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Analysis of polymer burnout during the start-up process of the MCFC stack

Filip Murawka[1]✉, Arkadiusz Szczęśniak[1], Alexander Martsinchik[1]

[1]Warsaw University of Technology, Faculty of Power and Aeronautical Engineering. Institute of Heat Engineering 21 Nowowiejska street, 00-665 Warsaw, Poland

✉ filip.murawka.stud@pw.edu.pl

Abstract

The paper contains a comprehensive summary of the current state of research on the polymer burnout process in molten carbonate fuel cells (MCFC). Outline information discussing both MCFC fundamentals and the start-up process are given along with references to the literature. The main part of the article presents the result of an on-site experiment regarding polymer burnout performed on an MCFC stack. The outcomes are discussed and conclusions are clearly stated.

Introduction

Concerns over climate change are driving a wide range of policies in the European Union member states. Many different fields of science must be sustainably developed to adapt to climate policies [1], [2]. Power engineering is the most prominent industry in terms of the search for alternative sources of energy.

Fuel cells, first developed in 1839 [3], represent a promising path to achieving climate goals, for instance, appliances cooperating with hydrogen production from renewable energy sources [4], [5]. Moreover, molten carbonate fuel cells, along with solid oxide fuel cells, provide various options for combined heat and power due to the high temperature in operating conditions.

The formative start-up of a fuel cell is crucial to exploiting its full potential. During such start-up, a mixture of gases is provided to flow through the stack and evenly distribute heat to gradually rise the stack temperature. As the mixture contains oxidants, mechanical factors must be considered when selecting materials. Oxidants appear necessary for processes such as polymer burnout, which will be the main focus of this paper. The potential replacement of gases for inert mixtures would be beneficial in mechanical and material matters.

Technology Overview

The basic electrochemical reaction taking place in molten carbonate fuel cells (MCFCs) [6]–[8] may be described as follows:

$$H_2 + \frac{1}{2}O_2 + CO_{2\_cathode} \rightarrow H_2O + CO_{2\_anode} \quad (1)$$

when specifying hydrogen as fuel.

As the formula above states, bonding hydrogen and oxygen molecules is the main process that allows fuel cells to generate energy. However, the presence of carbon dioxide molecules determines the type of fuel cell. In MCFCs molten carbonate anions are the carriers of charge between the cathode and the anode through the electrolyte. To obtain these anions, subsequent reactions are carried on the cathode and anode respectively:

$$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \quad (2)$$

$$H_2 + CO_3^{2-} \rightarrow H_2O + 2e^- \quad (3)$$

The electrolyte is not permeable to the electrons obtained during the anode reaction. Thus, an external circuit must be introduced to transport electrons from the anode to the cathode. This electron movement creates a difference in electric potential, which is the reason for the electric current and electricity obtained. This process is illustrated in Figure 1.

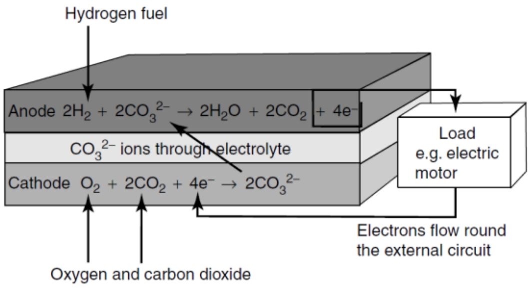

Figure 1: Working principle of MCFCs – scheme [9]

MCFCs are one of the types of high-temperature fuel cells. Their nominal operating temperature is 650°C (923.15 K). This temperature is strictly connected to the melting point of the electrolyte and the appropriate level of permeability of CO_3^{2-} anions through the electrolyte. Moreover, this temperature level allows for the use of nickel-based electrodes, instead of precious metals, considerably reducing manufacturing costs [10]–[12].

To obtain the assumed level of voltage, singular cells must be connected in series, creating a stack. Each singular cell consists of electrodes (cathode and anode) and electrolyte. Commonly, both cathode and anode are nickel-based. Due to its chemical properties, nickel acts as the catalyst in both semi-reactions at the electrodes. However, the pure Ni compound appears only on the anode side. Nickel oxide (NiO) is used on the cathode side. Electrolyte, however, is a much more complicated mixture of chemicals, especially the matrix to be precise. The matrix must be incorporated to store electrolyte, which usually comes in the form of either Li_2CO_3 or K_2CO_3, when forming the fuel cell. It is mostly composed of commercially available YSZ powder and PVB – $(C_8H_{14}O_2)_n$ – with the addition of other organic compounds. The mixture is then formed into thin layers of solid fabric in the 'tape casting' method. The aforementioned PVB polymer is the main subject of this paper.

Start-up process

To ensure proper behavior in design conditions, the MCFC stack must be correctly prepared during the first start-up process. The main aim of what is termed 'formative start-up' is to heat the fuel cells so that they reach the nominal temperature of 650°C. This temperature must be achieved in a gradual process to prevent any extreme local temperature gradients, which may cause damage due to heat stress [10], [13], [14].

The temperature is usually achieved in a five-stage process. Firstly, the stack is heated up from the ambient state to 250°C. The temperature rise in time is described by the linear function with a given coefficient determined by the individual stack. In the second stage, the stack is kept at a constant temperature for a specific time. This allows for the polymer additions in the fuel cell's matrix to be burned out – the process on which this paper focuses. Then the MCFCs are heated up linearly to the temperature of 500°C and once again kept at a stable temperature for a time. This is done to let the electrolyte melt and become a charge carrier. In the fifth stage, the stack reaches the nominal temperature of 650°C. The stages are summarized in Table 1.

Table 1: MCFC stack start-up stages [10], [15]

Stage	Description
Stage 1	Stack heat-up to 250°C
Stage 2	Polymer burnout in 250°C
Stage 3	Stack heat-up to 500°C
Stage 4	Electrolyte melting at 500°C
Stage 5	Stack heat-up to 650°C

The process can also be shown on the graph as a time function of stack temperature. The maximum temperature rise is assumed at 12°C/h, as stated by the manufacturer [15].

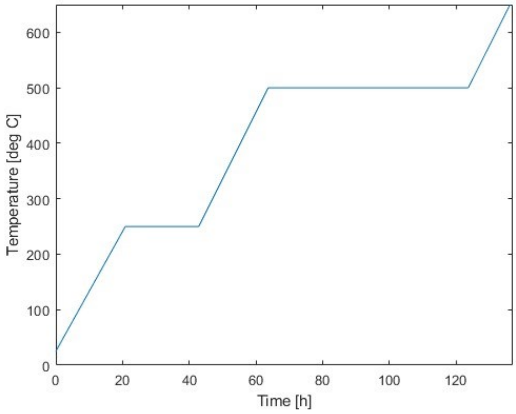

Figure 2: Change of stack temperature in time (simplified) [15]

This paper’s main focus is on the second stage of the formative start-up. Whereas the subject has not been widely researched, there are some papers regarding the burnout of PVB, the main polymer compound used in the MCFCs [16], and the stages of the formative start-up of MCFCs [10], [13]. There is considerable variability in the temperatures at which the polymers are supposed to burn out, lying in the range 150°C - 500°C. Multiple factors determine whether burnout actually takes place, such as humidity, the micro-pore configuration of the matrix, and oxygen concentration. While the details of the described processes differ, the high importance of polymer burnout is a common conclusion.

Experiment description

The test subject in the experiment was an MCFC stack FCP TNS 5000 manufactured by the company Fuel Cell Poland. The stack consists of 60 individual MCFCs stacked manually. Both electrodes were nickel-based and the electrolyte was held by the polymeric matrix. The appliance is shown in Figure 3.

Figure 3: FCP TNS 5000 MCFC stack

There were two MCFC stacks on site, placed in a prepared container.

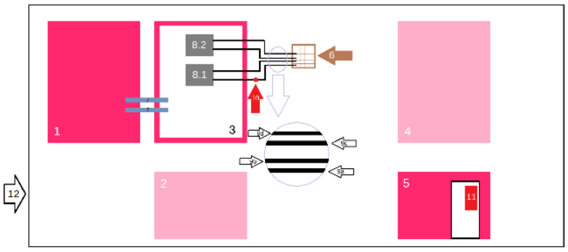

Figure 4: Research site simplified scheme

The exhaust gases, which were the main focus due to their importance in the experiment, were removed through four exhaust pipes divided equally between the stacks (pipes 9a to 9d - Figure 4). In each stack one pipe was responsible for anode exhaust gas removal and the other for cathode exhaust gas removal. Due to the high temperature of the exhaust gases (about 250°C), the pipe outlets were housed in a metal cage for health and safety reasons.

Samples of anode exhaust gases, which were crucial to the research, were collected by 10 - 100 ml syringes from a hole in anode exhaust gas pipe 9A from stack 8.1 (point 10 on Figure 4). A needle was placed in the hole to attach the syringe. Samples were taken and secured from leaks using thermal glue.

The samples were assigned to storage and experiment sets.

The storage set consisted of larger syringes (40+ ml). These samples were earmarked for storage elsewhere for future, separate research. These samples were taken throughout the whole period of the second stage of MCFC stack formative start-up – one sample per hour approximately. 20 samples were taken and labeled according to the set standards.

The experiment set samples were collected hourly, two samples in each period for use in the present gas composition analysis. This was because there were two studies carried out on-site. The volume of each sample was 10 ml.

The main study was based on the experiment set and carried out on-site.

Gas chromatography

The research was carried out with the use of a gas chromatograph. Gas chromatography is a field of science that regards the composition of sample gases. It is most commonly applied in the food production industry to determine if there are any unwanted additives in products [17]–[22].

Gas chromatography measures the peaks in voltage resulting from the presence of specific molecules in a mixture. Samples are gradually separated to exclude individual ingredients. The separated gas is then transported to a detector by a carrier gas, which is an inert compound that does not affect the results. The differences in voltage readings are caused by changing the thermal properties of gases in the detector. When the mixture is composed of only the carrier gas, the heat transfer is constant. When additives are present in the mixture, heat flux changes due to the new properties. The altered temperature results in a change in the detector's electrical resistance, which is then exported to the designed software as voltage peaks. The mass share of a specific compound can be obtained by the peak area method. It is defined by the following formula:

$$X_j[\%] = \frac{A_j}{\sum_{i=1}^{n} A_i} \cdot 100 \qquad (4)$$

where:

- X_j – the mass share of a specific compound or mixture of compounds;
- A_j – the area 'under' the determined peak;
- $\sum_{i=1}^{n} A_i$ – the area 'under' all peaks.

The separation of gases takes place in the furnace with a preset level of temperature (which can be changed during the study). Special columns are introduced to aid the separation.

The appliance used was the *SRI 310C Gas Chromatograph* equipped with a TCD detector (Thermal Conductivity Detector). Helium was the carrier gas which transferred the separated gases from the furnace plus *8600-PK1A 3' x 1/8" S.S. Silica Gel Packed Column* to the detector chamber [23].

Figure 5: SRI 310C Gas Chromatograph manufactured by SRI INSTRUMENTS, INC.

Preparation

The research was based on determining whether the share of CO_2 molecules was heightened. Carbon dioxide was assumed to be the main product of the burnout reaction of polymers, which are organic compounds with a considerable level of carbon.

Two temperature scenarios were defined before carrying out the research. The furnace temperature affects the retention of gases, meaning that the time in which a specific peak on the voltage graph happens is altered by the temperature level. Lower temperatures facilitate recognition of compounds with smaller retention, such as oxygen, hydrogen, and carbon dioxide. The higher the temperature, the shorter the retention, so increasing the temperature also shortens the research time, which was highly dependent on the on-site conditions. Moreover, long molecule chains of polymers could only be measured in high-temperature settings [17]–[19], [24].

The predefined scenarios A and B are shown in the following Figure 6 and Figure 8 accordingly.

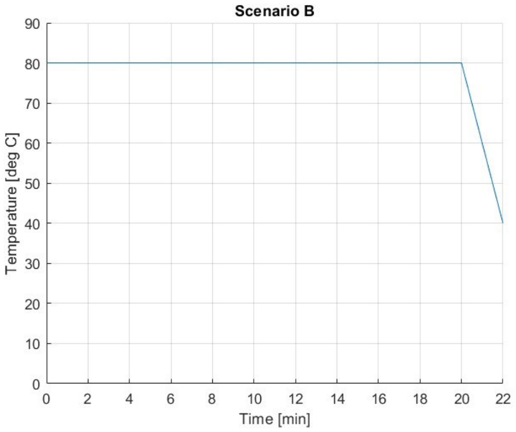

Figure 8: Temperature scenario B

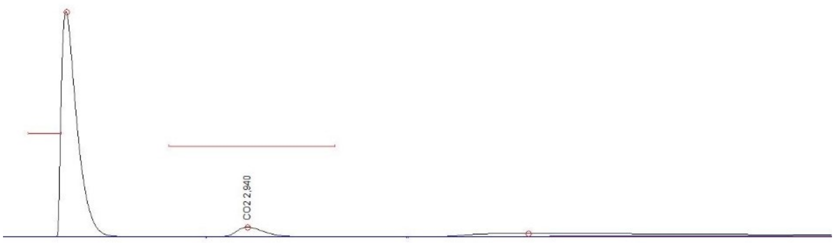

Figure 7: CO2-rich sample voltage graph

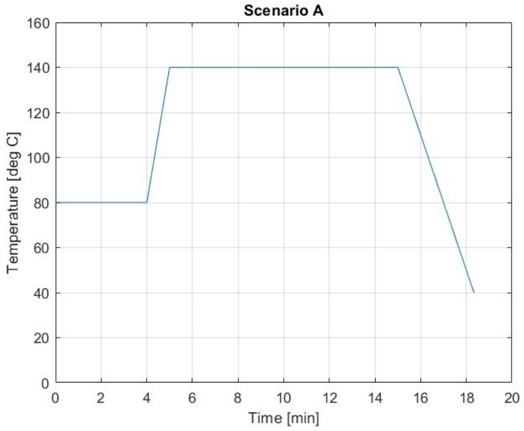

Figure 6: Temperature scenario A

The temperature is partly set at 80°C in both scenarios. This is due to the fact of the assumed retention of CO_2 at this temperature.

A dedicated study was conducted to confirm this assumption. A sample was prepared consisting of the gases contained in a bottle with highly carbonated water. It was then injected into the gas chromatograph, which was set to 80°C. The correct pressure of the carrier gas was also provided.

The voltage readings confirmed the retention of CO_2 molecules at 80°C as happening about 3 minutes after the start of the program. As air was the main component of the sample, as was also predicted for the experiment samples, its retention was determined as well. The measured results were then adapted to contain a margin in which the carbon dioxide peak can happen, as shown in Table 2.

Table 2: Gases retention assumptions

Gas	Retention – lowest value [min]	Retention – highest value [min]
Air	0.300	0.700
CO_2	2.000	4.000

Results

Knowledge of the retention time of CO_2 made it possible to conduct the main part of the research.

Scenario A

19 samples were taken and studied in temperature scenario A. The first two samples of the set were rejected due to issues concerning the connection between the chromatograph and the measuring software, leaving 17 valid samples examined on-site. The detailed results are presented in Table 3 (in both parts). The graph below shows the obtained values of the CO_2 mass share in the anode exhaust gases.

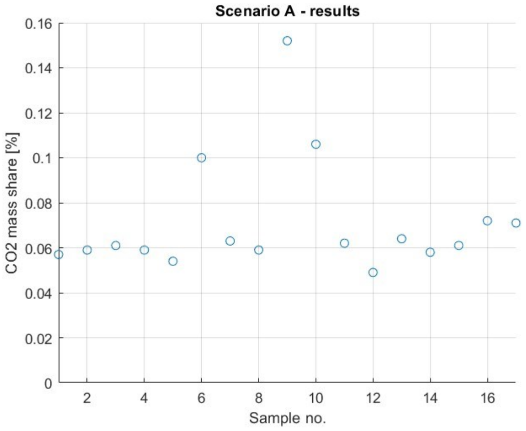

Figure 9: Scenario A results

Scenario B

19 samples were taken for testing in temperature scenario B. During the tests, some results were not complete due to connection problems. However, all problems appeared long after the time of the potential CO_2 peak. Thus, all of the samples were deemed valid and taken into consideration. The specific results are shown in Table 3 (both parts) and the cumulative graph of the CO_2 mass share is presented below.

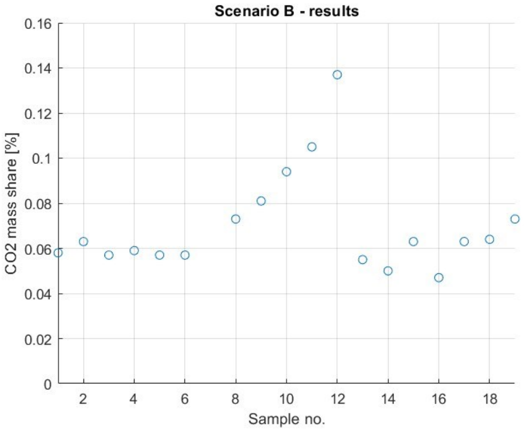

Figure 10: Scenario B results

Conclusions

Gases containing oxidants are much more harmful to the construction parts of fuel cells than inert compounds such as clear nitrogen. On the other hand, they may be crucial for some processes that require the presence of oxygen molecules in simple or complex forms. The main process that requires the presence of oxygen molecules is polymer burnout.

Polymers, including PVB, are organic compounds. Thus, the assumed product of the burnout process in the presence of oxidants are carbon dioxide molecules. The heightened presence of such in exhaust gases would suggest the ongoing process.

The share of CO_2 molecules was determined using a gas chromatograph. The peak area method was used to translate the voltage readings into the researched values. The highest determined percentage of CO_2 in the mixture with air was 0.152%, which is a marginal value. The most frequent value obtained was around 0.06%. These values are very low but non-nullifiable.

Readings higher than 0.00% may infer that the polymer burnout process does take place in these temperature conditions, but it cannot be classified as the leading process of polymer removal during the second stage of the formative start-up. However, it is not suggested to fully replace the start-up gases from those containing oxidants with inert gases. That is because there are

Table 3.1: Results – both scenarios – part 1

Timestamp	Scenario	Sample no.	Stack temperature [°C]	Air retention [min]	CO_2 retention [min]	CO_2 mass share [%]
17.08.2021 22:58	B	B1	250	0.686	2.646	0.058
17.08.2021 23:40	B	B2	250	0.743	2.800	0.063
18.08.2021 00:09	A	A1	250	0.713	2.760	0.057
18.08.2021 00:30	B	B3	250	0.720	2.876	0.057
18.08.2021 01:05	A	A2	250	0.746	2.876	0.059
18.08.2021 01:26	B	B4	250	0.763	3.026	0.059
18.08.2021 02:06	A	A3	250	0.720	2.856	0.061
18.08.2021 02:26	B	B5	250	0.776	2.930	0.057
18.08.2021 03:06	A	A4	250	0.773	2.833	0.059
18.08.2021 03:28	B	B6	250	0.746	2.846	0.057
18.08.2021 04:19	A	A5	250	0.700	2.780	0.054
18.08.2021 04:43	B	B7	250	0.736	2.896	0.070
18.08.2021 05:09	A	A6	250	0.740	2.903	0.100
18.08.2021 05:30	B	B8	250	0.700	2.910	0.073
18.08.2021 06:04	A	A7	250	0.680	2.890	0.063
18.08.2021 06:26	B	B9	250	0.713	2.943	0.081
18.08.2021 07:05	A	A8	250	0.676	2.903	0.059
18.08.2021 07:26	B	B10	250	0.696	2.953	0.094

some CO_2 molecules present in the exhaust gases. Moreover, various mechanisms regarding removal of organic compounds should be studied [16], [25] as well as the polymer burnout process at higher temperatures [25].

Table 3.2: Results – both scenarios – part 2

Timestamp	Scenario	Sample no.	Stack temperature [°C]	Air retention [min]	CO_2 retention [min]	CO_2 mass share [%]
18.08.2021 08:05	A	A9	250	0.710	2.936	0.152
18.08.2021 08:25	B	B11	250	0.706	2.976	0.105
18.08.2021 09:05	A	A10	250	0.716	2.936	0.106
18.08.2021 09:26	B	B12	250	0.710	2.990	0.137
18.08.2021 10:14	A	A11	250	0.703	2.906	0.062
18.08.2021 10:35	B	B13	250	0.696	2.903	0.055
18.08.2021 11:06	A	A12	250	0.713	2.890	0.049
18.08.2021 11:28	B	B14	250	0.720	2.936	0.050
18.08.2021 12:05	A	A13	250	0.713	2.933	0.064
18.08.2021 12:28	B	B15	250	0.706	2.976	0.063
18.08.2021 13:05	A	A14	250	0.720	3.003	0.058
18.08.2021 13:34	B	B16	250	0.736	3.046	0.047
18.08.2021 13:15	A	A15	250	0.740	3.046	0.061
18.08.2021 14:27	B	B17	250	0.740	3.070	0.063
18.08.2021 15:05	A	A16	300	0.710	3.013	0.072
18.08.2021 15:26	B	B18	300	0.726	3.060	0.064
18.08.2021 16:06	A	A17	300	0.733	3.010	0.071
18.08.2021 16:26	B	B19	300	0.730	3.020	0.073

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