Short communication

Assessment of the performance of a PEMFC in the presence of CO

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Abstract

Carbon monoxide is a conventional contaminant in the fuel obtained from reforming processes with an important influence on the performance of a proton exchange membrane fuel cell (PEMFC). The studies of transient and continuous injection of CO presented here give information about poisoning and recovery processes, and recommend strategies for fuel cell operation. Pulsing study shows that up to 100 ppm CO, has no significant effect on the performance. Constant current demand experiments show an oscillatory effect due to CO electro-oxidation at high over-potentials. In continuous poisoning process, kinetic and mass transfer affect the rate of CO removal. To recover the performance for continuous fuel cell operation, we propose cyclic feeding of hydrogen containing traces of CO (i.e. supplied by a reforming process) and pure hydrogen streams.
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1. Introduction

Hydrogen produced from hydrocarbon or alcohol reforming processes contains trace components (carbon monoxide, sulphur, ammonia, etc.) that may damage the electrode during a proton exchange membrane fuel cell (PEMFC) operation. One of them, carbon monoxide, when is adsorbed on the Pt anode, inhibits the dissociation of hydrogen to protons and electrons. The impact of CO on power output of a PEMFC that uses Pt as electrocatalyst increases with the concentration and this behaviour is more accentuated at the lower operating temperatures [1].

Overcoming the CO poisoning problem is of paramount interest and needs to be addressed in order to make reformate gas a viable fuel for PEM fuel cells. Even after a preferential oxidation (PrOx) reactor, the outlet CO concentration is about 50 ppm, although programmed targets for steady state and transient CO concentrations are 10 and 100 ppm, respectively [2]. Los Alamos National Laboratory (LANL) has developed both PrOx catalyst and reaction system and they can achieve low concentrations of CO (10–20 ppm) in a multistage reactor over a Pt/Al_2O_3 or Ru/Al_2O_3 catalyst [3]. In another study on low temperature PrOx reactors [4], up to 100 ppm CO in the effluent was obtained with the best catalyst studied.

Other methods to remove CO from the fuel cell are the mixing of the fuel feed with small amounts of air or oxygen ("air bleeding") between 1 and 5% content in the gas [5,6]. This stimulates the oxidation of CO over the catalyst. This method requires an extensive control system since the air content has to be closely monitored. The addition of hydrogen peroxide to the fuel stream has also been investigated as a method to minimise the CO contamination [7,8]. A method for operating PEM fuel cells using hydrogen from a reformate process, with reduced requirements for gas cleaning, is to apply electrical pulses while fuel cell is in operation. The pulses increase the anode potential to values at which the CO is oxidised to CO_2. In this way, the catalyst surface is continuously cleaned and the loss of cell voltage is minimised [9].

Springer et al. [10] tested PEMFC performance with CO concentrations between 10 and 100 ppm as impurity and de-

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veloped a model for operation on reformate feed at 80 °C. Due to higher CO poisoning effect at lower temperatures, it is important to know the performance at room temperature at which the start-up of the fuel cell system takes place. In a previous work [11], dynamic CO pulsing tests were carried out to evaluate the effect of CO during a PEMFC operation. In the present work we study the performance of a PEMFC under transient and steady state conditions. In the first case, we report the influence of pulses, at different concentrations of CO, in the decay and recovery rates. Long-time tests and simulation of performance using poisoning cycles were also carried out. For the second case, a study of the fuel cell performance under different CO concentrations has been carried out. The response to several cycles poisoning-recovering has been assessed and justified in order to obtain information for a continuous fuel cell operation using reformate gas.

2. Experimental

MEAs supplied by ETEK (active surface $3\,cm \times 3\,cm$, 20 wt% Pt on Vulcan XC-72, $0.5\,mg\,cm^{-2}$ Pt loading) were used to carry out the tests. The experimental system for fuel cell testing consists of a set of mass flow controllers (MFC) from Bronkhorst Hi-Tech, model F-201C-FAC-10-V, to feed the reactant gases in both anodic and cathodic sides. The mixtures of gases are passed through humidifiers to feed the necessary water for correct ionic conductivity in the membrane. In the anodic side, CO is fed by a MFC and then, by means of a capillary tube, it reaches a point of union with the anode tube. Gases continue along a heated pipe to the fuel cell. Finally the water from the exhausted gases is condensed before being removed. Control and data acquisition were developed in our lab. For the load demand, a dc electronic load (Höcherl & Hackl GMBH, model PL306) was used.

Different concentrations of CO (3–160 ppm) were tested using an initial gas mixture of 1000 ppm CO. The voltage of fuel cell was measured at a constant current density, room temperature and atmospheric pressure. Flow rates used in both cathodic and anodic sides were $50\,ml\,min^{-1}$ of oxygen and hydrogen, respectively.

Transient measurements were carried out by applying series of pulses with different concentrations of contaminants. Both the duration and the time between pulses were varied. Series of 10 pulses of 1, 2 and 5 min, with 5 min between pulses in all cases were carried out. The exposition time of the fuel cell to the contaminant was increased in order to obtain responses at long time. Initially, the concentrations of the contaminants were below the theoretical tolerance threshold and later over this value to know whether our results fit with other essays. Finally, long time tests were carried out for 18 h.
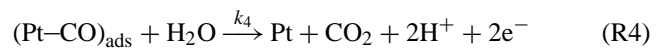
Continuous poisoning tests were realized for 6 h at different CO concentrations and the simulation of reformate fuel was made in a sequence modifying CO concentration.

3. Results and discussion

In previous tests (not presented) the influence of dilution on fuel cell performance was measured by feeding with an inert gas (nitrogen). A voltage decrease of 10 mV as maximum was observed, which supposed a negligible value compared with the poisoning effect. Several series of pulses varying both duration and waiting time were carried out. Fig. 1 shows the experiments at different CO concentration with 5 min duration and waiting time. No influence in the performance is observed up to 105 ppm CO is injected.

In order to verify that the poisoning process is cumulative and reversible, longer time and higher concentration transient tests were carried out (Fig. 2). Pulses of 5 min length with more than 100 ppm CO were injected with 10 min of waiting time during 18 h. When 105 ppm CO is used (Fig. 2a) a slight decrease of voltage happens after every cycle of CO adsorption–desorption. The initial voltage can be recovered after 30 min passing hydrogen. It suggests that the kinetic of adsorption is faster than desorption and that the process is completely reversible. For 130 and 160 ppm CO the effect is considerably stronger (Fig. 2b and c). However, the most interesting phenomenon observed is that after voltage drops significantly a fast removal of CO happens and the subsequent pulses affect the performance in a less way. This behaviour can be attributed to the electrochemistry processes of CO and hydrogen on the surface of platinum. In the absence of CO, hydrogen reacts onto active platinum sites. Nevertheless, when CO is present in the anodic side, it could occur through a replacement reaction or a free site attack [12].

There is still considerable controversy concerning the CO oxidation mechanism in fuel cells. It is commonly accepted, however, that the electrochemical CO oxidation in acidic solutions involves a surface reaction between adsorbed CO molecules and an oxygen-containing species, the exact nature of which is yet unclear [13]. A generally accepted mechanism for the H_2/CO oxidation [10,14] is

$$H_2 + 2Pt \xrightarrow{k_1} 2(Pt{-}H)_{ads} \tag{R1}$$

$$(Pt{-}H)_{ads} \xrightarrow{k_2} Pt + H^+ + e^- \tag{R2}$$

$$CO + Pt \underset{k_{-3}}{\overset{k_3,k_{-3}}{\rightleftarrows}} (Pt{-}CO)_{ads} \tag{R3}$$

$$(Pt{-}CO)_{ads} + H_2O \xrightarrow{k_4} Pt + CO_2 + 2H^+ + 2e^- \tag{R4}$$

where k_i, $i = 1, 2, 3, 4$ denotes the forward rate constants, and k_{-3} is the reversed rate constant. The corresponding reaction rate can be written as

$$v_1 = k_1 P_{H_2}(1 - \theta_H - \theta_{CO})^2 \tag{1}$$

$$v_2 = k_2 \theta_H\, e^{E/b_1} \tag{2}$$

$$v_3 = k_3 P_{CO}(1 - \theta_H - \theta_{CO}) - k_{-3}\theta_{CO} \tag{3}$$
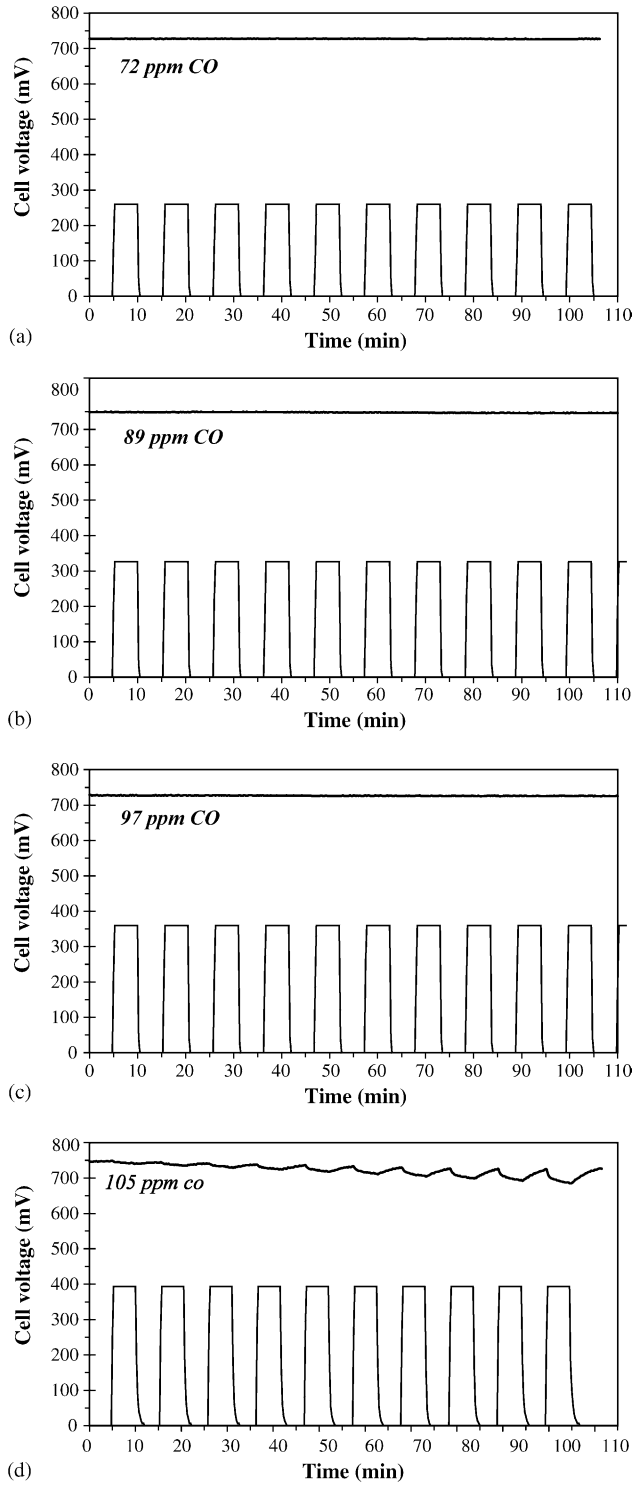
$$v_4 = k_4 \theta_{CO}\, e^{E/b_2} \tag{4}$$

Fig. 1. Influence of CO concentration in PEMFC performance for pulses with 5 min length: (a) 72.4 ppm; (b) 89 ppm; (c) 97 ppm and (d) 105 ppm.
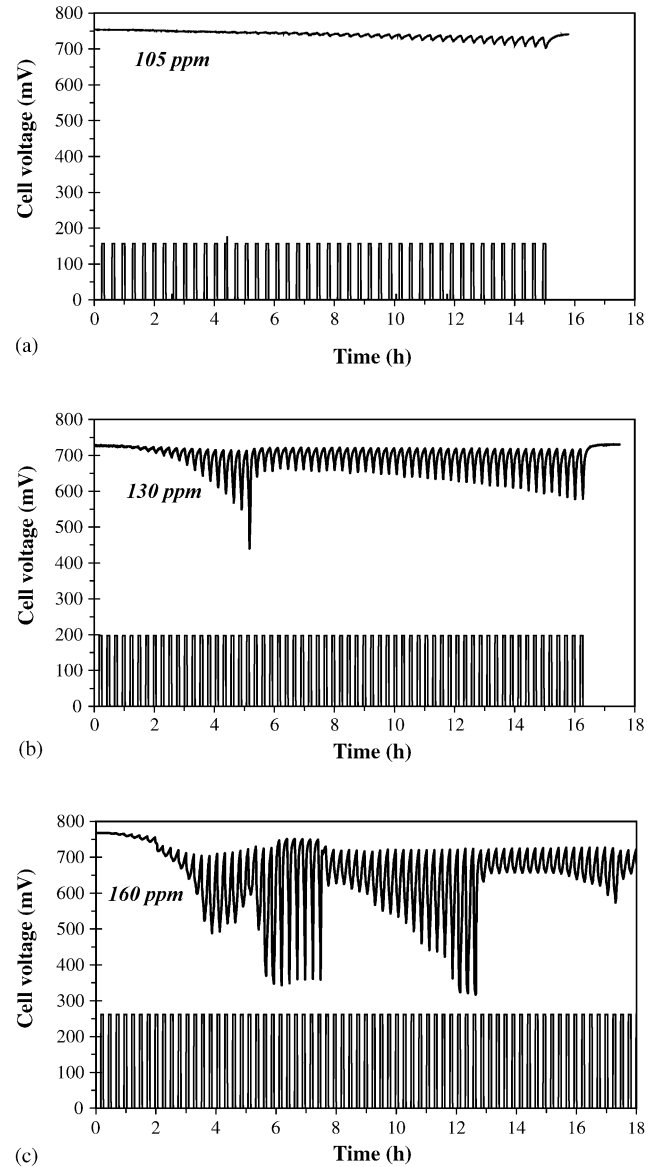

Fig. 2. Influence of CO concentration at long time exposition in PEMFC performance for pulses with 5 min length: (a) 105 ppm; (b) 130 ppm and (c) 160 ppm.

where P_{H_2} and P_{CO} are partial pressures of H_2 and CO; b_1 and b_2 are the Tafel slopes for R2 and R4; θ_H and θ_{CO} denote the surface coverage of Pt–H and Pt–CO, respectively.

The CO electro-oxidation rate (Eq. (4)) increases with the anode overpotential exponentially, as expected by the Butler–Volmer equation. To sustain a given current density, the anode potential is polarized to higher values, which also promotes the electro-oxidation of CO.

Continuous CO poisoning tests were also done (Fig. 3) to assess the effect in the fuel cell performance as an approach to a real case using reformate gas. In Fig. 3a we notice that a slight decrease in performance (<3% voltage) at CO levels up to 50 ppm occurs after 360 min of exposure. However, this behaviour changes significantly at 70 ppm CO levels where voltage drops to nearly 85% from the initial value. At 100 ppm CO voltage decreases to 82% although this process is not gradual, but shows variable rate. This behaviour may be attributed to cyclic adsorption–desorption processes that has been commented for the pulse experiments. After
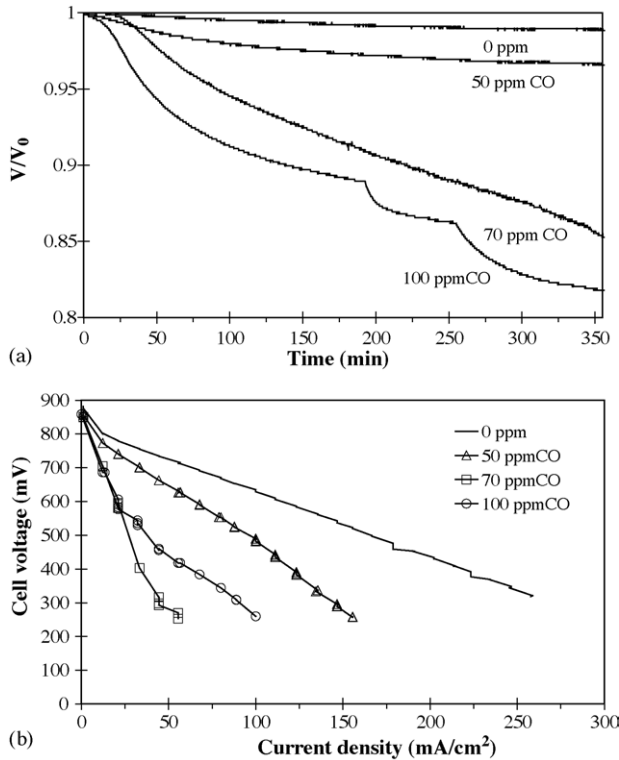
(a)

(b)

Fig. 3. (a) Normalized cell voltages for 6 h CO poisoning at different concentrations, (b) polarization curves after CO poisoning for the same concentrations.

every poisoning test, polarization curves were measured and, curiously, better performance was obtained for 100 ppm CO exposition than 70 ppm, for the same exposure time. This fact corroborates again that CO electro-oxidation is favoured operating at high enough current density. It might be due to an increase in the anode overpotential and/or water in the anode. The effect of CO can be controlled by humidifying the anode gases.

Again, to verify the complete CO cleaning, polarization curves were measurement before and after poisoning with a stream containing 100 ppm CO and after the poison removal (Fig. 4). After 15 min feeding clean hydrogen, the fuel cell
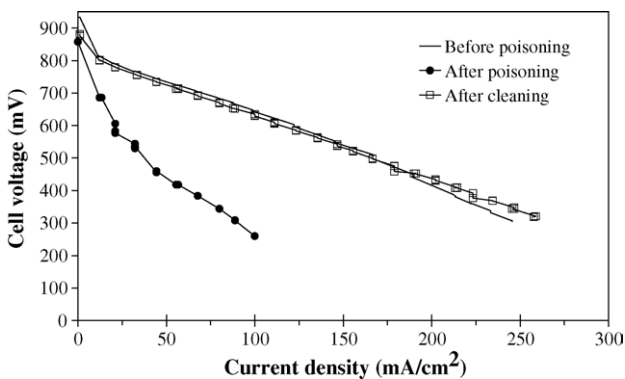

Fig. 4. Polarization curves before and after poisoning with 100 ppm CO during 6 h and after 15 min feeding clean hydrogen.
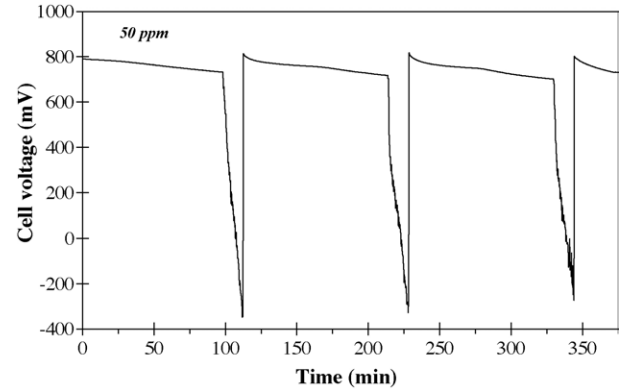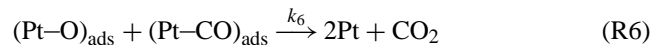

Fig. 5. Variation of cell voltage with time by employing current pulsing method for a 50 ppm CO concentration stream.

performance returns to the initial values, which is indicative of a completely reversible process.

The effect of current pulsing during poisoning with CO has been studied in previous works [15]. In order to verify it, a continuous exposure at 50 ppm was maintained during 6 h at constant current demand. When a significant voltage drop took place an increase of current demand was realized (Fig. 5). Once the current demand was turned to the initial value, the performance recovered completely. It was indicative that part of CO had been electrochemically oxidized due to the higher anodic overpotential during this time. Then, CO poisoning caused the drop of cell voltage again.

Another possibility to recover the performance after CO poisoning is to feed pure hydrogen when the cell voltage drops. Oxygen permeating through the membrane from the cathode contributes also to the CO clean up in the anode chamber. This nonelectrochemical reaction between CO and permeating oxygen is linearly dependent on the cathode O_2 partial pressure [16]. Evidently, oxygen permeated can react with hydrogen adsorbed to form water. The probably redox mechanism is the following:

$$O_2 + 2Pt \overset{k_5, k_{-5}}{\longleftrightarrow} 2(Pt{-}O)_{ads} \tag{R5}$$

$$(Pt{-}O)_{ads} + (Pt{-}CO)_{ads} \overset{k_6}{\longrightarrow} 2Pt + CO_2 \tag{R6}$$

Trying to avoid CO blocks too many platinum sites, the regeneration can be attempted with only the oxygen that permeate through the membrane. The conventional air bleeding method involves complicated control systems in order to maintain safe fuel cell operation. In order to compare with pulsing method, a dynamic test was carried out feeding cyclically hydrogen containing CO traces (72 ppm) and pure hydrogen streams (Fig. 6). This sequence shows that the performance also recovers the initial value rapidly and shows that the only oxygen that diffuses through the membrane is able to remove the CO. So, a cyclic feeding of hydrogen contains CO traces and pure hydrogen streams can be proposed to maintain the desired cell voltage range during the operation. It presents the advantage of preserving the useful life of
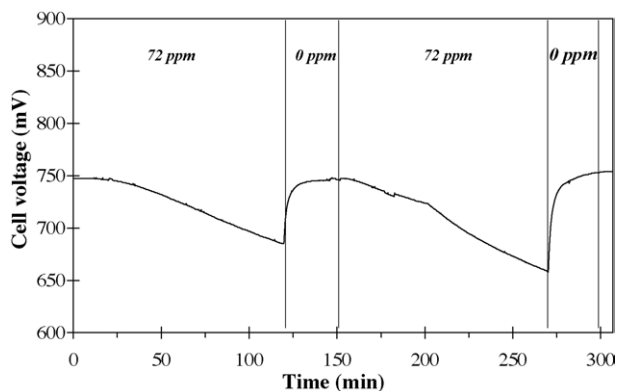
Fig. 6. Cyclic feeding of 72 ppm CO hydrogen stream and pure hydrogen.

the membrane, which could lose endurance due to potential changes.

4. Conclusions

The major conclusion withdrawn from this work is that reformate gas can be used as fuel for operation in a PEMFC but an exhaustive control of CO must be taken into account. Variations in CO concentration may suppose a significant decrease in the fuel cell performance. The poisoning process is reversible with only the injection of clean hydrogen. So, a suitable control of kinetic and mass transfer process can let operate a fuel cell system using reformate gas. The current demand in fuel cell causes an increase in anode overpotential and, as a consequence, favours the CO electro-oxidation reaction that recovers the initial performance. However, if a more constant voltage is desired, cyclic pure hydrogen injection can be proposed for continuous operation.

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