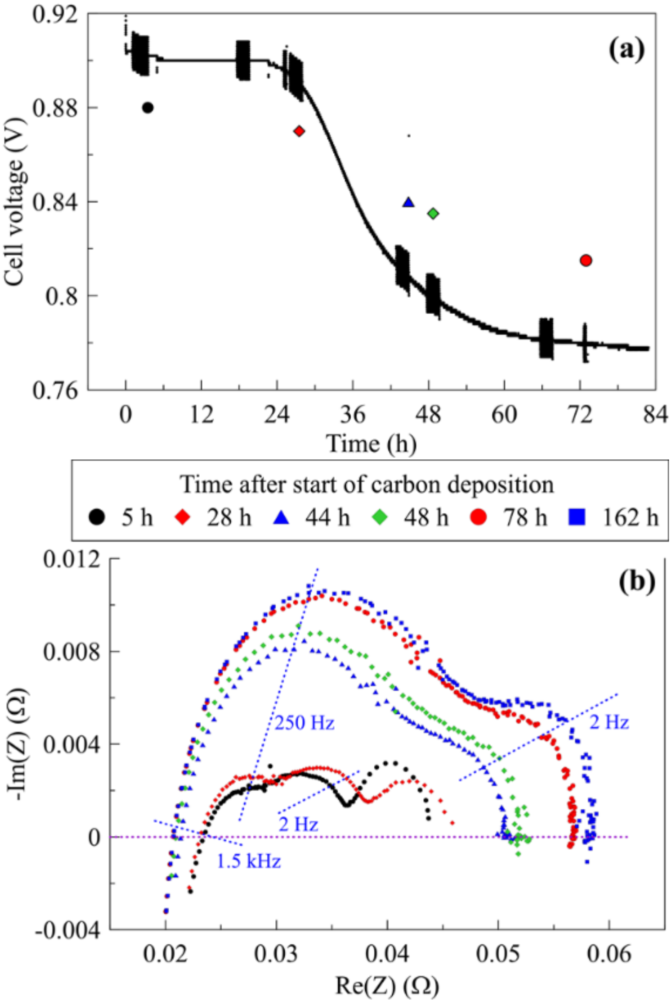


Figure 6: Cell degradation caused by carbon deposition. (a)—voltage drop; (b)—selected results of the EIS measurements, where Re(Z) and Im(Z)—real and imaginary parts of cell impedance. Symbols on plot A mark point of appropriate spectra on plot B. Anode gas velocity 0.7 m/s, current 3 A and S/C ratio 0

5. Conclusions

The experiments indicated that, in both open circuit and galvanostatic load (3 A) conditions, anode gas velocity affects carbon deposition in solid oxide fuel cells. The higher velocity of the fuel supplied to the anodic compartments of the SOFC results in faster and more rapid carbon formation on the anode. Later stages of carbon deposition may last up over ten hours, which is strictly correlated with anodic gas velocity, then it followed by a rapid drop in performance, concluded by continuous decay. The degradation rate during the

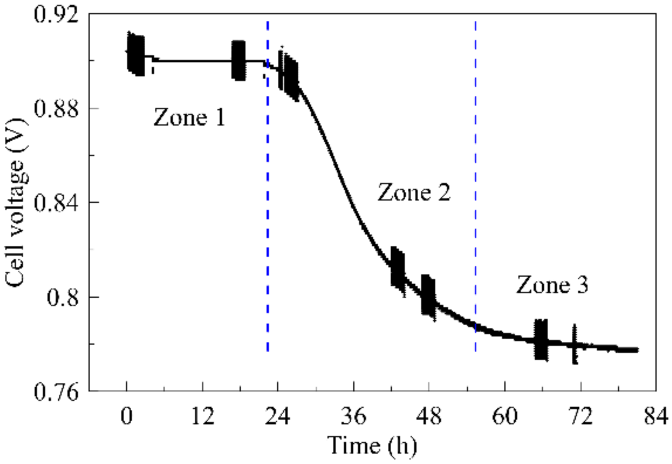


Figure 7: Cell degradation rate zones (measurement at constant current load of 3 A

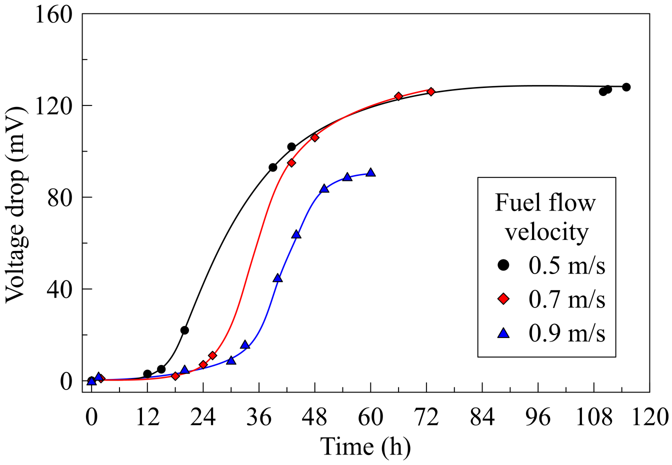


Figure 8: Fuel cell voltage drops and constant current load of 3 A for 3 anode gas velocities

rapid stage of degradation probably does not depend on the flow rate.

A formula was proposed which correlates gas velocity and the time needed to initiate rapid degradation of electrochemical performance due to the presence of solid deposits.

The experimental measurements which were performed in the work summarized in the article included analysis of the EIS spectra. This was done in order to determine the evolution of polarization during feeding of the SOFC with gas in conditions which correspond to carbon formation in the ternary diagram.

Results of the study can find application in the design of systems with high temperature fuel cells, which usually rely on steam reforming of hydrocarbonaceous fuels. SOFCs with internal reforming can adapt their operating strategies and implement safety measures with regard to selected faults or fluctuations of parameters in the fuel line. Potential problems can be factored into the control and automation system of SOFC-based power units and measures taken to mitigate the threats that are identified.

Acknowledgements

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