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Liquid Water Scavenging of PEMFC Contaminants

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Models were derived for the scavenging effect of product liquid water on airborne proton exchange membrane fuel cell (PEMFC) contaminants. A time scale analysis of contaminant mass transfer processes, product water accumulation in the gas diffusion electrode, and dissociation reactions indicated that the contaminant saturates the product liquid water simplifying model derivation. The baseline model only accounts for contaminant solubility. A multi-scale extension to this model was derived for the presence of contaminant dissociation reactions within the product liquid water using SO_2 as a model contaminant. The extended model demonstrates the large impact of dissociation reactions at low SO_2 concentrations. For both models, explicit expressions for the average gas phase contaminant concentration within the fuel cell were also derived and can be used as a surrogate for the effective contaminant concentration to correlate the fuel cell performance loss and facilitate the definition of tolerance limits and filtering equipment. The model was validated using a non-operating PEMFC. The water was transferred from the anode to the cathode by thermo-osmosis. Model contaminants, methanol and SO_2 , were injected with an inert carrier gas to avoid reactions. The model proved to be acceptable with parameters approximately equal to published values.

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The PEMFC, a cleaner alternative power generating device, still requires durability improvements to replace the incumbent internal combustion engine in automotive applications.^{1,2} Degradation is partly due to contaminant ingress because the system is open to the ambient atmosphere,³ the air filter is imperfect and lets gaseous species seep through the unit⁴ and the air filter is subject to failure.⁵ Contamination has also been linked to water management.^{6,7} However, the scavenging effect of the product liquid water on the numerous⁸ and in some cases soluble, gaseous contaminant species⁹ has not been studied.¹⁰ This is especially important for predictive purposes and the accurate determination of contaminant tolerance limits for the air intake.¹¹⁻¹³ Furthermore, two technology trends are particularly relevant to the scavenging effect of liquid water. Membranes are currently being developed for higher temperatures and drier reactant streams to optimize fuel cell systems (humidifier removal, more efficient heat removal, etc).14,15 Anion exchange membranes have also attracted interest to reduce Pt catalyst costs with the use of cheaper noble metals or nonnoble metals.¹⁶ In anion exchange membrane fuel cells, the water is produced on the anode rather than the cathode¹⁶ and the transport of water by electro-osmotic drag is directed toward the anode rather than the cathode.¹⁷ Therefore, drier conditions are expected in the cathode compartment. Current technology trends thus indicate that contamination will be more severe for soluble species because the presence of liquid water in the cathode compartment will be significantly reduced.

Pollutant scavenging by rain drops^{18–27} and gas absorbers²⁸ such as spray towers,^{29–32} packed columns^{33,34} and cables bundle contactors³⁵ are related cases because a contaminant is removed from a gas stream to a liquid either naturally or purposefully. The penetration model is useful to understand the scavenging process.³⁵ The local mass flux at the gas/liquid interface for diffusion into a falling liquid film is:²⁸

$$N = c \sqrt{\frac{D_l v}{\pi L}}$$
[1]

where *N* represents the molar flow rate (mol s⁻¹), *c* the dissolved species concentration at the interface (mol m⁻³), D_l the dissolved

species liquid phase diffusion coefficient (m² s⁻¹), v the liquid phase interfacial velocity (m s⁻¹) and L a characteristic dimension in the liquid phase flow direction (m). Figure 1a depicts the situation in a PEMFC. The penetration model readily applies to the water drops in the flow field channel.³⁶ However, for the liquid water in the gas diffusion electrode,³⁷ the penetration model no longer applies as the gas velocity is significantly reduced within the solid porous structure with a pore characteristic dimension of the order of or less than 100 μ m.³⁸ This difference significantly impact contaminant scavenging dynamics and it will be shown that the product liquid water in a PEMFC is always saturated by the contaminant greatly simplifying analysis.

A model is proposed for the water scavenging effect inside PEM-FCs. A time scale analysis of the different processes within the PEMFC revealed that the contaminant saturates water droplets in the gas diffusion electrode. This feature considerably simplifies the model resulting in a one dimensional along the flow field channel length description and explicit solutions. Experimental data that validate the model are also discussed. For the specific case of SO₂ that dissociates in water, the multi-scale model links molecular level information, a dissociation rate constant, with the macroscopic contaminant concentration profile.

Model

Time scale analysis.— Figure 1a depicts a schematic diagram of contaminant X transport pathways within the PEMFC. The contaminant X enters the PEMFC as a gaseous air stream component. Subsequently, contaminant X sequentially moves through the flow field channel and gas diffusion electrode before penetrating the solid ionomer phase to interact with the catalyst surface. For simplification purposes, the liquid water is not depicted in the catalyst layer. Contaminant X is also lost to the membrane bulk. Along the gaseous pathway, contaminant X comes into contact with liquid water droplets either in the flow field channel or the gas diffusion electrode. Contaminant X penetrates the liquid water and subsequently diffuses into the water bulk. The liquid water droplets which are entrained with the reactant stream thus eliminate a fraction of the contaminant X decreasing its effective concentration within the fuel cell. It is noteworthy that the

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Figure 1. Contaminant X transport pathways (a). The gas phase contamination path follows the flow field channel and an empty gas diffusion electrode pore to the membrane and the catalyst. Along the same path the contaminant X dissolves into liquid water drops located in the flow field channel and a partially filled gas diffusion electrode pore decreasing the average contaminant concentration. Contaminant X molar mass balance (b). The inlet atmospheric stream containing contaminant X saturates the product water leaving a depleted contaminated reactant stream.

water starts to scavenge the contaminant as it is produced. Therefore, water preferentially accumulates the contaminant in the gas diffusion electrode because at this location the contaminant concentration gradient is the steepest. Contaminant X pathway to the liquid water bulk defines three time scales: transport in the gas phase, transport by diffusion in the liquid phase and accumulation in the liquid phase (interphase transport is assumed to be rapid). The water phase is continuously replenished by the oxygen reduction reaction defining a fourth time scale, the water accumulation rate.

The gas phase transport time scale L^2/D_g with L the gas diffusion layer thickness (~200 µm)³⁸ and D_g the gas phase diffusion coefficient for SO₂ as a model contaminant (0.132 cm² s⁻¹)¹⁸ is ~3 ms. The aqueous phase transport time scale r^2/D_l with r the gas diffusion layer average pore radius (<50 µm)³⁸ and D_l the aqueous phase diffusion coefficient for SO₂ (1.8 × 10⁻⁵ cm² s⁻¹)¹⁸ is ~1 s. The contaminant accumulation in the liquid phase time scale is derived using the kinetic theory of gases,³⁹ the mass accommodation coefficient¹⁸ and the time required to fill a water saturated pore with the contaminant. The rate at which the contaminant X collides with the gas/aqueous phase interface is:

$$N = \frac{1}{4}\bar{v}Ac = \frac{1}{4}\sqrt{\frac{8RT}{\pi M}}Ac$$
[2]

where *N* represents the contaminant X collision with the gas/aqueous phase interface collision rate (mol s⁻¹), \bar{v} the average molecular velocity (m s⁻¹), *A* the gas/aqueous phase interface area (m²), *c* the contaminant X concentration (mol m⁻³), *R* the molar gas constant (8.314 J mol⁻¹ K⁻¹), *T* the temperature (K) and *M* the molecular mass (kg mol⁻¹). The mass accommodation coefficient β , the ratio of the number of contaminant molecules absorbed by the aqueous phase to the number of contaminant collisions with the gas/aqueous phase interface, was previously measured for SO₂ and is equal to ~0.06.¹⁸ The absorption rate per surface area *Q* (mol s⁻¹ m⁻²) is obtained by combining equation 2 with β :

$$Q = \frac{\beta N}{A} = \frac{\beta}{4} \sqrt{\frac{8RT}{\pi M}} c = Kc$$
[3]

The lumped parameter K is equal to 5.1 m s⁻¹ with $\beta = 0.06$, T = 353 K and $M = 6.4 \times 10^{-2}$ kg mol⁻¹ (SO₂). A water filled cylindrical pore of 50 µm radius and 200 µm length (gas diffusion electrode thickness) contains at saturation Vc moles of contaminant with V representing the pore volume in m^3 . This pore fills at a QA rate from one of its ends. The contaminant accumulation in the liquid phase time scale is therefore $Vc/QA = \pi r^2 Lc/Kc\pi r^2 = L/K = 2$ $\times 10^{-4}/5.1 = 39 \,\mu$ s. The water accumulation time scale is derived with an assumed water flux (Faraday law) and an experimental estimate for the water contained in the gas diffusion electrode. A maximum current density i of 10000 A m^{-2} and a gas diffusion electrode water content w/M (mass w per electrode area and molecular weight M) of ~2.8 mol m⁻² are used.⁴⁰ The time scale is thus 2Fw/iM = 2 \times 96500 \times 2.8/10000 = 54 s where F is the Faraday constant (96,500 C mol⁻¹). A comparison between all these time scales reveals that the mass transport related time scales do not exceed a second whereas the contaminant accumulation in the liquid phase time scale is of the order of a minute (a two orders of magnitude difference). Therefore, the liquid water is saturated by the contaminant. This conclusion also holds for smaller current densities down to 500 A m⁻² near the automotive fuel cell system idle point as the water accumulation time scale is inversely proportional to the current density.

In the presence of dissociation reactions, another time scale is needed. The time scale associated with SO₂ dissociation reactions is much smaller (3×10^{-7} s)¹⁸ than the liquid water accumulation in the gas diffusion electrode time scale. Therefore, for this specific case, the liquid water is also saturated by the contaminant as multiple species.

Contaminant dissolution model.— A contaminant mass balance is derived assuming the ideal gas law, an isobar,⁴¹ isothermal⁴¹ and saturated gas stream, Henry's law (deviations are not expected be-



Figure 2. Dimensionless contaminant concentration in the gas phase (c(x)/c(0)), equation 5) as a function of the dimensionless flow field channel length *x* and the dimensionless number characterizing the severity of the liquid water scavenging effect W_1 . $c_r = 100 \text{ mol m}^{-3}$, s = 2, $H = 6.9 \times 10^{-4}$, 2.4×10^{-2} and $4.2 \text{ m}^3 \text{ mol}^{-1}$ for respectively SO₂, NH₃ and ethylene glycol.

cause the contaminant is in trace concentration), the absence of water crossover⁴² and contaminant crossover, a constant volumetric gas flow rate (the oxygen consumption effect is relatively small at $\sim 11\%$ with a 2 stoichiometry and 79% N₂), a uniform current distribution⁴³ and the absence of a contaminant reaction (Figure 1b):

$$\frac{c_{in}}{c_a}Q = \frac{c(x)}{c_r}Q + Hc(x)Q_w(x), \ Q = \frac{sI}{4\varphi_0 F}, \ Q_w(x) = \frac{Ix}{2F}$$
[4]

where c_{in} represents the inlet contaminant X concentration in the ambient air on a dry basis (mol m⁻³), Q the air flow (mol s⁻¹), c_a the molar concentration of an ideal gas at a pressure of 1 atmosphere (mol m⁻³), c the molar concentration of contaminant X in the gas phase (mol m⁻³), x the dimensionless flow field channel length, c_r the molar concentration of non vapor gases at saturation conditions within the fuel cell (mol m⁻³), H the solubility constant (m³ mol⁻¹), Q_w the product water flow (mol s⁻¹), s the oxygen stoichiometry, I the total current (A) and φ_0 the fraction of oxygen in dry air (0.21). Rearrangement of equation 4 leads to:

$$c(x)/c(0) = 1/(1+W_1x), \ c(0) = \frac{c_{in}c_r}{c_a}, \ W_1 = \frac{2\varphi_0 H c_r}{s}$$
 [5]

where W_1 represents the dimensionless number characterizing the severity of the liquid water scavenging effect on the contaminant X. Equation 5 does not depend on current *I* and results equally apply to application relevant current values. The average contaminant X concentration is calculated by integrating equation 5:

$$\bar{c}/c(0) = \int_{0}^{1} \frac{1}{1 + W_{1}x} dx = \ln\left(1 + W_{1}\right)/W_{1}$$
 [6]

where \bar{c} represents the average molar concentration of contaminant X in the gas phase (mol m⁻³). Equation 6 is important because it can be used as a surrogate for the effective contaminant concentration. For W_1 equal to 2.51, the average dimensionless contaminant concentration is equal to 0.5. Equation 5 is plotted in Figure 2 for a few relevant contaminants using respective *H* values of 6.9×10^{-4} , 2.4×10^{-2} and $4.2 \text{ m}^3 \text{ mol}^{-1}$ for SO₂, NH₃ and ethylene glycol at room temperature. Figure 2 indicates that the scavenging effect widely varies with different contaminants and is significant especially for the relevant ethylene glycol species (the incumbent automotive coolant). At the cell outlet, ethylene glycol is virtually eliminated from the gas stream. For NH₃, the liquid water scavenging effect is important but not as drastic whereas for SO₂ the effect is barely perceptible. However, for the SO₂ case, equation 4 does not take into account known dissociation reactions.

Contaminant dissolution and dissociation model.— The baseline model extension with the addition of ionization reactions (contaminant species dissociation) demonstrates the importance of these processes for low contaminant concentrations. Sulfur dioxide is a model species for these ionization reactions (all equilibrium constants are given at 298 K):^{19,22}

$$SO_2 + H_2O \rightarrow H_2SO_3, K_H = [H_2SO_3]/[SO_2] = 30.9 \text{ mol mol}^{-1}$$
[7]

$$H_2SO_3 + H_2O \rightarrow H_3O^+ + HSO_3^-, K_1 = [H_3O^+][HSO_3^-]/[H_2SO_3]$$

$$= 13.3 \text{ mol m}^{-3}$$
 [8]

$$2H_2O \rightarrow H_3O^+ + OH^-, \ K_w = [H_3O^+][OH^-] = 10^{-8} \text{ mol}^2 \text{ m}^{-6}$$
[9]

=

Equations 7 to 9 are used to derive a relationship between the total quantity of sulfur species dissolved in the product water and the gas phase SO_2 concentration. The derivation includes a surrogate for Henry's law (equation 7), SO_2 dissociation equilibrium (equation 8), the water dissociation equilibrium (equation 9) and an electroneutrality condition. The resulting relationship is:¹⁹

$$[H_2SO_3] + [HSO_3^-] = K_H[SO_2] + \sqrt{K_1K_H[SO_2]} = Hc(x) + H'\sqrt{c(x)}$$
[10]

where K_H represents the SO₂ dissolution reaction equilibrium constant (mol mol⁻¹), K_1 the first SO₂ ionic dissociation equilibrium constant (mol m⁻³) and H' a solubility constant for the non-linear concentration dependence term (m^{3/2} mol^{-1/2}). It can be shown that the secondary HSO₃⁻⁻ to SO₃²⁻⁻ ionization is negligible.¹⁹ Equation 10 is used to correct the contaminant mass balance (equation 4):

$$\frac{c_{in}}{c_a}Q = \frac{c(x)}{c_r}Q + \left(Hc(x) + H'\sqrt{c(x)}\right)Q_w(x), \quad Q = \frac{sI}{4\varphi_0 F},$$

$$Q_w(x) = \frac{Ix}{2F}$$
[11]

Rearrangement of equation 11 leads to:

$$c(x)/c(0) = \left(\frac{-W_2 x}{1+W_1 x} + \sqrt{\frac{W_2^2 x^2}{(1+W_1 x)^2} + \frac{1}{1+W_1 x}}\right)^2,$$

$$c(0) = \frac{c_{in} c_r}{c_a}, \quad W_1 = \frac{2\varphi_O H c_r}{s}, \quad W_2 = \frac{\varphi_O H' c_r}{s\sqrt{c(0)}} \quad [12]$$

where W_2 represents the dimensionless number characterizing the severity of the liquid water scavenging effect on the contaminant X in the presence of dissociation reactions. Equation 12 also does not depend on current *I* as discussed for equation 5. For x = 1, a contour map is generated with equation 12 by assigning fixed values to c(1)/c(0) and plotting W_2 as a function of W_1 :

$$W_2 = \frac{1 - \frac{c(1)}{c(0)}}{2\sqrt{\frac{c(1)}{c(0)}}} - \frac{1}{2}\sqrt{\frac{c(1)}{c(0)}}W_1$$
[13]

The average contaminant X concentration is calculated by integrating equation 11 with a symbolic integration package:

$$\bar{c}/c(0) = \int_{0}^{1} \left(\frac{-W_2 x}{1+W_1 x} + \sqrt{\frac{W_2^2 x^2}{(1+W_1 x)^2} + \frac{1}{1+W_1 x}} \right)^2 dx$$
$$= \frac{2W_2}{W_1^2} \left(2 + (W_1 + 2) \left(\frac{W_2}{a_3} - a_2 \right) \right)$$
$$+ \frac{a_1}{W_1^3} \ln \left(\frac{a_3^2 (W_1 + 2W_2)^2}{(W_1 + 2W_2^2 + 2a_2 a_3 W_2) (a_3 W_1 - 2W_2^2 + 2a_2 a_3 W_2)} \right)$$
[14]



Figure 3. Dimensionless SO₂ contaminant concentration in the gas phase (c(x)/c(0)), equation 12) as a function of the dimensionless flow field channel length *x* and the dimensionless number characterizing the severity of the liquid water scavenging effect in the presence of dissociation reactions W_2 . $W_1 = 0.0145$, $c_{in} = 4.2 \times 10^{-4}$ mol m⁻³ (10 ppm, $W_2 = 0.139$), 4.2×10^{-5} mol m⁻³ (10 ppm, $W_2 = 0.441$), 4.2×10^{-6} mol m⁻³ (100 ppb, $W_2 = 1.39$), 4.2×10^{-7} mol m⁻³ (10 ppb, $W_2 = 4.41$) and 4.2×10^{-8} mol m⁻³ (1 ppb, $W_2 = 1.39$), $c_r = 100$ mol m⁻³, $c_a = 42$ mol m⁻³, s = 2, $H = 6.9 \times 10^{-4}$ m³ mol⁻¹¹ and $H' = 4.2 \times 10^{-4}$ m^{3/2} mol^{-1/2} for SO₂.

$$a_1 = W_1^2 - 4W_2^2$$
 [15]

$$a_2 = \sqrt{\frac{W_1 + W_2^2 + 1}{(1 + W_1)^2}}$$
[16]

$$a_3 = 1 + W_1$$
 [17]

It is noted that equations 14 to 17 reduce to equation 6 with $W_2 = 0$. The contaminant dissociation effect is depicted in Figure 3 for a relevant SO₂ concentration range of 1 ppb to 10 ppm in ambient air. The contamination dissociation effect is dependent on the contaminant concentration in ambient air (equation 12, $W_2(c(0))$). For a 10 ppm SO₂ inlet concentration, the outlet concentration is only reduced by ~20% whereas for a 1 ppb inlet concentration, the contaminant is practically eliminated from the gaseous stream.

Equation 13 is plotted in Figure 4 using a logarithmic W_1 scale rather than a linear scale because the W_1 values cover a wide range (Figure 2). Such a contour plot is useful to identify the potential impact of W_1 (solubility) and W_2 (dissociation) parameters on the liquid water scavenging effect for unknown contaminants. The SO₂ case is superimposed on the contour map and illustrates in a different manner the change in outlet SO₂ concentration in the gas phase as the inlet SO₂ concentration in ambient air is modified.

Experimental

Methanol was selected as a representative contaminant to validate the contaminant dissolution model whereas sulfur dioxide was chosen to confirm the contaminant dissolution and dissociation model. The fuel cell (50 cm² active area, double serpentine flow field channel for the anode, triple serpentine flow field channel for the cathode) was modified to focus on the liquid water scavenging effect (Figure 5). Hot liquid water was circulated in the anode compartment at a rate of ~2.3 mL min⁻¹, a value which is about 10 times the water crossover rate through the membrane/electrode assembly (Gore PRIMEA M715 catalyst coated membrane, SGL 25 BC gas diffusion layer on the cathode side). The liquid water was introduced into the cathode compartment by applying a small temperature difference of a few degrees (up to 4.5°C) across the cell by controlling the two heating pads and fans on the end plates (thermo-osmosis).⁴⁴⁻⁴⁷ The



Figure 4. Dimensionless number characterizing the severity of the liquid water scavenging effect in the presence of dissociation reactions W_2 as a function of the dimensionless number characterizing the severity of the liquid water scavenging effect W_1 for constant dimensionless contaminant concentration in the gas phase c(1)/c(0) values. The SO₂ case is illustrated with the dashed line at $W_1 = 0.0145$. The unfilled circles correspond to specific inlet concentrations. For respectively $c_{in}/c_a = 1$ ppb, 10 ppb, 100 ppb, 1 ppm and 10 ppm, $W_2 = 13.9, 4.41, 1.39, 0.441$ and 0.139. Equation 13 for c(1)/c(0) = 0.5 is also highlighted.

cathode temperature and pressure were respectively set to 80°C and 48.3 kPag. A gas diffusion layer was not inserted on the anode side to facilitate contact between the liquid water and the ionomer. Nitrogen (>99.999%, Airgas) saturated with water vapor was used as an inert carrier gas for the contaminant to minimize the presence of chemical or electrochemical reactions on the Pt catalyst surface. Methanol (certified ACS, Fisher Scientific) was evaporated by controlling the vaporizer temperature and the N₂ flow rate to achieve a 1000 ppm concentration in the cathode inlet stream. Gases composed of 140 and 676 ppm SO₂ in N₂ (certified plus grade, Matheson) were diluted with N₂ to accomplish contaminant concentrations of 1, 10 and 100 ppm.

The liquid flux through the membrane/electrode assembly was measured by collecting the liquid phase at the cathode outlet. The amount of water corresponded to an equivalent current density of 0.67 to 0.92 A cm⁻² for the methanol tests and 0.56 to 0.78 A cm⁻² for the sulfur dioxide tests. The temperature up to the collection point was controlled at 80°C to maintain the equilibrium between the contami-



Figure 5. Experimental setup schematic showing the transport of water through the PEMFC membrane/electrode assembly by thermo-osmosis, the injection of methanol and sulfur dioxide contaminants in a saturated and inert carrier gas, and the methods used to measure the amount of contaminant scavenged by liquid water (GC: gas chromatography, CV: cyclic voltammetry, TOC: total organic carbon).

nant in the gas and liquid phases. The methanol concentration in the cathode outlet liquid phase was measured by cyclic voltammetry^{48,49} and total organic carbon analysis.50,51

oxidation was carried out in a 0.5 M H₂SO₄ solution (18 MΩ deionized water, H₂SO₄ certified ACS Plus, Fisher Scientific) at room temperature with a RRDE-3A electrode system (ALS) using Bio-Logic VSP bi-potentiostat. The solution was de-aerated with N2 for at least 20 min prior to the measurements. A Pt/C catalyst thin film electrode was used as the working electrode. Its preparation is summarized here.^{52,53} The commercially available 46.6 wt% Pt/C catalyst (Ion Power) was used. An ink base solution (100 mL) was prepared by mixing 79.8 mL de-ionized water, 20 mL isopropyl alcohol (certified ACS, Fisher Scientific) and 0.2 mL of a 10.07 wt% Nafion solution (Ion Power). A 20 mL glass vial was employed to combine 15 mg of the Pt/C catalyst and 15 mL of the base solution. The ink was thoroughly mixed with a sonicator bath (model 50D, VWR) for 1 h, stirred overnight, then sonicated again for another 45-60 min before use. The bath temperature was kept below 40°C during sonication. The glassy carbon disk electrode was polished for 4 min to a mirror finish with a $0.05 \,\mu$ m alumina particle suspension (ALS) on a moistened polishing cloth before each use. A new film was used for the calibration curve and each fuel cell outlet water sample. The polished electrodes were thoroughly rinsed with de-ionized water and mounted onto the electrode rotator (RRDE-3A, ALS). The bare electrode was rotated at a rate of 800 rpm while a 5.41 µL aliquot of the well dispersed ink (20 μg cm⁻² Pt loading) was pipetted onto it. The electrode was rotated for 20 min to ensure that the film had sufficient time to completely dry. A spiral Pt wire and an Ag/AgCl/NaCl (3 M) electrode were used as the counter and reference electrodes, respectively. Cyclic voltammograms were first obtained in a potential range of -0.2 to 1 V vs Ag/AgCl at a rate of 50 mV s⁻¹ for several methanol concentrations by adding varied aliquots to the solution (Figure 6a). The measured methanol oxidation peak currents were subsequently used to create a calibration curve (Figure 6b). The fuel cell exhaust samples containing methanol stored in 125–250 mL vials (polypropylene, Nalgene) were then mixed with a sulfuric acid solution (30 mL of the sample was mixed with 40 mL of 0.875 M H₂SO₄ to obtain a 0.5 M H₂SO₄ electrolyte). The cyclic voltammetry procedure was repeated to extract the methanol oxidation peak current which was then fitted to the calibration curve.

The total organic carbon value was measured with a Shimadzu high temperature TOC-L combustion analyzer. The collected fuel cell exhaust liquid phase samples were also stored in the same polyethylene vials and were not altered before measurement. The SO₂ concentration in the cathode outlet gas phase was measured in triplicate by a Varian CP-3800 gas chromatography system with a pulsed flame photometric detector.54

Results and Discussion

Methanol.- Figure 7 depicts the dimensionless methanol concentration in the cathode outlet as a function of s, the hypothetical stoichiometry calculated by assuming the gas is air and converting the water flow rate through the membrane to an equivalent current density. Both cyclic voltammetry and total organic carbon data sets are consistent yielding similar dimensionless methanol concentrations. The contact time between the gas and liquid phases increases with a decrease in s, resulting in a larger scavenged proportion of methanol and a lower dimensionless concentration in the gas phase. Under nominal operating conditions of approximately s = 2, the scavenging effect is measurable but only amounts to 1-2% for methanol. Both data sets were aggregated and fitted to the model (equation 5), yielding a value of $H = 0.0019 \text{ m}^3 \text{ mol}^{-1}$ for methanol. This value favorably compares to H = 0.0032 and $0.0058 \text{ m}^3 \text{ mol}^{-1}$. ^{55,56} The H =0.0019 m³ mol⁻¹ value is also consistent with calculations completed for 80°C with parameters reported by Rolf Sander using a uniform



format (www.henrys-law.org):57

$$k_{H} = k_{H,ref} e^{\left(\frac{-\Delta H_{soln}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)}$$
[18]

where k_H represents Henry's law coefficient (mol L⁻¹ atm⁻¹), $k_{H,ref}$ Henry's law coefficient at 298.15 K (mol L⁻¹ atm⁻¹), ΔH_{soln} the molar enthalpy of dissolution (J mol⁻¹), R the gas constant (8.314 J mol⁻¹) K^{-1}), T the temperature (K) and T_{ref} the reference temperature (298.15 K). Conversion of k_H is carried out with $H = k_H p_a M_w / \rho_w c_a$ where p_a represents the atmospheric pressure (1 atm), M_w the molecular weight of water (18 g mol⁻¹) and ρ_w the liquid water density (1000 g L⁻¹). For methanol, $k_{H,ref} = 160$ and 220 mol L⁻¹ atm⁻¹ and $\Delta H_{soln}/R =$ -5600 and -5200 K leading to H = 0.0044 and 0.0075 m³ mol⁻¹. The reported values cover a wide range of 0.0032 to 0.0075 m³ mol⁻¹ implying significant measurement difficulties. On that basis, the measured value of $0.0019 \text{ m}^3 \text{ mol}^{-1}$ is reasonable.

Sulfur dioxide.- Figures 8a and 8b respectively show the SO2 concentration in the cathode outlet as a function of the dimensionless cathode inlet concentration and the hypothetical stoichiometry. The cathode outlet concentration decreases with a concurrent reduction in the dimensionless cathode inlet concentration as expected from a mass balance basis (Figure 8a). However, the quantity scavenged (the departure from the c(1) = c(0) line in Figure 8a equal to c(0)-c(1)) progressively increases at low dimensionless cathode inlet concentrations reflecting the increased contribution from SO₂ dissociation (second term on the right hand side of equation 10). The dimension-





Figure 7. Dimensionless methanol concentration c(1)/c(0) in the PEMFC cathode outlet gas stream measured by 2 different methods as a function of the hypothetical oxygen stoichiometry *s*. Dimensionless contaminant inlet concentration c_{in}/c_a approximately 1000 ppm methanol in N₂, 80°C, 48.3 kPag, 100% inlet relative humidity, $c_r = 34.9 \text{ mol m}^{-3}$.



Figure 8. SO₂ concentration c(1) in the PEMFC cathode outlet gas stream as a function of contaminant inlet concentration c(0) at a hypothetical oxygen stoichiometry *s* of approximately 2.5 (a). Dimensionless SO₂ concentration c(1)/c(0) in the PEMFC cathode outlet gas stream as a function of the hypothetical oxygen stoichiometry *s* at a dimensionless contaminant inlet concentration c_{in}/c_a of approximately 10 ppm (b). 80°C, 48.3 kPag, 100% inlet relative humidity, $c_r = 34.9 \text{ mol m}^{-3}$. $K_H = 1140 \text{ mol mol}^{-1}$ ($H = 0.021 \text{ m}^3 \text{ mol}^{-1}$), $K_1 = 0.0284 \text{ mol L}^{-1}$ ($H = 0.00324 \text{ m}^{3/2} \text{ mol}^{-1/2}$) for equation 12. $H = 0.0019 \text{ m}^3 \text{ mol}^{-1}$ for equation 5. GC: gas chromatography.

less cathode outlet concentration likewise decreases for lower *s* values (Figure 8b) which is accounted for by the longer contact time between the liquid and gas phases. Both data sets (Figures 8a and 8b) were simultaneously fit to equation 12 in two steps. In the first step, the 100 ppm data point was used with $W_2 = 0$ (the SO₂ dissociation has little impact at high *c*(0) concentrations) yielding $K_H = 1140$ mol mol⁻¹. In the second step, equation 12 is used with the fitted K_H value to find $K_1 = 0.0284$ mol L⁻¹. The resulting model curves adequately reproduce experimental data (Figures 8a and 8b). These experimentally derived parameter values are relatively close to the published values ($K_H = 700$ mol mol⁻¹, $K_1 = 0.00475$ mol L⁻¹).¹⁹

In Figure 8a, the c(1) = c(0) line is very close to the methanol case for the stated operating conditions ($s\approx 2.5$, $c_r = 34.9 \text{ mol m}^{-3}$) using the experimentally determined *H* value of 0.0019 m³ mol⁻¹ and equation 5 (c(1) = 0.989c(0)). Therefore, methanol is not scavenged as much as SO₂ by liquid water especially for smaller dimensionless inlet contaminant concentrations (c(0)-c(1) = 0.011c(0) or 1.1% for methanol in comparison to 82 and 49% for SO₂ and respectively c(0)= 0.0001 and 0.001 mol m⁻³). A similar conclusion is derived from Figure 8b which includes equation 5 for methanol (H = 0.0019 m³ mol⁻¹, $c_r = 34.9$ mol m⁻³).

Model extension.- Mass balances described by equations 4 and 11 were derived with the assumption that the contaminant does not undergo a chemical or electrochemical transformation. However, many of the airborne pollutants or species released into the air stream by system materials^{58,59} or leaks react in the fuel cell environment. This is not only the case for methanol⁶⁰ and sulfur dioxide⁶¹ but also for ammonia,⁶² ethylene glycol⁶³ and many other relevant species. As a result, the mass balance needs to be modified with the inclusion of an additional consumption term to better evaluate the role of liquid water scavenging under more practical operating conditions. The information required is not readily available. The reactivity of foreign species in a PEMFC environment is not envisaged to be the same as for other applications due to different operating conditions and materials. However, few reports provide this information for a limited number of airborne contaminants. Efforts in this direction are ongoing.^{64–66} With the proposed mass balance modification, the multi-scale model will have a stronger and more general connection between molecular (chemical and electrochemical reactions) and macroscopic (effective contaminant concentration) levels.

Conclusions

The scavenging effect of liquid water on airborne PEMFC contaminants was discussed using a modeling approach. The simple and advantageous solution avoiding the need to track the size and location of multiple water drops and their respective interfaces with the gaseous reactant phase was justified because the rate determining step was associated with the product liquid water buildup in the gas diffusion electrode. Therefore the product water is saturated by the contaminant. Methanol and SO₂ experimental data demonstrated the validity of this assumption. For methanol, a species that does not significantly dissociate, the dimensionless contaminant concentration along the flow field channel is independent of its inlet concentration. By contrast, SO₂ which dissociates in water, scavenging is particularly important for low concentrations. As a consequence, fuel cell contamination data reported in the literature may be misleading. The effect of SO₂ is usually determined using high concentrations because they accelerate degradation and minimize errors because the performance loss is larger.¹³ However, an extrapolation to lower concentrations would neglect the scavenging effect resulting in conservative air inlet tolerance limits. It is also instructive to consider current efforts to reduce or eliminate the need for reactant stream humidification with alternative ionomers.14,15,67 For this case, an extrapolation of data on contaminant effects for low concentration in humid conditions (in which the scavenging effect is significant) to dry conditions (where there is no scavenging) may not be valid. The model is extendible not only to reactive contaminants but also to other contaminant dissociation reactions, lower inlet relative humidities (change in fuel cell liquid water flow rate) and a net water crossover across the membrane/electrode assembly. In that regard, model validation with a sub-saturated stream and an operating cell will be considered.

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List of Symbols

- A gas/aqueous phase interface area, m²
- dissolved species concentration at the interface, mol m⁻³ С or molar concentration of contaminant X in the gas phase, $mol m^{-3}$
- average molar concentration of contaminant X in the gas \bar{c} phase, mol m⁻³
- molar concentration of an ideal gas at a pressure of 1 C_a atmosphere, mol m⁻³
- inlet contaminant X concentration in the ambient air on a C_{in} dry basis, mol m⁻³
- molar concentration of non vapor gases at saturation con- C_r ditions within the fuel cell, mol m⁻¹
- gas phase diffusion coefficient, m² s⁻¹ D_{g}
- dissolved species liquid phase diffusion coefficient, m² s⁻¹ D_l
- F Faraday constant, 96,500 C mol⁻¹
- solubility constant, m³ mol⁻¹ Η
- H' solubility constant for the non-linear concentration dependence term in equation 10, $m^{3/2} \text{ mol}^{-1/2}$
- current density, A m⁻² i
- total current, A I
- K lumped parameter defined in equation 3, m s^{-1}
- Henry's law coefficient, mol L⁻¹ atm⁻¹ k_H
- SO₂ dissolution reaction equilibrium constant, mol mol⁻¹ K_H
- Henry's law coefficient at 298.15 K, mol L⁻¹ atm⁻¹ k_{H,ref}
- water dissociation equilibrium constant, mol² m⁻⁶ K_w
- first SO₂ ionic dissociation equilibrium constant, mol m⁻³ K_1 characteristic dimension in the liquid phase flow direction, L
- m or gas diffusion layer thickness, m М molecular mass, kg mol⁻¹
- molecular mass of water, 18 g mol⁻¹ M_w Ν

molar flow rate, mol s⁻¹ or contaminant X collision with the gas/aqueous phase interface collision rate, mol s⁻¹ atmospheric pressure, 1 atm p_a

- absorption rate per surface area, mol $s^{-1}\ m^{-2}$ or air flow, Q $mol \ s^{-1}$
- product water flow, mol s⁻¹ Q_w
- gas diffusion layer average pore radius, m or correlation coefficient
- molar gas constant, 8.314 J mol⁻¹ K⁻¹ R
- Oxygen stoichiometry S
- Т temperature, K
- reference temperature, 298.15 K Tref
- pore volume, m³ V
- gas diffusion electrode water mass per electrode area, kg w m^{-2}
- dimensionless number characterizing the severity of the W_1 liquid water scavenging effect on the contaminant X
- W_2 dimensionless number characterizing the severity of the liquid water scavenging effect on the contaminant X in the presence of dissociation reactions
- х dimensionless flow field channel length

- β mass accommodation coefficient or ratio of the number of contaminant molecules absorbed by the aqueous phase to the number of contaminant collisions with the gas/aqueous phase interface
- ΔH_{soln} molar enthalpy of dissolution, J mol⁻¹
- liquid phase interfacial velocity, m s⁻¹ v
- \bar{v} average molecular velocity, m s⁻¹
- liquid water density, 1000 g L^{-1} ρ_w
- fraction of oxygen in dry air, 0.21 φ_0
- molar concentration of species j, mol m⁻³ [j]

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