



Electrochemical Removal of Carbon Monoxide in Reformate Hydrogen for Fueling Proton Exchange Membrane Fuel Cells

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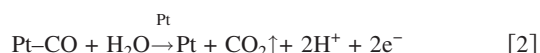
A twin-cell electrochemical filter is demonstrated to reduce the CO concentration in reformate hydrogen. In this design, the potential and gas flow are switched between the two filter cells so that alternative CO adsorption and oxidation occur in each cell while providing a continuous flow of H₂ to a fuel cell. The effects of filter switching time and applied potential on the CO concentration of gas exiting the filter are presented here for a CO concentration of 1000 ppm in nitrogen flowing at 100 cm³/min. The parasitic loss of hydrogen from a corresponding reformate stream was estimated to be 1.5%.
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Carbon monoxide (CO) in hydrogen reformed from carbon-based fuels is known to degrade the performance of a proton exchange membrane fuel cell (PEMFC) by poisoning the anode active sites, as shown in Reaction 1^{1–4}



To mitigate the detrimental effects of CO on the performance of a PEMFC, researchers have explored ways to modify fuel cell operation by using elevated temperatures (e.g., 120°C),^{5–7} air bleeding,⁸ or in situ voltage pulsing.^{9,3} Even with these techniques, fuel cells may not tolerate the concentration level of CO coming out of a reformer, which is typically 0.1–1% (1000–10,000 ppm). To reduce the CO concentration in reformate H₂ to parts per million levels, methods such as pressure swing adsorption,¹⁰ preferential oxidation,^{11–14} or catalytic methanation^{15–18} can be used. However, volume, weight, power, and fuel-efficiency penalties may be substantial when using these methods, particularly for small-scale fuel cell systems. Balasubramanian et al.¹⁹ proposed a single-cell electrochemical CO filter external to the fuel cell. This filter lowers the CO concentration by periodically oxidizing the adsorbed CO via the following reaction²



However, low exit CO concentrations and a high selectivity of CO to H₂ oxidation could not be simultaneously achieved due to the reformate continuously flowing through the filter cell during oxidation.

To achieve both low exit CO concentration and low H₂ consumption, we demonstrate here a twin-cell filter design in which the flow of the reformate and the potential are switched between two proton exchange membrane filter cells. In the adsorption mode, CO-contaminated H₂ is passed through the anode of one filter cell at open circuit. Simultaneously, a pulse potential is applied to the other filter cell, oxidizing the CO adsorbed a priori. Although hydrogen is also oxidized during pulsing, only the hydrogen confined to the anode compartment is lost. Here, we show the effect of switching time and applied potential on the concentration of CO in a gas exiting the filter cells. The stream tested here is 1000 ppm CO in nitrogen to isolate and to analyze the adsorption and oxidation rates of CO.

Experimental

Filter cell construction.—The electrodes (E-TEK) used in the filter cells had an active area of 10 cm² and a catalyst loading of 0.5 mg/cm² of platinum. The channels in the anode flow fields had a volume of 0.458 cm³. The membrane electrode assemblies for the filter cells were prepared as described previously.¹⁹ The gas flow, temperature, and pressure were controlled using a test station and hardware from Fuel Cell Technologies, Inc. All experiments were carried out at 25°C and 1 atm. A CO concentration of 1000 ppm in N₂ with no humidification flowing at 100 cm³/min was used as the CO source for the anode. The cathode, with fully humidified 4% H₂/N₂ gas flowing at 40 cm³/min, acted as the counter and reference electrodes. All the gases used were procured from Praxair, Inc. The CO concentration in the gas stream was quantified using an online gas chromatograph (Buck Scientific, model 910) equipped with a calibrated flame ionization detector. The electrochemical experiments were carried out with a potentiostat (Bio-Logic, model VMP3).

CO-SCV.—CO stripping cyclic voltammetry (CO-SCV) was used to quantify and remove the CO adsorbed on the anode of the filter cell. This was done by scanning the filter anode between 0.05 and 1.0 V for two cycles at a rate of 50 mV/s. The adsorbed CO was quantified by integrating the charge under the CO oxidation peak corrected for the background current.^{20–22}

CO breakthrough curve.—The CO breakthrough curves were generated by exposing a CO-free filter cell at open circuit to CO/N₂ for a period of time (i.e., adsorption time) and by analyzing the gas exiting the filter anode for CO concentration using a gas chromatograph flame ionization detector (GC-FID). Then, the CO adsorbed on the filter anode was quantified using CO-SCV. After removing the adsorbed CO by CO-SCV, the experiment was repeated for different adsorption times.

CO oxidation.—To understand the effect of the applied pulse potential during the oxidation mode, the filter anode was exposed to CO/N₂ for a period of time. Then, a pulse potential was applied for the same period of time, and the current response was monitored during the period. After the pulse, the CO adsorbed on the filter anode was quantified using CO-SCV. This experiment was repeated for pulses of different potentials.

Filter operation.—To demonstrate the filter operation, a CO/N₂ stream was fed to the anodes of the two filter cells, and the anode exits were connected to the GC-FID. A relay mechanism was used to switch gas flow between the filters and to synchronize the adsorption and oxidation modes of the filters according to a preset switching

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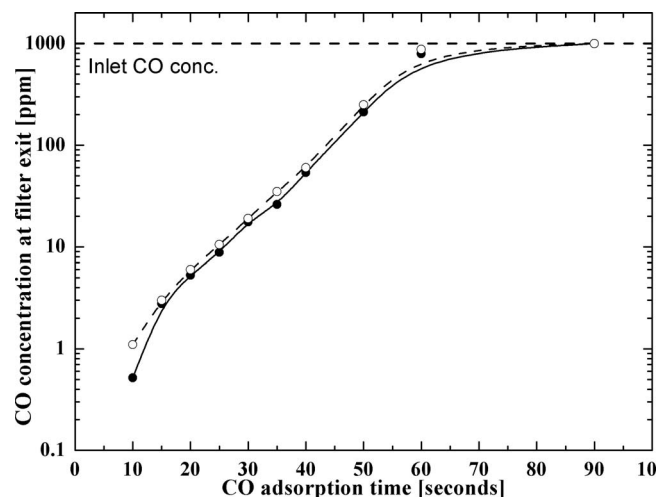


Figure 1. CO concentration at the anode exit of the filter cells measured as a function of adsorption time of 1000 ppm of CO/N₂ flowing at 100 cm³/min, 25°C, and 1 atm (closed symbols, filter 1; open symbols, filter 2).

time. The synchronized twin-cell filter experiments were carried out for different switching times and for a fixed oxidation potential.

Results and Discussion

CO breakthrough curve.—The CO breakthrough curves for each of the two filter cells are shown in Fig. 1. The concentration of CO in the exit stream increased from approximately 1 ppm after 10 s to 10 ppm after 20 s and, finally, to 1000 ppm (i.e., inlet concentration) after 90 s. The difference between the inlet and exit CO concentrations, as measured by the GC-FID, was equal to the amount of adsorbed CO estimated from CO-SCV, confirming the accuracy of the data. The breakthrough curves for CO in N₂ were similar to those for CO in H₂, confirming that CO adsorption is not greatly affected by the presence of H₂. This is consistent with Vogel et al.,²³ who showed that CO adsorption dominates hydrogen adsorption at low temperatures. The net CO adsorption capacity of each filter anode, as determined from CO-SCV from a CO saturated filter anode, was 4.65 μmol (0.465 μmol/cm²). An ideal filter, with no resistance to diffusion and adsorption, would adsorb all CO molecules entering the filter before any CO molecule exits the filter. Hence, a step change in the exit CO concentration from zero to the inlet concentration would be observed. For these filter cells under these flow conditions, the step change would have occurred after 60 s. The observed exponential increase in the exit CO concentration before reaching a steady-state value indicates a finite CO diffusion and adsorption rate. For an adsorption time of 20 s, the exit CO concentration was less than 10 ppm, and the corresponding coverage of the active sites was 0.155 μmol/cm², which was 33% of the CO adsorption capacity. Therefore, 20 s was chosen as the base case switching condition for demonstrating filter operation.

CO oxidation.—To determine the suitable pulse potential for a switching time of 20 s, the oxidation experiments were carried out for 20 s pulses of potentials 0.65, 0.7, and 0.75 V followed by CO-SCV. Figure 2 shows the current response of the filter anode, which was pre-exposed to CO/N₂ for 20 s. The current response shows two major features: (i) The initial sharp decline observed in the first 0.5 s is mainly attributed to the charging of the electrode double-layer capacitance, and (ii) the current decay afterward is attributed to the CO oxidation current. The amount of CO not oxidized by the pulse was quantified by integrating the CO oxidation peak from the CO-SCV results. The inset in Fig. 2 compares the CO left on the anode after the pulse to the initial CO adsorbed on the anode after 20 s of adsorption. Pulses of 0.65 and 0.7 V oxidized 85

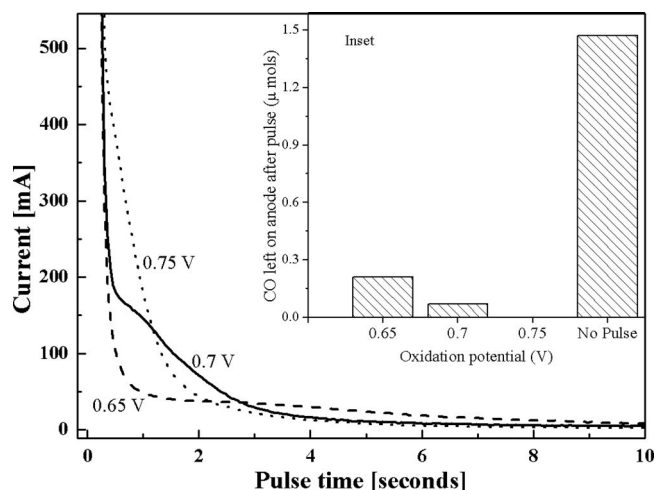


Figure 2. Current response of the filter anode exposed to 1000 ppm of CO/N₂ for 20 s at 100 cm³/min flow rate, 25°C, and 1 atm for different oxidation potentials of 0.65, 0.7, and 0.75 V vs 4% H₂/N₂ at the cathode. The inset compares the CO left adsorbed on the filter anode immediately after the pulse and when no pulse was applied.

and 95% of the CO adsorbed in 20 s, respectively, whereas a 0.75 V pulse oxidized the entire CO adsorbed. Because a complete removal of adsorbed CO occurred at 0.75 V, this was chosen as the oxidation potential for filter demonstration.

Filter operation.—To evaluate a continuous filtering of CO in a stream, two filter cells were connected. The filter was operated at a pulse potential of 0.75 V and at different switching times of 10, 20, and 30 s to see if the concentration of CO in a continuous stream of CO/N₂ can be controlled using the twin-cell electrochemical filter design. The gas was sampled and analyzed with GC-FID at the end of the adsorption time of a cycle, in which the CO concentration was maxima, and the results were plotted (see Fig. 3). For 20 and 30 s switching times, the exit CO concentration was around 10 and 40 ppm, respectively, which was consistent with the adsorption breakthrough curve (see Fig. 1). The steady concentration indicates the recyclability of active sites during the oxidation mode. However, for the 10 s switching time, the CO concentration increased from less

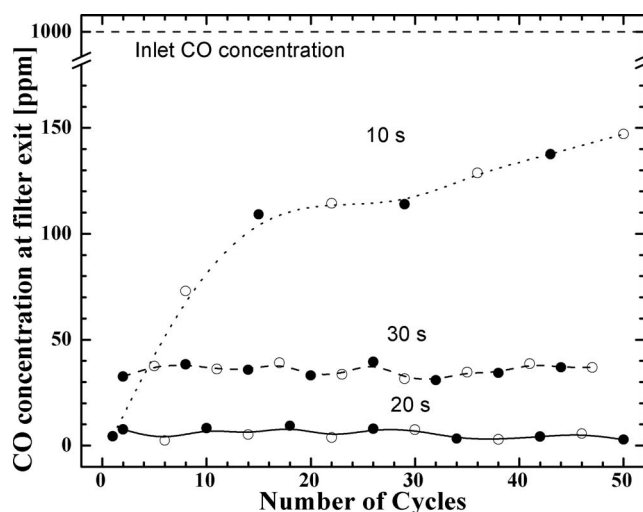


Figure 3. CO concentration of the gas exiting the filter operated with a pulse potential of 0.75 V vs 4% H₂/N₂ at the cathode. The inlet CO concentration was 1000 ppm in N₂ flowing at 100 cm³/min for different switching times at 25°C and 1 atm (closed symbols, filter 1; open symbols, filter 2).

than 10 ppm after the first cycle to 150 ppm with continuous operation. Despite a shorter adsorption time, the increase in the exit CO concentration was attributed to the incomplete recovery of the active sites through the oxidation of the adsorbed CO. The incomplete recovery of the active sites led to a decrease in the CO adsorption capacity of the filter during the adsorption mode with time. Despite the oxidation of most of the CO in the first 10 s (see Fig. 2), the CO oxidized and the active sites recovered in the last 10 s are important for a steady filter performance. The filter performance for 20 and 30 s switching times shows the importance of adsorption time in achieving the desired CO concentration, whereas the 10 s switching time shows the limitation of a low switching time in recovering the electrode active sites during oxidation.

The difference between filtering CO from H₂ and filtering CO from N₂ is the additional oxidation due to hydrogen. However, only H₂ trapped in the cell during the oxidation step is consumed. Therefore, the parasitic loss of H₂ from a reformat stream can be calculated from the operating parameters of the filter and fuel cells. Consider, for example, a twin-cell filter for removing CO from a reformat stream (50% H₂, 1000 ppm CO, and balance inert gases) feeding a fuel cell. Assume that each filter cell has the same active area as the fuel cell, so the ratio of the twin-cell filter area to the fuel cell stack area is 2:1. Furthermore, assume that the fuel cell runs at 85% utilization and at a current density of 0.6 A/cm². Therefore, the flow of hydrogen through the filter and the fuel cell is 3.7 μmol/cm² s. For a filter operating as demonstrated here (i.e., switching time of 20 s), the average CO oxidation rate is 0.00775 μmol/cm² s (i.e., 0.155 μmol CO/cm² divided by 20 s). Hydrogen oxidation involves hydrogen atoms adsorbed onto 67% of the active sites, those not covered by CO (0.155 μmol H₂/cm²), and hydrogen in the gas phase (1.02 μmol H₂/cm² because, for this reformat stream, 10.2 μmol H₂ occupies the 0.458 cm³ volume of the 10 cm² cell). Therefore, the average hydrogen oxidation rate is 0.0588 μmol/cm² s, and the CO:H₂ selectivity is 1:7.6 (i.e., 0.00775:0.0588). This corresponds to a loss of ~1.5% of hydrogen in the reformat stream. If the reformat stream was a more realistic 0.5% CO (5000 ppm), and the capacity per area of the filter was increased by a reasonable factor of 5, the loss of hydrogen would still be less than 5%.

Conclusions

We demonstrated a twin-cell filter design to decrease the CO concentration in nitrogen from 1000 to 10 ppm in a gas stream flowing at 100 cm³/min through 10 cm² filter cells. It was observed that the performance of the filter is usually determinable from the

adsorption breakthrough curve. For example, the exit CO concentration decreased with a decrease in switching time from 30 to 20 s, consistent with the breakthrough curve. However, a limit is reached such that a small switching time is not sufficient to remove CO during the oxidation step. Therefore, at a switching time of 10 s, the CO concentration exiting the filter eventually surpassed that of the 20 s switching time. The parasitic loss of hydrogen from a corresponding reformat stream was estimated to be 1.5%.

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References

1. J. W. Ha, J. H. Jang, J. H. Gil, and S. H. Kim, *Int. J. Hydrogen Energy*, **33**, 2059 (2008).
2. H. F. Oetjen, V. M. Schmidt, U. Stimming, and F. Trila, *J. Electrochem. Soc.*, **143**, 3838 (1996).
3. L. P. L. Carrette, K. A. Friedrich, M. Huber, and U. Stimming, *Phys. Chem. Chem. Phys.*, **3**, 320 (2001).
4. J. J. Baschuk and X. Li, *Int. J. Energy Res.*, **25**, 695 (2001).
5. S. J. Lee, S. Mukerjee, E. A. Ticianelli, and J. McBreen, *Electrochim. Acta*, **44**, 3283 (1999).
6. B. Lakshmanan, W. Huang, D. Olmeijer, and J. W. Weidner, *Electrochem. Solid-State Lett.*, **6**, A282 (2003).
7. Y. Song, J. M. Fenton, H. R. Kunz, L. J. Bonville, and M. V. Williams, *J. Electrochem. Soc.*, **152**, A539 (2005).
8. S. Gottesfeld and J. Pafford, *J. Electrochem. Soc.*, **135**, 2651 (1988).
9. P. S. Fedkiw, C. L. Traynelis, and S.-R. Wang, *J. Electrochem. Soc.*, **135**, 2459 (1988).
10. E. H. Majlan, W. R. W. Daud, S. E. Iyuke, A. B. Mohamad, A. A. H. Kadhun, A. W. Mohammad, M. S. Takriff, and N. Bahaman, *Int. J. Hydrogen Energy*, **34**, 2771 (2009).
11. S. H. Oh and R. M. Sinkevitch, *J. Catal.*, **142**, 254 (1993).
12. C. D. Dudfield, R. Chen, and P. L. Adcock, *Int. J. Hydrogen Energy*, **26**, 763 (2001).
13. M. Echigo and T. Tabata, *Appl. Catal., A*, **251**, 157 (2003).
14. A. Manasilp and E. Gulari, *Appl. Catal., B*, **37**, 17 (2002).
15. S. Kasaoka, E. Sasaoka, Y. Okazaki, and M. Hanaya, *Kagaku Kogaku Ronbunshu*, **17**, 732 (1991).
16. M. A. Vannice, *J. Catal.*, **37**, 462 (1975).
17. J. L. Bousquet and S. J. Teichner, *Bull. Soc. Chim. Fr.*, **10**, 3687 (1972).
18. M. Echigo and T. Tabata, *J. Chem. Eng. Jpn.*, **37**, 75 (2004).
19. B. Lakshmanan, W. Huang, and J. W. Weidner, *Electrochem. Solid-State Lett.*, **5**, A267 (2002).
20. H. A. Gasteiger, N. Markovic, P. N. Ross, and E. J. Cairns, *J. Phys. Chem.*, **98**, 617 (1994).
21. T. Vidakovic, M. Christov, and K. Sundmacher, *Electrochim. Acta*, **52**, 5606 (2007).
22. V. A. Sethuraman, B. Lakshmanan, and J. W. Weidner, *Electrochim. Acta*, **54**, 5492 (2009).
23. W. Vogel, L. Lundquist, P. Ross, and P. Stonehart, *Electrochim. Acta*, **20**, 79 (1975).