We studied the operation of a twin-cell electrochemical filter for removing carbon monoxide (CO) from reformate hydrogen by periodically adsorbing and then electrochemically oxidizing CO on the electrode. During the adsorption step, we studied the effects of feed CO concentration, flow rate, electrode catalyst loading, type of feeder gas, and temperature on CO breakthrough. We then applied a fixed bed adsorber model to show that the breakthrough time could be accurately correlated to the adsorption-step operating parameters. Since the oxidation step was found to be much faster than that for CO breakthrough, adsorption time should dictate switching time. This insight was used to predict steady-state filter performance, and the prediction was validated for an electrochemical filter operated with CO contaminated hydrogen to decrease the CO concentration from 10,000 to 10 ppm. The model was also used to explore the employability of an electrochemical filter over a range of operating conditions by considering the comparative electrode area of a filter with that of a fuel cell.

## Theory

In the twin-cell filter design (Figure 1), two electrochemical cells (F-1 and F-2) undergo alternating cycles of CO adsorption and electro-oxidation. During adsorption mode, CO contaminated reformate H2 is passed into the anode chamber of F-1 at open circuit. Carbon monoxide in reformate adsorbs onto the catalyst (e.g., Pt) as in the reaction 1.

\[
\text{Pt} + \text{CO} \rightarrow \text{Pt} - \text{CO}
\]

The gas exiting the anode of F-1 would have decreased levels of CO concentration due to CO adsorption on the catalyst sites. After a certain duration (which we will refer to as the switching time), we periodically adsorbing and then electrochemically oxidizing CO on the electrode. During the adsorption step, we studied the effects of feed CO concentration, flow rate, electrode catalyst loading, type of feeder gas, and temperature on CO breakthrough. We then applied a fixed bed adsorber model to show that the breakthrough time could be accurately correlated to the adsorption-step operating parameters. Since the oxidation step was found to be much faster than that for CO breakthrough, adsorption time should dictate switching time. This insight was used to predict steady-state filter performance, and the prediction was validated for an electrochemical filter operated with CO contaminated hydrogen to decrease the CO concentration from 10,000 to 10 ppm. The model was also used to explore the employability of an electrochemical filter over a range of operating conditions by considering the comparative electrode area of a filter with that of a fuel cell.

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the reformate flow is switched to F-2 for CO adsorption, while a potential pulse is applied to F-1 for oxidizing the adsorbed CO from the previous cycle. The switching time between the cycles of adsorption and oxidation is chosen such that the CO concentration at the filter exit is always maintained at a desirable level for fuel-cell operation. The applied potential is chosen to ensure that Pt anodes are regenerated for continuous operation of filter cells. The application of potential pulse oxidizes the adsorbed CO as in reaction 2.

\[ \text{Pt} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Pt} + \text{CO}_2 + 2\text{H}^+ + 2e^- \]  

[2]

The oxidation of CO trapped during filter adsorption mode leads to the regeneration of Pt sites for CO adsorption during the adsorption mode of the next cycle. During the oxidation mode, H₂ co-adsorbed or present as gas in the anode compartment also undergoes oxidation as in the reaction 3.

\[ \text{H}_2 \xrightarrow{\text{in}} 2\text{H}^+ + 2e^- \]  

[3]

The corresponding cathode reaction is,

\[ 2\text{H}^+ + 2e^- \xrightarrow{\text{in}} \text{H}_2 \]  

[4]

The H₂ generated at the filter cell’s cathode can be sent back to fuel cell with no loss of H₂ as is the case of catalytic methanation or preferential oxidation. Alternatively, oxygen (or air) could also be fed to the filter cathode (as in Figure 1) and the resulting oxygen reduction reaction at the filter cathode would then lower the operating potential of the filter, but will result in a net consumption of hydrogen. The choice of the cathode feed would probably be application specific, and is beyond the scope of this paper.

Fixed bed adsorber model.— The cell during CO adsorption on the Pt anode is modeled as a fixed bed adsorber under isothermal conditions. Assuming axial dispersion and porosity effects are negligible, a differential material balance for CO concentration along the serpentine channels of the filter is written as (variables are defined in the List of Symbols),

\[ \frac{\partial C}{\partial t} + \frac{v}{L} \frac{\partial C}{\partial z} + \frac{Q}{L} \frac{\partial Q}{\partial t} = 0 \]  

[5]

\[ C = 0, \quad \text{at } t = 0, \text{ for all } z \]  

[6]

\[ C = C_{in}, \quad \text{at } z = 0, \text{ for all } t \]  

[7]

\[ Q = 0, \quad \text{at } t = 0, \text{ for all } z \]  

[8]

The rate of CO adsorption is limited by various resistances: external film diffusion resistance, internal pore diffusion resistance, surface diffusion resistance and surface adsorption kinetic resistance. A sum of all of these resistances that impede the adsorption of CO can be represented by a parameter \( 1/k \). Assuming a linear relation between gas phase CO concentration (\( C \)) and adsorbed phase CO concentration (\( Q \)), the adsorption rate equation is then written as

\[ \frac{\partial Q}{\partial t} = k \left( C - Q \right) \]  

[9]

Rewriting the governing Equations 5 and 9 in dimensionless form with normalized concentrations of CO in gas phase (\( c = C/C_{in} \)) and adsorbed phase (\( \theta = Q/Q^* \)) in reference to inlet gas concentration (\( C_{in} \)) and saturated adsorbed phase CO concentration (\( Q^* \)), respectively, results in,

\[ \frac{\partial \theta}{\partial \tau} + \frac{c}{z} \frac{\partial \theta}{\partial \xi} = 0 \]  

[10a]

\[ \frac{\partial c}{\partial \xi} = -\xi_L \left( c - \theta \right) \]  

[10b]

\( Q^* \) is estimated from stripping cyclic voltammogram (SCV) of a CO saturated electrode as described in the Experimental section and also in the reference.⁴² \( \tau \) and \( \xi \) are dimensionless time and channel length variables and are defined as,

\[ \tau = k \left( t - \frac{z}{v} \right) \]  

[11]

\[ \xi = \frac{Q}{C_{in}} \left( \frac{z}{L} \right) \]  

[12]

and \( \xi \) is evaluated at \( z = L \). A solution is obtained by solving the coupled PDEs in Equation 10 along with the dimensionless form of boundary conditions in Equations 6–8 for the CO concentration at the exit of the filter (i.e., \( z = L \)).⁴⁴–⁴⁶

\[ C_{out(t)} = C_{in} \left[ 1 - \int_0^{\xi_t} \exp(-\tau - \xi)I_0 \left( \sqrt{4\xi \xi} \right) d\xi \right] \]  

[13]

In Equation [13], \( I_0 \) is the modified Bessel function of first kind with zeroth order.

Experimental

The membrane electrode assembly (MEA) was procured from Lynntech Inc. The MEA has two platinum black electrodes, each with a geometrical area of 25 cm², coated on either side of a Nafion-115 membrane. Unless specified a Pt loading of 4 mg/cm² was used in the electrode. The gas diffusion layer (GDL) was used a woven carbon cloth without any microporous carbon coating on it. The MEA along with two GDLs (one for each electrode) were assembled into filter cells’ hardware, which has triple serpentine channelled graphite flow fields (Fuel Cell Technologies Inc.). The gas flow, temperature and pressure were monitored using a test station (Fuel Cell Technologies Inc.). The gas flow, temperature and pressure were monitored using a test station (Fuel Cell Technologies Inc.). The MEAs assembled into filter cell hardware were initialized and humidified by following a break-in procedure, in which each of the filter cells were operated like a fuel cell for 8 hours at 75 °C and 0.5 V with pure hydrogen and oxygen as fuel and oxidant feeds, respectively. A polarization curve was taken to characterize the performance of each MEA in comparison to that of a standard MEA. To obtain \( Q^* \), the electrode was exposed to CO containing gas for certain duration sufficient enough to saturate the filter anode. Then 100% humidified gas (N₂ or He) was fed for a minute to purge out the CO in gas phase. The remaining CO adsorbed on the filter anode was quantified using CO stripping cyclic voltammetry (SCV). The CO covered anode was scanned from 0.05 to 1.1 V at a scan rate of 50 mV/s for two cycles, while 4% H₂/N₂ flowing through the filter cathode acted as the counter and reference electrodes for the SCV. The resulting current response during the forward sweep of the first cycle was corrected for background current by subtracting out the current response of the forward sweep of the second cycle. The background current corrected response shows a peak that corresponds to the CO oxidation current peak time indicates the quantity CO adsorbed on the filter anode.⁴⁵–⁴⁶

CO breakthrough.— For determining the CO breakthrough, a conditioned MEA was exposed to the CO containing gas and the change in the CO concentration in the gas at the filter anode’s exit with time was quantified using GC-FID. To quantify the concentration of CO at the filter exit, the gas was sampled using a purge and trap system connected with a solid state relay. No sampling bags were used. At the precise time, controlled by a computer, a relay kicks in and collects the
gas sample from the exit. This sample was then fed to a GC column, which was on line with FID (i.e., the filter exit → purge-trap → GC column → FID). After the sampling for a GC run was completed, the CO containing gas flow was stopped. The remaining adsorbed CO was oxidized and quantified using CO-SCV. As each GC run takes about 10 minutes, it is impossible to collect all of the samples for different adsorption time in one adsorption experiment. So the adsorption run was repeated for sampling at different adsorption times. Despite repeated runs of adsorption and oxidation the CO adsorption capacity of the MEA was constant and the breakthrough curves were consistent. Unless specified, the general conditions for the experiments were a gas flow rate of 100 cm³/min, a temperature of 25 °C and a pressure of 1 atm.

Choosing oxidation potential.— The suitable potential to oxidize the adsorbed CO within the switching time estimated from the CO-breakthrough curves, was obtained by carrying out a combination of chronoamperometry and CO-SCV on a CO covered filter anode. The clean filter anode was exposed to CO gas for a certain switching time and then the gas flow was stopped. With 4%H₂/N₂ flowing through the cathode, a pulse potential, for e.g. 0.7 V, was applied for a time interval, followed by a CO-SCV to quantify the leftover CO and recovered active sites. The lowest potential at which all of the adsorbed CO can be oxidized within the switching time was chosen as the suitable oxidation potential.

Filter setup and operation.— In a twin-cell filter, each of the cells undergo alternating cycles of adsorption and oxidation. To demonstrate the operation of a filter, we used a single filter cell and simulated the cycles of CO adsorption and oxidation. A set of solid state relays were used to switch gas flows and potentiostat, according to preset switching time. The gas stream exiting filter anode was sampled and the CO concentration in it was measured using GC-FID. The filter experiments were carried out for various switching times and exit CO concentrations were measured.

Results and Discussion

CO concentration effects.— Figure 2 shows the experimental breakthrough curves (symbols) and model fit (lines) for different CO concentrations in hydrogen (10,000, 5,000 and 1,000 ppm of CO in H₂) at 25 °C, 100 cm³/min and 4 mg Pt/cm². The initial CO break through (i.e., the CO concentration at the exit reached 10 ppm) occurred at around 25, 45 and 190 seconds as the CO feed concentration increased, and leveled to the feed concentration at around 43, 90 and 285 seconds, respectively. The model fit for the respective feed concentrations was predicted using a single value for the mass transfer coefficient (k = 414 s⁻¹) fitted for the entire set of data shown in the Figure 2. Hence the breakthrough curve scales with the CO concentration and does not show significant deviation in mass transfer resistance with a change in CO concentration.

CO flow rate effects.— Figure 3 shows the experimental breakthrough curves (symbols) and model fit (lines) for different flow rates (50, 100 and 150 cm³/min) at 25 °C, 10,000 ppm CO in H₂ and 4 mg Pt/cm². The initial CO break through occurred at around 50, 25 and 15 s as the flow rate increased, and leveled to the feed concentration at around 80, 43 and 30 s, respectively. The decrease in breakthrough time scaled with a corresponding increase in the molar flow rate, since more CO is being fed in a shorter about of time. However, one mass transfer coefficient value (k = 414 s⁻¹) fit all three breakthrough curves at the different flow rates. If the mass transfer rate in the filter was affected by the film diffusion resistance, then increase in flow rate should have improved the mass transfer (i.e., increased k). A constant value of k suggests that the dominant resistance came from either or both of the internal mass transfer resistance (macro- and/or micro-pore diffusion) and surface adsorption reaction resistance.

Effects of catalytic loading.— Figure 4 shows the experimental breakthrough curves (symbols) and model fit (lines) for different Pt loadings (1.5, 4.0 and 8.0 mg/cm²) at 25 °C, 10,000 ppm CO in H₂ and 100 cm³/min. The initial break through occurred at around 15, 25 and 45 seconds as the loading increased, and leveled to the feed concentration at around 30, 43 and 90 seconds, respectively. The decrease in breakthrough time scaled with a corresponding decrease in the Pt loading since there are fewer sites to adsorb the CO. Again, one mass transfer coefficient value (k = 414 s⁻¹) fits the breakthrough curves at the three different catalyst loadings. If the mass transfer rate in the filter was affected by macro-pore diffusion, then decreasing the Pt loading (i.e., decreasing the film thickness) should have improve mass transfer. A constant value of k suggests that the dominant resistance came from either or both micro-pore diffusion and surface adsorption reaction resistance.
Figure 4. CO adsorption breakthrough curves showing the effect of different catalyst loadings for a feed CO concentration of 10,000 ppm in hydrogen at 25°C and 1 atm. pressure on a filter cell. Symbols and lines ( ● and dotted – 1.5, ■ and solid – 4.0 and ◀ and dashed – 8.0 mg/cm²) represent experimental data and the model fit of the Equation 13, respectively.

Since the fit to the breakthrough curves in Figs. 2–4 result in the same mass-transfer coefficient (i.e., $k = 414$ s⁻¹), the performance of the filter could be described by a characteristic performance curve. Therefore, the breakthrough curves shown in Figs. 2–4 were replotted on a dimensionless scale (i.e., $C_{in}/C_{out}$ vs $\tau$) in Figure 5. Indeed, all the data followed a single dimensionless breakthrough curve. The only outliers were two data points for the shortest sampling times at the highest flow rates. Considering the concentration is on a log scale, the error at those short times is reasonable. Therefore, the filter performance for CO in H₂ at 25°C can be accurately predicted over a range of feed CO concentrations, flow rates and catalyst loadings with no adjustable parameters.

Effect of temperature.— Figure 6 shows the experimental breakthrough curves (symbols) and model fit (lines) for different temperatures (25, 45 and 60°C) at 10,000 ppm CO in H₂, 100 cm³/min, and 4 mg Pt/cm². The initial breakthrough occurred at around 25, 16 and 13 seconds with increasing temperatures, and the respective $k$ values are 414, 128.6 and 94.6 s⁻¹. That is, the resistance to CO adsorption is increasing with temperature. Diffusional resistance of a gas should decrease with an increase in temperature. However, CO adsorbs more strongly at lower temperature. The contradictory increase in mass transfer resistance indicates that the CO adsorption resistance is more dominant than the diffusion resistance over this temperature range.

Effects of inert gas.— Figure 7 shows the experimental breakthrough curves (symbols) and model fit (lines) for different carrier gases (N₂, H₂, and He) at 25°C, 1000 ppm CO, 100 cm³/min, and 4 mg Pt/cm². The initial breakthrough occurred at around 160, 200, and 230 seconds as the carrier gas changed from N₂, H₂, and He, respectively. The $k$ values obtained from the fit changed from 3115, 414, and 114.6 s⁻¹ respectively. The diffusional resistance for CO in N₂, H₂ and He should decrease in that order since the diffusion coefficient increases with decreasing molecular weight of the carrier gas.

Figure 5. Normalized CO adsorption breakthrough at the exit of a filter cell plotted against the corresponding normalized time. Symbols represent experimental data and the line represents the model fit for a single mass transfer coefficient.

Figure 6. CO adsorption breakthrough curves showing the effect of different temperatures for a feed CO concentration of 10,000 ppm in hydrogen at 1 atm. pressure on a filter cell with a Pt loading of 4.0 mg/cm². Symbols and lines (● and solid – 25, ▶ and dashed – 45 and ★ and dotted – 60°C) represent experimental data and the model fit of the Equation 13, respectively.

Figure 7. CO adsorption breakthrough curves showing the effect of different filler gases for a feed CO concentration of 1,000 ppm at 1 atm. pressure on a filter cell with a Pt loading of 4.0 mg/cm². Symbols and lines (*) and solid – CO/N₂, ★ and dotted – CO/H₂ and ◀ and dashed – CO/He) represent experimental data and the model fit of the Equation 13, respectively.
Figure 8. Oxidation response cycle of a filter operating with a switching cycle of 20 seconds and 0.7 V.

This trend is consistent with the k values of CO/N₂ and CO/He breakthrough. However, the CO/H₂ resistance is in between those two, indicating another resistance dominates for this case. This additional effect is attributed to the competing adsorption reaction between CO and H₂, which slows down the adsorption of CO and hence contributes to an increase in the overall resistance to the CO removal. Neither N₂ nor He competes with CO for adsorption sites.

Electro-oxidation of carbon monoxide.— A suitable value for the oxidation potential (0.7 V with a 5 A current maximum) was chosen so that sufficient adsorbed CO oxidized during the pulse without causing undesired side reactions. Figure 8 shows the current response (solid line) and the corresponding applied potential (dashed line). The 5 A current maximum was used to simulate more closely how an actual filter would be run to avoid current spikes. The initial high current observed from 0 to 7 seconds is due to the oxidation of hydrogen trapped in the cell. After the oxidation of the trapped hydrogen, the potential increases to 0.7 V, where CO oxidation starts. The current decays to zero as the adsorbed CO is fully oxidized between 7 to 20 seconds.

Figure 9. Comparison of the exit CO concentration (symbols) of a filter operating for a feed CO concentration of 10,000 ppm CO/H₂ at 25 °C and 1 atm.

CO filter demonstration.— The exit CO concentration from a continuously operating filter cell, which undergoes alternating cycles of adsorption and oxidation of CO, is shown in Figure 9. The feed to the cell was 10,000 ppm CO in H₂ at 100 cm³/min. The cell operated 25 °C and 1 atm, and the catalyst loading was 4.0 mg of Pt/cm². The corresponding breakthrough curve for these conditions is shown in Figure 2. As seen in this figure, to reach an outlet concentration of 10 ppm CO, the adsorption time must be less than 25 seconds. Therefore, a switching time of 20 seconds was chosen for this filter demonstration.

Comparing the coulombs pass during the oxidation step to the amount of CO adsorbed shows that 82% of the charge went to H₂ oxidation, with the remaining going to CO oxidation. This means that 5 H₂ molecules are pumped across the cell for a net gain of one H₂ molecule for every CO molecule oxidized. This comes at the expense of parasitic power loss to the overall system. The power loss can be reduced by using air as the cathode gas for the filter cell, in which the oxygen reduction reaction at the cathode will decrease the overall potential required for the oxidation of CO. However, this will result in a net consumption of hydrogen (approximately 1.5% for a CO concentration of 1,000 ppm). For an exit CO concentration level of 10 ppm, the hydrogen loss in electrochemical filtering compares favorably with other technologies like PSA (8%) and catalytic methanation (11%). The tradeoff in decreasing the losses between power and hydrogen would need to be analyzed for a particular application.

While the fuel and power loss may further be decreased with optimization and design improvements to filter, the other important factor is the volume occupied by the CO handling equipments.

The significant decrease in the volume of filter cell required for a low feed CO concentration is exemplified in the Figure 10. Assuming a switching time of 20 seconds, it relates the ratio of filter cell area to fuel cell area with the CO adsorption capacity per cm² of the electrode. Hydrogen concentration in the fuel is assumed to be 40%. For a feed CO concentration of 10,000 ppm fed to a fuel cell operating at 1.0 A/cm² requires the filter cell (at 4 mg of Pt/cm²) to be almost 10 times the fuel cell area. However, the required filter area decreases to one fifth of the fuel cell area, if the feed CO concentration is 1,000 ppm and an operating fuel cell current density is 0.2 A/cm², which is typical for stationary fuel cells operating at high voltage efficiency. In case of direct methanol fed fuel cells require a catalyst loading of the order of 4–8 mg/cm², which is comparable to the catalyst loading expected for a filter cell.

The volume required for PrOx or catalytic methanation units increases by a factor of 10, if the desired exit CO concentration decreases from 250 to 10 ppm. This is due to the limitation of catalyst volume required for PrOx or catalytic methanation units in increases by a factor of 10, if the desired exit CO concentration decreases from 250 to 10 ppm. This is due to the limitation of catalyst volume required for PrOx or catalytic methanation units in case of direct methanol fed fuel cells require a catalyst loading of the order of 4–8 mg/cm², which is comparable to the catalyst loading expected for a filter cell.

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Figure 10. Figure relates the area ratio of filter cell to fuel cell required to feed a fuel cell operating at a certain current density and a certain feed concentration required for a given loading of molar active sites per unit electrode area. The vertical lines represent the Pt loading / cm² of the MEA used in this work.

The vertical lines represent the Pt loading / cm² of the MEA used in this work.
selectivity at low CO concentrations. In the electrochemical filter described herein, the filter volume scales with the quantity of CO to be removed. Therefore, decreasing the CO concentration from 1000 to 10 ppm requires 10 times less filter volume than from going to 10,000 to 10 ppm. Hence, instead of treating the entire reformate containing 10,000 ppm of CO with either a PrOx reactor or an electrochemical filter, CO removal can be done in stages. The reformate gas with higher CO concentrations (~10,000 ppm) can be treated initially in a carbon monoxide filter, CO removal can be done in stages. The reformate gas with 10,000 ppm of CO with either a PrOx reactor or an electrochemical filter can be separated into two sections: one for CO removal at a low concentration, and the other for CO removal at a high concentration. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit. The model was validated by predicting a suitable switching time for an MEA with known desired CO concentration at the filter exit.