Influence of high concentrations of SO_2 on Molten Carbonate Fuel Cell operation

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Abstract

Molten Carbonate Fuel Cells (MCFCs) can be used as CO_2 separators in fossil fuel power plants. Fossil fuel power plants emit flu gases with SO_2 contaminants, thus the influence of SO_2 on the operation of MCFC is investigated both experimentally and theoretically. The influence of SO_2 contaminants (up 680 ppm) on MCFC performance was examined. The experimental investigation revealed there is a boundary limit where SO_2 contamination could increase the MCFC voltage.
Keywords: CO_2 capture, Molten Carbonate Fuel Cells, sulfur contaminants.

1 Introduction

The European Union has placed limits on CO_2 emissions by Member States as part of its Emission Trading Scheme. This impacts fossil fuel power plants to a significant degree, as their emissions are governed by the number of emission allowances they receive from the Member State allocation. Excess CO_2 emissions have to be covered by purchasing extra allowances, which is in effect a penalty (€100/Mg). In contrast, undershooting emission limits enables the emitter to sell CO_2 allowances. The selling price of a traded allowance is estimated at €15/$\mathrm{Mg}_{\mathrm{CO_2}}$.

Various types of fuel cells may be distinguished by: different catalysts, different ions as proton carriers, different operating temperatures and different fuels. In general, we may recognize low- (e.g. Polymer Exchange Fuel Cells [1]) and high-temperature fuel cells and among the latter Solid Oxide Fuel Cells (SOFC) [2–4] and Molten Carbonate Fuel Cells (MCFC) [5, 6]. They both feature high efficiencies and have the priceless feature of methane utilization—already available as a fuel including in bio-fuels. Others need hydrogen feeding, which requires a significant amount of energy to produce. Additionally, a high

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temperature fuel cell can be coupled to a gas turbine for ultra-efficient power generation. Alternatively, small units based on fuel cells can be utilized as power sources in a Distributed Generation system.

Furthermore, MCFCs make it possible to concentrate carbon dioxide, e.g. from coal or gas fired power plants [7], and might form part of a Carbon Capture and Storage system [8]. To operate, an MCFC requires a flow of CO_3^{2-} as the proton carrier through the electrolyte. This is achieved by feeding CO_2 to the cathode, where it reacts and flows as CO_3^{2-} to the anode. There, after another reaction, it becomes carbon dioxide once again and, after removing water vapor, may be transported as pure gas to the storage point. One might say that MCFCs work as a filter, allowing exclusive flow of CO_2.

The idea of adopting a molten carbonate fuel cell to reduce CO_2 emissions was developed by Campanari [9]. In that paper it was shown that an estimated reduction of 77% in CO_2 emissions can be achieved in a steam turbine power plant. A few years later Campanari *et al.* [10] investigated the possibility of separating CO_2 from combined cycles integrated with Molten Carbonate Fuel Cells. The results obtained show that CO_2 reduction can reach 80% while electrical efficiency remains virtually unchanged, with the power of the cell contributing 17% of the entire system. Amorelli *et al.* [11] described an experimental investigation into the use of molten carbonate fuel cells to capture CO_2 from gas turbine exhaust gases. They obtained an emission reduction of 50%. Those experiments were performed using a singular cell. Lusardi *et al.* [12] investigated the application of a fuel cell system for separating CO_2 from thermal plant exhaust. They found that, even without CO_2 separation, the relative emission of carbon dioxide could be reduced to below the Kyoto Protocol limit. If a separator is used, emissions could be reduced by 68%. The use of an MCFC as a carbon dioxide concentrator was investigated by Sugiura *et al.* [13]. In this work the experimental results of CO_2 sequestration through the use of an MCFC are given. One key conclusion from this work is that the CO_2 removal rate can be obtained by making calculations using electrochemical theory. In [14] consideration was given to reducing CO_2 emissions from a coal fired power plant through the use of a molten carbonate fuel cell and in [15] from a gas turbine power plant and in [16]—from Fossil Power Plants. Jung-Ho in [17] analyzed three fields (mobile application, transportation application and stationary application) in terms of CO_2 emission reduction through the use of fuel cells. Only the last of them considered the possibility of using MCFC for the separation of CO_2. Cryogenic separation of CO_2 from combined cycles integrated with molten carbonate fuel cells was shown in Chiesa *et al.* [18]. The considered system affords the possibility to separate 80% CO_2, while the increase in power as a result of the proposed solution is 22% with nearly unchanged efficiency (59% LHV). In [19] Xu *et al.* presented tests of a new composite—a dual phase mixed carbonation and electron conducting membrane (molten carbonate and silver). The possibility of separation of CO_2 from simulated flue gas was explored, yielding higher CO_2 and O_2 flux densities compared with molten metal carbonate systems. Based on experimental investigations [20], the achievable CO_2 separation rate

Table 1: Exemplary flue gas composition.

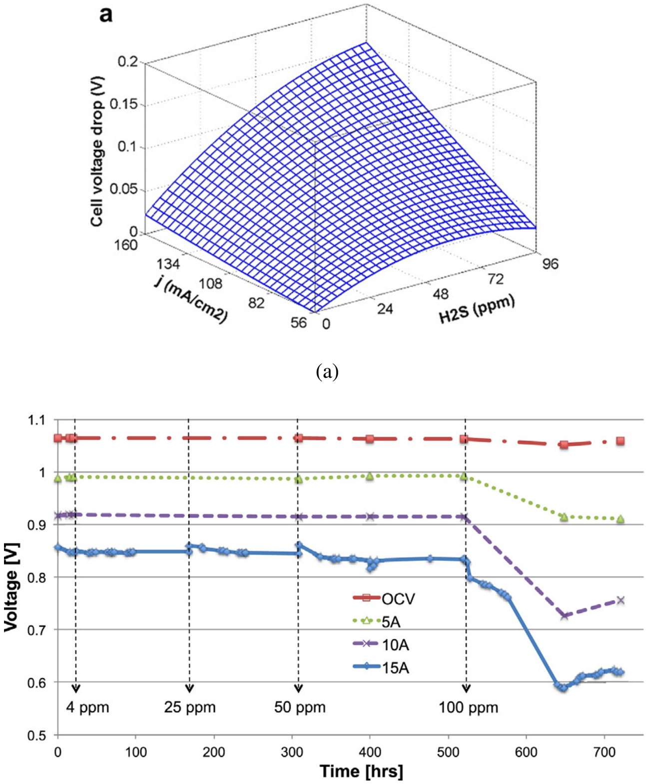
Component	Hard coal	Lignite	Oil	Natural gas
O_2, vol. %	2.5...10	5	2..6	1..5
CO_2, vol. %	11...16	10...14	8...10	6...8
N_2, vol. %	balance	balance	balance	balance
H_2O, vol. %	5...10	16...20	2...6	3...8
NO_X, vol. %	0.1	0.1	0.06	0.05
SO_2, ppm	**<2,000**	**<2,600**	**<1,000**	**0**
SO_3, ppm	11	40	<6	0
dust, mg/m^3	50..150	50	0.05..0.3	0

from lignite fired boiler flue gas was determined at above 90% by adjusting the cathode inlet flow.

Typical compositions of the flue gases from various sources are presented in Table 1. There are several pollutants which can influence MCFC operation as CO_2 separator, the highest content concerns SO_x compounds. One of the issues that should be examined is the effect of sulfur dioxide on the parameters of the MCFC. The sources of sulfur dioxide in flue gas are the sulfur compounds contained in fossil fuels. Although the exhaust gases are desulfurised, they are not deprived of certain quantities of sulfur dioxide. In order to determine the separation capacity with regard to exhaust gas produced by conventional power plants one must examine the effect of sulfur dioxide on the side of the cathode.

The MCFC can act as a sulfur scrubber [21], SO_2 is known to accumulate in the electrolyte as sulphate, and readily transferred to the anode where it can react with the hydrogen to form H_2S. This in turn has a strong poisoning effect on the nickel based anodes.

The formation of hydrogen sulphide at anode is the most harmful and damaging reaction product in the conversion process [24], and it is advised to remove the sulfur species before the gas enters the fuel cell anode. Hydrogen sulphide poisoning of nickel-based materials can occur through several paths, such as chemical reactions to form bulk nickel sulphides, physical and chemical adsorptions to form a sulfured surface, and electrodic reactions to deposit nickel sulphides by a predominance of electrochemical reactions over chemical reactions [22]. In addition, the analysis shows that the poisoning effect is a quadratic function (see Fig. 1(a)) of hydrogen sulfide which is expressed by the cell voltage, and the drop in voltage asymptotically tends toward a maximum value corresponding to dynamic steady state conditions of poisoning. To investigate these issues, in [25] an experimental campaign was carried out for the purpose of a preliminary analysis of the effect of H_2S on MCFC performance, highlighting



(a)

(b)

Figure 1: (a) Response surface and contour plot for the effect of H_2S and current density on cell voltage drop. The H_2 concentration for this plot is set at 40.5% [22]; (b) effect of different SO_2 concentration in KIST condition [23].

how the main operating parameters affected poisoning phenomena. The results obtained provided new insights for approaching phenomena-reading, confirming the possibility of using MCFCs when a number of ppm of H_2S is also present in the feeding fuel.

In [23], the particular effects of the presence of SO_2 at cathode side on MCFCs were studied. The experimental campaign carried out allowed for a preliminary analysis of the SO_2 up to 100 ppm—see Fig. 1(b)—effect on MCFC performance, highlighting the poisoning mechanisms and the influence of the main operating parameters. The poisoning mechanisms proposed in the literature have been confirmed and experimental tests on single-cells showed that SO_2 reacts with the electrolyte at cathode side forming SO_4^{2-} ions which, migrating to anode side, cause the formation of H_2S, whose effects at anode side are described above. In particular, the effect of SO_2 poisoning was significant even at OCV conditions, suggesting that the chemical reaction for the formation of sulfur ions in the electrolyte is fast and well-favored.

This paper continues the investigation into the effect of SO_2 on MCFC performance, but for higher concentrations of sulfur dioxide:100...680 ppm, which is closer to the amount of SO_2 presented in flue gases.

2 Influence of high concentrations of SO_2 on Molten Carbonate Fuel Cell operation

Studies were carried out for three levels of sulfur dioxide concentration. The cells used in the experiments were previously tested in other investigations. Previous tests were conducted without any sulfur content in cathoded (and anoded) gas. The cells have a slightly different chemical composition of the cathode and anode. Basic data characterizing the cells used is shown in Table 2.

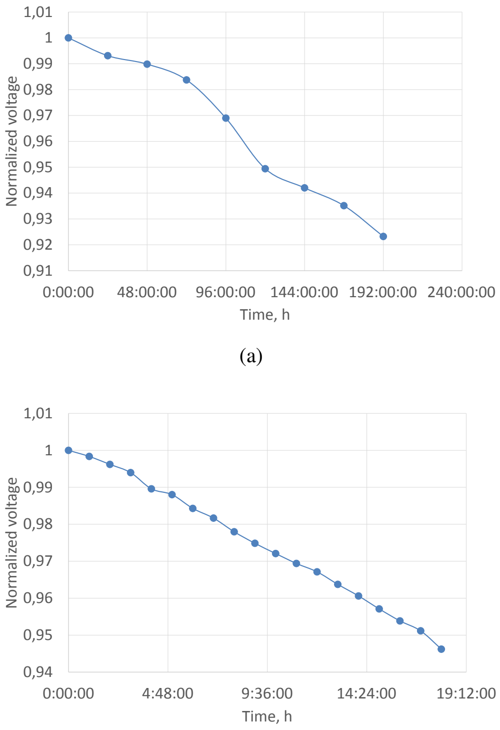
Table 2: Characteristics of the used single-cells.

Test	SO_2 concentration, ppm	Anode	Cathode	Size, cm^2	Daily decrease of voltage, %/day	Current density (constant in time), A/cm^2
1	100	Ni	Ni	20.25	0.7	0.05
2	320	NiO	NiO	20.25	7.2	0.05
3	680	Ni	NiO	20.25	12	0.05

Effect of 100 ppm of sulfur dioxide cell voltage variation is depicted in Fig. 2(a). The experiment lasted about 220 hours. The negative effect of sulfur dioxide was already noticeable in the first few hours. On average, the voltage drop is about 0.7%.

The influence of 320 ppm on sulfur dioxide is shown in Fig. 2(b). There is an observed constant decrease in nominal voltage in time until the 36th hour of operation. The visible peak, which occurred in ca. the 36th hour, is presumed to be a measurement error. The chemical processes occurring in the fuel cell, which was operated more than 40 hours, are more dynamic and result in an increase in the rate of voltage drop with respect to the cell operating 30 hours.

Fig. 3(a) shows the voltage drop in time caused by the presence of a sulfur dioxide concentration of 680 ppm. The rate of voltage drop in time is higher than in the previous cases. After 48 hours of operation, the total voltage drop of the fuel cell exceeds 20%.



(a)

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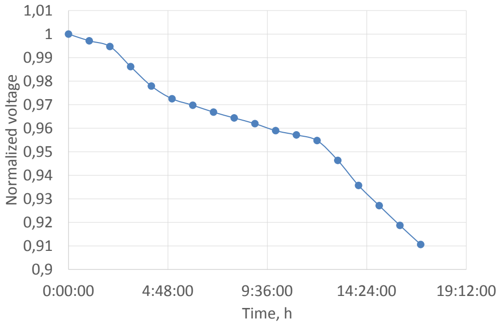
Figure 2: (a) Effect of 100 ppm sulfur dioxide concentration; (b) effect of 320 ppm sulfur dioxide concentration.

Fig. 3(b) presents a comparison of experimental results. It is observed that the increase in sulfur dioxide concentration in gases results in an increase in the rate of voltage drop in time. The presence of a sulfur dioxide concentration which is not higher than 100 ppm results in a slight voltage drop in time. After 48 hours of operation the voltage drop does not exceed 2% of nominal voltage, whereas an SO_2 concentration higher than 680 ppm results in a significant voltage drop. The different shapes of those lines are the result of slight differences in the composition of the fuel cell.

3 Discussion

In the available literature, there is a limited amount of papers on the influence of sulfur dioxide on performance of the molten carbonate fuel cell. Results are published in [23]. Fig. 4 shows a comparison of experimental results by KIST and IHE. Both experiments were conducted in similar conditions, i.e. the sulfur dioxide concentration was 100 ppm and the composition of inlet gases was similar.



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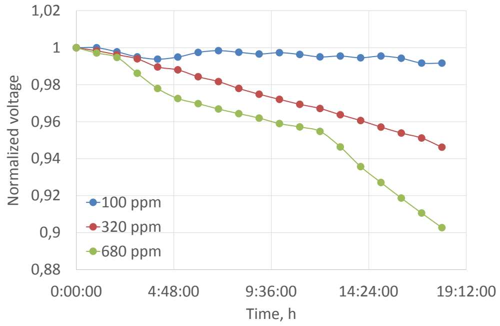

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Figure 3: (a) Effect of 680 ppm sulfur dioxide concentration; (b) effect of different sulfur dioxide concentration during the initial phase.

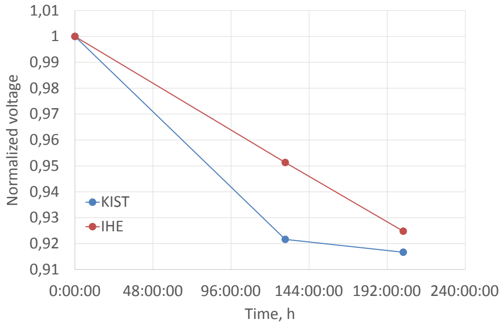
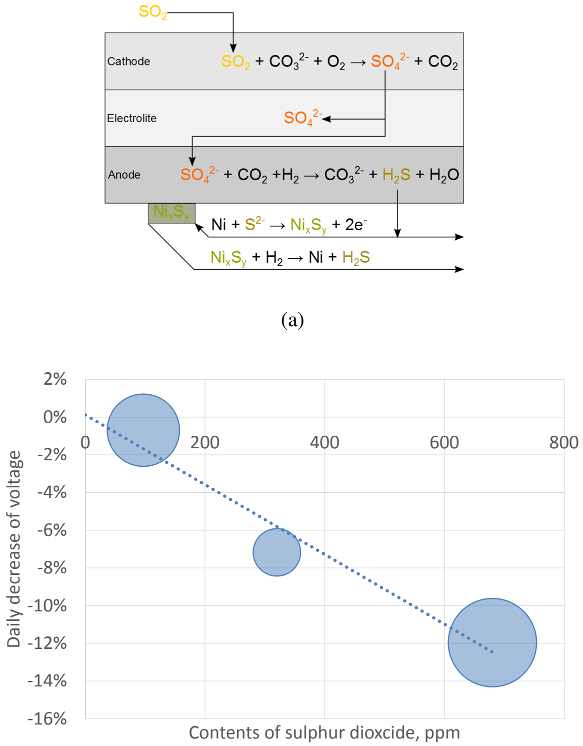


Figure 4: Comparison of KIST and IHE results.

The results were analyzed and the supposed approximate mechanism of sulfur dioxide influence on MCFC performance presented in Fig. 5(a). The presented



(a)

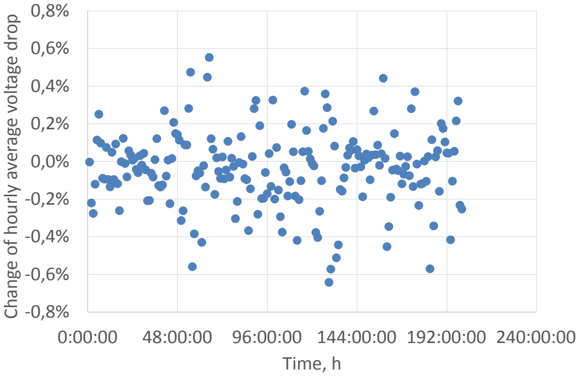
(b)

Figure 5: (a) The mechanism of the impact of sulfur dioxide on MCFC; (b) impact of content of sulfur dioxide on the daily decrease in voltage. The radii of the circles are proportional to the standard deviation of the individual experiments.

mechanism has primary chemical reactions which significantly effect fuel cell operation during exposure to sulfur dioxide contamination at cathode side. The supposed mechanism is initiated by a reaction of sulfur dioxide with an electrolyte. The reaction is dynamic and very rapidly achieves a state of equilibrium. Hence, in the conditions present in an MCFC, the total amount of sulfur dioxide delivered reacts and forms sulfate ions. The sulfate ions from the resulting reaction (SO_4^{2-}) could either remain in and degrade the electrolyte or migrate to the anode side and be converted to hydrogen sulfide by the reaction $SO_2 + CO_3^{2-} + O_2 \rightarrow SO_4^{2-} + CO_2$. The influence of hydrogen sulfide at anode side of the MCFC is widely presented in many papers [22, 24–26]. In general, it is assumed that the hydrogen sulfide present in a potential determining reaction with nickel $xNi + yS^{2-} \rightleftharpoons Ni_xS_y + 2e^-$ (which is a main component of electrodes) creates nickel sulfide, which precipitates on the porous anode surface and decreases the active surface of the cell. Under certain conditions (especially significant hydrogen excess), the reverse reaction can occur. This reaction allows for partial regeneration of the fuel cell.

Fig. 5(b) shows the average daily drop in voltage as a function of the sulfur dioxide concentration at cathode side. The diameter of the circles is proportional to the standard deviation of the results obtained. A review of the available literature revealed a noticeable negative influence on performance after a relatively short time period of MCFC exposure to ca. 100 ppm sulfur dioxide. However, that does not mean that sulfur dioxide concentrations lower than 100 ppm do not have a deleterious effect on fuel cells. A sulfur dioxide concentration of ca. 100 ppm causes a significant, but not immediate drop in voltage.

Fig. 6(a) presents an average hourly change in voltage during consecutive days of the experiment's duration. An increase in fuel cell voltage occurred.



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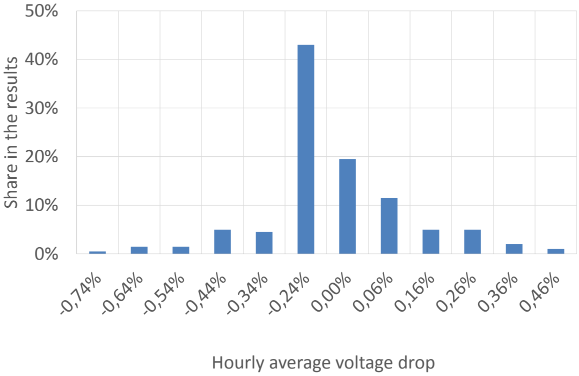
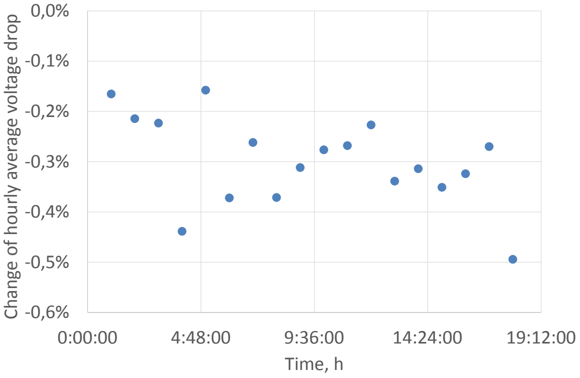


(b)

Figure 6: (a) Change in hourly average voltage drop during 100 ppm test; (b) share of hourly average voltage drop in all 100 ppm test results.

Fig. 6(b) presents a share of average hourly drops in voltage at present ranges across the spectrum of the results. The most of the results obtained lie in the range 0% to −0.238%, while over 40% of results have a positive value (i.e. an increase in voltage). The negative effect of sulfur dioxide contamination is indisputable (as shown in Fig. 2(a)). Fig. 7(a) shows average hourly changes of FC voltage in the presence of sulfur dioxide at a concentration of 320 ppm. Positive changes in voltage are absent in these conditions. As in the case presented in Fig. 7(b), positive hourly changes in voltage are not observed. Evidently, there is a limit of SO_2 contamination at which positive changes in voltage no longer occur.



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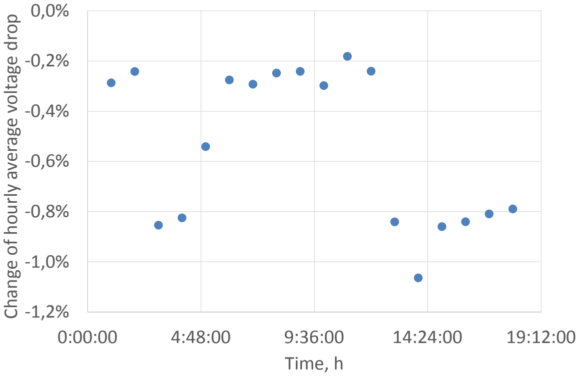

(b)

Figure 7: (a) Change in hourly average voltage drop during 320 ppm test; (b) change in hourly average voltage drop during 680 ppm test.

4 Conclusions

Molten Carbonate Fuel Cells (MCFCs) can be used as a CO_2 separator in fossil fuel power plants. Fossil fuel power plants emit flue gases with SO_2 contaminants, thus the effect of SO_2 on the operation of MCFC is investigated both experimentally and theoretically. With regard to MCFC performance the examined range of SO_2 contamination was 100...680 ppm. The experimental investigation revealed that there is a boundary limit, where SO_2 contamination could increase MCFC voltage. The investigation revealed that SO_2 contamination of ca. 100 ppm does not cause an immediate voltage drop. Qualitative and quantitative analyzes are presented, but the mechanism of the poisoning effect of SO_2 is not deeply understood to date. A few common behaviors can be observed for experiments done by various laboratories.

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