

Removal of Carbon Monoxide from Reformate for Polymer Electrolyte Fuel Cell Application

by

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[Introduction](#)

[Experimental](#)

[Results and Discussion](#)

[Conclusions](#)

[Acknowledgment](#)

[References](#)

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INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are being actively developed worldwide for transportation applications. The fuel gas generated from reforming hydrocarbon fuels contains small amounts of carbon monoxide (CO) (0.5-1 vol%), even after the water-gas shift reaction. Carbon monoxide is preferentially adsorbed on the platinum electrocatalyst in the PEFC, thus blocking the access of H₂ to the surface of the catalyst and resulting in the degradation of the cell performance. Therefore, the CO concentration in the PEFC reformate must be reduced to a tolerable level of 100 ppm (1). Catalytic preferential oxidation (2), anode air bleed (3), or a combination of the two can be used to reduce CO to trace levels, but their use in a dynamically varying system is problematic. We are developing a sorption process based on the reversible complex-forming and dissociation reactions of CO with Cu(I). These reactions are well documented in patent and literature (4,5).

EXPERIMENTAL

We have studied the CO sorption/desorption characteristics of two types of porous, high-surface-area, solid supports (designated as A and B) on which CuCl is dispersed or reacted. The sorbent

was tested at atmospheric pressure and at temperatures ranging from 25 to 250°C for CO uptake in a thermogravimetric analyzer (TGA) with a synthetic reformat test gas containing 30-50% H₂, 12-19% CO₂, 3-14% CO, and the rest N₂. In the TGA test, the sorbent was first exposed in the same reformat test gas but without CO until the constant weight of the sorbent is established. Then, we switched to the test gas that contained a controlled amount of CO. The increase in weight of the sorbent represents the amount of CO uptake. When the weight gain reached a plateau, we switched back to the test gas without CO; the sorbent lost weight because of desorption of the adsorbed CO.

A dynamic column test setup was also constructed to demonstrate the capability of this sorption process to reduce CO to 100 ppm. The 1.9-cm o.d. x 1.17-m-long (3/4-in. o.d. x 46-in.-long) column was packed with 0.16-cm o.d. x 0.32- to 0.95-cm-long (1/16-in. o.d. x 1/8- to 3/8-in.-long) sorbent extrudates and was heated by a three-zone clamshell-type furnace. It was tested with a simulated reformat gas mixture containing 49% H₂, 19% CO₂, 1% CO, 0-25% H₂O vapor, and the rest N₂. After the CO sorption cycle, the column is regenerated using a gas containing 12% H₂, 31% CO₂, 0-25% H₂O vapor, and the rest N₂ to simulate the anode exhaust of the PEFC. The column exit gas is analyzed by an on-line CO analyzer for CO breakthrough from the column.

RESULTS AND DISCUSSION

TGA Tests for CO Sorption/Desorption

Figure 1 shows TGA thermograms for sorbent B tested with 3 vol% CO at temperatures ranging from room temperature to 150°C. These thermograms show rapid sorption of CO by the sorbent, as well as CO desorption from the sorbent by the gas mixture containing no CO. The rate and amount of CO sorption by sorbent B increase with increasing temperature.

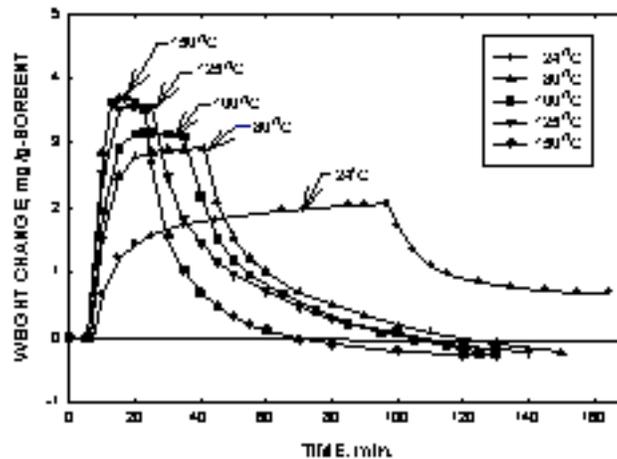


Fig. 1. TGA Thermograms for Sorbent C Showing CO Sorption and Desorption as a Function of Temperature. Test gas contained 3% CO.

Effect of Temperature. Figure 2 summarizes the CO sorption capacity as a function of temperature for both sorbents A and B tested with 3% CO. For sorbent A, two different CuCl dispersion methods were used. One sample had significantly higher CO sorption capacity than the other, indicating the influence of the technique used to disperse CuCl on the surface of the substrate. However, both samples showed that the amount of CO uptake decreased with increasing temperature, and that CuCl lost its CO sorption capability at about 200°C. In contrast, the CO sorption capacity of sorbent B increased with increasing temperature up to 150°C and then decreased slightly at higher temperatures. These results indicate that a combination of sorbents A and B offers the potential for high CO sorption capacities over a wide temperature range from room temperature to 250°C.

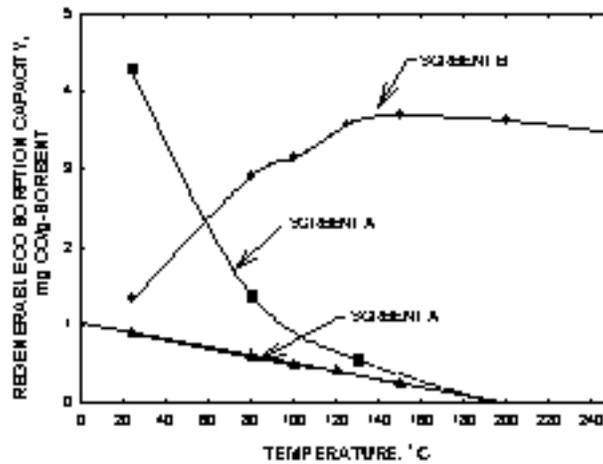


Fig. 2. CO Sorption Capacity as a Function of Temperature for Sorbents A and B.

Two different dispersion methods were tested with sorbent A.

Effect of CO Partial Pressure. Although the CO concentration in reformat varies from 0.5 to 1.0 vol% after the water-gas shift reaction, it can significantly increase when the vehicle is operated in transient conditions. To protect the fuel cell, the CO cleanup device should be capable of handling a wide range of inlet CO concentrations. Therefore, sorbent B was tested as a function of CO partial pressure to study its effect on the CO sorption capacity. The results are shown in Fig. 3. The CO sorption capacities of the sorbent increased with increasing CO partial pressure over temperatures ranging from room temperature to 250°C. These results show that the CO sorption capacity increases significantly with increasing inlet CO concentrations, at least from 0 to 3% CO.

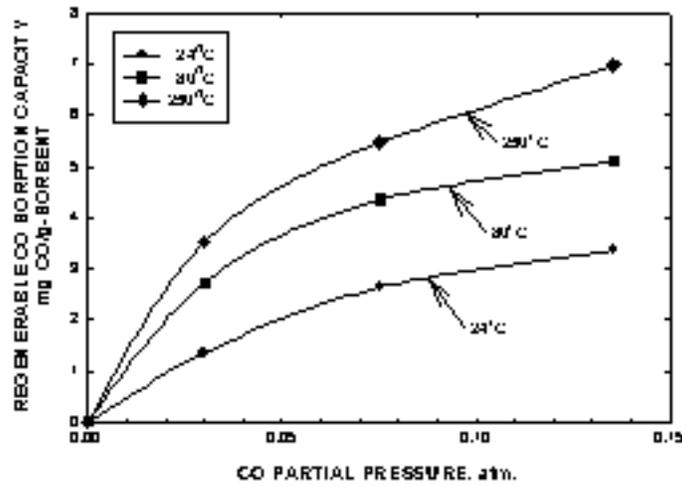


Fig. 3. CO Sorption Capacity as a Function of CO: Partial Pressure at Three Different Temperatures

Sorbent Stability. A useful sorbent needs to be stable in terms of CO sorption/desorption cycling. For this investigation, sorbent B was tested with 3 vol% CO at 250°C for 10 repeated CO sorption/desorption cycles. Figure 4 is a plot of CO sorption capacity as a function of sorption/desorption cycle number. Within the limits of experimental and analytical errors, the sorption capacity of the sorbent remains reasonably constant over the 10 cycles, showing that the sorbent is stable with repeated cycling.

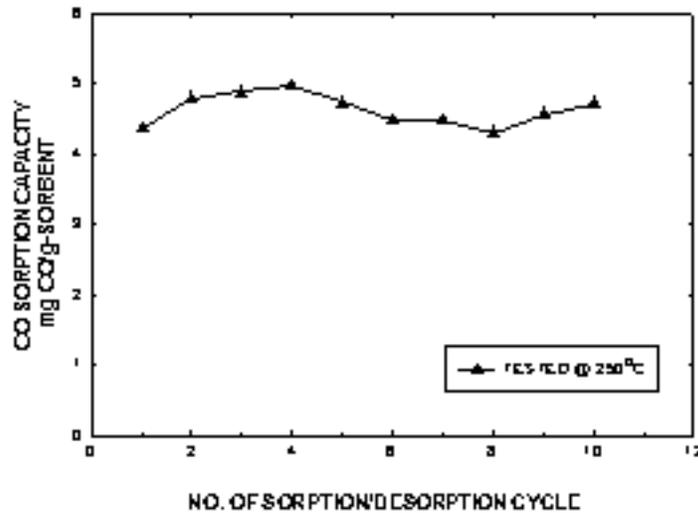


Fig. 4. CO Sorption Capacity of Sorbent B as a Function of Sorption/Desorption Cycling

Dynamic Column Tests

With the promising TGA test results shown above, a dynamic column of sorbent B was tested at 25 and 110°C to obtain breakthrough data for verifying the sorption process to reduce CO to 100 ppm.

25°C Test. Figure 5 is the CO breakthrough/desorption curve for the 25°C test. After the CO analyzer was calibrated with dry test gas containing 1% CO, the test gas was switched to the dynamic column at 9:23. The flow rate was 250 mL/min. As shown in Fig. 5, the 1% CO in the test gas was totally captured until the CO started to breakthrough the column at 11:12. This indicates that the column had achieved 100 ppm CO in the column exit for a breakthrough time of 105 min. After breakthrough, the CO concentration rapidly increased and reached a plateau of 1% CO. At 13:36, the column was switched to the regeneration gas, and the captured CO started to release from the column, as shown in the desorption curve. This test demonstrated that the column possesses the instantaneous cold-start capability at room temperature to reduce 1% CO to <100 ppm.

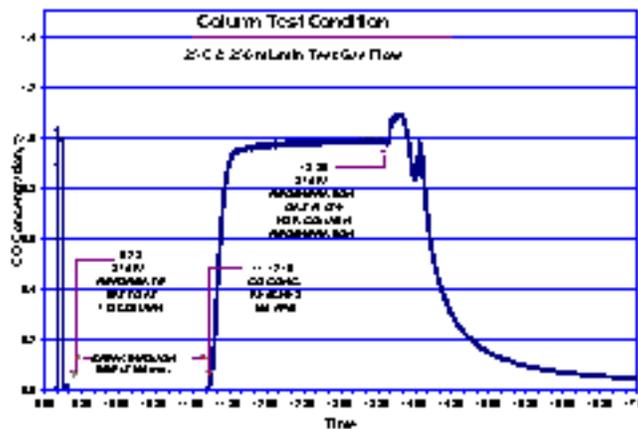


Fig. 5. CO Breakthrough/Desorption Curve for 25°C Test.

At the test gas flow rate of 250 mL/min, the CO broke through after 105 min.

110°C Test. The column was further tested at 110°C with the wet (25 vol% water vapor) test gas containing 1% CO, as shown in Fig. 6. For this test, the flow rate was 560 mL/min. The CO was totally captured by the column for a breakthrough time of 80 min. This shorter breakthrough time was expected because the flow rate used in this test was twice as high as in the 25°C test. As observed in the 25°C test, the CO concentration rapidly increased after breakthrough, and the column was easily regenerated by the wet (25% water vapor) regeneration gas. (The regeneration was begun when the exit gas reached 0.44% CO.) This test further demonstrated the sorbent's capability of dynamic removal of CO to <100 ppm in the temperature range of the PEFC fuel cell.

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