

Effect of CO in the anode fuel on the performance of PEM fuel cell cathode

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Abstract

Even trace amounts of CO in the fuel for a proton-exchange membrane fuel cell (PEMFC) could poison not only the anode, which is directly exposed to the fuel, but also the cathode, which is separated from the fuel by a proton-exchange membrane; and the performance decline of the cathode is sometimes more than that of the anode. Adsorption of CO on the cathode catalyst has been detected electrochemically, and this indicates that CO can pass through the membrane to reach the cathode. To reduce such a poisoning effect, fuel cell operation conditions (e.g. level of membrane humidification, gas pressure difference between cathode and anode), membrane and catalyst layer structures, and CO-tolerant cathode catalysts should be further explored.

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1. Introduction

A proton-exchange membrane fuel cell (PEMFC) performs best when pure hydrogen is used as the fuel. However, due to the difficulty in transporting and storing hydrogen, on-site generation of hydrogen by reforming hydrocarbons and alcohols seems to be more realistic [1,2]. Partial oxidation, steam reforming and autothermal reforming are the most common reforming techniques [3–8]. Immediately after reforming, a few CO cleaning steps such as high and low temperature water-gas shift reactions and CO preferential oxidation are needed to reduce the concentration of CO in the reformat. CO has a strong tendency to adsorb on the surface of the catalyst and thus to block the sites that hydrogen needs for reactions. Even parts per million levels of CO can cause serious poisoning. Various CO-tolerant catalysts such as Pt-Ru, Pt-Mo, and Pt-Ru-Mo are used in the anode to alleviate this kind of poisoning [9–11]. On the other hand, Pt is the most effective and proven catalyst for oxygen reduction and is commonly used in the cathode [12]. Since a CO-containing fuel is only fed to the anode side, which is separated by a membrane from the cathode side, it had not been expected that CO would affect the cathode until recently we found that CO in the fuel could sometimes pass

through the membrane to the cathode side to cause a decline in the cathode performance [13]. This paper reports some detailed studies by focusing on the effect of CO on the performance of both the anode and cathode.

2. Experimental

Catalyst mixtures were prepared by a direct mixing of the catalyst with other components such as Nafion and PTFE. The mixtures were stirred, sonicated, and even homogenized in order to achieve a thorough mixing. They were then applied onto Teflon-treated carbon paper-type gas diffusion medium. A membrane-electrode assembly (MEA) was then obtained by hot-pressing the electrodes onto a Nafion membrane at 130 °C.

The MEA was tested using a 10 cm² single cell (Fuel Cell Technologies Inc., Albuquerque, NM). The cell is composed of a pair of graphite plates with serpentine flow-fields. A small circular section, about 2 mm away from the edge of the anode, was used to host a reference electrode. When the performance of the anode and cathode was assessed individually, their potentials were measured against this reference electrode. If only the cell voltage was needed, the cathode was measured directly against the anode without referring to the reference electrode. The fuel passes through the reference section first before flowing through the channels of the anode flow-fields. The cell was operated at 70 °C,

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and both anode and cathode gases were humidified at 70 °C by passing them through stainless steel water bottles. Due to the simplicity in the design of the humidifiers, less than 100% humidification was expected to be achieved if the humidification temperature was the same as the cell temperature. Both the anode and cathode gases had an inlet pressure of about 5 psig, and no backpressure was applied to either side. Air was the oxidant used throughout the experiments. The stoichiometries of air, pure hydrogen and mixed gas were controlled at 2.5, 3.0 and 2.0, respectively. The voltage–current density curves were collected using an HP 6050A load bank.

When a cyclic voltammetry of the cathode of an MEA was studied, the anode was used as both the counter and reference electrode. Pure hydrogen or hydrogen containing CO was fed to the anode and argon or nitrogen was fed to the cathode, respectively. After a waiting period, the cathode potential was scanned between 0.15 and 0.70 (or 0.75) V for a few cycles. A Gamry EIS300HFC electrochemical impedance system was used to carry out the cyclic voltammetry.

3. Results and discussion

Fig. 1 shows the voltage (V)–current density (I) curves of an MEA when the anode fuel, hydrogen, contained 0, 10 and 50 ppm CO, respectively. The anode was made using E-TEK 40% Pt-Ru/C (atomic ratio Pt:Ru = 1:1) with a Pt-Ru loading of 0.60 mg/cm², while the cathode was made using Pt black with a Pt loading of 1.7 mg/cm². Nafion 1135 was used as the membrane. As expected, the fuel cell performance declines when CO exists in the fuel, and a higher CO concentration causes a larger decline. These V – I curves are typical, and have been widely observed.

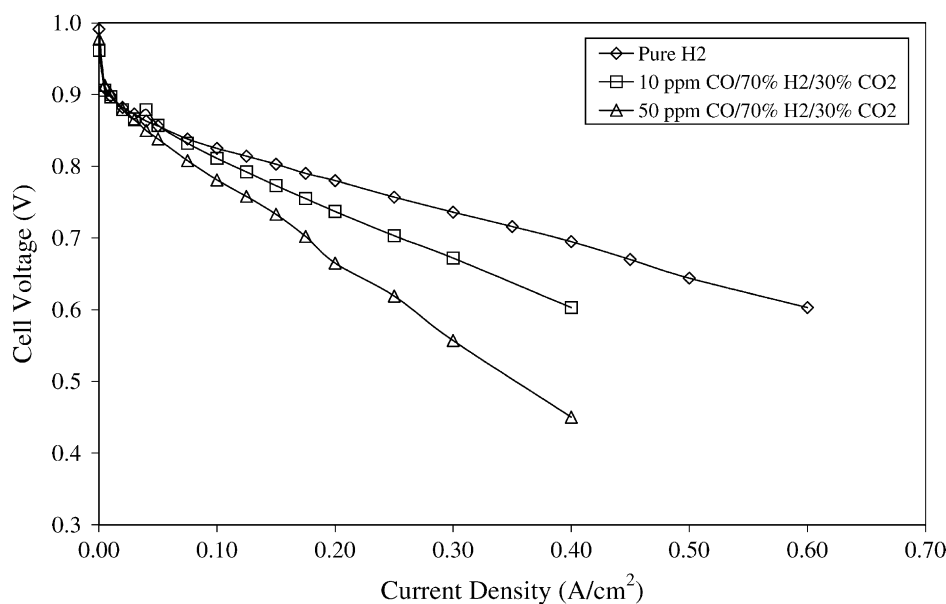


Fig. 1. Cell performance of an MEA when the anode fuel was H₂, 10 ppm CO/70% H₂/30% CO₂, and 50 ppm CO/70% H₂/30% CO₂, respectively. Anode, Pt-Ru = 0.60 mg/cm²; cathode, Pt = 1.7 mg/cm²; Nafion 1135 membrane.

In order to evaluate the effect of Pt-Ru loading on CO-tolerance, MEAs with different Pt-Ru (E-TEK, 40% Pt-Ru/C) loadings were prepared and tested. Fig. 2 shows the cell voltage change with time at a current density of 200 mA/cm² after the fuel was switched from pure H₂ to 10 ppm CO/70% H₂/30% CO₂. Firstly, the performance of all the MEAs declined pretty fast within the first 10 min after the gas was switched, but after about 1 h, the cell voltage got stabilized. Secondly, MEAs with higher anode Pt-Ru loading sustained a higher cell voltage. For example, the MEA with an anode Pt-Ru loading of 0.19 mg/cm² could sustain a cell voltage of 0.69 V, while other MEAs with higher anode Pt-Ru loadings could sustain a cell voltage higher than ca. 0.74 V. The relatively lower performance of the MEA with an anode Pt-Ru loading of 1.06 mg/cm² was probably due to higher conducting resistance and mass transport limitations caused by its thicker catalyst layer.

Fig. 3 shows the cell voltage change with time for the same MEAs after the fuel was switched from 10 ppm CO/70% H₂/30% CO₂ to 50 ppm CO/70% H₂/30% CO₂. Since the MEA with an anode Pt-Ru loading of 0.19 mg/cm² could not maintain a stable voltage at a current density of 200 mA/cm², no curve for this MEA was able to be obtained. In the presence of 50 ppm CO, the poisoning proceeded much faster, and a maximum CO adsorption was reached within about 15 min. A Pt-Ru loading of 0.60 mg/cm² or higher was needed in order to achieve the best performance in the presence of 50 ppm CO and at a current density of 200 mA/cm². If the cell current density were set at a higher value, it is expected that the minimum Pt-Ru loading would need to be higher than 0.60 mg/cm² in order to achieve the best performance.

We have become accustomed to attributing the performance decline of the whole cell to CO poisoning to the

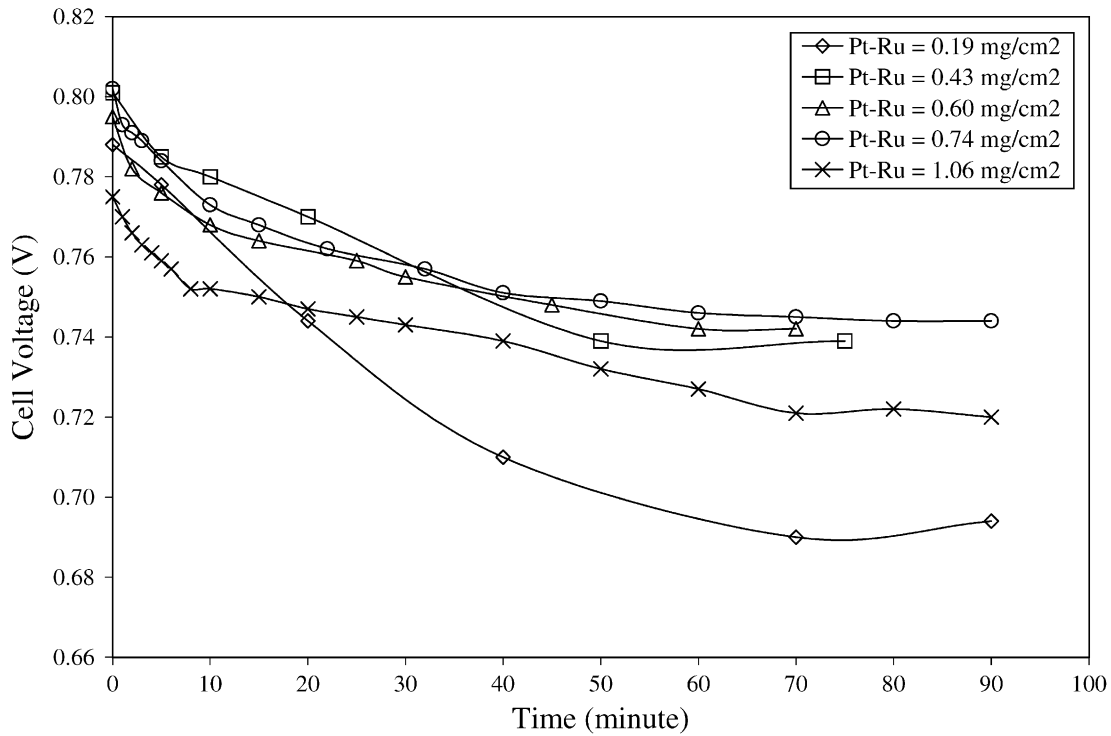


Fig. 2. Cell voltage change with time after the fuel was switched from pure H₂ to 10 ppm CO/70% H₂/30% CO₂ for MEAs with different anode Pt-Ru loadings. Current density = 200 mA/cm²; Nafion 1135 membrane.

anode when CO exists in the fuel. However, when a reference electrode was used to separate the cell performance into anode and cathode performance respectively, we discovered that along with the anode performance declining, the cathode performance very often also declined if the fuel contained CO. Fig. 4 shows the *V-I* curves of both the anode and cathode

of an MEA with an anode Pt-Ru (E-TEK 40% Pt-Ru/C) loading of 0.26 mg/cm² and a cathode Pt loading of 1.7 mg/cm². When pure hydrogen is switched to a gas mixture containing 10 ppm CO, the anode overpotential increased from 0.036 to 0.190 V, while the cathode potential decreased from 0.724 to 0.688 V, at a current density of 400 mA/cm².

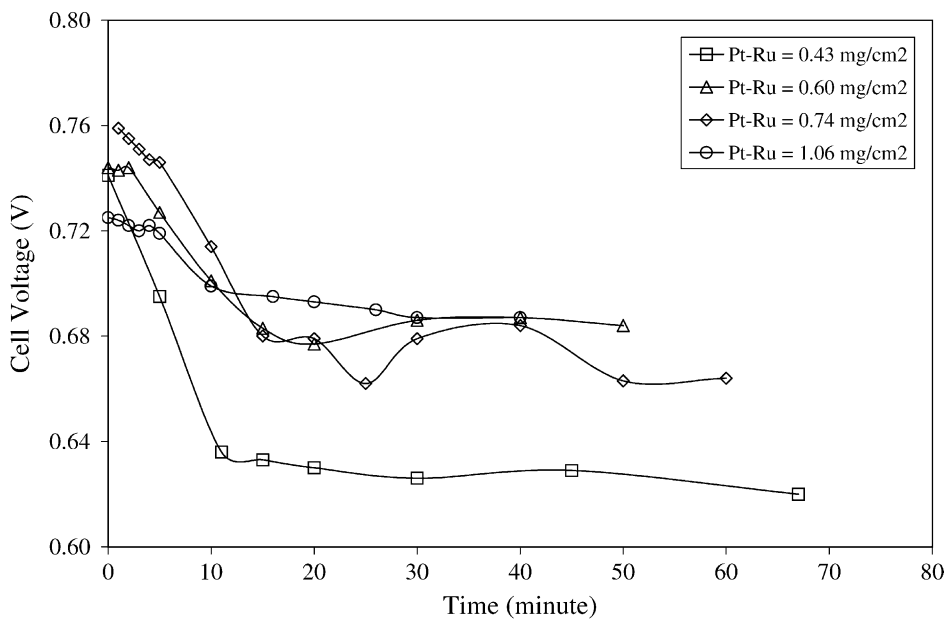


Fig. 3. Cell voltage change with time after 10 ppm CO/70% H₂/30% CO₂ was switched to 50 ppm CO/70% H₂/30% CO₂ for MEAs with different anode Pt-Ru loadings. Current density = 200 mA/cm²; Nafion 1135 membrane.

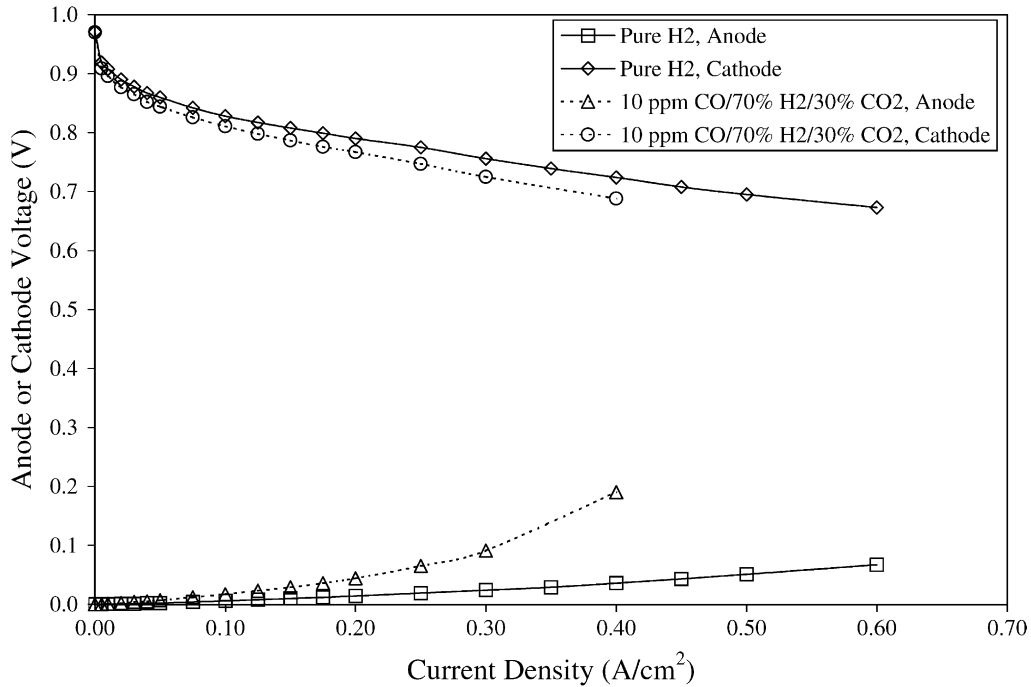


Fig. 4. Anode and cathode performance of one MEA in pure H₂ and 10 ppm CO/70% H₂/30% CO₂, respectively. Anode, Pt-Ru = 0.26 mg/cm²; cathode Pt = 1.7 mg/cm²; Nafion 1135 membrane.

We tested a variety of MEAs and found that different MEAs showed different CO-tolerance. Fig. 5 shows an MEA whose anode (Pt-Ru = 0.67 mg/cm²) and cathode (Pt = 0.40 mg/cm²) were affected dramatically by 50 ppm CO. For example, at a current density of 600 mA/cm², the anode overpotential increased from 0.012 to 0.281 V, while

the cathode potential declined from 0.644 to 0.321 V. The absolute potential change of the cathode (0.323 V) was even higher than that of the anode (0.269 V). These catalysts were experimental samples provided by a catalyst manufacturer. On the other hand, some other MEAs were pretty CO-tolerant, such as the one shown in Fig. 6. This MEA had an anode

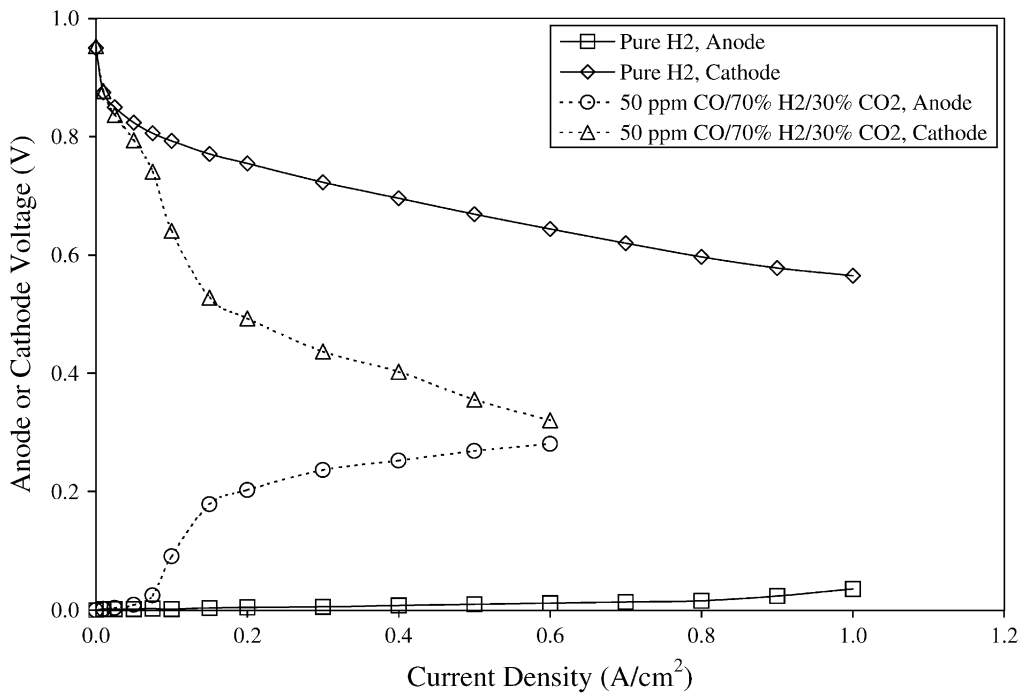


Fig. 5. Anode and cathode performance of another MEA in pure H₂ and 10 ppm CO/70% H₂/30% CO₂, respectively. Anode, Pt-Ru = 0.67 mg/cm²; cathode, Pt = 0.40 mg/cm²; Nafion 1135 membrane.

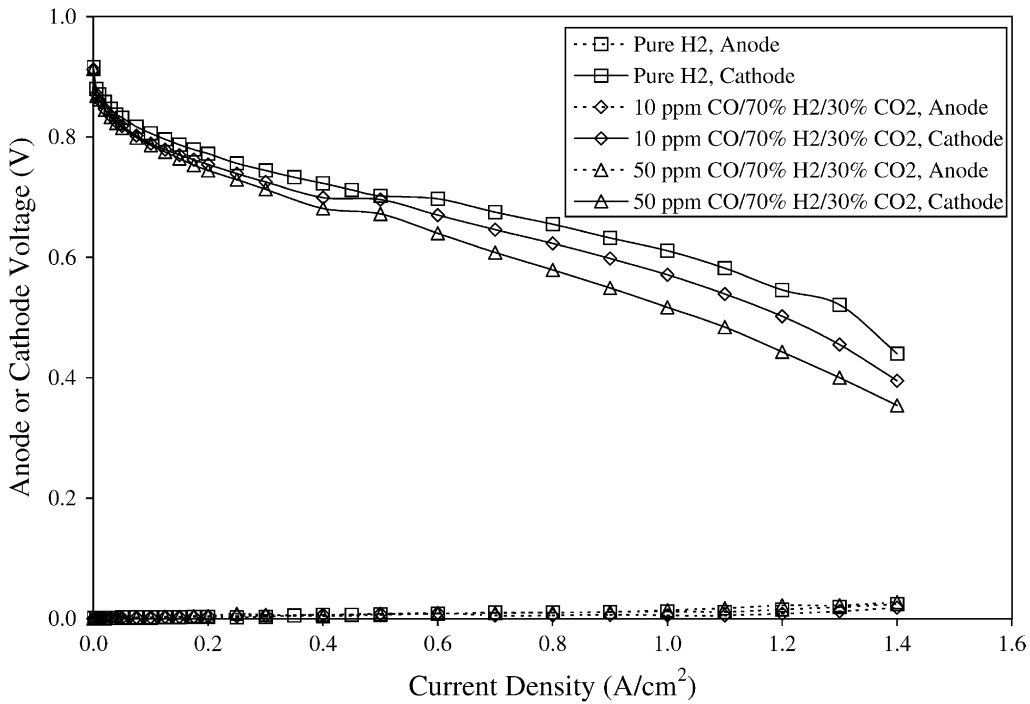


Fig. 6. Anode and cathode performance of a third MEA in pure H₂, 10 ppm CO/70% H₂/30% CO₂, and 50 ppm CO/70% H₂/30% CO₂, respectively. Anode, Pt-Ru = 0.60 mg/cm²; cathode, Pt = 0.40 mg/cm²; a 25 μm thick membrane.

Pt-Ru loading of 0.60 mg/cm² and cathode Pt loading of 0.40 mg/cm², and a membrane of ca. 25 μm thick. We obtained this MEA from another fuel cell developer.

Figs. 4–6 illustrate three typical patterns we have observed with various kinds of MEAs. In Fig. 4, CO causes anode to

decline more than the cathode. In Fig. 5, both anode and cathode performance declines largely. In Fig. 6, anode shows little decline but the cathode performance declines slightly.

The effect of CO on the performance of both anode and cathode is presented in another way as shown in Fig. 7

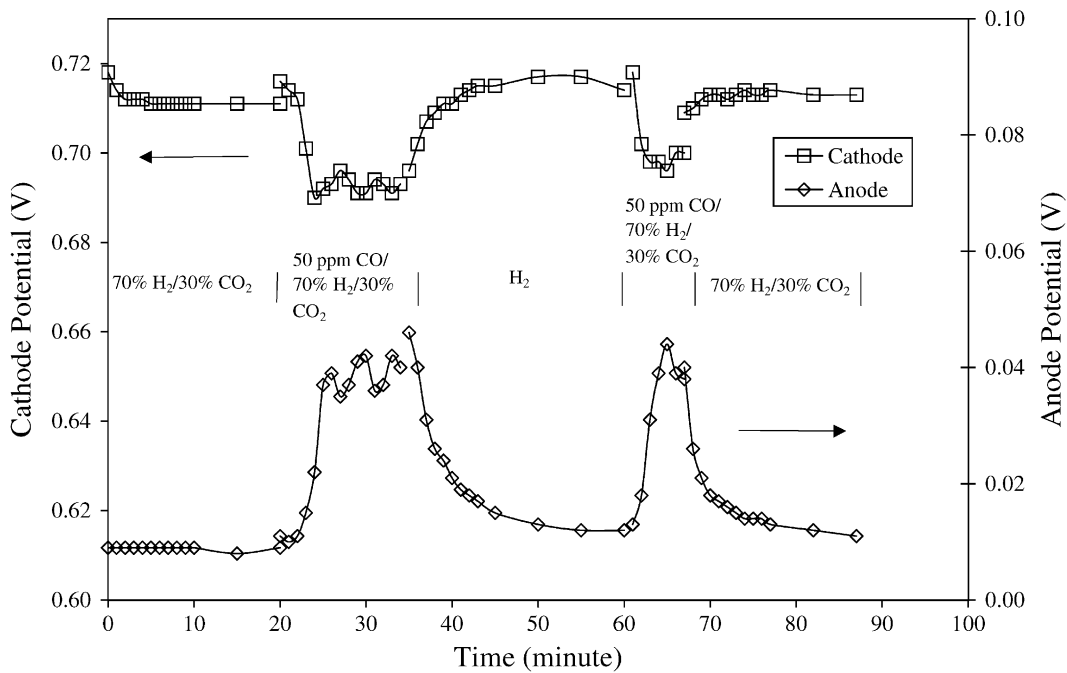


Fig. 7. Anode and cathode voltage change with time in the presence of different anode fuel gases. Anode, Pt-Ru = 0.62 mg/cm²; cathode, Pt = 1.8 mg/cm²; Nafion 1135 membrane; current density = 300 mA/cm².

(Engelhard 40% Pt-Ru/C). The anode fuel gas was switched sequentially from 70% H₂/30% CO₂, to 50 ppm CO/70% H₂/30% CO₂, to pure H₂, to 50 ppm CO/70% H₂/30% CO₂ again, and finally back to 70% H₂/30% CO₂. The results enable us to draw the following conclusions. Firstly, the anode and cathode potentials changed simultaneously whenever the anode fuel was changed, which clearly demonstrated that CO in the fuel did affect the cathode performance, along with the anode performance. Secondly, 70% H₂/30% CO₂ gave similar results as pure H₂, which indicates that CO₂ did not poison the Pt-Ru anode, and that the hydrogen concentration dilution by 30% CO₂ did not affect the performance, at least at a current density of 300 mA/cm². Thirdly, electrodes poisoned by CO could be recovered quickly when fuels containing no CO was used. Fig. 8 shows more clearly (only anode) that when the fuel gas was switched, both poisoning and recovering proceeded quite quickly, although the recovery seemed to be a little slower than poisoning. Another interesting observation was the voltage oscillation in the plateau region in the presence of 50 ppm CO. Our interpretation to such an oscillation is as follows. Since the cell current density was set at 300 mA/cm², the cell had to maintain this number at whatever a voltage. When more CO adsorbs on the anode catalyst surface, less active sites will be available for hydrogen oxidation. In order to support the current density, the anode overpotential has to increase. At the same time, such an increase in overpotential weakens CO adsorption strength, which causes some CO desorbs from the catalyst surface. Now more active sites are available for hydrogen oxidation, leading to a lower anode overpotential to support the same current density. Such adsorption–de-sorption–re-adsorption repeats continuously, resulting in the voltage oscillating.

The cathode performance decline due to the presence of CO in the anode fuel can only be explained by postulating that CO transports through the membrane and adsorbs onto the cathode catalyst to cause a reduction of the available sites for oxygen reduction. Due to its high sensitivity, cyclic voltammetry was chosen to test if there was any CO on the cathode side. During the experiments, the anode was fed with pure hydrogen or hydrogen containing 50 ppm CO, while the cathode was fed with argon. After a waiting period, cyclic voltammograms of the MEA were recorded with the cathode as the working electrode and the anode as both the counter and reference electrode. Figs. 9 and 10 show the result of an MEA with Nafion 112 as the membrane, a Pt-Ru (E-TEK 40% Pt-Ru/C) anode with a loading of 1.1 mg/cm², and a cathode with Pt loading of 1.7 mg/cm². In Fig. 9, the fuel contains no CO. When the voltage was scanned from 0.15 to 0.75 V, no peaks were observed between 0.4 and 0.6 V, which is the region where CO oxidation would occur. The conditions in Fig. 10 were similar to those in Fig. 9, except that a fuel containing 50 ppm CO was passed through the anode side. Evidently, a large oxidation peak due to CO oxidation was observed at 0.55 V during the first positive scan, but no corresponding reduction peak was observed. In the following cycles, only a tiny bump existed in this potential region. Clearly, CO transported from the anode side to the cathode side and accumulated on the catalyst surface during the 10 min waiting period. It was then oxidized to CO₂ and stripped off the electrode surface during the first positive scan. The shoulder at ca. 0.47 V could evolve into an apparent peak if more CO adsorbed onto the catalyst surface when 30 min was waited before the first scan was started [13]. These two oxidation peaks have been attributed to the

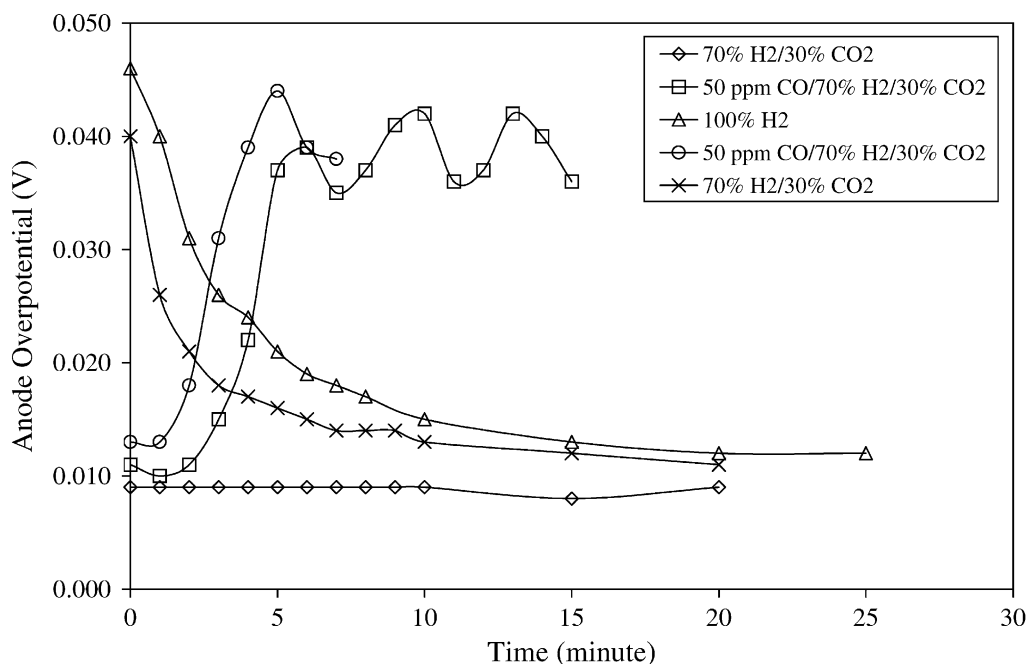


Fig. 8. Anode voltage change with time when the anode fuel was switched sequentially from 70% H₂/30% CO₂, to 50 ppm CO/70% H₂/30% CO₂, to pure H₂, to 50 ppm CO/70% H₂/30% CO₂ again, and finally back to 70% H₂/30% CO₂. The conditions were same as in Fig. 7.

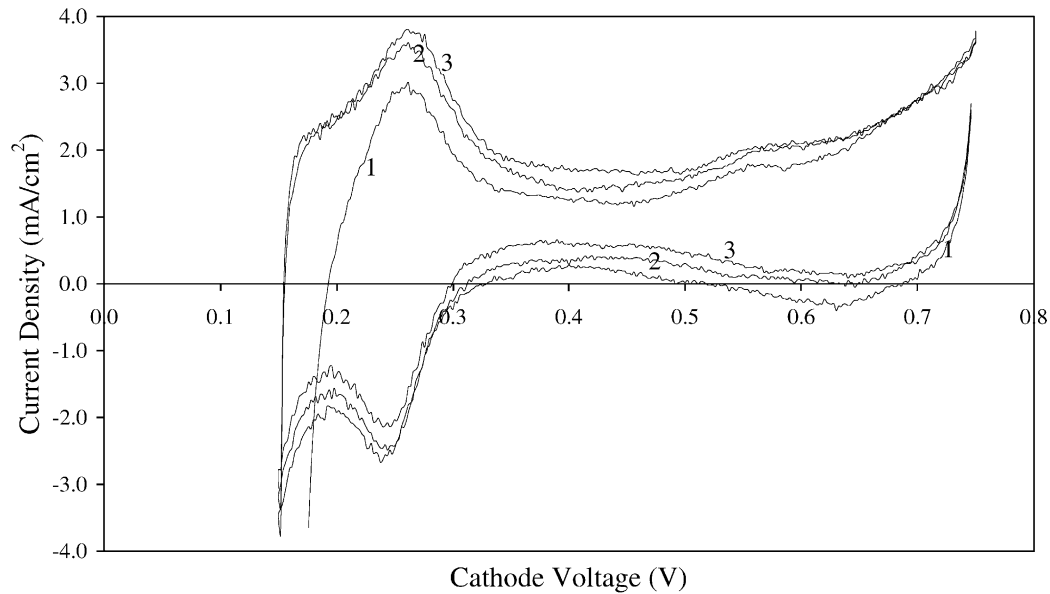


Fig. 9. Cyclic voltammograms of the cathode of an MEA with pure H_2 as the anode feeding gas. The cathode feeding gas was argon. Anode, Pt-Ru = 1.1 mg/cm²; cathode, Pt = 1.7 mg/cm²; Nafion 112 membrane; potential scan rate = 20 mV/s. Cycle numbers are shown on the curves.

different facets of the low index planes of the catalyst surface [14,15]. The ratio of CO_{ads} oxidation charge (the area of CO region) to the H_{ads} desorption charge (the area of H region) is 0.38. Based on a previous study concluding that a ratio of 2 represented a full CO monolayer coverage [15], a value of 0.38 means that 19% of the total cathode active sites is covered by CO after a 10 min waiting period. It is expected that CO adsorption onto the cathode catalyst sites is not

evenly distributed throughout the whole cathode catalyst layer. Since CO enters through the membrane, more CO will adsorb onto the catalyst sites that are near the membrane. Such a distribution is likely to have a more severe effect on the cathode performance than if CO mainly adsorbs onto catalyst sites that are near the gas diffusion medium, because the catalyst near the membrane plays a more important role in determining the electrode performance [16].

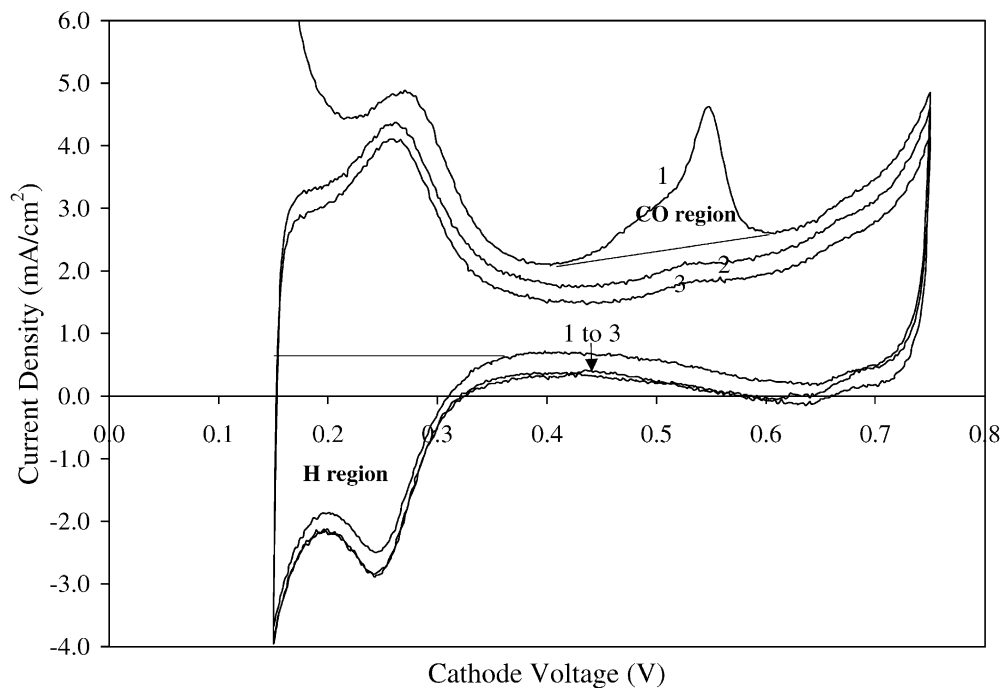


Fig. 10. Cyclic voltammograms of the cathode of an MEA with 50 ppm CO/70% H_2 /30% CO_2 as the anode feeding gas. The conditions were same as in Fig. 9, and the MEA was exposed to the fuel gas for 10 min.

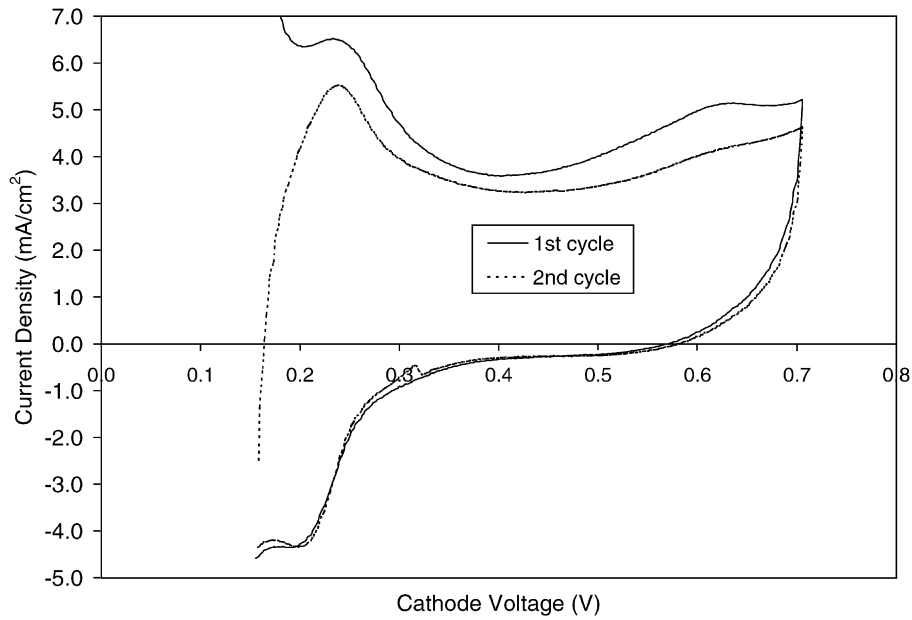


Fig. 11. Cyclic voltammograms of the cathode of a fully humidified MEA with 50 ppm CO/70% H₂/30% CO₂ as the anode feeding gas. The cathode feeding gas was nitrogen. Anode, Pt-Ru = 0.42 mg/cm²; cathode, Pt = 0.99 mg/cm²; Nafion 1135 membrane; potential scan rate = 20 mV/s. The MEA was exposed to the fuel gas for 10 min.

Many factors could affect the transportation of CO from the anode to the cathode. These factors could include the porosity, level of humidification and thickness of the membrane, the oxidation efficiency of CO on the anode, and the pressure difference between the cathode gaseous reactant and the anode gaseous reactant. Figs. 11 and 12 show the effect of membrane humidification. In Fig. 11, the membrane was

fully hydrated (the humidifier was modified), and no CO was detected at the cathode after a 10 min waiting period. Similar cyclic voltammograms were observed when pure H₂ was used. The membrane was then dehydrated by not humidifying the reactants (pure hydrogen and air) for 15 min, followed by a 5 min humidification. During this 5 min humidification, hydrogen was replaced by 50 ppm CO/70% H₂/30% CO₂, but

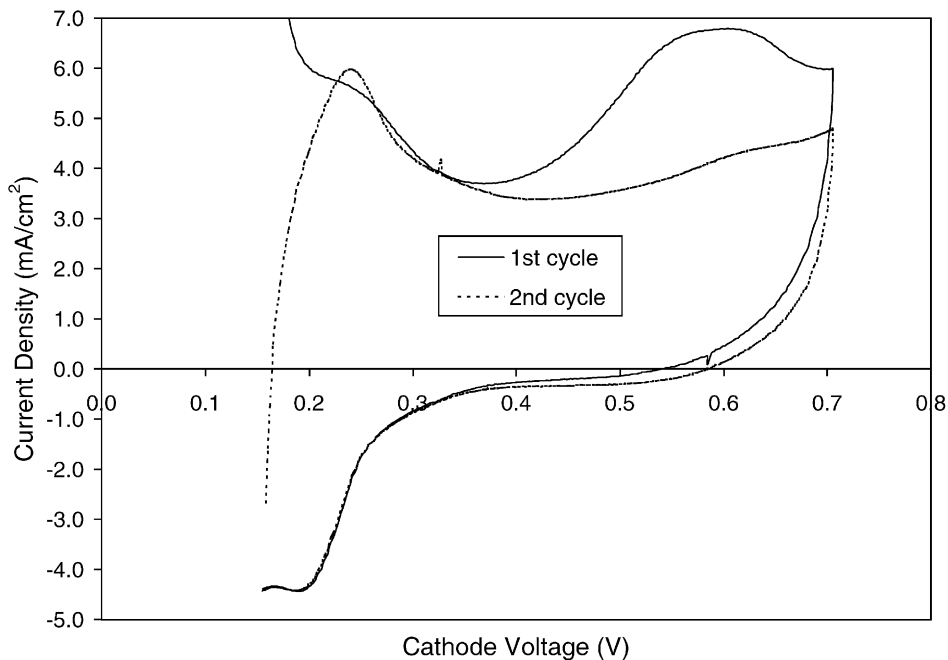


Fig. 12. Cyclic voltammograms of the cathode of a partially humidified MEA with 50 ppm CO/70% H₂/30% CO₂ as the anode feeding gas. The conditions were same as in Fig. 11, except that the MEA was exposed to the fuel gas for 5 min.

the level of humidification achieved during this time period was not certain. When the cyclic voltammetry was performed again, a much higher current was observed in the CO oxidation potential region, indicating that some CO transported through the membrane to the cathode side. This experiment seems to indicate that a fully hydrated membrane will reduce the likelihood of CO crossover.

It is not clear how CO transports through the membrane. The above experiment may suggest that CO mainly transports through pin-holes in the membrane. High level of membrane humidification fills the pin-holes with liquid water so that CO crossover is reduced or hindered. These pin-holes could be intrinsic to the membrane, or be created when MEAs were made using a hot-pressing technique, or formed due to membrane deterioration.

The decline of the cathode voltage when CO is present in the anode fuel may be suspected to be due to voltage increase of the reference electrode. Of course, CO will adsorb onto the reference electrode too because it is in the passage of the fuel gas. However, CO adsorption has little effect on the voltage of the reference electrode because there is only an extremely tiny current density passing through the reference electrode during the measurement using a voltmeter, and such a tiny current density guarantees the stabilization of the voltage of the reference electrode. This conclusion is supported by the experimental results that the cell open circuit voltage does not change with the fuel containing CO or not, and that the cell voltage does not change much in the small current density region with either pure H₂ or H₂ containing CO. It is also supported by the experimental result that when the anode was fed with 50 ppm CO/70% H₂/30% CO₂ and the cathode with 100% H₂, the open circuit voltage difference between the two electrodes (cathode minus anode) was ca. -5 mV, which just corresponded to the difference caused by the difference in H₂ concentrations [$\Delta V = (RT/2F)/\ln(0.7/1.0)$]. It is further supported by the fact that the cell voltage obtained by using the difference between cathode voltage versus reference and anode voltage versus reference electrode was the same as measured directly from cathode versus anode voltage.

4. Conclusions

The effect of CO in the anode fuel on the performance of both the anode and cathode was studied using various MEAs. It was surprising to find that CO could poison not only the anode, but also the cathode, and sometimes, the cathode potential drop is even larger than that of the anode. Cyclic voltammetry was used to detect the adsorption of CO on the cathode catalyst. Fully hydrated membrane could reduce or even prevent CO crossover, especially for thicker membranes. It seems likely that that CO transports to the cathode via diffusion through pin-holes in the membrane.

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