On-board removal of CO and other impurities in hydrogen for PEM fuel cell applications

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Abstract

Carbon monoxide (CO) in the hydrogen (H_2) stream can cause severe performance degradation for an H_2 polymer electrolyte membrane (PEM) fuel cell. The on-board removal of CO from an H_2 stream requires a process temperature less than $80\,^\circ C$, and a fast reaction rate in order to minimize the reactor volume. At the present time, few technologies have been developed that meet these two requirements. This paper describes a concept of electrochemical water gas shift (EWGS) process to remove low concentration CO under ambient conditions for on-board applications. No on-board oxygen or air supply is needed for CO oxidation. Experimental work has been carried out to prove the concept of EWGS and the results indicate that the process can completely remove low level CO and improve the performance of a PEM fuel cell to the level of a pure H_2 stream. Because the EWGS electrolyzer can be modified from a humidifier for a PEM fuel cell system, no additional device is needed for the CO removal. More experimental data are needed to determine the rate of CO electrochemical removal and to explore the mechanism of the proposed process.
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Keywords: Carbon monoxide (CO); Removal; Electrolysis; Hydrogen; PEM fuel cell

1. Introduction

Low-level carbon monoxide (CO) (ppm level) is one of the most common impurities in hydrogen (H_2) fuel streams that can cause significant performance degradation of H_2 polymer electrolyte membrane (PEM) fuel cells. The on-board removal of CO from an H_2 stream is a challenge due to the fact that it requires a low process temperature and a fast removal rate. An H_2-powered vehicle requires a fast H_2 volumetric flow rate and the conventional technologies have limitations for the on-board removal of CO for vehicle applications. Considering a 100 horsepower (75 kW) automobile powered by H_2, under the assumption that an H_2 fuel cell is operated at 0.75 V with a 50% overall efficiency, the electrical current required from the fuel cell can be calculated as 200 kA. Based on Faraday's Law, theoretical (or minimum) H_2 flow rate required for a PEM fuel cell to generate 1 A current can be calculated from either anode or cathode reaction as follows:

Based on an anode reaction: $H_2 = 2H^+ + 2e^-$, 1 mol of H_2 makes two equivalents ($n = $ eq. mol^{-1}). Therefore, a 1 A (1 A = $1\,C\,s^{-1}$) current is produced by an H_2 flow (at standard conditions): $1\,C\,s^{-1} \times 60\,s\,min^{-1} \times 22{,}414\,mL\,mol^{-1}/(96{,}458/eq. \times 2\,eq.\,mol^{-1}) = 6.97\,mL\,min^{-1}$. A 200 kA current requires an H_2 flow of: $200 \times 1000 \times 6.97\,mL\,min^{-1}/(1000\,mL\,L^{-1}) = 1394\,L\,min^{-1}$.

If the calculation is based on a cathode reaction: $4H^+ + O_2 + 4e^- = 2H_2O$, $n = 4\,eq.\,mol^{-1}$, then a 1 A current requires: $1\,C\,s^{-1} \times 60\,s\,min^{-1} \times 22{,}414\,mL\,mol^{-1}/(96{,}458/eq. \times 4\,eq.\,mol^{-1}) = 6.97/2\,mL\,min^{-1}$. So 200 kA current requires: $6.97/2 \times 200/2 = 1394/2\,L\,min^{-1}$.

It should be pointed out that the above flow rate ($1394/2\,L\,min^{-1}$) represents minimum O_2 flow that is equal to two times of H_2 based on the reaction: $2H_2 + O_2 = 2H_2O$. So the theoretical H_2 flow rate should be: $2 \times O_2$ flow rate $= 2 \times (1394/2) = 1394\,L\,min^{-1}$.
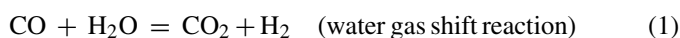
Assuming CO removal residence time is 10 s; the reactor volume can be calculated as 232.3 L. If the residence time could be reduced to 0.1 s, the reactor volume could be reduced to 2.3 L. Because of cost, selectivity and elevated temperature and pres-

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sure, most currently available technologies are precluded from applicability for on-board CO removal.

Present technologies possibly applicable for on-board CO removal can be separated into off-fuel cell and on-fuel cell approaches. The former removes CO from the H_2 fuel in advance of the fuel cell apparatus, while the latter process occurs at the anode of a PEM fuel cell. In off-fuel cell CO removal, the goal is to maximize the adsorption of CO onto the catalyst surface in order to separate it from H_2. However, in on-fuel cell CO removal, the objective is to minimize the CO adsorption on the fuel cell anode catalyst so that H_2 adsorption and oxidation can be enhanced. In order to have a better understanding of the challenges and the principles for the removal of low concentration CO in an H_2 stream, some analyses and discussions are needed.

Off-fuel cell CO removal methods include water gas shift (WGS) reaction, catalytic methanation, and catalytic preferential CO oxidation as follows:

$$CO + H_2O = CO_2 + H_2 \quad \text{(water gas shift reaction)} \tag{1}$$

$$CO + 3H_2 = CH_4 + H_2O \quad \text{(CO methanation)} \tag{2}$$

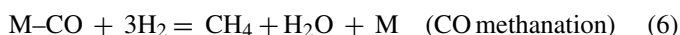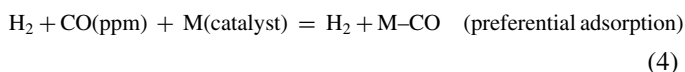$$CO + O_2 = CO_2 \quad \text{(preferential oxidation)} \tag{3}$$

It should be noted that Pd-based membrane purification method is expensive and requires both high operating temperature and a high-pressure differential. Therefore, it is not suitable for on board applications. Thermocatalytic WGS processes, including high temperature and low temperature WGS reactions, are suitable for treatment of different CO concentrations. The low temperature WGS is normally operated at temperatures as high as $200\,^{\circ}C$ to ensure a reasonable reaction rate, and therefore cannot be used for on-board applications based on the temperature requirement. Catalytic CO methanation is the hydrogenation of CO on supported metal catalysts in H_2 fuel. The advantages of the methanation process are that it avoids the introduction of O_2 or air to the fuel cell system, and the generated methane (CH_4) gas does not deactivate the anode catalyst. However, its disadvantages are the consumption of H_2 and the requirement of high temperature. The CO preferential oxidation process uses less than 2% of air by volume mixed with an H_2 fuel stream and fed into a metal-based catalyst. This catalyst preferentially adsorbs CO and adsorbed CO then reacts with O_2 to form CO_2. The typical metal catalysts for the oxidation of CO are alumina-supported Pt-group metal catalysts and metal oxide-supported gold (Au) catalysts. In this oxidation process, part H_2 is oxidized to produce water resulting in a fuel loss. A great effort has been devoted to reduce the oxidation temperature to lower than $80\,^{\circ}C$ in order for the process to be applicable in an H_2 PEM fuel cell system. Some important advances of catalytic preferential CO oxidation are summarized below.

Fenton and co-workers reported a 100% CO conversion with an Ir/CoO$_x$–Al$_2$O$_3$/carbon catalyst at an O_2/CO ratio of 1.5 in a humidified H_2 environment and a temperature near $75\,^{\circ}C$ [1]. They also showed that Co–Ru/C catalysts are very effective for CO methanation. Muradov et al. investigated the catalytic activity of a wide range of carbon-based materials and examined their structural and surface properties [2]. Chen et al. reported a 100% conversion of CO oxidation using 7% CuO/CeO$_2$ catalysts in an H_2 rich environment (H_2/CO/O_2/He = 50/1/1/48) at 87–$147\,^{\circ}C$ [3]. Furthermore, the partial substitution of the Ce lattice with Zr^{+4} (7% CuO/Ce$_{0.9}$Zr$_{0.1}$O$_2$) resulted in 100% CO conversion at about $77\,^{\circ}C$. Zhou et al. showed that CO conversion in excess H_2 can reach up to 99.5% at a temperature range between 130 and $150\,^{\circ}C$ in the presence of activated carbon supported Co–Ni metal catalyst [4]. Goerke et al. reported a 95% selective oxidation of CO in micro-channeled reactors using Ru/ZrO$_2$ catalysts at $150\,^{\circ}C$ and average residence time of 14 ms [5].

However, it is difficult for any of these three methods to completely remove CO because, fundamentally, the ppm level of CO is thermodynamically stable in an H_2 stream at ambient conditions. To remove low concentration CO from an H_2 fuel stream requires a two-step process in order to overcome these thermodynamic obstacles. The first step is the preferential adsorption of CO on metal-based catalysts to increase the CO concentration locally because CO has a higher catalytic adsorption capability than H_2. The second step is the thermochemical conversion of CO to CO_2 (reaction (3)) or CH_4 (reaction (2)). The two-step process can be described in reactions (4) and (5) or reactions (4) and (6).

$$H_2 + CO(ppm) + M(catalyst) = H_2 + M\text{–}CO \quad \text{(preferential adsorption)} \tag{4}$$

$$M\text{–}CO + O_2 = CO_2 + M \quad \text{(CO selective oxidation)} \tag{5}$$

$$M\text{–}CO + 3H_2 = CH_4 + H_2O + M \quad \text{(CO methanation)} \tag{6}$$

Note that reaction (4) is favored at low temperatures to increase the adsorption rates, whereas, CO oxidation and methanation require a higher temperature to enhance reaction kinetics. Therefore, there exists a contradictory condition favoring both CO adsorption and the CO reaction kinetics. On the other hand, it is essential to recognize that for the on-board removal of CO the reaction temperatures cannot exceed the fuel cell optimal operating temperature of $80\,^{\circ}C$. If the reaction temperature is at $80\,^{\circ}C$ or below, the low reaction rates for reactions (5) or (6) would require large reactor volume or complicated reactor configurations to compensate the slow reaction rate.

Low-level CO in an H_2 stream can also be removed on fuel cell anodes. The advantage of on-fuel cell CO treatment is that no additional processing is required. Three fundamental technologies have been reported for on-fuel cell applications: high temperature process, air or O_2 bleeding, and anode catalyst alloying.

In the high temperature process Fenton and co-workers showed that CO adsorption on fuel cell anode catalysts was reduced at temperatures higher than $100\,^{\circ}C$, thereby alleviating the CO poisoning effects [6]. This is due to the fact that CO adsorption on a Pt catalyst exhibits high negative standard entropy. It should be noted that increasing the PEM fuel cell operating temperature might have some adverse impacts on fuel cell performance. Firstly, higher operating temperature greatly increases the resistance of the Nafion® membrane, resulting in

a reduction of fuel cell performance. In order to maintain the membrane's low resistance a 100% relative humidity is preferred. When temperature is above 100 °C, maintaining high humidity for a PEM fuel cell requires a system pressure greater than 1 atm, which again reduces the efficiency of the fuel cell. Secondly, operating a PEM fuel cell at temperature greater than 100 °C will enhance the aggregation rate of Pt particles as well as the Pt dissolution in the fuel cell electrocatalyst layer, both of which decrease the performance of the cell. Finally, above 100 °C PEM fuel cells suffer a higher rate of membrane degradation, shortening membrane long-term stability.

In the approach of air or O_2 bleeding, air or O_2 is introduced into the H_2 stream fed to the anode of a PEM fuel cell to oxidize CO adsorbed on the anode catalyst. This technology has been extensively reported and the results have shown some alleviation of the deleterious effect of CO in the H_2 stream. However, since the H_2 lower and upper flammable limits (in air) are 4% and 75% by volume, a malfunction of the O_2 inlet flow could result in very undesirable consequences. Also, as indicated in literature, air-bleeding technology is only effective at CO concentration less than 50 ppm and at low H_2 flow rates. As discussed previously, a hydrogen-powered vehicle requires a very high H_2 flow rate (minimum 1394 L min^{-1} for a 75 kW vehicle). Therefore, air-bleeding technology is unlikely to be suitable for on-board CO removal in a PEM fuel cell system.

For the anode catalyst alloying approach, considerable efforts have been made to develop CO tolerant electrocatalysts. It has been found that adding Ru, Rh or Ir to the Pt anode catalyst reduces CO adsorption, but it cannot fundamentally eliminate CO poisoning. Other alloys such as Pt–Sn and Pt–Mo have been investigated. Still, the Pt–Ru alloys are the most promising candidates and have attracted the most attention. However, at an 80 °C fuel cell operating temperature the Pt alloy method is unable to completely resolve the CO poisoning issue. Thus, there is need for developing a novel technology.

The objective of this paper is to address a concept for the removal of CO in H_2 streams with the focus on the effect of CO removal on fuel cell performance. More specifically, we proposed a concept of electrochemical water gas shift (EWGS) process for the on-board removal of CO in the PEM fuel cell anode H_2 stream. Along with the CO removal, the reduction of other impurities in the H_2 stream is also investigated experimentally. These impurities include sulfur components (*i.e.* hydrogen sulfide (H_2S), carbonyl monosulfide (CS)), carbon dioxide (CO_2), and nitrogen oxide (NO).

2. Technical concept

Most commercial H_2 is produced from natural gas *via* steam methane reformation (SMR) followed by a water gas shift (WGS) reaction in which CO is oxidized to CO_2 while water is reduced to H_2. The gas effluent from the WGS varies from a few ppm to 2% by volume of CO in excess of H_2. This low concentration of CO in the H_2 outlet stream from the WGS cannot be avoided. However, eliminating the CO is beneficial in increasing PEM fuel cell performance. As discussed previously, in order to remove CO, a two-step process is needed.

Firstly, locally increase CO concentration on the surface of a catalyst to separate it from H_2, and secondly oxidize CO to CO_2 or through a methanation process to convert CO to CH_4. One feature of these processes is that CO adsorption and oxidation (or methanation) processes occur at the same time in one reactor. Differing from CO oxidation or methanation, a WGS process not only removes the CO, but also uses the CO as a reducing reagent to reduce water for the production of additional H_2. In the EWGAS, electrical energy is used to replace thermal heat for remove CO from H_2 while reduce water to produce H_2. The process is possibly applicable for on-board removal of CO because it can be operated at ambient temperatures and atmospheric pressures. The process can also potentially be used as an off-board application to replace the currently used low temperature water gas shift reaction. The EWGS can be performed using an electrolyzer modified from a PEM fuel cell humidifier, so that no additional devices would be needed in an H_2 fuel cell system. It is expected that EWGS process can also remove other H_2 contaminants, such as H_2S, CS, NO$_x$, NH$_3$, etc.

Fig. 1 depicts the flow diagram of the as proposed technology. On the left, H_2 stream containing ppm level of CO is introduced
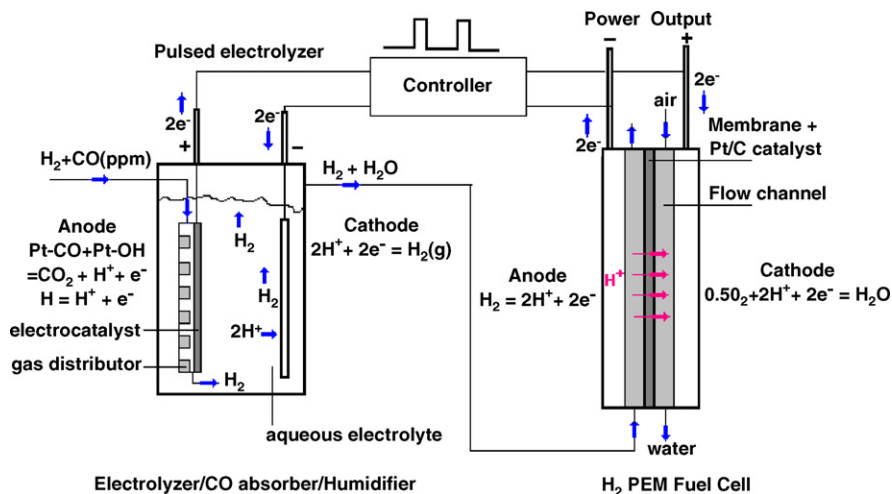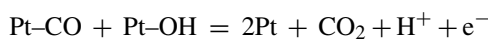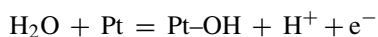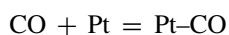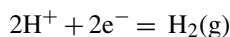

Fig. 1. Flow diagram depicting the proposed process for removal of low level CO and other impurities from the PEMFC anode H_2 feed stream.

to the anode of the electrolyzer where the majority of CO is adsorbed onto the surface of the electrocatalyst. The remaining CO is absorbed by the aqueous electrolyte. After adsorption, pure H_2 is sent to the PEM fuel cell. A small portion of electricity generated from the fuel cell is used to electrolyze water into hydroxide group (OH^-) and proton (H^+). CO adsorbed on the surface of the electrocatalyst is oxidized by OH^- into CO_2 and proton (H^+). The two H^+ are reduced at the cathode of the electrolyzer to produce H_2, which is then combined with the purified H_2 stream and fed to the fuel cell. For convenience, we use Pt as an electrocatalyst. Some other metal catalysts, such as nickel and copper, can also be applicable for the adsorption of CO. Non-Pt catalysts will reduce the cost of CO removal. The reactions at the electrolyzer can be describes as follows:
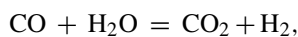
Anode reaction :

$CO + Pt = Pt–CO$

$H_2O + Pt = Pt–OH + H^+ + e^-$

$Pt–CO + Pt–OH = 2Pt + CO_2 + H^+ + e^-$

Cathode reaction :

$2H^+ + 2e^- = H_2(g)$

Overall reaction :

$CO + H_2O = CO_2 + H_2,$

$\Delta E = 0.4–0.6\,V$

As shown in Fig. 1, CO is adsorbed and stored on the catalyst surface or absorbed by the aqueous electrolyte until the adsorber is saturated, with CO reaching its breakthrough condition. This step is carried out at ambient temperature without the addition of heat or electricity or O_2 input to the adsorber. If the CO concentration is at a very low level and the CO storage capacity of the catalyst in the adsorber is sufficient, the breakthrough time for the absorber can be prolonged for several hours. After the electrocatalyst is saturated with CO, electricity is applied to the electrolyzer to split water into OH^- and H^+. The OH^- group reacts with the adsorbed CO on the catalyst surface of the electrolyzer and converts it to CO_2, while H_2 produced in the cathode combines with the main H_2 stream and is fed to the fuel cell. Because CO adsorption and removal processes are separated, the H_2 loss during the CO oxidation will be minimized.

As long as CO breakthrough time is greater than CO removal time, the as proposed EWGS can be operated in two parallel reactor systems. One reactor serves as a CO adsorber and the alternate one as an CO remover (electrolyzer). Two reactors can be shifted according to the CO breakthrough time. During the electrolytic process no H_2 passes through the electrolyzer so there would not be an H_2 oxidation issue. Differing from other conventional process, the alternative operation for CO removal from the adsorber could avoid the H_2 fuel loss issue that needs to be dealt with for conventional processes. The advantages of this alternative operation are: first, CO breakthrough time of an adsorber depends upon CO concentration, absorbent, and absorber volume. Since CO concentration in an H_2 stream is at a very low level (ppm); a CO adsorber therefore can have a reasonable CO breakthrough time in an on-board condition. Second, CO adsorption is favored at low temperature conditions. An ambient temperature will promote CO adsorption. No energy is needed for the CO adsorption process, so the total energy needed to remove CO is for the brief oxidation process. Comparing to conventional processes that operate continuously the EWGS process may reduce the energy required to maintain the reactor temperature. Third, when an adsorber is saturated with CO its concentration reaches the highest level. Therefore the CO is thermochemically more reactive, easier to remove, and at a higher kinetic rate.

Detailed experimental studies to verify as proposed concept of the EWGS and the effect of the performance of a fuel cell on the removal of CO are given in the following sections.

3. Experimental

Three case studies were carried out to prove the concept and investigate the scientific merits of the as proposed EWGS. The impact of CO removal on the performance of a PEM fuel cell is also included in this study. Two fuel cell hardware (Fuel Cell Technologies, NM) were used. One fuel cell was used to simulate an electrolyzer to purify the H_2 feed stream, and another one was used to investigate the fuel cell performance. The operating conditions of the electrolyzer in all experiments were at 25 °C, 1 atm, and 100% relative humidity. The electrolyzer consists of a 25 cm^2 membrane electrode assembly (MEA) with 0.4 mg cm^{-2} Pt loading on carbon. The volume of the flow channels of both the anode and the cathode is 0.875 mL. Two gas tanks containing 500 ppm CO in high purity N_2 gas and 100 ppm CO in H_2 were purchased from Linde Gas LLC. Those gases were served as CO sources for the investigation of the effect of CO removal in the EWGS processes. Potentiosatatic measurement and linear sweep voltammetry were carried out using a potentiostat (Model 263A, Princeton Applied Research). The measurement of low level of impurity gases in an N_2 stream was carried out using a GC/MS (JEOL GC mate-II GC/MS-MS) to the gas samples before and after the electrolyzer.

4. Results and discussion

4.1. Case study I: proof-of-concept of EWGS

In order to demonstrate that adsorbed CO in the anode of the electrolyzer can be electrochemically oxidized to CO_2 and water can be reduced to H_2, the small amount of H_2 produced at the cathode of the electrolyzer needs to be detected. In the first step of the experiment, as shown in Fig. 2A, a 500 mL min^{-1} N_2 stream containing 500 ppm CO was introduced to the anode of the electrolyzer modified from a PEM fuel cell. A potentiostatic measurement was carried out by applying potential of 0.6 or 0.8 V between the two electrodes for 30 min. Protons (H^+) produced at the anode migrated through the MEA and were reduced to H_2 in the cathode. Because both inlet and outlet ends of the cathode channel were sealed, any H_2 produced is stored in
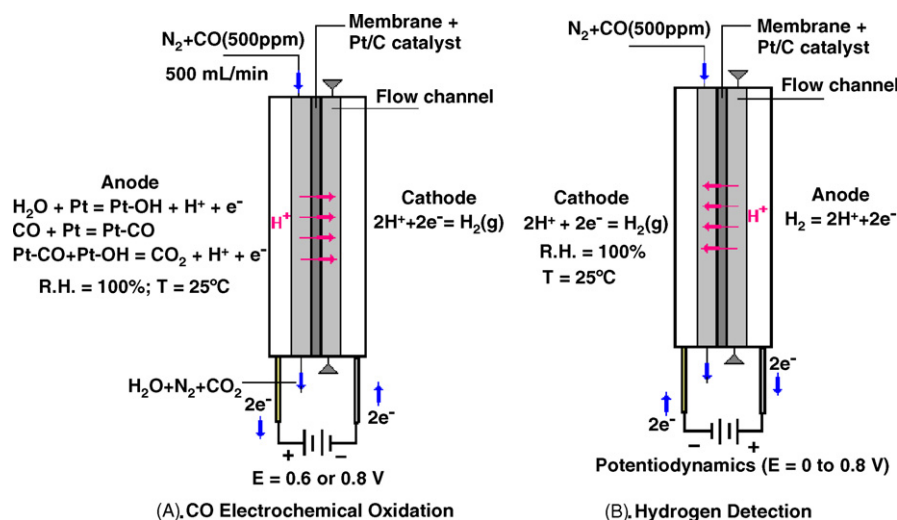
Fig. 2. Proof-of-concept of electrochemical gas water shift (EWGS) reaction.

the cathode compartment. In the second step of the experiment (Fig. 2B), a linear sweep voltammetry (from 0 to 1.0 V) was performed to detect H_2 stored in the cathode of the electrolyzer.

Fig. 3 shows the results of the potentiostatic measurement of $N_2 + CO$ stream. The CO conversion, which correlates to the H_2 yield, can be calculated using Faraday's Law as 52.28%. The power input to the electrolyzer is estimated at $(0.8\,V) \times (0.00075\,A\,cm^{-2}) \times (25\,cm^2) = 0.015\,W$, indicating that the electrical energy required for the EWGS reaction is a small value. The potentiodynamic curves in Fig. 4 show a typical H_2 peak at 0.2 V for both 0.6 and 0.8 V electrolytic processes, confirming the production of H_2.

It should be noted that the detection of H_2 shown in Figs. 3 and 4 may not necessarily mean that H_2 produced results from the EWGS processes. To ascribe H_2 production to the EWGS process requires a proof from a blank test, when a potential is applied between the anode and cathode of the electrolyzer as shown in Fig. 2B, the steady state current density under the potential of 0.8 V for N_2 and water system is about $0.001\,A\,cm^{-2}$. Compared to this blank test, the current densities for $N_2 + CO +$ water system increases to $0.00175\,A\,cm^{-2}$ for potential 0.8 V and $0.0015\,A\,cm^{-2}$ for 0.6 V potential, respectively. The increased current density must indicate the generation of H_2 from an EWGS process because a Nafion membrane used

in this electrolyzer is only conductive to H^+ but not conductive to electrons. Therefore the current increase must result from the migration of protons (H^+) through the Nafion membrane from the anode to cathode of the electrolyzer. Fig. 4 proves that H_2 is detected at the cathode of the electrolyzer. As discussed in the following section, H_2 generated must result from as proposed EWGS process not other mechanisms.

In the case of the $N_2 + CO$ system under a 100% humidity, no initial H_2 was inlet to the electrolyzer. Any H_2 detected must have come from electrochemical processes when a potential was applied to the electrolyzer. There are basically three possible mechanisms that can generate H_2: (1) water electrolysis ($H_2O + \Delta E = H_2 + 0.5O_2$), (2) water carbon reformation ($H_2O + C + \Delta E = CO + H_2$). Carbon here refers to the support of Pt/C catalyst, and (3) water gas shift reaction ($H_2O + CO + \Delta E = CO_2 + H_2$). The blank test for pure N_2 system (Figs. 3 and 4, curve 0.8 V N_2) showed that there was no H_2 detected at the cathode of the electrolyzer, implying that under 0.8 V potential water will be reduced to generate H_2 because water electrolysis requires a potential greater than 1.23 V. The blank test result also proves that water carbon reforming is not possible as no H_2 peak is detected (Fig. 4, curve 0.8 V N_2).
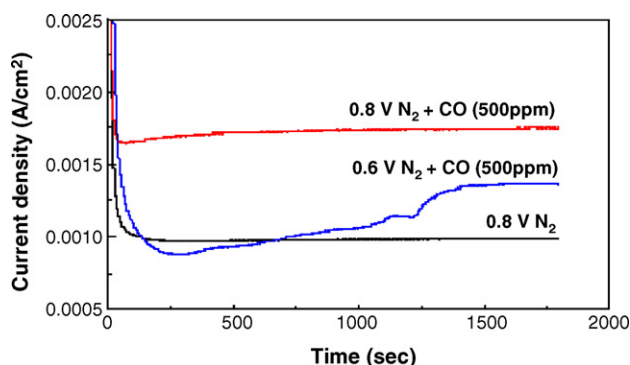
Fig. 3. Potentiostatic measurements of $N_2 + CO$ (500 ppm) stream.
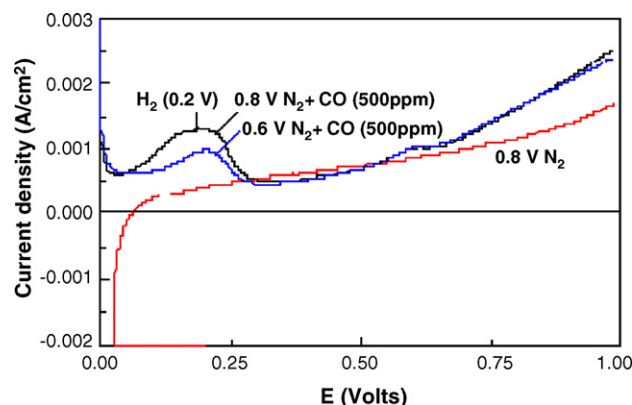
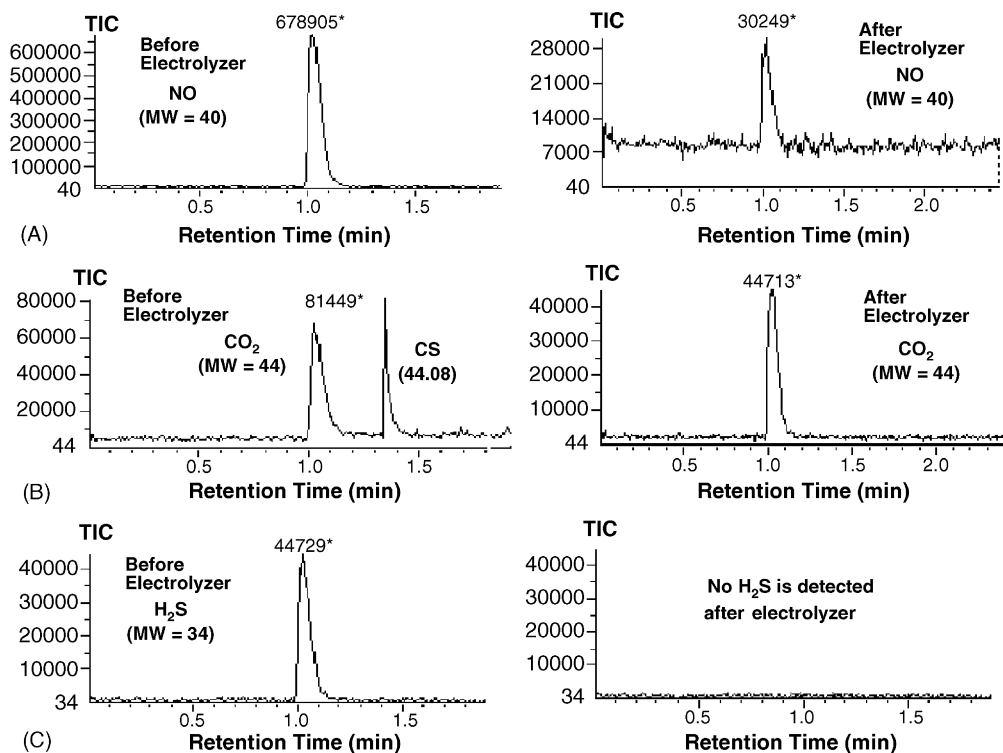Fig. 4. Potentiodynamic curves of $N_2 + CO$ (500 ppm).

Fig. 5. GC/MS measurement for adsorption of impurity gases.

Therefore, we preclude all these possibilities and the only source of H_2 must be from the EWGS reaction.

Gas chromatograph/mass spectrometer (GC/MS) measurements were carried out to test the level of impurities before and after introducing $N_2 + CO$ stream to the EWGS electrolyzer. The results of the CO_2 and other impurities are shown in Fig. 5. Fig. 5A shows that approximately 50% of nitrogen monoxide (NO) was adsorbed by the electrolyzer at a volumetric flow rate of $500\,mL\,min^{-1}$ and residence time of 0.11 s (calculated upon the volume of 0.875 mL for the anode flow chamber). Fig. 5B and C shows that the carbon monosulfide (CS) and hydrogen sulfide (H_2S) were completely adsorbed. Interestingly, CO_2 in N_2 is also detected before the electrolyzer, indicating that there already exists CO_2 in the N_2 and CO gas mixture. After the electrolyzer, CO_2 can be produced by the EWGS reaction and is supposed to have a higher concentration than that before the electrolyzer. However, the result of GS/MS measurement indicates (Fig. 5B) that only 50% CO_2 is detected in the outlet stream of the electrolyzer compared to that in the inlet stream. This result indicates that the electrolyzer has a capability for CO_2 adsorption.

Based on these results, we can conclude that it is highly possible that other sulfur-based gases, such as sulfur dioxide (SO_2), carbonyl sulfide (COS), and carbon disulfide (CS_2) can also be adsorbed and eliminated *via* the EWGS process. Similarly, the electrolyzer could also be used for the adsorption of trace amount of impurity nitrogen dioxide (NO_2) and ammonia (NH_3), with high efficiency and a short residence time. It should be pointed out that the elimination of these ppb level impurity gases in an H_2 fuel stream could enhance the performance of a PEM fuel cell as indicated in Section 4.3.

4.2. Case study II: effect of CO removal on fuel cell performance (50 vol.% N_2 with 500 ppm CO and 50 vol.% ultra pure H_2)

In this case study, a 500 ppm CO concentration in an N_2 stream with $100\,mL\,min^{-1}$ flow rate was introduced to the electrolyzer. After the EWGS, the purified outlet stream from the electrolyzer was mixed with a pure H_2 stream with a flow rate of $100\,mL\,min^{-1}$, and fed into a PEM fuel cell. The flow diagram is shown in Fig. 6. A fuel cell testing station was applied to monitor the cell output voltage as a function of CO removal at a constant current density of $200\,mA\,cm^{-2}$. The purpose of this case study is to investigate the effect of CO removal on the performance of a PEM fuel cell. The introduction of an $N_2 + CO$ is not to simulate a real H_2 fuel cell system, rather, to investigate the EWGS process simultaneously monitoring the output voltage of a fuel cell. It should be noted that we will not be able to conduct such an experiment using an $H_2 + CO$ fuel stream. Our test stand does not allow us to apply a potential to the electrolyzer for the $H_2 + CO$ stream because the migration of H^+ under a potential greater than 0.2 V will cause electrical current in excess of the maximum allowable value of the test stand. This limits us to testing fuel cell performance during the electrolysis process. In other words, for an $H_2 + CO$ system, the test of the fuel cell performance has to be separated for the electrolytic process. This is the main reason why an $N_2 + CO$ system was applied in this case study.

The results of the fuel cell performance are depicted in Figs. 7 and 8. As shown in Fig. 7, the fuel cell output voltage dropped significantly when the $N_2 + CO$ stream was mixed with an H_2 stream (containing 250 ppm CO) and was fed to the
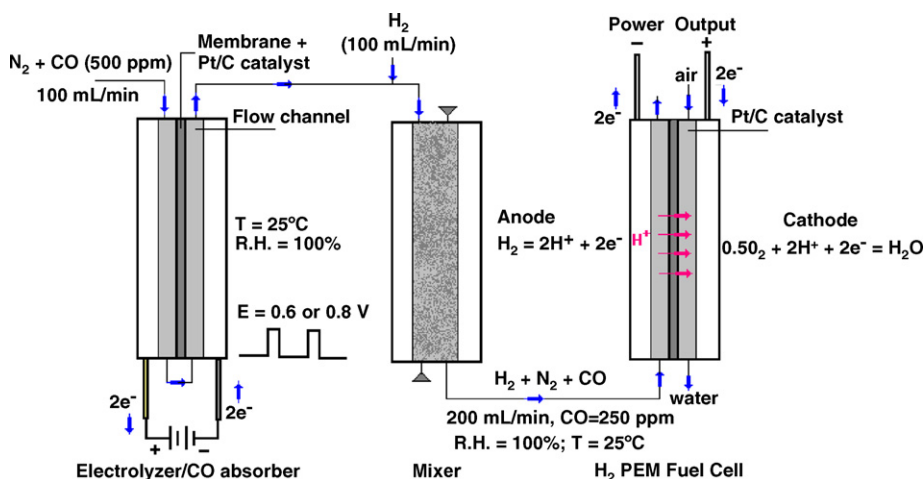
Fig. 6. Experimental setup for measuring PEM fuel cell performance ($N_2 + H_2 + CO$ (250 ppm)).
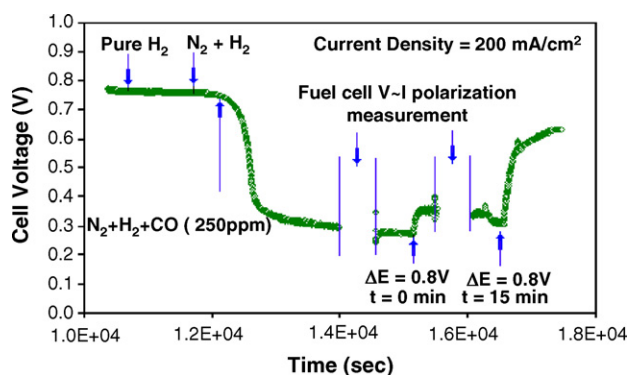

Fig. 7. Fuel cell output voltage as a function of CO removal.

fuel cell. When applying 0.8 V potential to the electrolyzer, CO was oxidized to CO_2 rapidly, and the fuel cell output voltage increased simultaneously. After electrolyzing for about 15 min, the potential applied to the electrolyzer was turned off. The fuel cell output voltage was gradually improved to a pure H_2 level at 0.757 V. The fuel cell output voltage under a current density of 200 mA cm^{-2} only decreased slightly after more than 6 h (Fig. 8). This result indicates that the electrolyzer could continuously adsorb CO up to 6 h before it was saturated with CO. To confirm this finding, we disconnected the electrolyzer and introduced $N_2 + CO$ directly into the main H_2 stream and then the gas mixture was introduced to the fuel cell. This caused the
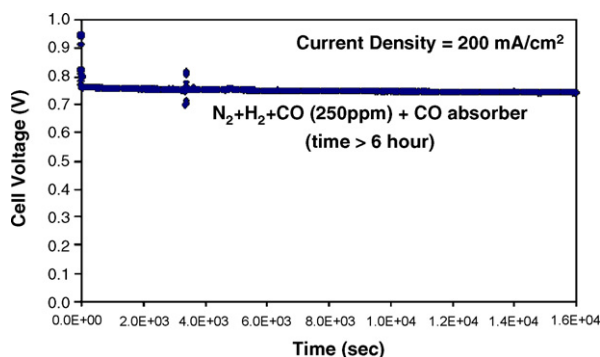

Fig. 8. Fuel cell performance including CO absorber.

output voltage of the fuel cell to drop immediately to the initial $N_2 + CO + H_2$ fuel level ($\sim$0.3 V). After reconnecting the electrolyzer the fuel cell voltage was restored to about 0.75 V. With this result, we can conclude that even though electricity is turn off, the electrolyzer still has a capability to adsorb CO for a few hours to maintain a high fuel cell output voltage. The measurements of fuel cell polarization curve (V–I) under different current densities were also conducted as shown in Fig. 7. Since the measurements were not carried out under steady state conditions, the fuel cell polarization curves are not shown in this paper.

One interesting observation derived from Fig. 7 shows that during the EWGS process fuel cell output voltage did not improve significantly. However, after electricity was turned off, the cell voltage increases dramatically. This may be due to the interaction between CO adsorption and the EWGS process. The detailed mechanism is unclear and a research effort is needed. The complete proof of the interaction concept and the mechanism study is beyond the scope of this paper.

4.3. Case study III: effect of CO removal on fuel cell performance (H_2 with 100 ppm CO)

The objective of this case study was to investigate the effect of electrochemical removal of CO from an H_2 stream. The experimental setup is depicted in Fig. 9. During this experiment, an H_2 stream containing 100 ppm CO was fed to an electrolyzer at a flow rate of 200 mL min^{-1}. The electrolyzer was operated at room temperature, atmospheric pressure and saturated at 100% water vapor.

Fig. 10 shows the effects of CO removal on the performance of the PEM fuel cell. When an H_2 stream containing 100 ppm CO was directly fed into a PEM fuel cell, the fuel cell output voltage significantly dropped. When the cell voltage reached a minimum level ($\sim$0.3 V), we shut down the $H_2 + CO$ fuel supply to the system. At this very moment, the test stand automatically switches from $H_2 + CO$ fuel to N_2 gas inlet to the electrolyzer and the fuel cell system in order to protect the cell from damage. It should be noted that in a real system no N_2 is needed to flush the adsorbed CO from an electrolyzer. In fact, N_2 flush will not
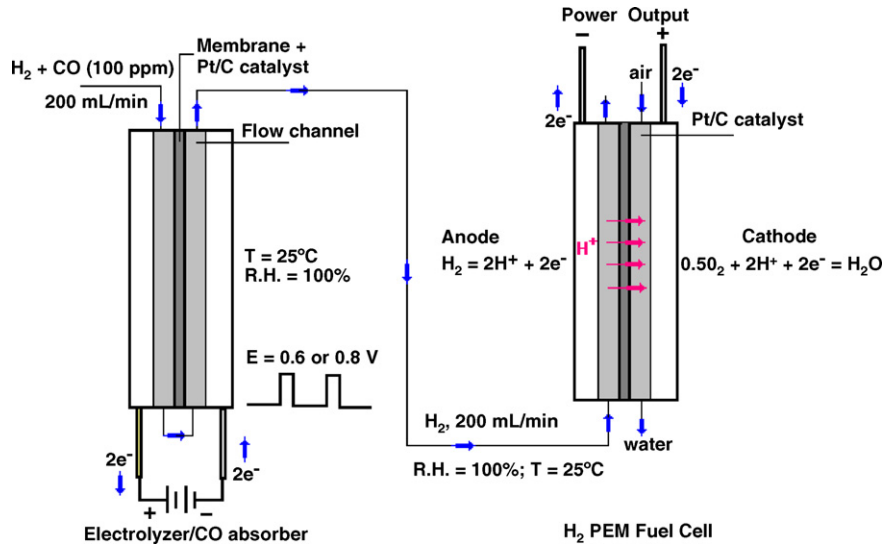
Fig. 9. Experimental setup for testing PEM fuel cell performance (H_2 with 100 ppm CO).

reduce the CO absorption because N_2 does not competitively adsorb on the Pt catalyst with CO. With the N_2 stream provided by the fuel cell test stand to the electrolyzer, we applied a potential of 0.8 V to the electrolyzer for 10–15 min (arbitrary time) to remove CO adsorbed in the Pt catalyst in the electrolyzer. After that, the H_2 + 100 ppm CO fuel was reconnected from the test stand to the electrolyzer and the fuel cell to record the output voltage of the fuel cell. The process was repeated for four times as shown in Fig. 10 to verify the regeneration of the electrocatalyst in the electrolyzer under an H_2 + CO feed stream. Although in this preliminary experiment we did not directly measure the CO concentration at the outlet of the electrolyzer, the output voltage of the fuel cell could serve as an indicator for indirectly monitoring the effect of CO removal.

One interesting observation is shown in Fig. 10. After the EWGS process, the fuel cell output voltage recovered to slightly higher level than that of the pure hydrogen input condition (from 0.747 to 0.762 to 0.784 V). The figure also shows that the CO breakthrough time can reach up to 1 h as indicated in the fuel cell output voltage curve. This effect may be due to the fact that other impurity gases (*i.e.* sulfur-based components) in the H_2 stream were also removed by the electrolyzer as indicated by the GC-MS measurements shown in Fig. 5.
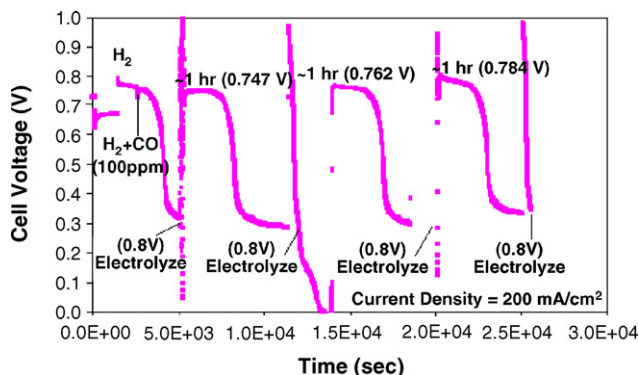
It should be pointed out that the CO breakthrough time in the H_2 stream is much less than that in the N_2 stream. This result may be attributed to the competitive adsorption of H_2 in the electrocatalyst leading to the reduction of CO storage capability. The 1 h CO storage time in this case study could be prolonged by either selecting a better electrolyte or by increasing the volume of the anode flow chamber. The volume of the electrolyzer in this research is 0.875 mL and the breakthrough time is about 1 h (Fig. 10), with CO concentration of 100 ppm. As an estimation, if the CO concentration in H_2 is 10 ppm, or if the volume of the electrolyzer increases by a factor of 10, the breakthrough time can be increased to 10 h, meaning that in this time period the electrolyzer would have a capacity to store CO up to 10 h. This result may indicate that the conceptual design proposed in this paper has potential to enable an H_2 powered vehicle to drive for a few hours before electricity would have to be applied to remove CO, and the as proposed process could occur at ambient temperature and pressure.

As discussed in Section 2, if the CO removal time is shorter than CO storage time, we can operate CO removal between two parallel systems with one electrolyzer serving as a CO adsorber and the alternative one as a CO remover. Two systems can be shifted according to the CO breakthrough time. During the electrolytic process no H_2 will pass through the electrolyzer so there would not be an H_2 oxidation issue. This differs from conventional processes that operate under a continuous condition which requires energy to maintain the reactor's temperature during the whole process. Compared to CO removal time (10–15 min in this case study), the CO breakthrough time ($\sim$1 h) is about four to six times longer than the removal time. This result shows a possibility of application of this technology in an on board condition.

5. Conclusions

The proposed EWGS process has been shown to be effective for the removal of a ppm level CO and trace amount of other

Fig. 10. Performance of PEM fuel cell (H_2 + CO (100 ppm)).

impurities from an H$_2$ stream. The EWGS could be a rapid reaction for CO removal. Two electrolyzer systems can be operated alternatively for on board applications using a pulse power supply at ambient conditions and 100% relative humidity. The CO breakthrough time for a Pt/C catalyst is about 1 h for 100 ppm CO in an H$_2$ stream. The effect of electrochemical removal of CO on the performance of PEM fuel cells was also investigated and the results showed that the process is safe since no on-board oxygen or air sources are needed. The process is also highly efficient because the CO serves as a fuel for the production of H$_2$. Furthermore, the electrolyzer is stable under electrochemical conditions for more than 70 h with no sign of catalyst degradation. The overall advantages of the proposed EWGS reaction can be summarized as:

(1) Favorable operating conditions: The electrolyzer operates at 25 °C, 1 atm, and 100% relative humidity; the conditions are compatible with the operating conditions of a PEM fuel cell at 60–80 °C, 1 atm, and 100% relative humidity.
(2) High efficiency: Differing from conventional thermocatalytic oxidation of CO, in which CO is wasted as an energy source and H$_2$ loss cannot be avoided, the proposed electrolyzer operates at ambient conditions, generates H$_2$ and minimizes overall H$_2$ fuel loss.
(3) Low electricity consumption: The EWGS of the electrolyzer first serves as a CO adsorber. Once it is saturated with CO, a potential is applied to oxidize CO to CO$_2$ while reducing water to produce H$_2$. The electricity consumption for CO oxidation is as low as 0.015 W for the flow rate of 500 mL min^{-1} of N$_2$ + 500 ppm CO gas.

(4) Multiple impurity removal: The electrolyzer can also absorb other impurity gases in the H$_2$ stream such as NO, H$_2$S, CS, and CO$_2$.
(5) Greater safety: The proposed process does not require O$_2$ or air input and the system is safe.

Acknowledgements

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