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Optimization of operating conditions of a mini fuel cell for the detection of low or high levels of CO in the reformate gas

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Abstract

A prototype of a miniaturized fuel cell has been studied in order to detect carbon monoxide in hydrogen-rich atmosphere for PEM-FC (Protonic Exchange Membrane fuel - cell) applications. It consists in a home-made Membrane –Electrode – Assembly (MEA) developed by the CEA. Experiments have been carried out on a laboratory testing bench with simulated reformed gases. For low CO concentrations (≤ 20 ppm), an amperometric mode is suitable but regeneration in air is necessary to obtain a good reversibility of the sensor response. On the contrary, for higher CO concentrations (250 to 4000 ppm), a good reversible response is observed without air regeneration by using a potentiometric or quasi-potentiometric mode. Therefore, this prototype of mini CO sensor seems to be convenient for monitoring reformed gases and ensures the correct operation of a PEM-FC.

Keywords:

CO sensor ; PEM ; fuel-cell ; hydrogen

I. Introduction

In the field of PEM-FC, the CO poisoning of platinum based anode which is used to dissociate H_2, is well known [1]. CO strongly adsorbs on the Pt catalyst surface, causing a decrease of the available catalytically active Pt surface area for H_2 electro-oxidation. Consequently, CO sensors are very important in order to monitor the reformed gas purity. Classical tin oxide based semiconductor sensors are not well adapted to work without oxygen because the detection principle is related to the reaction of reducing gas (like H_2 or CO) with the adsorbed oxygen species. Only a few articles are related to the detection of reducing gases in the absence of oxygen using semiconductor SnO_2 based sensors. A promising solution proposed for such application is to use mini-fuel cells (solid oxide fuel cell (SOFC) or PEM-FC) and to follow the degradation of the fuel cell performances due to the presence of CO [2,3].

In this work, a mini PEM-FC prototype developed by the CEA has been used to detect CO concentrations (0-4000 ppm) in a simulated reformate fuel mixture. Working modes have been optimized in order to detect low (< 20 ppm) or high (up to 4000 ppm) CO concentrations.

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II. Experimental

The mini fuel cell sensor prototype (Figure 1) is a self breathing PEM-FC that can be placed directly on line in the gaseous flow (anode side), while the second electrode (cathode) is exposed to ambient air. It consists in a home-made Membrane-Electrode-Assembly (MEA) composed of two 1.5 cm^2 gas diffusion electrode hot pressed on a Nafion® 212 membrane. The MEA is inserted between two chambers, one of them being connected to the H_2-rich gaseous flow, the other being supplied with a porous area directly exposed to the ambient air.
The sensor prototype has been tested on a laboratory gas bench. For the present study, the carrier gas is generally a simulated reformate fuel mixture composed of H_2 diluted in N_2 (5%), with CO_2 (1.9 %) and H_2O (1.8%) as additional components. The concentration of O_2 in the gas mixture, measured by various O_2 probes, is still less than 50 ppm. The signal from the mini PEM-FC is first stabilized in the carrier gas and injections of increasing concentration of CO are performed. Each injection is followed by an exposure to the carrier gas. The gas flow is maintained at 6 l h^{-1} throughout the test. Two operating modes are envisaged placing an electrical resistance loading (R) in the electrical circuit. Amperometric mode corresponds to the case where R is less than 10^3 ohm, whereas if R is located between 10^4 and 10^6 ohm, we then speak of quasi-potentiometric mode .The open circuit voltage is recorded at zero current when there is no loading resistance (case of the potentiometric mode).

III. Results

In the case of amperometric mode, the introduction of low CO content causes a large decrease in the voltage measured at the terminals of the mini-PEM. However, the signal is not reversible when CO is removed from the gas stream and a regeneration step under air is absolutely necessary to oxidize the adsorbed CO (see Figure 2, in the case of a load resistance of 10 ohm and a CO content of 50 ppm). The sensitivity of the device is very interesting since CO levels as low as 5 ppm can be easily detected for lower values of load resistance (R close to 1 to 10 ohm); moreover, for low values of R, a saturation of the response appears at 10-20 ppm CO. However, this sensitivity decreases when the load resistance increases (see Figure 3).
On the contrary, with high resistance load (quasi-potentiometric method) or without load resistance (potentiometric method), detection of high CO levels is possible. The results obtained for CO levels between 250 and 4000 ppm are shown in Figure 4 (quasi potentiometric mode with R = 10^6 ohm) and Figure 5 (potentiometric mode, without load resistor). We find that in both cases, the injection of high levels of CO in the simulated reformate is reflected by large responses of the mini PEM-FC. Furthermore the reversibility is virtually complete in a reasonable period of time and a step of regeneration in pure air does not seem absolutely necessary. Moreover, the value of the emf obtained under high levels of CO remains almost stable during long-term injection (see Figure 4).
Nevertheless, the amperometric mode could also be interesting to detect high CO level with a very short response time. Thus one finds that a CO content of 1000 ppm can be detected in less than one minute (30 s) for a value of load resistance of 10 ohm. (see Figure 6). In this figure, we also see that the recovery occurs in two steps: the first, fast and possibly accompanied by oscillations, is related to the oxidation of adsorbed CO by water vapour [4] in the absence of O_2 gas; the second, much slower, is probably due to desorption of remaining CO. The transition between these two stages is likely to depend on the value of oxidation potential of CO (0.6 V) and the corresponding value of the emf is close to 0.3- 0.4 V in most cases. If the value of the emf in the presence of CO is below 0.3 - 0.4 V, the phenomena related to the adsorption and oxidation of CO are very fast: amperometric mode can then be useful for detecting changes in the CO content around a mean value (typically 100 ppm) with response times of several seconds (Figure 7).

IV. Conclusion

In this study, the CO detection performances of a mini-PEM-FC developed by the CEA were evaluated on a test bench. The goal is to detect carbon monoxide in hydrogen-rich atmosphere for PEM-FC applications. Two operating modes were envisaged: an amperometric mode with a load resistance less than or equal to 10^3 ohm and a quasi-potentiometric where the load resistance is between 10^3 and 10^6 ohm. According to the selected mode, this type of sensor can detect low or high levels of CO with response time and sensitivity depending on the chosen application. In the case of a low temperature PEM-FC for which CO poisoning is critical, an amperometric mode seems preferable with a periodic regeneration in pure air. For high temperature PEM-FC, the CO poisoning is less severe and it seems that potentiometric or quasi-potentiometric are suitable modes for continuous operation.

References

[1] Uribe F.A., Valerio J.A., Garzon F.H., Zawodzinski T.A. PEMFC reconfigured anodes for enhancing CO tolerance with air bleed. Electrochem Solid-State Lett 2004; 7(10): A376-9.

[2] Hashimoto A., Hibino T., Sano M. Solid oxide fuel cells that enable the detection of CO in reformed gases. Sens. Act. B 2002; 86:12-19

[3] Kirby K.W., Chu A.C., Fuller K.C. Detection of low level carbon monoxide in hydrogen-rich gas streams. Sens. Act. B 2003; 95:224-31.

[4] Farrell C.G., Gardner C.L., Ternan M. Experimental and modelling studies of CO poisoning in PEM fuel cells. J.Power Sources 2007; 171:282-93.

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Figures

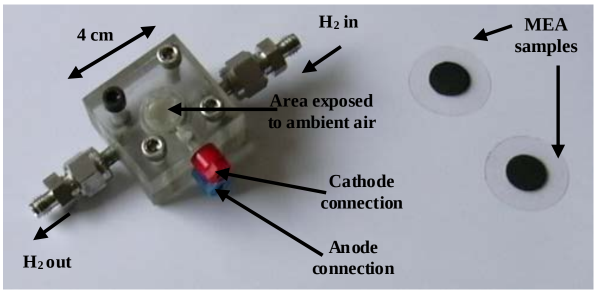

Figure 1: Prototype of mini fuel cell.

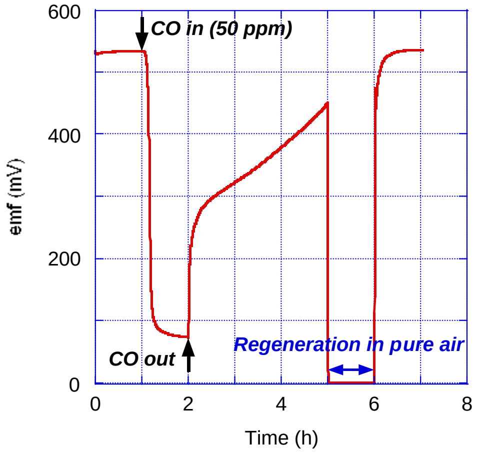

Figure 2: Response of the fuel-cell to 50 ppm CO with a step of regeneration in pure air. Carrier gas: $[H_2]$ =5%/N_2 with $[H_2O]$ (1.8%) and $[CO_2]$ (1.9%) Amperometric mode: R = 10 ohm

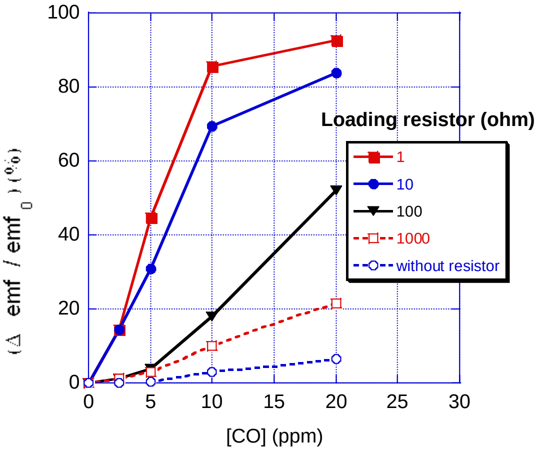

Figure 3: Relative response of the fuel cell as a function of CO content (0-20 ppm) for several values of load resistor

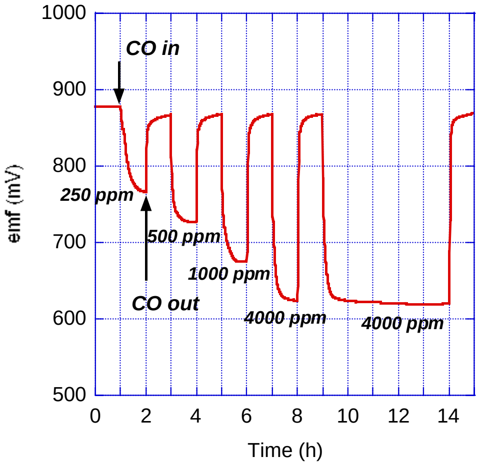

Figure 4: Response of the fuel-cell to injections of CO from 250 to 4000 ppm Carrier gas: [H_2] =5%/N_2 with [H_2O] (1.8%) and [CO_2] (1.9%) Quasi potentiometric mode; R=10^6 ohm

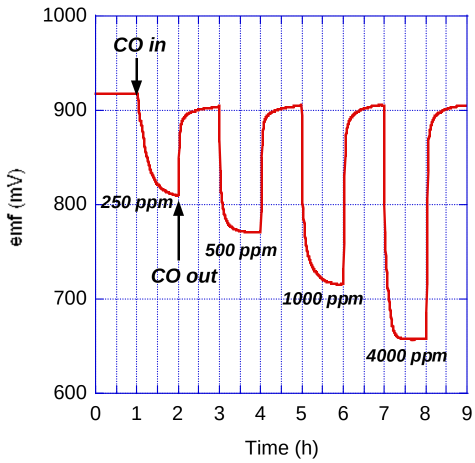

Figure 5: Response of the fuel-cell to injections of CO from 250 to 4000 ppm Carrier gas: [H_2] =5%/N_2 with [H_2O] (1.8%) and [CO_2] (1.9%) Potentiometric mode

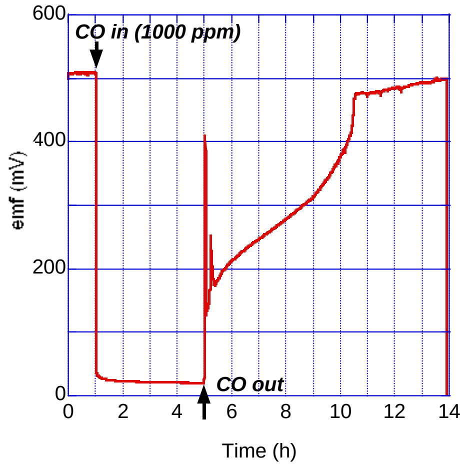

Figure 6: Transient response of the fuel-cell to 1000 ppm CO without regeneration in pure air Carrier gas: [H_2] =5%/N_2 with [H_2O] (1.8%) and [CO_2] (1.9%) Amperometric mode: R = 10 ohm

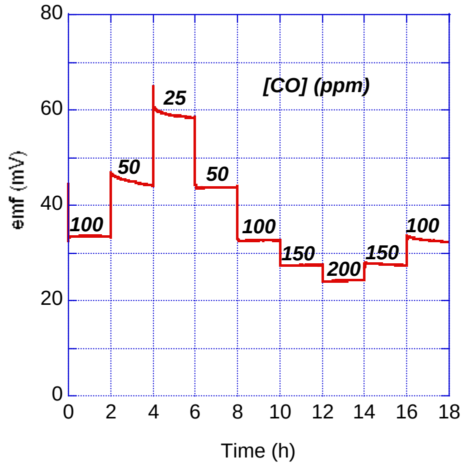

Figure 7: Evolution of the emf of the fuel-cell for changes in the CO content in the range 25-200 ppm Carrier gas: [H_2] =5%/N_2 with [H_2O] (1.8%), [CO_2] (1.9%) and [CO] (100 ppm) Amperometric mode: R = 10 ohm