

1-1-2005

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J. X. Zhang

Ravindra Datta

Worcester Polytechnic Institute, rdatta@wpi.edu

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## Suggested Citation

Zhang, J. X., Datta, Ravindra (2005). Electrochemical Preferential Oxidation of CO in Reformate. *Journal of the Electrochemical Society*, 152(6), A1180-A1187.

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## Electrochemical Preferential Oxidation of CO in Reformate

Jingxin Zhang<sup>\*,a</sup> and Ravindra Datta<sup>\*\*,z</sup>

Fuel Cell Center, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA

An electrochemical preferential oxidation (ECP<sub>PrOx</sub>) process, an alternative to the conventional preferential oxidation (PrOx), is developed to cleanse CO from a hydrogen-rich gas mixture using a device similar in structure to the proton exchange membrane fuel cell. In this process, the selective CO electro-oxidation is achieved at the anode by rendering the process electrochemical and by utilizing autonomous anode potential oscillations when operated at a constant low current density. The oscillation period and amplitude of the ECP<sub>PrOx</sub> device adjust automatically to the CO levels in the feed stream so that a self-controlled autonomous potential pulsing is achieved with a low level of CO in the cleansed reformat. Some supplemental electrical power is produced from the ECP<sub>PrOx</sub> device while CO is removed from the reformat gas, without any H<sub>2</sub> or CO being wasted. The ECP<sub>PrOx</sub> device can be operated at near room temperature, high anode pressure, atmospheric air pressure, and without external humidification. However, the operating conditions or the structure of ECP<sub>PrOx</sub> are not optimized in this paper, but rather the feasibility of the concept is evaluated with a single cell unit.

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Manuscript submitted July 19, 2004; revised manuscript received December 28, 2004. Available electronically May 5, 2005.

Proton exchange membrane (PEM) fuel cells have the potential to serve as the power systems for a new generation of “green” vehicles, as well as off-road power plants operating with increased efficiency and reduced emissions. A key issue limiting immediate fuel cell application, however, is that PEM fuel cells require pure hydrogen as the fuel. Because H<sub>2</sub> storage on-site or on-board vehicles is as yet impractical and its widespread availability is not likely for some time, conventional fuels, *e.g.*, natural gas, gasoline, or alcohols, must be reformed catalytically into H<sub>2</sub> at the point of usage.<sup>1</sup> The conventional reforming process produces substantial amounts of CO in addition to CO<sub>2</sub> and H<sub>2</sub>. This is reduced via the water-gas-shift (WGS) reaction. The exit gas from the low-temperature shift (LTS) reactor following the high-temperature shift (HTS) stage still contains roughly 5000-10,000 ppm (0.5-1%) CO, which cannot be tolerated by PEM fuel cells. Thus, preferential oxidation (PrOx) reactors are used following the shift reactors to reduce CO to tolerable levels. The preferential oxidation (PrOx) reactor oxidizes CO into CO<sub>2</sub> typically over a Pt or other precious metal based catalyst by carefully bleeding small amounts of air or oxygen. This is able to reduce the CO level to 50-100 ppm. Due to the limited selectivity, however, O<sub>2</sub> in excess of stoichiometry is required to reduce CO to low levels, which burns the hydrogen present in the reformat, thus reducing the overall efficiency.<sup>2</sup> The PrOx stage is also bulky and complex.

The success of the PrOx stage relies heavily on complex control of O<sub>2</sub> and temperature and on the high activity and selectivity of the catalyst in order to minimize the CO content in the effluent while keeping H<sub>2</sub> consumption at a low level. Much of the research on PrOx has focused on searching for better catalysts. Thus, Los Alamos National laboratory (LANL) has developed a PrOx catalyst and reaction system which reportedly can achieve low concentrations of CO (10-20 ppm) in a multistage PrOx reactor over a Pt/Al<sub>2</sub>O<sub>3</sub> or Ru/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>3</sup> A variety of catalytic materials were examined by Oh and Sinkevitch in an integral flow reactor.<sup>4</sup> It was found that both Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> are very active in CO oxidation, achieving nearly complete CO conversion at temperatures as low as 100°C (compared to ~200°C required for Pt/Al<sub>2</sub>O<sub>3</sub>). Au/MnO<sub>x</sub> has been tested for the selective oxidation of CO in simulated reformat as well.<sup>5</sup> The performance was found to be superior at 323-353 K, with a CO conversion of over 95% (*i.e.*, less than 500 ppm in the outlet for a feed CO content of 1%). However, CO conversion dropped greatly for temperatures out of this range. Igarashi *et al.*<sup>6</sup>

found that Pt-Ru supported on mordenite exhibited fairly high selectivity over a wide flow rate range at 150°C. Borup *et al.*<sup>7</sup> disclose in their patent that in the presence of an Ir-based supported catalyst, CO is selectively oxidized in the desired temperature range, preferably 210-260°C. He *et al.*<sup>8</sup> reported CO selective oxidation in a reactor having a fuel cell type of configuration and under conditions similar to those in a fuel cell (60-80°C, high humidity). For the best catalyst tested (5% Ir/CoO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub>/carbon), CO concentration in the effluent is found to be less than 100 ppm at 76°C and 100% humidity (1% CO in the feed, at O<sub>2</sub>/CO ≤ 2).

A key variable determining selectivity in the PrOx reactor is temperature. Therefore, the CO selective oxidation reactor requires careful cooling and temperature control, which is a major technical challenge. Thus, a two-stage reactor with three heat exchangers to carefully control the temperatures of the process stream before, in between, and after the reactor was used by Vanderborgh *et al.*<sup>9</sup> Both of the O<sub>2</sub> streams to the reactors were predetermined and carefully controlled. Edwards *et al.*<sup>10</sup> report that the CO cleanup unit in the HotSpot methanol processor uses several small and highly selective catalytic stages instead of one large catalyst bed.

Pilot-scale CO preferential oxidation reactors have been successfully demonstrated. Thus, LANL has developed and tested a 50 kW catalyzed PrOx CO cleanup system.<sup>11</sup> A simulated methane partial oxidation reformat was used with an inlet CO concentration of 1%. The three-stage PrOx system consistently produced outlet CO concentrations below 50 ppm. Dudfield *et al.*<sup>12</sup> describe a dual-stage CO preferential oxidation reactor based upon catalyst coating of high-surface-area heat-transfer technology. The catalyst used is Pt-Ru promoted by mixed transition metal oxide. Lee *et al.*<sup>13</sup> also demonstrated a PrOx reactor using Pt-Ru/Al<sub>2</sub>O<sub>3</sub> as catalyst. The reactor adopted the dual-stage design as well, with interstage cooling and controlled air injection. It was found that for fast start-ups, the reactant temperature had to be at least 150°C and the amount of air injected should be such that the O<sub>2</sub>:CO molar ratio is ≥ 3. With these start-up procedures, it took about 3 min for the outlet CO concentration to fall below 20 ppm, experiencing a CO peak of about 2000 ppm.

Despite the fact that the PrOx technology is now universally adopted in fuel reformers, the process is, in fact, cumbersome, involving two or more stages with intercooling and distributed air or water injection. The PrOx stage is bulky as well, being roughly 10-15% of the total size of the reformer plant. There is also a relatively long reactor warm-up period and large transient CO concentration during reactor start-up. Recently, the idea of using electrochemistry for selective CO oxidation was proposed by Lakshmanan *et al.*,<sup>2</sup> based on the periodic use of an external power source. A PEM fuel cell was used as an electrochemical filter (EF) for the periodic selective oxidation of CO in H<sub>2</sub> with an external pulse

\* Electrochemical Society Student Member.

\*\* Electrochemical Society Active Member.

<sup>a</sup> Present Address: General Motors Corporation, Fuel Cell Activities, Honeoye Falls, NY 14472, USA.

<sup>z</sup> E-mail: rdatta@wpi.edu

potential control. At low potentials, the CO in reformat is allowed to adsorb on anode. Then the potential is increased to 0.6-1.0 V in order to oxidize it. While unlike in the PrOx process there is no net consumption of H<sub>2</sub>, this reaction does represent substantial *net power consumption*, because the device works like an electrochemical hydrogen pump.<sup>14</sup> A similar approach was proposed by Stimming *et al.* as well, where by periodically pulsing the fuel cell anode potential using an *external* signal generator, the fuel cell performance was improved when the anode feed contains low concentration of CO.<sup>15</sup>

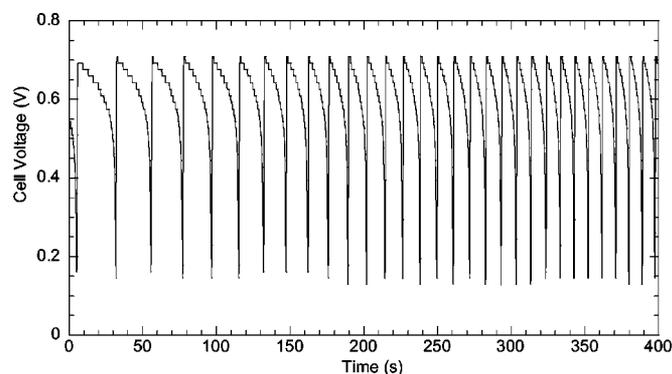
In this paper, we present an entirely novel approach involving electrochemical preferential oxidation (ECPrOx) which can effectively remove CO from reformat gas.<sup>16</sup> In addition, this ECPrOx unit can simultaneously produce some supplementary power, which can be integrated into the fuel cell power plant. The design of ECPrOx is similar, but not identical, to the conventional PEM fuel cells and exploits the strong adsorption of CO at the anode along with the use of electric potential to selectively oxidize CO with air fed at the *cathode*. The necessary electric potential in our approach is supplied *not* by an external power source but rather produced *in situ* by the potential difference established by O<sub>2</sub> reduction reaction and CO electro-oxidation as well as the hydrogen electro-oxidation reaction (HOR). The outlet CO is thus maintained at the desired level because the potential oscillates autonomously in an effort to maintain the desired current.<sup>17</sup> Experimental results that prove the feasibility of the concept of ECPrOx are presented for a single-cell device. The effect of feed CO concentration, catalyst loading, operating temperature and pressure, and humidification are investigated.

### Experimental

The basic construction of the electrochemical preferential oxidation (ECPrOx) unit is similar to a PEM fuel cell. A gas diffusion electrode loaded with 20 wt % Pt/C at a metal loading of 0.4 mg/cm<sup>2</sup>, acquired from E-TEK, was used as the cathode, while 20 wt % PtRu/C at a 0.35 mg/cm<sup>2</sup> metal loading, or 40 wt % PtRu/C at a 0.7 mg/cm<sup>2</sup> metal loading were used as the anode. The electrodes were hot-pressed onto a Nafion 117 PEM to form the membrane-electrode assembly (MEA) at 130°C and under a pressure of 4000 lbs for about 2 min.

The MEA was then incorporated into a 5 cm<sup>2</sup> single cell from ElectroChem, Inc. (Woburn, MA), and tested in a test station with temperature, pressure, humidity, and flow rate control. The graphite bipolar plate has serpentine flow channels. The ECPrOx unit was operated at the room temperature unless otherwise noted. The room temperature recorded in the laboratory varied between 25 and 30°C. The anode and cathode gases were humidified in stainless steel bottles containing water at room temperature before introduction into the unit. The total pressure of both anode and cathode sides was maintained at 30 psig except in the experiments investigating the effect of pressure. The volumetric flow rates reported in this study are in units of standard (1 atm and 25°C) cubic centimeters per min.

The current-voltage characteristics were recorded using a HP 6060B dc electronic load, interfaced with a PC using LabVIEW software (National Instruments, Austin, TX), with a data sampling rate of 0.226 s. The anode exit gas stream was monitored by a model 200 IR CO/CO<sub>2</sub> gas analyzer (California Analytical Instruments, Orange, CA). The FP-AI-100 analog input module/FP-1000 network module (National Instruments, Austin, TX) was used to collect data from the gas analyzer using LabVIEW. Simulated reformat (from premixed gas cylinder) was introduced to the anode at a flow rate controlled by a mass flow controller. A variety of feeds was tested, namely, H<sub>2</sub>/100 ppm CO, H<sub>2</sub>/200 ppm CO (MG Industries, Morrisville, PA); H<sub>2</sub>/1000 ppm CO (Spec Air, Auburn, ME); and H<sub>2</sub>/24.1% CO<sub>2</sub>/9380 ppm CO (AGA Gas, Maumee, OH). These premixed gases were used as anode feed, while oxygen was fed to the cathode.

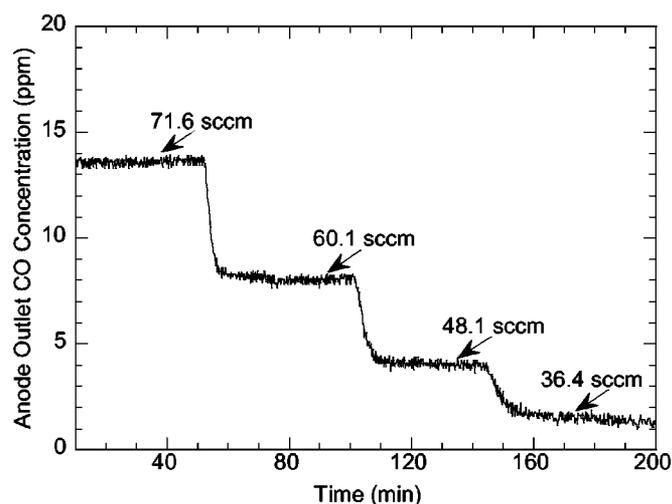


**Figure 1.** Cell voltage pattern for anode feed change from H<sub>2</sub>/200 ppm CO to H<sub>2</sub>/1000 ppm CO. Current density 100 mA/cm<sup>2</sup>; anode inlet flow rate 60.1 sccm; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

### Results and Discussion

*Proof of concept of ECPrOx.*—The electrochemical preferential oxidation (ECPrOx) is based on the recent advances in our fundamental understanding of CO electro-oxidation and CO-induced potential oscillations in PEM fuel cells.<sup>17,18</sup> It has been found that when a PEM fuel cell is operated at a constant current density and the anode feed contains low concentration of CO, the fuel cell voltage oscillates at lower temperatures (<80°C). It is further observed that the potential oscillations adjust automatically according to the CO concentration in the feed stream. For example, the cell voltage pattern when the anode feed is switched from H<sub>2</sub>/200 ppm CO to H<sub>2</sub>/1000 ppm CO is shown in Fig. 1. It can be seen that with the introduction of higher concentration of CO in the anode feed, the oscillation period decreases, *i.e.*, the oscillation becomes faster, which is predicted by our dynamic model.<sup>18</sup>

The mechanistic modeling of such potential oscillations has indicated that a significant amount of CO entering the anode is electro-oxidized on the catalyst surface.<sup>18</sup> Such a prediction is further confirmed by our experimental observations. A typical result of the anode outlet CO concentration with the step change in anode inlet flow rate is shown in Fig. 2. The anode feed is H<sub>2</sub> containing 200 ppm CO. The cell is operated at room temperature and a current density of 200 mA/cm<sup>2</sup>. It can be seen that the exit CO concentration responds quickly and is very stable over time for different inlet



**Figure 2.** Anode outlet CO concentration at different inlet flow rates. Anode feed H<sub>2</sub>/200 ppm CO; current density 200 mA/cm<sup>2</sup>; room temperature; anode 0.35 mg/cm<sup>2</sup>PtRu.

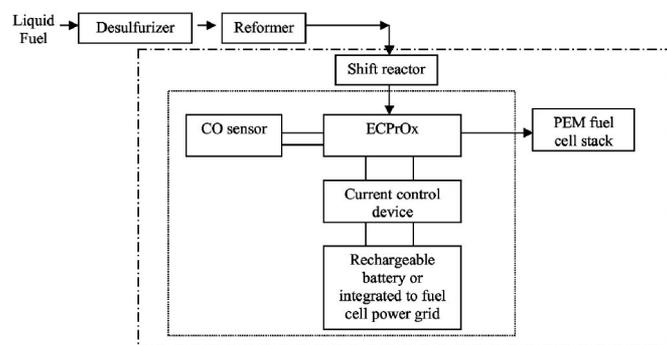


Figure 3. Schematic of reformer/PEM fuel cell system with ECPrOx unit.

flow rates. The CO concentration can be brought down to about 13 ppm at an inlet feed rate of 71.6 sccm, and below 2 ppm at 36.4 sccm for a feed containing 200 ppm CO. It is thus evident that the CO concentration in hydrogen can be reduced without resorting to an external power supply.

Based on these experimental observations, we propose the ECPrOx process for selectively removing CO from H<sub>2</sub>-rich gas by utilizing the anode potential oscillations in a device with a structure similar to that of a fuel cell. A schematic of the proposed ECPrOx unit in the overall fuel processing system is shown in Fig. 3. The ECPrOx unit has the same function as the conventional PrOx reactor. A CO sensor could be put in series with the ECPrOx exit stream to monitor the CO concentration and possibly for control. A current control device is used to control the hydrogen consumption rate and the CO conversion. The supplemental power produced by the ECPrOx unit could be stored in a rechargeable battery or integrated directly into the fuel cell power plant. The ECPrOx unit can be built in the same modular structure as PEM fuel cells. In some cases, it may even be possible to replace the low-temperature shift reactor with the ECPrOx unit.

*Performance of ECPrOx at different feed CO concentrations.*—Substantial hydrogen consumption is not desirable in the ECPrOx unit, although the H<sub>2</sub> consumed generates electrical power. In fact, there might be an optimal value of operating current in ECPrOx as far as the overall system efficiency is concerned. Hence, the preliminary results shown in this paper are obtained at low but arbitrary current densities (less than 200 mA/cm<sup>2</sup>), and without any consideration to the question of optimization of the overall system efficiency. Thus, the outlet CO concentration as a function of inlet flow rate is plotted in Fig. 4a at various current densities for an anode feed containing 1000 ppm CO. It is seen that the CO concentration increases with the inlet flow rates at a given current density. Furthermore, the outlet CO concentration decreases with an increase of the current density at a given inlet flow rate. However, these differences in exit CO concentration become increasingly small for higher current densities.

Because a two-stage ECPrOx may be required depending upon inlet CO concentration and flow rate, experiments were conducted using higher feed CO concentrations as well. Thus, a feed gas of H<sub>2</sub>/24.1% CO<sub>2</sub>/0.938% CO was also used to simulate the reformat gas stream from the LTS reactor. The exit CO concentration for this feed as a function of inlet flow rate is plotted in Fig. 4b for an anode catalyst loading of 0.7 mg/cm<sup>2</sup> PtRu. It is seen that the CO concentration can be lowered from 9380 ppm to about 140 ppm for an inlet flow rate of 21.9 sccm, and to about 500 ppm at a flow rate of 55.6 sccm, and a current density of 150 mA/cm<sup>2</sup>. Thus, in a two-stage ECPrOx, the first stage might reduce the CO level from around 10,000 to 500 ppm, while the second stage would reduce it to about 50 ppm.

It may be noticed that the trends observed in Fig. 4b are different from that for the lower CO concentration shown in Fig. 4a. This is due to transition of cell voltage between stable stationary and oscillatory states.

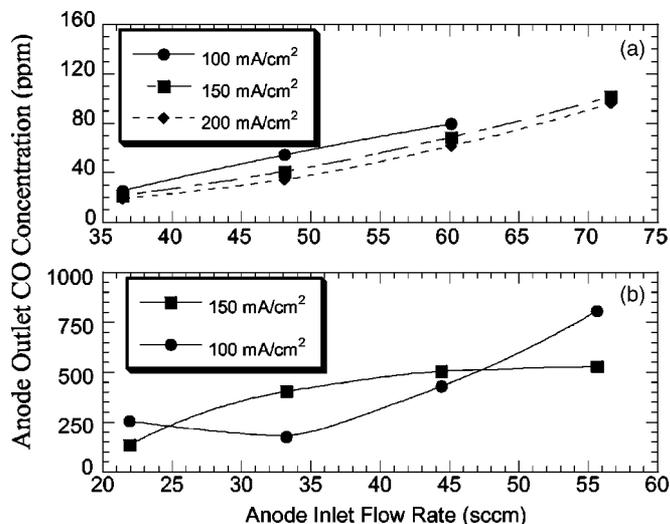
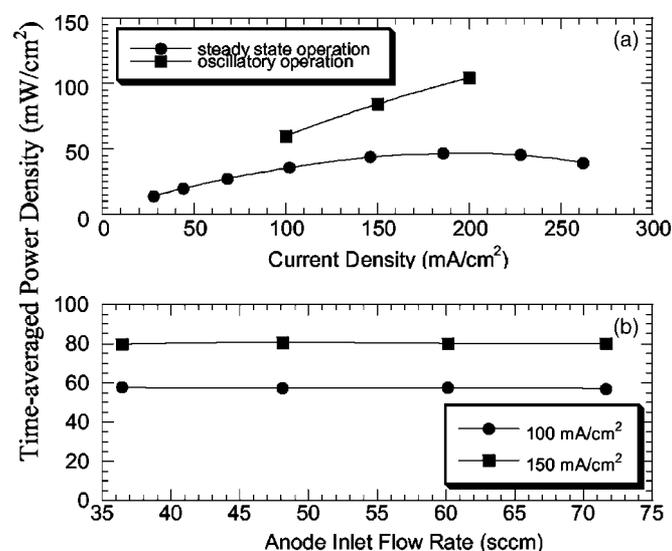


Figure 4. Anode outlet CO concentration as a function of inlet flow rates at various current densities. (a) Anode feed H<sub>2</sub>/1000 ppm CO; room temperature; anode 0.35 mg/cm<sup>2</sup> PtRu. (b) Anode feed 75% H<sub>2</sub>/24% CO<sub>2</sub>/9380 ppm CO; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

latory states. We have found that the current density and flow rates are two key parameters that affect the onset of potential oscillations.<sup>17</sup> The effect of current density on the onset of potential oscillation was consistent with our previous observation, in that oscillations appeared at larger current densities for a given inlet flow rate. However, the onset of oscillations in terms of flow rate was opposite to our earlier observations at the lower CO levels. Thus, the oscillations born at relatively smaller flow rates were suppressed when the flow rate was increased. For example, at a current density of 100 mA/cm<sup>2</sup>, oscillations disappeared when the inlet flow rates exceeded 33.2 sccm, while at a current density of 150 mA/cm<sup>2</sup>, the oscillations disappeared when the inlet flows was greater than 55.6 sccm. Due to the transition from an oscillatory state to a stable stationary one, the monotonic change in exit CO concentration with flow rates is not observed in Fig. 4b for the current density of 100 mA/cm<sup>2</sup>. The lower exit CO concentration at the stable stationary state is because the cell voltage at stable stationary states is much lower than the time-averaged cell voltage at oscillatory states (*i.e.*, the anode overpotential is higher at a stable stationary state than the time-averaged anode overpotential at oscillatory state).<sup>19</sup> The higher anode overpotential leads to a higher CO electro-oxidation rate. However, for a given state of cell operation (either oscillatory or stationary), the exit CO concentration always increases with the inlet flow rates.

Due to the high concentration of CO<sub>2</sub> (24.1%) in the feed, there is the distinct possibility for the reverse water gas shift reaction to proceed on the anode catalyst as well. However, the reverse water gas shift reaction is not favored at low temperatures both kinetically and thermodynamically. We have previously measured the steady-state outlet CO concentration of fuel cell anode fed with H<sub>2</sub>/20% CO<sub>2</sub> but without any CO. It was found that the CO concentration exiting the anode is only about 2–4 ppm when the fuel cell is operated at 80°C, even though the calculated equilibrium CO concentration is over 100 ppm under these operating conditions. Furthermore, the CO concentration in the anode exit was found to decrease with a decrease of the fuel cell temperature. Therefore, the contribution of reverse water gas shift reaction to the CO concentration in the exit of ECPrOx unit is likely to be small even though there is a significant amount of CO<sub>2</sub> (>20%) in the simulated reformat feed. Of course, the overpotential at anode promotes WGSR while constraining the reverse WGSR by virtue of the Butler-Volmer equation.

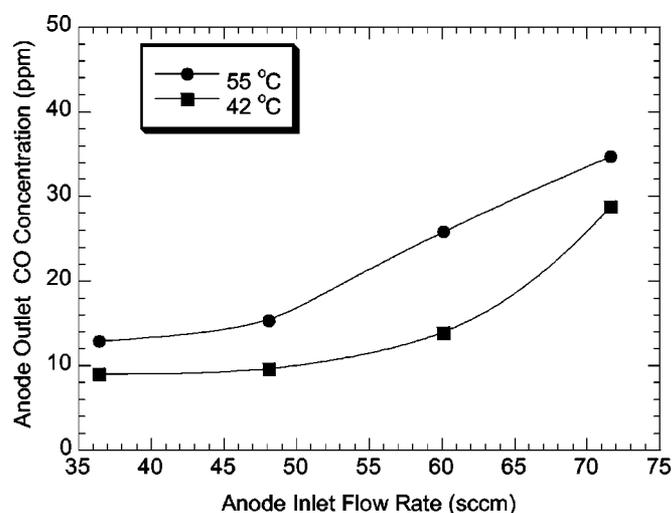


**Figure 5.** (a) Comparison of power outputs at stationary and oscillatory states. Anode feed H<sub>2</sub>/200 ppm CO; anode inlet flow rate 48.1 sccm; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu. (b) Effect of anode inlet flow rate on the time-averaged power density. Anode feed H<sub>2</sub>/1000 ppm CO; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

*Supplemental electrical power.*—As has been mentioned in the previous section, no external electrical power source is needed for the ECPrOx. On the contrary, supplemental electrical power is generated. In fact, it has been previously found by us that the power output of a PEM fuel cell operating under an oscillatory state is significantly higher than that at stable stationary state when the anode feed containing around 100 ppm CO.<sup>19</sup> Such enhanced power output was observed for higher CO concentration (e.g., 200 and 1000 ppm CO) as well in the ECPrOx operation. A comparison of the supplemental power output under stable stationary and oscillatory states at the same experimental conditions is shown in Fig. 5. It is seen in Fig. 5a (for 200 ppm CO) that the maximum power density under steady-state operation is about 47 mW/cm<sup>2</sup> at a current density of around 200 mA/cm<sup>2</sup>. However, the power output under the oscillatory state is over 100 mW/cm<sup>2</sup> and has not yet peaked. Even when the anode feed contains 1000 ppm CO (Fig. 5b), the power output under the oscillatory state does not fall appreciably even though the CO concentration in the feed has risen 5-fold. It can be further noticed that the power output at the oscillatory state does not change appreciably with inlet feed rates.

Thus, it is evident that the proposed ECPrOx process can effectively remove CO from reformat gas to produce clean hydrogen on the one hand, while also generating supplemental electrical power, which (at oscillatory state) is even higher than that at a stable stationary state at otherwise identical conditions. Although the power density is lower than that in fuel cell, such a characteristic of ECPrOx increases the overall energy efficiency of the reformer/fuel cell system.

*Effect of operating temperature.*—Figure 6 shows the exit CO concentration at two different operating temperatures. In this experiment, the anode feed is hydrogen containing 100 ppm CO. It is seen that the exit CO increases with the cell temperature, exceeding 30 ppm for an inlet flow rate of 71.6 sccm at 55°C. This indicates that lower temperature operation is preferable for ECPrOx to remove CO from the hydrogen-rich gas stream. Similar results were obtained for the feed containing 9380 ppm CO representative of that in the first stage ECPrOx. At a current density of 140 mA/cm<sup>2</sup> and a flow rate of 44.4 sccm (catalyst loading 0.35 mg/cm<sup>2</sup>), the exit CO concentration was 638 ppm at 35°C, while the exit CO concentration was above 1000 ppm (over the detection range of the gas analyzer) when the unit was operated at 80°C.



**Figure 6.** Effect of temperature on the outlet CO concentration. Anode feed H<sub>2</sub>/108 ppm CO; current density 300 mA/cm<sup>2</sup>; anode 0.35 mg/cm<sup>2</sup> PtRu.

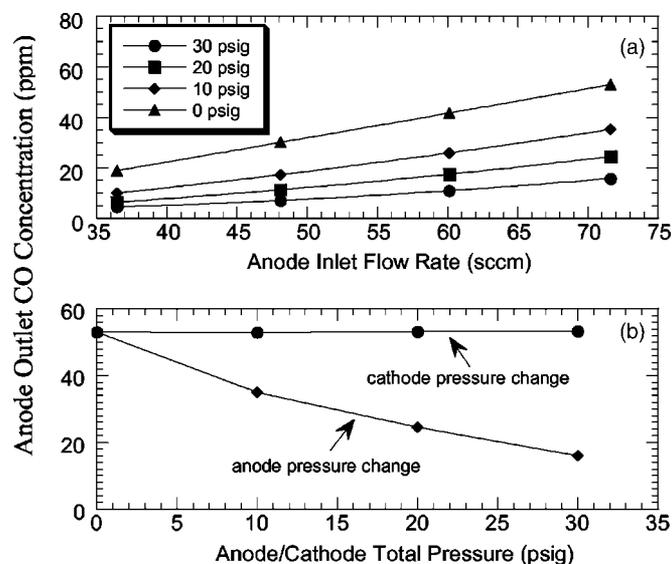
The kinetic and mechanistic study by Schubert *et al.*<sup>20</sup> showed that the selectivity of conventional CO preferential oxidation is determined by the steady-state surface coverage. Thus, there is a loss in selectivity with decreasing surface coverage of CO as CO partial pressure decreases. Similarly for ECPrOx, the CO surface coverage decreases at elevated temperatures and reduced CO partial pressures. The adsorption of CO on noble metal catalyst surface is an exothermic process, the enthalpy change being about -115 kJ/mol on Ru, and around -130 kJ/mol for Pt. The heat of adsorption decreases with an increase of surface coverage of CO, but is still about -45 kJ/mol at near saturation coverages.<sup>21</sup> Therefore, the majority of the experiments reported here were conducted at room temperature. This means that a heat exchanger would be required between the reformer and the ECPrOx to cool the reformat.

*Effect of operating pressure.*—In order to study the influence of operating pressure on the performance of ECPrOx, the total pressure of both the anode and the cathode were lowered from 30 to 0 psig in a stepwise manner while the other experimental conditions remained fixed. The corresponding exit CO concentration as a function of inlet flow rate is shown in Fig. 7a for a feed containing 200 ppm CO with the unit operated at 100 mA/cm<sup>2</sup>. It is clear that with the decrease of the operating pressure, there is a significant increase in the exit CO concentration. At a feed rate of 60.1 sccm, the CO concentration jumped from 10 ppm at 30 psig to 42 ppm at 0 psig. The increase in exit CO concentration becomes more significant as the total pressure approaches atmospheric pressure.

Because in the experiment the pressure of both electrode compartments was lowered simultaneously, further experiments were conducted to single out the effect of individual pressure change (Fig. 7b). Thus, at an inlet flow rate of 71.6 sccm, the anode pressure was fixed at 0 psig while the cathode pressure was increased stepwise from 0 to 30 psig. The anode exit CO concentration remained unchanged (Fig. 7b). However, when the cathode oxygen total pressure was fixed at 30 psig while the anode total pressure was increased in the same manner as cathode, the exit CO concentration dropped in exactly the same manner as observed in Fig. 7a. Therefore, it is evident that it is the anode pressure that is responsible for the change in exit CO concentration with varying operating pressures.

The same result was observed for a feed containing 9380 ppm CO. It is seen in Fig. 8 that at a current density of 100 mA/cm<sup>2</sup> and at a feed rate of 44.4 sccm, the exit CO concentration decreases with an increase of the anode pressure. The CO concentration thus dropped from about 680 ppm at 10 psig to about 380 ppm at 30 psig.

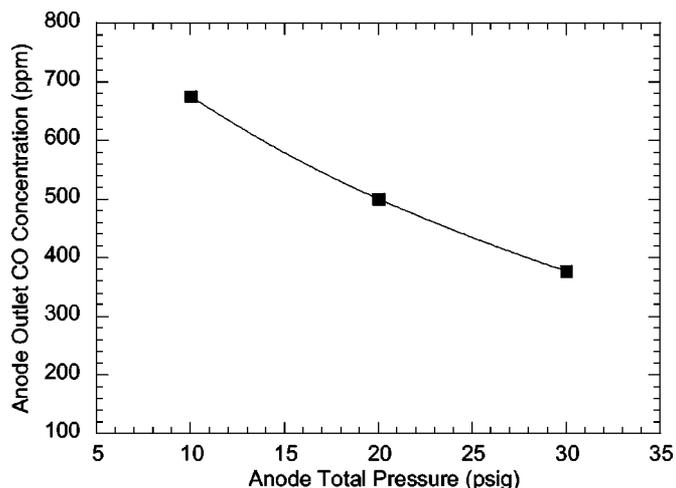
A high anode total pressure (*i.e.*, high CO partial pressure) is thus beneficial to the removal of CO from the gas stream. A high CO



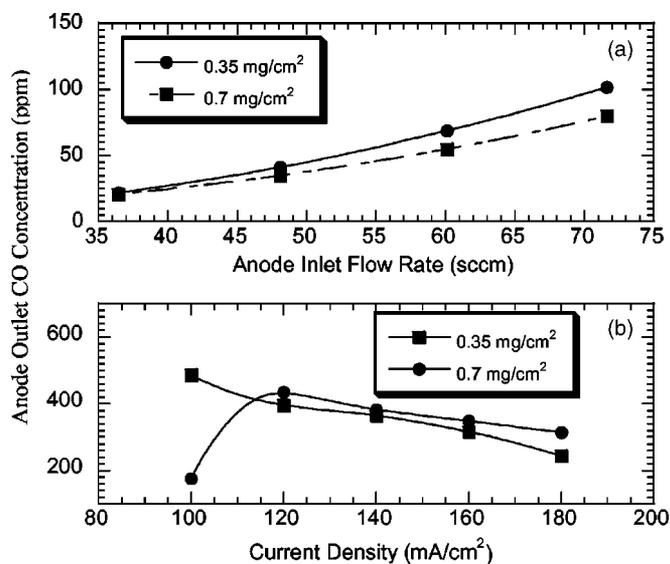
**Figure 7.** Effect of total pressure on the anode outlet CO concentration: (a) lowering the pressures of both electrodes and (b) lowering the pressure of either electrode at an anode inlet flow rate of 71.6 sccm. Other conditions: anode feed  $\text{H}_2/200$  ppm CO; current density 100 mA/cm<sup>2</sup>; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

partial pressure leads to an increase in the CO adsorption rate and a high CO surface coverage. Therefore, the CO electro-oxidation rate increases. Although we had found in our previous work that  $\text{O}_2$  permeating through the membrane from the cathode also contributed partially to the CO removal in the anode compartment,<sup>22</sup> the effect is apparently not significant for the thicker membrane (Nafion 117) used here for ECP<sub>2</sub>Ox, especially for the high CO concentration and feed rates used in the present work. Therefore, contribution of any permeating oxygen from the cathode to the removal of CO can be assumed to be negligible here. This observation also indicates that the ECP<sub>2</sub>Ox can be operated at low cathode pressures, likely with air at ambient pressure.

*Effect of catalyst loading.*—The effect of catalyst loading is shown in Fig. 9. A higher catalyst loading is beneficial in lowering the exit CO concentration. The improvement becomes more apparent at higher flow rates (Fig. 9a) and at higher inlet CO concentra-



**Figure 8.** Effect of total pressures on the outlet CO concentration. Anode feed 75%  $\text{H}_2/24\%$   $\text{CO}_2/9380$  ppm CO; anode inlet flow rate 44.4 sccm; current density 100 mA/cm<sup>2</sup>; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

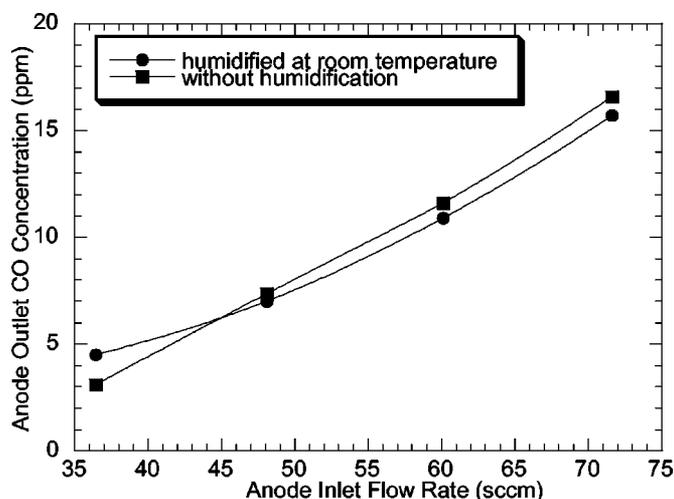


**Figure 9.** Effect of PtRu catalyst loading on the outlet CO concentration. (a) Anode feed  $\text{H}_2/1000$  ppm CO; current density 150 mA/cm<sup>2</sup>; room temperature. (b) Anode feed 75%  $\text{H}_2/24\%$   $\text{CO}_2/9380$  ppm CO; anode inlet flow rate 33.2 sccm; room temperature.

tions, typical of the first stage of the ECP<sub>2</sub>Ox. At a flow rate of 71.6 sccm, the difference in exit CO concentration is about 5 ppm for the two different catalyst loadings investigated for a feed containing 200 ppm CO (not shown in the figure). However, as shown in Fig. 9a, for a feed containing 1000 ppm CO, the difference is around 25 ppm.

The effect of catalyst loading for a feed containing 9380 ppm CO is shown in Fig. 9b. In this figure, the exit CO concentrations are compared at a given inlet flow rate but at varying current density. It is seen that at a given inlet flow rate, the exit CO concentration decreases monotonically with the increase of operating current density for catalyst loading of 0.35 mg/cm<sup>2</sup>. For this case, the cell voltage remained at a stable stationary state. However, the CO concentration experienced a large jump as current density increased from 100 to 120 mA/cm<sup>2</sup> for the case of the higher catalyst loading of 0.7 mg/cm<sup>2</sup>. This sudden concentration change is due to the transition of the cell voltage from a stable stationary state to an oscillatory state as a result of increasing current density. At the upper branch (cell voltage in oscillatory state), however, the CO concentration decreased monotonically with increasing current density, and is in fact somewhat higher than that at the lower catalyst loading. It thus appears that the trends are similar although the performance depends upon whether the unit is in a steady or oscillatory state of operation. In the oscillatory state, the CO outlet content is higher but so is the supplemental power produced. For appropriate comparison of catalyst loading, the state of operation must be the same. Thus, *e.g.*, for 100 mA/cm<sup>2</sup>, the exit CO concentration for the lower catalyst loading is more than double as compared to that for the higher loading. Thus, higher catalyst loadings are desirable, although clearly there would be an optimum. Further, the supplemental power output increases as well at higher catalyst loadings in the anode. For example, at a current density of 150 mA/cm<sup>2</sup> and a feed containing 1000 ppm CO, the average power output is 43.5 mW/cm<sup>2</sup> for a catalyst loading of 0.35 mg/cm<sup>2</sup>, while it is about 80 mW/cm<sup>2</sup> for an anode loading of 0.7 mg/cm<sup>2</sup>.

*Effect of humidification.*—The exit CO concentration was also compared with and without humidification of the feed gases at room temperature and otherwise identical experimental conditions. Thus, the anode and cathode feed were introduced directly into the ECP<sub>2</sub>Ox unit, with the humidifier bypassed, for an anode feed containing 200 ppm CO. It can be seen in Fig. 10 that the exit CO



**Figure 10.** Effect of humidification on the outlet CO concentration. Anode feed  $\text{H}_2/200$  ppm CO; current density  $100 \text{ mA/cm}^2$ ; room temperature; anode  $0.7 \text{ mg/cm}^2$  PtRu.

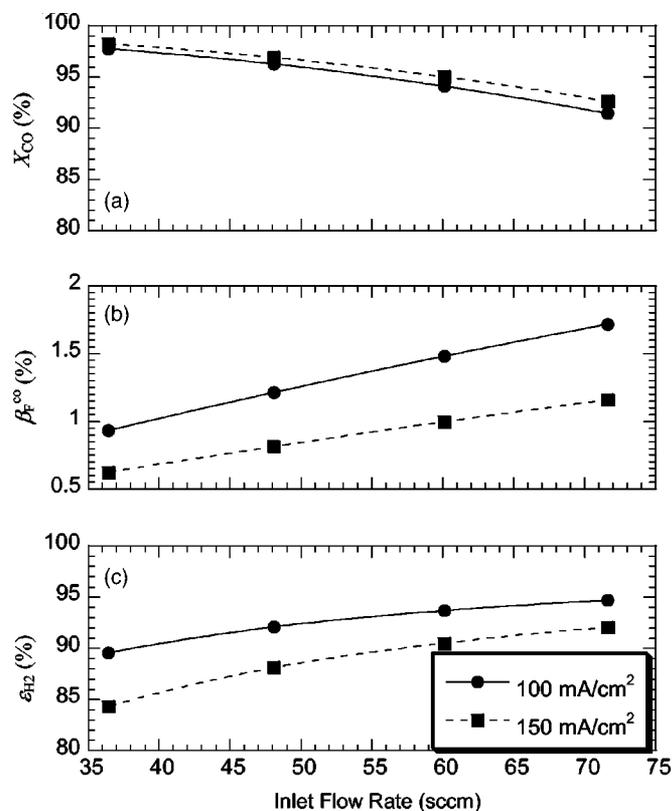
concentrations are virtually identical. This result is not surprising because even in the case of humidification at room temperature, the water partial pressure is relatively small (0.032 atm, assuming a 100% relative humidity). Thus, for this case water produced by the electrochemical reaction at the cathode is more significant in terms of contribution to the hydration of the membrane.

In the operation of PEM fuel cells, membrane resistance may increase at the anode side at larger current densities due to the dehydration of membrane when insufficient water back diffusion occurs for a thicker membrane, as has been demonstrated by Buchi and Scherer.<sup>23</sup> However, it has been shown by Slade *et al.*<sup>24</sup> that for Nafion 115 membrane, the membrane conductivity does not change appreciably with current density up to about  $1000 \text{ mA/cm}^2$ , which is well above the current densities for ECPrOx in this work ( $100$ – $200 \text{ mA/cm}^2$ ). Therefore, water transport due to any electroosmotic drag can be counterbalanced by the back-diffusion of liquid water produced at the cathode membrane-electrode interface. Furthermore, membrane hydration is not a significant concern as high current densities is not a goal here. In fact, a drier membrane may be desirable because the goal is to provide the necessary anode overpotential for CO electro-oxidation rather than high current densities. According to this logic, furthermore, thicker membranes may also be more desirable.

#### Further Discussions

*Electrochemical potential as an additional tool.*—PEM fuel cells are currently accepted as an efficient energy conversion device. When CO is present in the anode feed (using reformat as anode fuel), the fuel cell performance is seriously degraded. However, it has been shown in our previous work that there is finite CO electro-oxidation in the fuel cell anode for both Pt and PtRu anode catalysts.<sup>17,22</sup> Thus, in the proposed ECPrOx, this is exploited by rendering the preferential oxidation of CO electrochemical so that electrode potential may be used as an additional tool to control the PrOx activity and selectivity. The conventional chemical processes utilize only thermal means for enhancing reaction rate on a given catalyst. Although temperature is an extremely effective tool for rate control, there are limitations of thermodynamics, selectivity, coking, catalyst sintering, and reactor material. In particular, frequently one runs into thermodynamic limitations at elevated temperatures for exothermic reactions, so that enhanced activity and reduced equilibrium conversion must be balanced.

It so happens that in addition to temperature, electrical potential is a particularly powerful tool for controlling the rate of a reaction

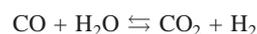


**Figure 11.** (a) CO conversion, (b) fraction of CO electro-oxidation current, and (c) hydrogen recovery as a function of inlet flow rates at two current densities. Anode feed  $\text{H}_2/1000$  ppm CO; room temperature; anode  $0.7 \text{ mg/cm}^2$  PtRu.

for electrochemical and sometimes even for nonelectrochemical reactions. The reaction that occurs in ECPrOx at anode is, in fact, the electrochemical WGS, or EWGS, reaction



which could simply be viewed as the WGS reaction



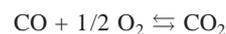
followed by the HOR, *i.e.*



At the cathode, the normal oxygen reduction reaction (ORR) occurs, namely



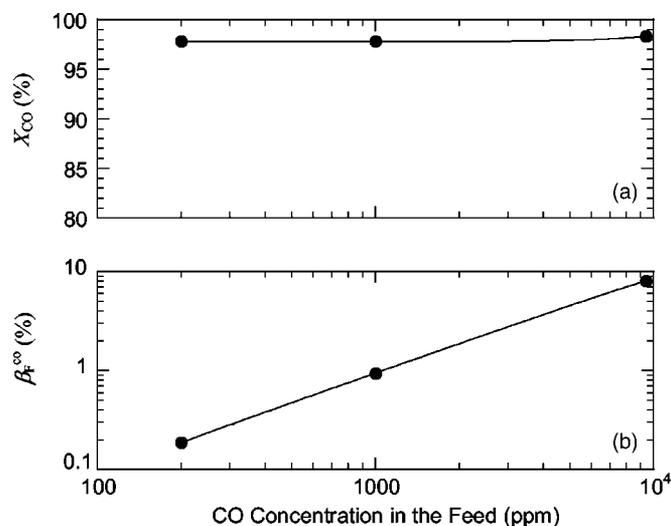
so that the overall reaction in ECPrOx is the same as in PrOx, *i.e.*, simply the CO oxidation reaction



Thus, while the overall chemistry remains unchanged, by rendering the reactions electrochemical, the additional tool of potential available in ECPrOx can be effectively utilized. Furthermore, the thermodynamics is also improved by potential as explained by the Nernst equation.

*Characterization of ECPrOx unit.*—In order to characterize and compare the performance of ECPrOx unit with the conventional PrOx reactor, three quantities are defined.

The first is CO conversion,  $X_{\text{CO}}$ , which is defined similarly to that in the PrOx reactor, and evaluated by the CO concentration entering and exiting the ECPrOx unit



**Figure 12.** (a) CO conversion and (b) fraction of CO electro-oxidation current at different CO concentrations. Anode inlet flow rate 36.4 sccm; current density 100 mA/cm<sup>2</sup>; room temperature; anode 0.7 mg/cm<sup>2</sup> PtRu.

$$X_{\text{CO}} = \frac{f_{\text{in}}x_{\text{CO,in}} - f_{\text{out}}x_{\text{CO}}}{f_{\text{in}}x_{\text{CO,in}}} \quad [1]$$

where  $f_{\text{in}}$  and  $f_{\text{out}}$  are the total molar flow rates at inlet and outlet, respectively, and  $x_{\text{CO,in}}$  and  $x_{\text{CO}}$  are the CO mole fractions in the inlet and outlet gas stream.

In ECPrOx unit, a predetermined (by the selected current density) amount of hydrogen is consumed to generate a current in order to polarize the anode. Meanwhile, CO electro-oxidation contributes to the total faradaic current drawn from the ECPrOx unit as well. Thus, the fraction of CO electro-oxidation current in the total faradaic current,  $\beta_{\text{F}}^{\text{CO}}$ , is defined as

$$\beta_{\text{F}}^{\text{CO}} = \frac{i_{\text{CO}}}{i_{\text{CO}} + i_{\text{H}_2}} = \frac{2Ff_{\text{in}}^{\text{CO}}X_{\text{CO}}}{I} \quad [2]$$

where  $f_{\text{in}}^{\text{CO}}$  is the inlet molar flow rate of CO,  $F$  is the Faraday constant, and  $I$  is the total current.

In principle, if the CO concentration is high enough, the ratio could approach one, *i.e.*, almost all the faradaic current and anode polarization is contributed from CO electro-oxidation. Then, CO may be viewed as a fuel instead of a poison.

The last factor to consider is the hydrogen recovery, defined as the ratio between the inlet and outlet hydrogen molar flow rate

$$\varepsilon_{\text{H}_2} = \frac{f_{\text{out}}^{\text{H}_2}}{f_{\text{in}}^{\text{H}_2}} = \frac{f_{\text{in}}^{\text{H}_2} - I(1 - \beta_{\text{F}}^{\text{CO}})/2F}{f_{\text{in}}^{\text{H}_2}} \quad [3]$$

Thus, the three characteristic quantities of the experimental results with 1000 ppm CO feed are illustrated in Fig. 11a-c. It can be seen in Fig. 11a that the CO conversion decreases from 98 to 92% with the increase of inlet flow rate. This is because the cell voltage does not change appreciably with inlet flow rate.

It is seen in Fig. 11b that for an anode feed containing 1000 ppm CO, the CO contribution in the overall current is only about 0.6-2%. The ratio of CO electro-oxidation current in the total current increases with the inlet flow rates. This ratio is higher as CO content of feed increases, as discussed below.

The recovery of hydrogen is predominantly determined by the operating current at a certain inlet flow rate. For a current density of 100 mA/cm<sup>2</sup>, the hydrogen recovery is between 90 and 95% in the flow rates investigated. The recovery increases with the inlet flow rate for a given current density.

The CO conversion (Fig. 12a) and CO contribution to the overall current (Fig. 12b) are also compared at 100 mA/cm<sup>2</sup> and a flow rate

of 36.4 sccm for different CO concentrations in the feed. The catalyst loading is 0.7 mg/cm<sup>2</sup>. It can be seen from Fig. 12a that the conversion of CO is nearly independent of the feed concentration. This is a special feature of the ECPrOx unit. It shows that this unit is self-regulated and naturally stable. The fraction of CO electro-oxidation current increases with the CO concentration in the feed as shown in Fig. 12b. It is seen that for a feed containing 9380 ppm CO, the contribution of CO electro-oxidation has increased to almost 10%, which is a substantial fraction of the total current drawn from the ECPrOx unit. Thus, CO can be viewed a fuel instead of poison.

Thus, we have shown that the ECPrOx can effectively remove CO from reformat gas while wasting no H<sub>2</sub> and producing a part of the power of the overall fuel cell power plant. Unlike conventional PrOx, no complex temperature or air flow control is required in order to attain desired activity and selectivity, especially for variable conditions such as those that might be encountered in automotive applications.

## Conclusions

An electrochemical preferential oxidation (ECPrOx) process is proposed here for the selective oxidation of CO from H<sub>2</sub>-rich reformat gas. This process exploits the strong adsorption of CO on the PtRu catalyst at low temperatures and the anode overpotential (in oscillatory state) to selectively electro-oxidize CO over hydrogen. In addition to the cleansing of CO, supplemental electrical power is generated from the ECPrOx device. Thus, both hydrogen and CO are not wasted but used to produce power. Room temperature and high anode pressure can facilitate CO adsorption, thus increasing the CO surface coverage and CO electro-oxidation while lowering the CO concentration in the anode exit. The cathode total pressure is found to have no effect on the performance. Further, humidification is not necessary.

With further improvement and optimization, the ECPrOx technology may be a promising alternative to the conventional preferential oxidation of CO. It is also an interesting example of utilizing electrical potential besides temperature to enhance catalytic reaction. Moreover, the electrical potential used is not supplied from an external source but is generated *in situ* and is in an autonomous oscillatory state.

Although the basic structure and construction of ECPrOx units is similar to a PEM fuel cell in that the MEA consists of a PEM flanked on either side by an electrode, the design objective is completely different. The results presented in this paper simply demonstrate the feasibility of ECPrOx, without any effort to optimize the structure or operating conditions of the device. Significant additional work is needed to optimize the design of the catalyst layer (*e.g.*, more catalyst at anode, less at cathode), the catalyst used, as well as the operating conditions.

## Acknowledgment

J.Z. gratefully acknowledges a Dr. Yoo Fellowship.

Worcester Polytechnic Institute assisted in meeting the publication costs of this article.

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