



The effect of low concentrations of tetrachloroethylene on H₂ adsorption and activation on Pt in a fuel cell catalyst

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ABSTRACT

The poisoning effect of tetrachloroethylene (TTCE) on the activity of a Pt fuel cell catalyst for the adsorption and activation of H₂ was investigated at 60 °C and 2 atm using hydrogen surface concentration measurements. The impurity was chosen as a model compound for chlorinated cleaning and degreasing agents that may be introduced into a fuel cell as a contaminant at a fueling station and/or during vehicle maintenance. In the presence of only H₂, introduction of up to 540 ppm TTCE in H₂ to Pt/C resulted in a reduction of available Pt surface atoms (measured by H₂ uptake) by ca. 30%, which was not enough to shift the H₂–D₂ exchange reaction away from being equilibrium limited. Exposure of TTCE to Pt/C in a mixed redox environment (hydrogen + oxygen), similar to that at the cathode of a fuel cell, resulted in a much more significant loss of Pt surface atom availability, suggesting a role in TTCE decomposition and/or Cl poisoning. Regeneration of catalyst activity of poisoned Pt/C showed the highest level of recovery when regenerated in only H₂, with much less recovery in H₂ + O₂ or O₂. The results from this study are in good agreement with those found in a fuel cell study by Martínez-Rodríguez et al. [2] and confirm that the majority of the poisoning from TTCE on fuel cell performance is most likely at the cathode, rather than the anode.

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1. Introduction

With the ever decreasing supply of liquid fossil fuels and the fear of global warming looming on the horizon, the ongoing search for alternative energy, especially for the automotive industry, is of even greater importance. From the list of possible alternatives, including batteries, biofuels, and solar energy, proton exchange membrane fuel cells (PEMFC) have been shown to be the most promising due to their advantageous characteristics such as high current density, quick startup, and zero pollution emissions [1]. However, partly due to the detrimental effects impurities have on the durability and performance of PEMFCs, successful commercialization of this technology is still limited at best.

While the numbers of studies investigating the impurity effects on PEMFCs have been increasing rapidly in the past years, most of them have concentrated mainly on the impurities that are present in the hydrogen fuel stream as a result of hydrogen production from hydrocarbon reforming, namely CO, CO₂, and NH₃. There exists very limited information of other impurities, such as chlorinated hydrocarbons, that may be introduced into the fuel cell via other sources, such as the fueling station and/or during vehicle maintenance. Due

to their non-polar nature, such compounds are used extensively in cleaning and degreasing applications as excellent solvents for organic materials. In fact, the International Organization for Standardization (ISO) and the Society of Automotive Engineers (SAE) have proposed the regulation of these chlorinated hydrocarbons as part of the hydrogen fuel quality standards, setting the limit of total chlorinated species to be 0.05 ppm [2].

A recent study by Martínez-Rodríguez et al. [2] on the impact of one such chlorinated hydrocarbon, tetrachloroethylene (TTCE), also known as perchloroethylene (PCE), on the performance of a PEMFC showed a 98% degradation in current density in the span of 3 h when 30 ppm of TTCE was introduced into the hydrogen fuel stream. Furthermore, while a decrease in the concentration of TTCE did result in a slower rate of poisoning, the amount of current loss at steady-state after 200 h with 0.05 ppm TTCE was still 84% of its initial value. Compared to the cell polarization results in the presence of CO [3], it is clear that the impact of TTCE [2] on fuel cell performance is far greater, at similar concentration levels. Yet, results from the TTCE study [2] were inconclusive as to exactly how the impurity was causing such a detrimental effect on the fuel cell performance. For example, results from a hydrogen pump experiment [H₂(anode)/N₂(cathode)], used to characterize changes in the anode and membrane during poisoning, and the electrochemical impedance spectroscopy (EIS) characterization of the membrane resistance before and after TTCE exposure showed

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that the poisoning effects of TTCE are neither related to the anode nor the membrane. On the other hand, analysis of both anode inlet and outlet showed a reduction in TTCE concentration from 164 ppm to 41 ppm, respectively, during open circuit, which was further reduced to 5.4 ppm upon application of a current. However, no TTCE was detected at the cathode outlet. Thus, while this fuel cell study was very informative in measuring and determining the effect of TTCE on overall fuel cell performance, more information is required in order to understand the poisoning mechanism of the impurity, especially on the catalyst and associated reactions.

This study is a follow-up to the fuel cell work by Martínez-Rodríguez et al. [2] to further delineate the effect of TTCE on the H₂ activation and surface coverage of Pt in order to better understand the poisoning mechanism of the impurity. It is important to note that the impurity was chosen as a model chlorinated compound to simulate poisoning effects similar to chlorinated cleaning and degreasing agents. As mentioned previously, while these types of impurities are not directly associated with the production of fuel cell feed streams (i.e., hydrocarbon reformation), the use of cleaning and degreasing agents between the fueling station and the vehicle during everyday maintenance can inadvertently introduce these contaminants into the fuel stream. Due to the fast reaction rate of H₂ activation on Pt, kinetic measurements of the reaction could not be made at typical fuel cell operating conditions. Instead, a modified H₂-to-D₂ switch procedure, H₂-D₂ switch with Ar purge (HDSAP) [4,5], was used to measure in situ the surface concentrations of hydrogen on Pt/C and on Nafion-Pt/C with time-on-stream (TOS) in the presence of varying concentrations of TTCE (150–540 ppm). Chlorine elemental analyses were performed subsequently on the TTCE poisoned catalysts. Furthermore, in order to mimic conditions at the cathode, Pt/C was also exposed to 150 ppm TTCE under mixed redox conditions.

2. Experimental

2.1. Catalyst preparation

A carbon supported Pt fuel cell catalyst (Pt/C), with a nominal Pt-loading of 20 wt%, was purchased from BASF and used as-received. The carbon support used for the synthesis of the catalyst was Vulcan XC-72 (Cabot Co.).

The Nafion supported on Pt/C (Nfn-Pt/C) catalyst used in this study was the same as that prepared in our previous work [6]. Briefly, Nfn-Pt/C was prepared via incipient wetness impregnation of the commercial 20 wt% Pt/C catalyst with a Nafion ionomer solution (LQ-1105, DuPont, 5 wt% Nafion) to give a target weight loading of 30 wt% for the Nafion. The high Nafion loading of 30 wt% has been shown in the literature to be the optimum Nafion content in a PEMFC catalyst layer [7–10]. The impregnated material was then dried at 90 °C overnight in a static air oven, crushed and sieved to obtain a particle size distribution of 60–150 μm. The catalyst was then stored in the dark prior to use. Elemental analysis of Pt-content (performed by Galbraith Laboratories) showed a Pt-loading of ca. 17.5 wt% and 13.7 wt% for Pt/C and Nfn-Pt/C catalysts, respectively.

2.2. Characterization methods

2.2.1. BET

The BET surface area, pore size, and pore volume measurements of Pt/C and Nfn-Pt/C were carried out using a Micromeritics ASAP 2020 unit. Samples of catalysts were degassed under vacuum (10⁻³ mm Hg) at 110 °C for 4 h prior to analysis. Results were obtained from N₂ adsorption isotherms at -196 °C.

2.2.2. TEM

Transmission electron microscopy (TEM) images of Pt/C and Nfn-Pt/C catalysts were obtained using a TEM-Hitachi 9500, which offers 300 kV high magnification TEM and is designed for atomic resolution. The preparation method of copper sample grids was the same as that used in our previous work [5]. Briefly, catalyst samples were immersed in small aliquots of isopropyl alcohol and sonicated until an even dispersion of the catalyst was observed. A small drop of the dispersed sample was then transferred onto a copper grid (200 mesh copper Formvar/carbon) and allowed to dry at room temperature overnight prior to measurement. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images.

2.2.3. Static H₂/CO chemisorption

Static chemisorption experiments using H₂ and CO were performed at 35 °C in a Micromeritics ASAP 2010 unit equipped with a chemisorption controller station. Prior to the start of the analysis, the catalysts were first reduced in flowing H₂ at 80 °C for 3 h, followed by an evacuation at 80 °C (10⁻⁵ mm Hg) for another 3 h. After evacuation, the temperature was then adjusted to 35 °C and the H₂ or CO isotherms were obtained from 50 to 450 mm Hg pressure at increments of 50 mm Hg. Volumetric uptakes of H₂ or CO on the catalysts were determined from the total adsorption isotherms of the specified gas. These values were then used in the determination of total Pt surface atom concentration (Pt_s) and metal dispersion by assuming stoichiometric ratios of 1:1 for H:Pt_s and CO:Pt_s. Calculation of average Pt particle size for Pt/C and Nfn-Pt/C were made using metal dispersion measured by chemisorption, which has been shown to correlate reasonably well with TEM results [5,6].

2.2.4. Surface hydrogen concentration measurements

The method, H₂-D₂ switch with an Ar purge (HDSAP), was developed and verified in our previous work [4–6] for determining in situ the concentration of strongly adsorbed surface hydrogen on Pt/C and Nfn-Pt/C. The use of HDSAP is preferred over other surface concentration measurements, such as TPD, due to the non-destructive nature of the methodology (Nafion is not stable above ca. 120 °C) and its ability to obtain TOS measurements.

HDSAP measurements were initiated by first exposing the catalyst to a flowing gas mixture of H₂/Ar (1:1) at 100 cm³ min⁻¹ (sccm) for 30 min. Afterwards, the H₂ was stopped and 50 sccm of Ar was passed through the plug flow reactor for 30 min [5] or 50 min [6] for Pt/C and Nfn-Pt/C, respectively. The purge with Ar was done to flush out as much of the gas-phase and/or weakly adsorbed H₂ from the catalyst as possible. After the Ar purge, a flow of 50 sccm of D₂ (along with the 50 sccm of Ar) was introduced to the catalyst, resulting in two transient signals being observed for hydrogen-containing species (H₂ and HD) in the Pfeiffer Vacuum mass spectrometer (MS). The amount of H₂ and HD were calculated by integrating the area under the peaks (signal vs. time) and using the area obtained from a pulse of known quantities of H₂ and HD via a 6-port valve equipped with a 2 mL sample loop as calibration. Total surface concentration of hydrogen was calculated by adding the amount of hydrogen (H) in H₂ and HD, as given by the equation below:

$$\begin{aligned} \text{Surface H} \quad (\mu\text{mol}(\text{g.cat})^{-1}) \\ = \mu\text{mol HD}(\text{g.cat})^{-1} + 2 \times \mu\text{mol H}_2(\text{g.cat})^{-1} \end{aligned} \quad (1)$$

After the initial measurement of hydrogen surface concentration on the freshly reduced catalyst, specified concentrations of TTCE were exposed to the catalyst by flowing 10 sccm of either H₂

or Ar through a KIN-TEK Trace Source™ permeation tube type LFH filled with approximately 30 mL of the liquid component. Based on the emission rate of the membrane inside the tube, control of the TTCE concentration at the outlet was maintained by placing the permeation tube in an insulated oven and adjusting its temperature accordingly. The calibrated effluent of the permeation tube was diluted further with a mixture of H₂/Ar or H₂/O₂/Ar, depending on the experiment, to achieve a total flow rate of 100 sccm and the desired concentration of TTCE. Time-on-stream (TOS) measurements of the effect of TTCE exposure of Pt/C and Nfn–Pt/C on hydrogen surface concentration were taken sequentially such that one sample could be used for the entire experiment. Preliminary results showed that the Ar purge periodically did not have any effect on the poisoning behavior of TTCE compared to an uninterrupted exposure of Pt/C to either 150 or 540 ppm TTCE for 12 h (non-sequential), resulting in the same 12 h hydrogen surface concentration being measured as one with HDSAP measurements periodically during a 12 h run (sequential).

2.3. H₂–D₂ exchange reaction

The H₂–D₂ exchange reaction was chosen as the model reaction for the hydrogen oxidation reaction (HOR) primarily because both reactions share the same rate-limiting step, which is the dissociative adsorption of hydrogen. Furthermore, as shown by Ross and Stonehart [11], for the temperature range of 30–80 °C, the first-order rate constants for H₂–D₂ exchange on Pt and electrochemical hydrogen oxidation are in close agreement with each other. Thus, not only is the H₂–D₂ exchange reaction a good probe reaction for hydrogen activation, it is also a very good model reaction for the electrocatalytic oxidation of hydrogen on Pt, within the temperature range specified.

Using a conventional plug flow, micro-reactor system maintained at 60 °C and 2 atm, the H₂–D₂ exchange reaction was started by flowing a reactant gas mixture comprised of (25:25:50) H₂:D₂:Ar, with the specified concentration of impurity, over the catalyst for 15 min. The reactor effluent gas (comprised of the reactants H₂ and D₂, the product HD, and the inert Ar) was analyzed online with a MS. To obtain the MS signals of H₂ and D₂ in the absence of the catalyst for the purpose of calculating the exchange conversion, the flow was switched to reactor bypass for 5 min. The exchange conversion for H₂ or D₂ was obtained via Eq. (2) using the H₂ (m/z=2) and D₂ (m/z=4) MS signals in the presence and absence of catalyst:

Conversion (%)

$$= \frac{(\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{No Cat.}} - (\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{Cat.}}}{(\text{H}_2 \text{ or D}_2 \text{ Signal})_{\text{No Cat.}}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET

The BET surface area, pore size, and pore volume results for the carbon support (XC-72) were 225 m² g⁻¹, 16.4 nm, and 0.63 cm³ g⁻¹, respectively, which correspond very well with literature values [12,13]. Similar results were observed for the carbon-supported Pt catalyst where the BET surface area, pore size, and pore volume were found to be 170 m² g⁻¹, 15.9 nm, and 0.44 cm³ g⁻¹, respectively. Due to the fact that the bulk of the surface area of a support comes from its pores, reductions in the BET surface area and pore volume suggests that significant amounts of the Pt particles were most likely situated in the pore

structure rather than just on the external surface of the carbon support granules.

Addition of Nafion to Pt/C resulted in a further reduction of BET surface area and pore volume to 38 m² g⁻¹ and 0.28 cm³ g⁻¹, respectively, while increasing the average pore size to 32.7 nm. As was shown in our previous work [6], the severe reduction in BET surface area was due to a substantial filling/blocking of the smaller pores by the Nafion, while the larger sized pores appear to have been much less affected.

3.1.2. Average particle size

Measurements of average Pt particle sizes for the Pt/C and Nfn–Pt/C catalysts were obtained from TEM images and were determined to be 2.6 ± 0.4 nm and 2.8 ± 0.5 nm, respectively, indicating no apparent change in Pt particle size (within experimental error) from the addition of Nafion [6]. Furthermore, analysis of TEM results indicated a relatively even distribution of Pt particles on the carbon support for both catalysts.

3.1.3. Static H₂ and CO chemisorption

Due to differing Pt loadings for Pt/C and Nfn–Pt/C, static chemisorption results were scaled to a “per g of Pt” basis rather than “per g of catalyst” in order for a more valid comparison (Table 1). The results can easily be converted back to “per g of catalyst” basis by dividing by the appropriate Pt weight fraction for the associated catalyst (i.e., 17.5 wt% and 13.7 wt% for Pt/C and Nfn–Pt/C, respectively). Surprisingly, the addition of such large amounts of Nafion did not appear to affect the ability of the Pt to adsorb either hydrogen or CO since the amounts of hydrogen and CO uptake were relatively similar for both catalysts, within experimental error. Furthermore, based on the severe loss of pores with pore sizes of 20 nm and below due to being filled/blocked by the Nafion [6] and the fact that N₂ molecules have a critical diameter similar to that of CO (3.0 Å vs. 2.8 Å, respectively), the minimal effect Nafion had on the amount of CO uptake also suggests that the majority of the Pt particles were most likely not situated in the smaller pores of the carbon support. A more in-depth analysis of these results and the reasoning behind our conclusions can be found elsewhere [6], as the point of this work is not on the effect of Nafion.

Comparison of the average Pt particle sizes from chemisorption results, calculated based on the metal dispersion, with those obtained from TEM shows good agreement, within experimental error. This suggests that the amount of Pt_s measured from hydrogen chemisorption, based on the assumed stoichiometric ratio of 1:1 for H:Pt_s, is reasonably accurate and that the Pt surface is essentially not blocked by Nafion [6].

3.2. Hydrogen surface concentration measurements

3.2.1. Effect of TTCE poisoning on Pt in H₂ for Pt/C

Fig. 1 shows the TOS measurements of hydrogen surface concentration on 100 mg of Pt/C in the presence of 150–540 ppm TTCE in a (50/50) H₂/Ar mixture at 60 °C and 2 atm. Even in the presence of such high concentrations of TTCE, the hydrogen surface concentration, at steady-state, showed a loss of only 18% when exposed to 150 ppm TTCE over a 12 h period. Increase in the TTCE concentration resulted in a further decrease in hydrogen surface concentration such that at 290, 400, and 540 ppm TTCE, the reductions in hydrogen surface concentration were ca. 24%, 29%, and 35%, respectively. While the loss in hydrogen surface concentration is not minor, it should be noted that, due to the extremely high activity Pt has for adsorbing and activating hydrogen, a much more substantial loss in Pt surface atoms (ca. 66%) is required to shift the reaction away from equilibrium for the conditions used and to start inhibiting the performance of a PEMFC [5]. Because of this, the conversion of H₂–D₂ exchange on Pt, even in the presence of 540 ppm TTCE, remained at equilibrium at steady-state. This

Table 1
Static H₂ and CO chemisorption results at 35 °C for Pt/C and Nfn–Pt/C.

Catalyst ^a	Adsorption gas	Analysis temp. (°C)	Amount of CO/H adsorbed ^b ($\mu\text{mol}(\text{g Pt})^{-1}$)	Metal dispersion (%)	Avg. Pt particle size (nm) ^c
Pt/C	H ₂	35	1806	35	3.1
	CO	35	1669	33	3.3
Nfn–Pt/C	H ₂	35	1861	36	3.0
	CO	35	1452	28	3.9

^a Catalysts were pretreated in H₂ at 80 °C for 3 h.

^b Experimental error for all results was ca. $\pm 5\%$.

^c Avg. Pt particle size calculated from: Avg. Pt particle size (nm) = 1.08/Metal Dispersion, assuming CO/Pt₅ = 1 and H/Pt₅ = 1 [29].

result can also be observed from fuel cell hydrogen pump experiments, where polarization scans using a H₂(anode)/N₂(cathode) setup, with 30 ppm TTCE in the anode feed, showed that the impurity had no effect on the overpotential of the hydrogen oxidation reaction (HOR) over a 4 h period [2]. However, introduction of the same TTCE concentration to a H₂(anode)/O₂(cathode) fuel cell for 3 h showed almost a complete degradation in fuel cell performance.

Even though the exposure of Pt/C to TTCE was not able to shift the H₂–D₂ exchange reaction away from equilibrium, the loss of up to 35% of available Pt surface atoms was determined and was a cause of concern. According to hydrodechlorination studies (dechlorination in the presence of hydrogen) of chlorinated hydrocarbons, coke, chlorine deposition, and possibly HCl are attributed to be the main possible reasons for catalyst deactivation [14–18]. However, the majority of these deactivation effects were observed more for the hydrodechlorination of chloroalkanes instead of the chloroalkenes. For example, hydrodechlorination of trichloroethane (TCA) and dichloroethane (DCA) on 3 wt% Pt/ η -alumina at 250 °C in 10% H₂ started to deactivate as early as 8 h TOS. However, no signs of deactivation were evident for dichloroethylene (DCE) at the same conditions for up to 24 h TOS, with the conversion of DCE at 100% for the entire duration and the product distribution being primarily ethane and HCl [19]. Further addition of an equimolar amount of HCl to a feed stream with 1 mol% DCE had essentially no effect on the initial activity or stability of a Pt/ η -alumina catalyst at 250 °C, proving that the presence of HCl does not contribute to the deactivation of the catalyst.

While no deactivation was observed above for the hydrodechlorination of DCE on Pt/ η -alumina at higher reaction temperatures, at lower temperatures such as 60 °C, the hydrogenation of Cl-species on the Pt surface may not be as fast, resulting in a reduction of hydrogen surface concentration or Pt surface atoms available for adsorbing hydrogen on the Pt/C catalyst. However, elemental analysis of Cl concentration (performed by Galbraith Laboratories)

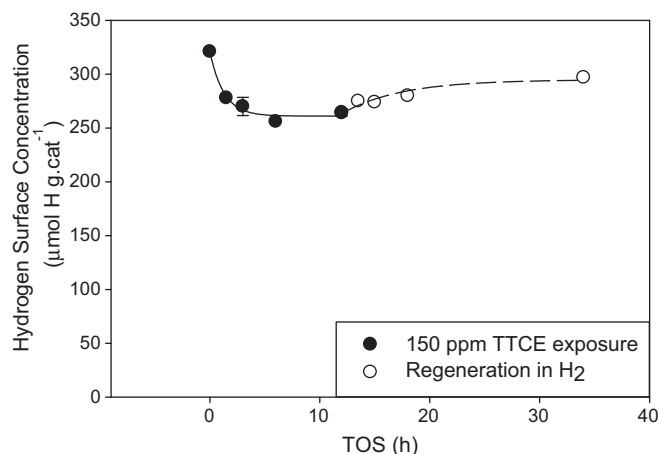


Fig. 2. Regeneration in H₂ after TTCE poisoning for Pt/C.

using ion chromatography for Pt/C samples exposed to 150, 290, 400, or 540 ppm TTCE for 12 h resulted in a retention of only ca. 13, 20, 23, and 26 $\mu\text{mol Cl g.cat}^{-1}$, respectively. While this low concentration of Cl would not account for the reduction in hydrogen surface concentration on a 1:1 Cl:Pt₅ basis, surface science results for Cl adsorption on Pt(1 0 0) single crystals suggest that the stoichiometric ratio of Cl to Pt₅ is actually closer to 1:2 [20]. Furthermore, results from low-energy electron diffraction (LEED) for the adsorption of Cl on Pt(1 1 0) and Pt(1 1 1) single crystals show clear evidence of surface reconstruction [21]. Thus, based on this and the steady-state behavior of TTCE poisoning on the hydrogen surface concentration of Pt in the presence of excess H₂, it can be concluded that the poisoning effect of the impurity, at the lower reaction temperatures, is mainly due to the deposition of Cl-species on the Pt surface, resulting in Pt₅ blockage, effects on the chemisorption of hydrogen on neighboring Pt surface atoms, and/or Pt surface reconstruction. It should also be noted that, similar to how electropositive alkali metal atoms can affect not only the site they are adsorbed on but also four neighboring sites through electrostatic interactions [22], the presence of electronegative Cl atoms on a Pt surface can potentially poison multiple active Pt sites for adsorbing and dissociating H₂ [23,24].

3.2.2. Reversibility of TTCE poisoning on Pt in H₂ for Pt/C

Fig. 2 shows the regeneration of Pt/C after exposure to 150 ppm TTCE in H₂ for 12 h. The regeneration was performed by flowing a mixture of (50/50) H₂/Ar over the poisoned catalyst at 60 °C and 2 atm for a period of 22 h with hydrogen surface concentration measurements at 1.5, 3, 6, and 22 h of regeneration. As can be observed from the figure, some partial recovery of the Pt surface is evident after only 1.5 h of regeneration. However, similar to the results observed for the regeneration of CO poisoning on Pt/C [5], complete recovery of hydrogen surface concentration could not be achieved, even after 22 h of exposure to H₂. Elemental analysis of Cl on the poisoned Pt/C, after 22 h of regeneration, shows a concentration of

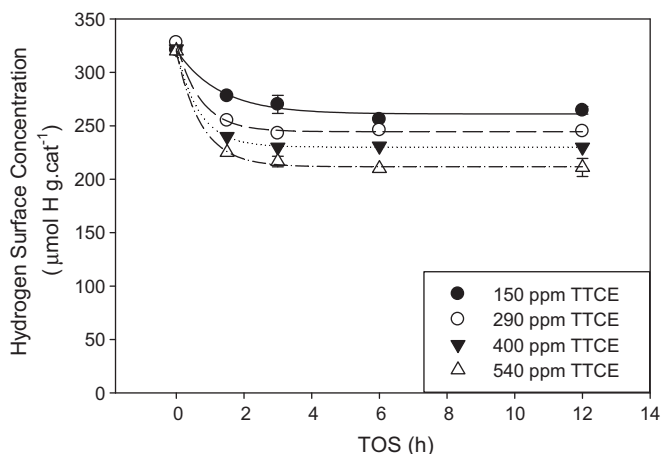


Fig. 1. Effect of TTCE exposure on the hydrogen surface concentration on Pt/C in the presence of only H₂.

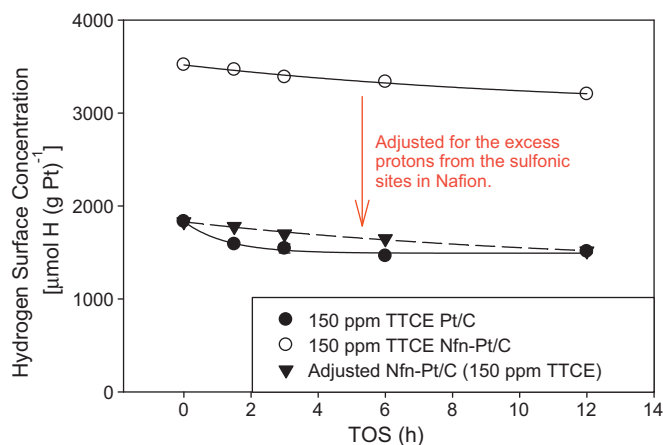


Fig. 3. Effect of Nafion on the poisoning behavior of TTCE in H_2 on Pt.

ca. $7 \mu\text{mol Cl g.cat}^{-1}$ remaining of the original $13 \mu\text{mol Cl g.cat}^{-1}$. This lack of a complete recovery may be due to the difficulty in removing adsorbed Cl and/or in reconstructing at 60°C the surface modified by the adsorption of Cl-species.

3.2.3. Effect of Nafion on TTCE poisoning on Pt in H_2 for Nfn–Pt/C

The effect of Nafion on the poisoning behavior of TTCE on Pt is shown in Fig. 3. It should be noted that, based on the effect Nafion has for obstructing the diffusion of gas-phase H_2 away from the catalyst, the purge time used for the hydrogen surface concentration measurements for Nfn–Pt/C was increased to 50 min [6].

Similar to the effect Nafion has in obstructing the rate of diffusion of CO to the Pt surface [6], the presence of the polymer apparently also decreased the diffusion of TTCE to the Pt surface. After taking into account the excess protons available from the sulfonic sites in the Nafion, the effect of Cl on the strongly adsorbed hydrogen surface concentration on the Pt surface for Nfn–Pt/C was the same as for Pt/C, within experimental error. No evidence of physical and/or chemical interaction between the Nafion and the Pt surface atoms exists based on these results, as also previously found [6].

3.2.4. Co-adsorption of TTCE and CO on Pt in H_2 for Pt/C

The poisoning effect of 150 ppm TTCE + 30 ppm CO on Pt/C was investigated via hydrogen surface concentration measurements, with the results plotted in Fig. 4. While the poisoning effect of

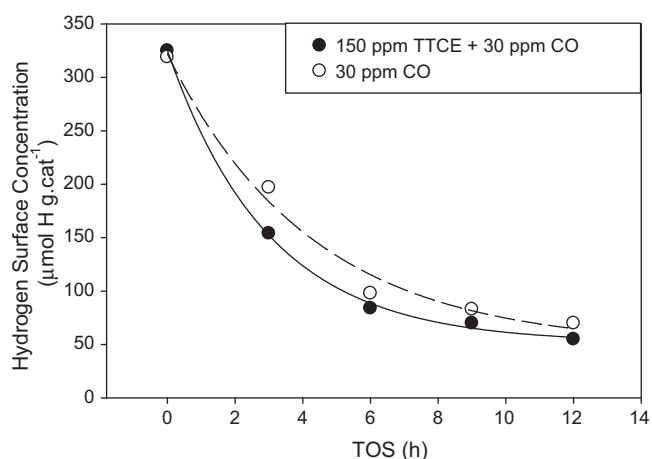


Fig. 4. Effect of 30 ppm CO + 150 ppm TTCE in H_2 on the hydrogen surface concentration on Pt/C.

two impurities is always interesting due to possible synergistic effects, the co-poisoning experiment was further motivated by FT-IR results suggesting that the presence of Cl on the Pt surface may block similar sites for CO adsorption. In a study by Gracia et al. [25], two batches of Pt/SiO₂ catalysts were prepared with one using a Pt-precursor containing Cl (H_2PtCl_6) and the other using a Pt-precursor without Cl [$Pt(NH_3)_4(NO_3)_2$]. Results from FT-IR obtained by exposing each catalyst to 0.3% CO in He at varying temperatures ($45\text{--}200^\circ\text{C}$) show a significant reduction in the absorbance for the IR band corresponding to the linear-bonded CO, especially at the lower temperatures.

Based on Fig. 4, the poisoning behavior of 150 ppm TTCE + 30 ppm CO on the hydrogen surface concentration of Pt/C appears to have been relatively similar to that of 30 ppm CO by itself, suggesting that the poisoning effect of CO is more dominant over that of Cl. This result is somewhat surprising, especially considering the highly electronegative nature of Cl. Furthermore, theoretical surface science studies of electrostatic adsorbate–adsorbate interactions show that an adsorbing molecule like CO, which extracts electrons from the surface, will be destabilized by nearby electronegative atoms like Cl [22,26]. This result suggests that the presence of Cl should decrease the adsorption behavior of CO and is in agreement with what was observed from the FT-IR results mentioned above. So why then is CO the dominant poison in our CO + TTCE study? While the presence of such large amounts of H_2 may have some effect on the adsorption of the two impurities, the reason is more likely due to the method of Cl deposition or, more specifically, the hydrodechlorination of TTCE. In other words, unlike the Pt/SiO₂ study [25], where Cl was directly deposited on the catalyst using a Pt-precursor containing Cl, the surface Cl in our study is from the decomposition reaction of TTCE.

Whenever a reaction involves the breaking of chemical bonds, in this case four C–Cl bonds to form ethane and HCl, that reaction is often structure sensitive, requiring site containing up to 12 contiguous surface metal atoms in order to carry out the reaction. Even the $H_2\text{--}D_2$ exchange reaction, which is essentially hydrogen activation, exhibits evidence of structure sensitivity at specific reaction conditions [27]. Furthermore, the extent to which the reaction is structure sensitive does not need to be extreme for the presence of a small amount of impurity to completely poison the reaction. For example, for a moderately structure sensitive reaction such as cyclopropane hydrogenolysis, a K^+ -coverage on the Pt surface of ca. 0.4 resulted in a 90% reduction in the rate of propane formation (i.e., from 96 to $10 \mu\text{mol g.cat}^{-1} \text{s}^{-1}$) [28]. Thus, if the hydrodechlorination of TTCE is structure sensitive, as the surface coverage of CO increases, the rate of TTCE decomposition would decrease, resulting in a much slower deposition of Cl on the Pt surface. It should be emphasized that this is just a hypothesis as data regarding the structure sensitivity of the hydrodechlorination of TTCE is extremely limited. However, with such a hypothesis, all the results can be explained. One can also hypothesize that if Cl_2 gas was used instead of TTCE, at the same Cl concentrations, the poisoning effect of Cl would most likely be more severe. However, this is outside the scope of this paper.

3.2.5. Effect of TTCE poisoning on Pt in O_2 and $H_2 + O_2$

While the exposure of Pt/C to TTCE in a reducing environment (H_2) has been shown to have a negligible effect on the activity of Pt for adsorbing and activating H_2 and only a small effect on hydrogen surface coverage, the detrimental effect the impurity has on the performance of a fuel cell still remains to be answered. While no TTCE was detected at the cathode outlet during any of the fuel cell tests, this does not eliminate the possibility of chlorinated species being present at the cathode. In fact, it was hypothesized by Martínez-Rodríguez et al. [2] based on their results that the poi-

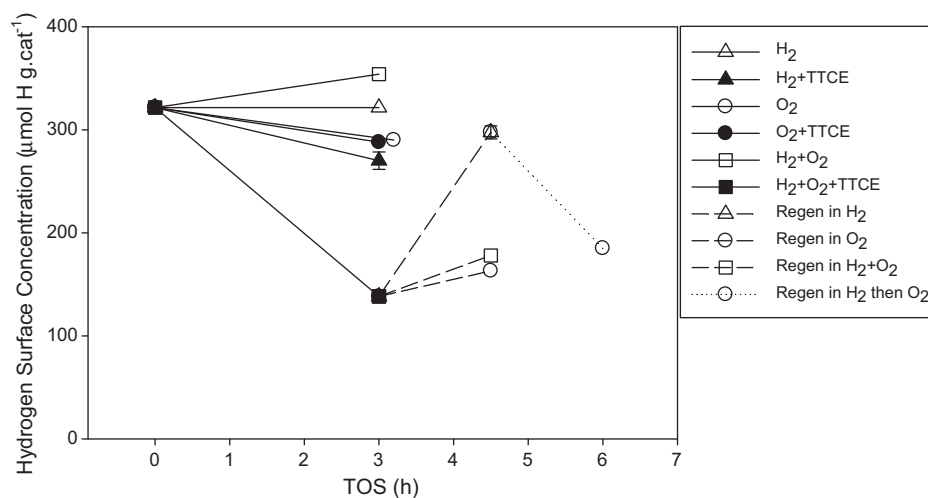


Fig. 5. Comparison of exposure and 150 ppm TTCE poisoning of Pt/C in different gases (H_2 , O_2 , and $H_2 + O_2$). Effect of different regeneration gases. The data point for exposure to O_2 for 3 h has been moved slightly to the right due to overlapping with the data point for exposure to $O_2 + TTCE$.

soning effect observed in their fuel cell was most likely due to the migration of a chlorinated compound, resulting from the decomposition of TTCE, across the membrane to the cathode where the oxygen reduction reaction (ORR) was poisoned.

The effect of TTCE in O_2 alone was first investigated. Exposure of the Pt/C to 1.8% O_2 for 1 h at 60 °C and 2 atm, followed by a H_2 exposure time of 30 min, was shown to be adequate to saturate the Pt surface with hydrogen [5], i.e., the amount of surface hydrogen obtained after the O_2 exposure was the same as before O_2 exposure, suggesting that the amount of available Pt surface atoms remained the same. Increase in the duration of exposure to 1.8% O_2 to 3 h resulted in a minor loss of available Pt surface atoms based on the measured hydrogen surface concentration (from 322 to 288 $\mu\text{mol H g cat}^{-1}$). This slight reduction in the Pt surface atom availability was most likely due to the H_2 exposure time of 30 min being too short to completely re-reduce all of the oxidized Pt surface atoms. However, in order to allow for a valid comparison and based on the relatively minor loss in hydrogen concentration, the H_2 exposure time of 30 min was used for all subsequent experiments involving O_2 .

Exposure of Pt/C to 150 ppm TTCE in 1.8% O_2 in Ar (no H_2) for 3 h showed no further decrease in Pt surface atom availability (as measured by hydrogen uptake), suggesting that the O_2 in conjunction with TTCE was not the cause for the severe deactivation observed in the fuel cell. This is most likely because, at low temperatures (<100 °C) and in the absence of H_2 , the decomposition of TTCE on Pt in O_2 is nearly 0% [18], resulting in almost no deposition of Cl on the Pt surface.

In order to fully investigate the effect chlorinated compounds might have on the ORR, it is important to duplicate the mixed redox conditions present (hydrogen + O_2) at the cathode of a fuel cell, where water vapor is also produced. To this end, the poisoning effect of 150 ppm TTCE on Pt/C was investigated in a mixture of 4% H_2 and 1.8% O_2 in Ar. Besides being below the flammability range of a $H_2 + O_2$ mixture, the 2:1 ratio of $H_2:O_2$ was chosen due to evidence suggesting a reasonably high conversion of TTCE in this stoichiometric mixture at low temperatures (ca. 20% at 75 °C) [18]. In addition, the combination of both H_2 and O_2 on Pt also allows for the investigation of the effect that water vapor might have on the TTCE poisoning, which, at the partial pressures of H_2 and O_2 used would be equivalent to ca. 30%RH, assuming 100% conversion.

From Fig. 5, it can be observed that the exposure of Pt/C to the mixture of 4% $H_2/1.8\% O_2$ in Ar for 3 h resulted in a slight increase in the hydrogen surface concentration measured. This excess sur-

face hydrogen was most likely contributed by the formation and retention of some H_2O on the catalyst surface, and should not be confused with an increase in Pt surface atom availability [4]. In contrast to the lack of effect observed in the presence of H_2 , exposure of Pt/C to 150 ppm TTCE in the H_2-O_2 mixture for 3 h resulted in a substantial decrease in Pt surface atom availability. The effect of this poisoning was repeated 5 times at the same conditions on fresh samples of Pt/C, with reproducibility being $< \pm 5\%$. Elemental analysis of Cl content on the Pt/C exposed to 150 ppm TTCE in the presence of $H_2 + O_2$ for 3 h resulted in a Cl concentration of ca. 118 $\mu\text{mol Cl g cat}^{-1}$, which is substantially more than the 13 $\mu\text{mol Cl g cat}^{-1}$ observed for the catalyst exposed to 150 ppm TTCE in H_2 alone. Furthermore, based on the fuel cell hydrogen pump results [$H_2(\text{anode})/N_2(\text{cathode})$] of Martínez-Rodríguez et al. [2], with 30 ppm TTCE in the humidified anode feed, no decrease in the overpotential of the HOR was observed over a 4 h period in the presence of $H_2 + H_2O$. This suggests that the significant loss in the hydrogen surface concentration on Pt/C, from the exposure of TTCE in the H_2-O_2 mixture, was not due to either H_2 or H_2O , but clearly shows the role O_2 plays in enhancing the deactivation process of the catalyst. It should be re-emphasized that, in the absence of H_2 , no effect from Cl poisoning was observed due to the TTCE being unable to decompose in O_2 at the lower reaction temperatures, resulting in little or no deposition of Cl on the Pt surface.

Thus, the poisoning effect of TTCE on the performance of a fuel cell is really the combination of processes that are occurring at both the anode and the cathode. In other words, while the addition of TTCE to the anode has a minor effect on the Pt surface atom availability, the presence of the H_2 plays a crucial role in initiating the poisoning process by facilitating the decomposition of TTCE to ethane and HCl. Once formed, the HCl then migrates from the anode to the cathode, where the presence of O_2 enhances the poisoning effect from the halogen. Without the H_2 being present to first decompose the TTCE via hydrodechlorination, the poisoning effect from the TTCE would most likely not be as severe, as $O_2 + TTCE$ had no further effect on the Pt surface atom availability compared to O_2 by itself. This is again due to the fact that the decomposition of TTCE on Pt in O_2 is nearly 0% at the lower temperatures (<100 °C) [18].

Similar to the results observed in the performance recovery studies of a fuel cell poisoned with TTCE [2] and what was shown in Fig. 2, regeneration of the poisoned Pt/C in 4% H_2 showed an almost complete recovery of Pt surface atom availability (based on hydrogen uptake) in 1.5 h. In contrast, regeneration of the poi-

soned Pt/C in 1.8% O₂ or 4% H₂ + 1.8% O₂ resulted in little recovery in the same period of time. Interestingly, subsequent exposure to 1.8% O₂, with no TTCE, following regeneration in 4% H₂ showed a re-poisoning (i.e., loss of Pt surface atom availability) of the catalyst. This re-poisoning effect from subsequent exposure to O₂, after regenerating in H₂, was also observed by Martínez-Rodríguez et al. [2] and was suggested to be from residual TTCE desorbing from the gas lines. However, due to the fact that all gas lines were heated to 100 °C with heating tape in our experimental system and the long time since TTCE was removed from the feed stream, a more likely reason may be associated with a study by Garcia et al. [25], where it was suggested that O₂ facilitates the migration of adsorbed Cl from the support to the metal surface, a process which H₂ helps reverse. However, more work is needed to validate this hypothesis.

4. Conclusions

The poisoning effect of TTCE on the ability of Pt to activate and adsorb H₂ was investigated at 60 °C and 2 atm using hydrogen surface concentration measurements on both Pt/C and Nfn–Pt/C catalysts exposed to varying concentrations of the impurity (150–540 ppm). Even at as high as 540 ppm TTCE, the reduction in hydrogen surface concentration was observed to be only ca. 33%, which was not enough to shift the H₂–D₂ exchange reaction away from being equilibrium limited. Decrease in the concentration of TTCE resulted in a decrease in the amount of surface hydrogen lost. As expected, the addition of Nafion to Pt/C decreased the rate of TTCE poisoning, due to the polymer inhibiting the rate of diffusion [6], but had very little/no effect on the poisoning behavior of TTCE at steady-state. Considering the high activity Pt has for the adsorption and activation of H₂, these results suggest that the presence of TTCE should have no observable effects on the HOR, due to not being able to shift the reaction away from equilibrium. These results also suggest that the detrimental loss in fuel cell performance in the presence of TTCE is not from the anode but most likely from the cathode.

Co-adsorption of CO and TTCE (30 ppm CO + 150 ppm TTCE) on Pt/C in H₂ showed that the poisoning effect from the mixture to be primarily dominated by the CO. This result is surprising considering overwhelming evidence from FT-IR [25] and surface science studies [22–24,26] suggesting that the presence of Cl should actually destabilize the adsorption of CO due to electrostatic adsorbate–adsorbate interactions. However, because the deposition of Cl on the Pt surface is from the hydrodechlorination of TTCE, it can be speculated that the structure sensitivity of the reaction plays a role. The presence of CO, which has a much more direct method of adsorption, would then severely poison the reaction and limit the deposition of Cl. It should be emphasized that this is only speculation at this point as data regarding the structure sensitivity of the hydrodechlorination of TTCE is extremely limited.

While only a slight reduction in amount of available Pt surface atoms (measured based on H₂ uptake from HDSAP) was observed from the exposure of TTCE to Pt/C in a H₂-only environment, a much

more significant loss of available Pt surface atoms was observed when the catalyst was exposed to TTCE in the presence of both H₂ and O₂. This increase in the poisoning effect of TTCE was found to be contributed by the combination of H₂ and O₂, as the absence of either one resulted in little/no poisoning at the experimental conditions studied (60 °C and 2 atm). This enhancement in the poisoning effect of TTCE in the presence of O₂ clearly shows the role O₂ plays in enhancing the deactivation process of the catalyst and further confirms that the actual poisoning of fuel cell performance by TTCE is at the cathode, rather than the anode. Similar to the recovery results obtain in a fuel cell [2], regeneration of Pt surface atoms (based on hydrogen surface concentration measured) of a poisoned Pt/C showed the highest level of recovery when regenerated in only H₂, followed distantly by H₂ + O₂ and O₂.

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