Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2015 September 3; 119(35): 20328–20338. doi:10.1021/acs.jpcc.5b06362.

Chlorobenzene Poisoning and Recovery of Platinum-Based Cathodes in Proton Exchange Membrane Fuel Cells

Yunfeng Zhai^{a,*}, Olga Baturina^b, David Ramaker^b, Erik Farquhar^c, Jean St-Pierre^a, and Karen Swider-Lyons^b

^aHawaii Natural Energy Institute, University of Hawaii, Honolulu, Hawaii 96822, USA

^bChemistry Division, Naval Research Laboratory, Washington DC 20375-5342, USA

^cCase Western Reserve University Center for Synchrotron Biosciences, Brookhaven National Laboratory, Upton, NY 11973, USA

Abstract

The platinum electrocatalysts found in proton exchange membrane fuel cells are poisoned both reversibly and irreversibly by air pollutants and residual manufacturing contaminants. In this work, the poisoning of a Pt/C PEMFC cathode was probed by a trace of chlorobenzene in the air feed. Chlorobenzene inhibits the oxygen reduction reaction and causes significant cell performance loss. The performance loss is largely restored by neat air operation and potential cycling between 0.08 V and 1.2 V under H₂/N₂ (anode/cathode). The analysis of emissions, in situ X-ray absorption spectroscopy and electrochemical impedance spectra show the chlorobenzene adsorption/reaction and molecular orientation on Pt surface depend on the electrode potential. At low potentials, chlorobenzene deposits either on top of adsorbed H atoms or on the Pt surface via the benzene ring and is converted to benzene (ca. 0.1 V) or cyclohexane (ca. 0 V) upon Cl removal. At potentials higher than 0.2 V, chlorobenzene binds to Pt via the Cl atom and can be converted to benzene (less than 0.3 V) or desorbed. Cl[−] is created and remains in the membrane electrode assembly. Cl[−] binds to the Pt surface much stronger than chlorobenzene, but can slowly be flushed out by liquid water.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered a promising clean energy technology, primarily for use in automotive and propulsion applications and for materials handling. Unfortunately, over 200 airborne pollutants¹, most of which are volatile organic compounds, can be introduced into the PEMFC cathode and cause degradation to the system performance.^{2–5}

Most of these organic compounds adsorb and react on the Pt surface⁶ and compete with the oxygen reduction reaction (ORR) that is the key reaction in the fuel cell processes. Cathode

*Corresponding author. Tel.: 18085931714; Fax: 18085931719; yunfeng@hawaii.edu.

Supporting Information Description

Supporting information provides the configuration and settings of the Spectro-electrochemical cell for XAS, the initial GC-MS and GC graphs, and initial EXAFS data.

poisoning occurs when the contaminant species occupies the surface of the platinum electrocatalysts in the PEMFC catalyst layer, decreases the effective electrochemical surface area (ECSA) of the electrocatalyst, and eliminates the ability of the Pt to convert O_2 to H_2O in the kinetically limited oxygen reduction reaction (ORR) shown in Eq. 1.

Fortunately, most of the contaminants can be removed, and the full or nearly full Pt ECSA can be recovered. In many cases, the cathode simply undergoes recovery or self-recovery after the PEMFC is exposed to neat (e.g., contaminant-free) air, and the contaminants simply desorb. This situation is the case for most unsaturated hydrocarbons and oxygen-containing hydrocarbon contaminants, e.g., aromatics, alkynes, alkenes, carbonyls, ketones, aldehydes and alcohols (toluene, acetylene, propene, acetone, acetaldehyde and iso-propanol).^{7–11}

Highly polar contaminants, such as SO and Cl^- , require electrochemical cycling to remove them from the Pt surface. For SO_2 (H_2S , COS), the electrode must be cycled to high potentials to electrochemically convert the adsorbed S_x species to SO_4^{2-} . The SO_4^{2-} is subsequently desorbed by decreasing the cathode potential to below 0.1 V to decrease the electrostatic attraction between the cathode and the anionic impurity and allow the anion to desorb¹² or at the open circuit potential in N_2 .¹³ Similar cycling to low potentials is required for chloride species, which adsorb proportionately to the charge on the cathode.¹⁴ Extensive exposure to Cl^- should be avoided because it causes irreversible ECSA loss due to Pt conversion to chloroplatinate.¹⁵ The nanoparticulate form of the Pt electrocatalysts in the PEMFC cathode also plays a role in the loss and the recovery of the ECSA because the corners and edges of the Pt cuboctahedra preferentially adsorb the poisons. In the case of Pt poisoning by S_x species, electrochemical studies in combination with X-ray absorption spectroscopy (XAS) showed that additional cycling is required to remove the S from the edge sites of the nanoparticle compared with the faces.¹⁶

Recently, our groups attempted to determine the overall impact of airborne pollutants on PEMFC performance by considering functionality, reactivity, atmospheric concentrations, literature reports, industry suggestions, and toxicity to humans.^{10, 11} Twenty-one contaminants were selected from the more than 150 airborne and indoor pollutants detected by the U. S. Environmental Protection Agency (USEPA) for experimentation.^{10, 11} The single cell performance response to each of these 21 contaminants was investigated under operating conditions that accelerate contamination.¹¹ Chlorobenzene (CIB, C_6H_5Cl), one of the most critical contaminants, was found to degrade cell performance by greater than 90%. Airborne CIB originally arises from applications in industry, including solvents, heat transfer agents, deodorants and degreasers and intermediates), in the production of commodities (e.g., dyestuffs, and rubbers), in agriculture (e.g., herbicides and pesticides) as well as in medical practice (e.g., disinfectants).^{17, 18} Chlorobenzenes are toxic but stable, can accumulate in the surroundings for long time periods, and therefore are labeled as persistent organic pollutants (POPs).¹⁸ Chlorobenzenes are listed as priority pollutants by the USEPA (1988). The catalytic and electrochemical dechlorination of chlorobenzenes has been frequently studied to find proper solutions for detoxifying or decomposing chlorobenzenes using environmentally friendly processes.^{17–23} The CIB is also a residual

solvent in many inexpensive gaskets, adhesives, and membranes under consideration for use in lower cost systems. Study of CIB poisoning is also of academic interest because it offers the opportunity to determine how poisoning by an organohalide compares with that of the organic compound benzene and the halide Cl^- .

Similar to other aromatic compounds, adsorption of CIB on a Pt surface in the gas phase proceeds non-dissociatively with the aromatic ring parallel to the substrate bonding through the π electrons of the ring.²⁴ Theoretically, the most stable point is that at which the chlorinated aromatics are adsorbed through the chlorine atom on a corner platinum atom if the surface is stepped.²⁵ Under vacuum conditions, thermal dechlorination (when heated on platinum from 270 K to 500 K) results in the formation of HCl and benzene. A stable cyclohexadiene intermediate forms above 270 K. In addition to the interaction of benzene with the Pt surface, the strong interaction of chlorine with the Pt surface likely plays an important role in dechlorination.²⁶ In the presence of excess co-adsorbed atomic oxygen, dechlorination of the adsorbate/surface system is substantially inhibited, and desorption of weakly bound molecular CIB is observed at 212 K. Co-adsorbed CIB and atomic oxygen react to form H_2O , CO_2 , and CO over the range of 200–445 K.²⁶ In an H_2 atmosphere, CIB on a Pt surface can be hydro-dechlorinated to HCl, benzene and cyclohexane at room temperature.²⁰

When the CIB adsorbs on a Pt electrode in aqueous electrolyte, the chlorine acts as an electron acceptor and decreases the aromatic adsorption.²⁷ The adsorption is still sufficiently strong to displace water completely and irreversibly from the Pt surface. Conversely, water does not displace the chemisorbed aromatic compound layers already on a smooth polycrystalline Pt electrode.²⁸ The orientation and attachment mode of the aromatic compounds, which are irreversibly adsorbed from aqueous solutions onto smooth platinum electrodes, are dependent on the chemical structure and concentration of the adsorbate, the surface activity, the supporting electrolyte and the pH of the solution.²⁸ The hydrogenation of CIB begins at 0.4 V vs. standard hydrogen electrode (SHE), and it desorbs as chloro-cyclohexane at approximately 0.4 V, as benzene at 0.24 V, and as 1-chlorocyclohex-1-ene at 0.23 V.²⁹ At potentials less than 0.05 V, CIB is reduced to cyclohexane with benzene as an intermediate. The CIB begins to desorb without oxidation or reduction at the potentials where the oxide layers are formed (~ 0.9 V), and at potentials above 1.2 V, CIB is oxidized to CO_2 within several cycles.^{29, 30} The chlorinated aromatic reactions are potential-dependent processes; the potential of course affects the adsorption orientation and attachment mode. However, CIB has not been studied as an air contaminant of PEMFC, and reactions of chlorinated aromatics on Pt surfaces have not received much attention. In addition to the potential variations on the PEMFC cathode, the atmosphere in an operating PEMFC involves H_2 and O_2 , vapour and liquid water, all of which are conditions that make the CIB reactions and contamination mechanisms in PEMFC more complicated.

The XAS technique can be used on electrochemical cells exposed to contaminants to reveal electronic and structural information on the catalysts and the speciation of the adsorbate. Specifically, the μ X-ray absorption near edge structure (XANES) technique produces adsorbate coverage and binding site information using a difference method to isolate the changes in the XANES between a clean sample and one with adsorbates.³¹ This

methodology has been advanced to another level of specificity by determining the μ between the extended X-ray absorption fine structure (EXAFS) of the clean and contaminated electrodes to determine specific adsorption sites and adsorbate coverage on a metal catalyst.³¹ The XANES, EXAFS and μ XANES techniques have been applied to unravel the complex kinetic mechanisms of fuel cell reactions^{31–37} as well as the effect of CO^{38, 39}, SO^{16, 40}, and anions etc.^{41–46}, which are contaminants on Pt and Pt alloy electrochemical catalysts. Specific applications have been summarized in the literature, including H adsorption on supported Pt in the gas phase, water activation at a Pt cathode, methanol oxidation at a Pt anode in an electrochemical cell, sulfur oxidation on Pt, and oxygen reduction on an Au/SnO_x cathode.³¹

In this paper, the PEMFC performance responses to CIB were investigated with CIB at the cathode. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear scanning voltammetry (LSV) and polarization measurements (V-I) were applied to characterize the temporary electrochemical reaction effect and the permanent performance effect. Gas chromatography (GC), gas chromatography mass spectroscopy (GC-MS) and ion chromatography (IC) were used to detect the contaminant reaction products, and X-ray adsorption fine structure (XAFS) analysis in a spectroelectrochemical cell was performed to identify the adsorption structure of CIB on the Pt electrode surfaces under different potentials. All of these characterization results were combined to develop the CIB contamination mechanisms in a PEMFC cathode.

2. Experimental

Experiments were conducted at the FCATS™ G050 series test station (Green Light Power Technologies Inc.) using an internal 50 cm² single cell. The anode flow field was a double channel serpentine shape, and the cathode flow field was a triple channel serpentine. The membrane electrode assembly (MEA) used for the contamination tests was purchased from Gore (GORE® PRIMEA® M715 catalyst coated membrane, CCM) and had a Pt loading of 0.4 mg Pt cm⁻² on each side. The cells were assembled with 25 BC gas diffusion layers (GDL, SGL Tech.) at both the anode and the cathode. The common operating conditions at the anode/cathode were 2/2 flow stoichiometry and 100/50% RH. The outlet back pressures were 10/10 kpag, which correspond to the dry reactant pressure in the cell chamber at 1 atm for cell temperatures of 45 °C. The CIB concentration in the cell cathode chamber was either 20 ppm or 10 ppm.

The contamination experiments applied either a constant current or constant voltage during the three phases of operation: (i) pre-poisoning with neat air, (ii) poisoning until a steady cell performance was achieved, and (iii) self induced performance recovery with neat air until a steady performance was reached. To expose the MEAs, mixed gases of 100 ppm CIB in air (supplied by Matheson Tri-Gas Inc.) were injected into the humidified air feed stream of the cathode, and the humidity of the gas was maintained at a constant level by increasing the temperature setting of the humidifier unit. For the constant current tests, the current density was set at 1 A cm⁻². For the constant voltage tests, the cell voltage was held at OCV (open circuit voltage), 0.85 V, 0.65 V, 0.5 V, 0.3 V or 0.1 V.

For the constant current tests, the V-I curves were obtained under H₂/Air and LSV and CV was under H₂/N₂ mode, respectively, before and after the contamination experiments. The V-I curves were measured from high current to OCV with a stabilizing time of 15 min at each current set point and under operating conditions similar to those of the constant current tests. The CV was conducted at 35 °C with fully humidified hydrogen at the reference electrode and nitrogen at the working electrode with a flow rate of 0.466 L min⁻¹. A total of 10 scans were performed with a scan rate of 20 mV s⁻¹. The potential range was 0.08 V to 1.2 V vs. the hydrogen reference electrode (HRE). During the constant current tests, EIS data from 0.1 Hz to 10 kHz (10 points per decade) were obtained using a Solartron SI1260 Impedance/Gain-Phase Analyzer and a Stanford Research SR560 Low Noise Preamplifier with ZPlot® (Scribner Associates) software. An AC current perturbation of 0.75 A was applied to the single cell operated at a constant current density of 1 A cm⁻². The perturbation resulted in a voltage change of approximately 5 mV.

For the constant voltage tests, the gas composition in the inlet and outlet of the cell were analysed during the contamination experiments via GC (Varian CP-3800) and GC-MS (Bruker SCION 456-GC SQ). For GC, the HCs were separated using a CP 5CB column, and the CO₂ and CO were separated using a Haysep DB/Mol Sieve 5A column. All carbon species were quantified by a flame ionization detector (FID). For GC-MS, the HCs were separated using a J&W CP7413 column and detected by a single quadrupole mass detector. The effluent water was collected and post analysed via IC (Dionex ICS-1100 with a Dionex AS14A anion column).

The X-ray absorption spectroscopy (XAS) experiments were performed on the X3A beamline at the National Synchrotron Light Source at Brookhaven National Laboratory. A Si(220) monochromator with sagittal focusing of the second crystal was used with a downstream Pd-coated cylindrically bent mirror providing vertical focusing and harmonic rejection. The X3A beamline was equipped with a flexible sample stage in which a custom-made spectroelectrochemical cell was mounted. The beam was focused to a 1 mm² spot size at the sample. The Pt L₃ edge spectra were acquired in fluorescence mode using a 13-element Canberra germanium fluorescence detector by scanning the incident energy between 11400 eV and 12400 eV with step of 5 eV in the pre-edge region up to 11544 eV, with 0.5 eV steps in the edge (11544 – 11594 eV) and 0.05/k steps (e.g., at 12000 eV, the step is 0.05 × 12 = 0.6 eV) in the EXAFS region covering 11594 – 12400 eV. A Pt foil was used as a reference to ensure proper instrument calibration with the Pt L₃ absorption edge set to 11564 eV. Where necessary, Zn filters were placed between the sample and germanium detector to reduce scattering photons and ensure that the Ge detector counts were in the linear region (<100 kHz).

The design of a custom-made cell was reported previously.⁴⁰ As shown in Fig. S1 of the supplemental information, the cell consists of two compartments separated by a commercial Ion Power catalyst coated membrane (CCM, 50 wt% Pt/C, 0.4 mg Pt cm⁻² at the anode/cathode, Nafion 212, 10 cm² coated area). The CCM is sandwiched between two pieces of E TEK carbon cloth soaked in 0.1 M HClO₄ solution. One side of the CCM, which is covered with carbon cloth and connected to a current collector (Au foil), serves as a working electrode (WE), whereas the other side (also covered with carbon cloth and connected to a

Pt wire) serves as a counter electrode (CE). The WE compartment is exposed either to a flow of research grade N₂ (99.9999%, Air Liquide) or 500 ppm ClB in synthetic air (Alfa-zero, Air Liquide), and the CE compartment is filled with 0.1 M HClO₄ solution. A no-leak Ag/AgCl electrode (Cypress Systems, Inc.) is mounted in the CE compartment of the cell. All potentials are given vs. the reversible hydrogen electrode (RHE) in 0.1 M HClO₄ solution.

The spectroelectrochemical measurements were performed in potentiostatic mode using an Autolab PGSTAT30 potentiostat. The WE potential was held at 0.1 V, 0.2 V, 0.3 V, 0.5 V or 0.6 V while purging the WE chamber either with N₂ or ClB in air. The potentiostatic experiments were preceded and followed by measurements of three cyclic voltammetry curves at a scan rate of 50 mV s⁻¹ under flow of N₂ through the cell. Prior to a 30-min exposure of the WE to ClB in air, the chamber was held in the flow of N₂ for 10 min. Exposure to ClB in air was followed by a N₂ flush. The XAS were collected before and after exposure of the WE to ClB in air. At least two spectra were collected, and each experiment was repeated twice. For comparison, similar experiments were conducted on a clean WE, which was exposed to only the N₂ flow.

3. Results and Discussion

3.1 Cell performance response to chlorobenzene contamination

3.1.1 Degradation and recovery under constant current—After activation and BOT diagnostics of a new MEA, ClB contamination was investigated in an operating PEMFC using a three-phase experiment. Fig. 1 shows the cell voltage response to 20 ppm ClB at a current density of 1 A cm⁻². For the first 5 hours under neat H₂/Air operation, the MEA exhibited a steady cell voltage of approximately 0.655 V. The slight variation in cell voltage arises from the responses to the AC perturbation of the impedance tests. When the cell was exposed to ClB, the cell voltage rapidly dropped to approximately 0.15 V within 20 min. The cell performance loss is approximately 0.50 V. Then a slow transient degradation appeared until the cell voltage reached a relative steady state value of 0.07 V at 1 hour of exposure. At the end of a 2.5-hour ClB exposure, the cell voltage decreased slightly to reach 0.057 V. This final poisoned state represents an approximate 91% loss in cell performance. These results show the significant impact of ClB on the cathode of these single cells.

When the ClB injection was stopped, the cell voltage partially recovered within three time phases. As shown in Fig. 1, within the first 1.5 hours of recovery, the cell voltage was slowly restored to 0.13 V with a voltage oscillation at approximately 0.10 V for approximately one hour. In the following 2 hours, the voltage increased rapidly up to approximately 0.53 V. The voltage recovery subsequently slowed and reached a steady value of 0.62 V after approximately 8 hours of recovery. After self-recovery, the cell voltage represented a 95% recovery of cell performance. To further restore the cell performance, CV scans and V-I measurements were conducted, and the results are presented in Section 3.1.3. After the CV scans and V-I measurement, the voltages increased up to 0.65 V. The final voltages after the V-I measurements show nearly complete recovery of the cell performance. These results indicate that the cell performance loss can be only partially restored after switching to neat air operation, and fortunately, the irreversible performance loss can be

restored by the CV scans and V-I measurement except for an irrecoverable 1% cell performance loss.

As the literature review reveals, CIB can strongly adsorb on the Pt surface in competition with O_2 and H_2O , and the adsorption/reactions of CIB on Pt surfaces depend on the potential. The cell voltage response to CIB exposure in Fig. 1 is attributed to the adsorption, reaction, and desorption of CIB on the PEMFC electrode. Before exposure to CIB, the cell voltage was 0.655 V. The ohmic resistance of the MEA, which was measured by AC impedance, was approximately $0.063 \Omega \text{ cm}^2$. Considering the ohmic polarization of the MEA and disregarding the hydrogen oxidation over potential at the anode, the cathode potential is approximately 0.72 V. This potential is much lower than the CIB oxidation/desorption potential and much higher than the reduction/desorption potential on the Pt surfaces. Therefore, upon introduction of CIB into the cell cathode, the strong adsorption of CIB poisons the Pt sites for the ORR and results in a significant and rapid cell performance loss. When the cell voltage further decreases, the cathode potential drops to approximately 0.45 V, where the Pt electrode should be relatively free of Pt oxide or hydrogen, but intermediates in the ORR (i.e., OOH and HOOH) are known to be located on the surface.⁴⁷ However, the adsorption/desorption equilibrium and orientation of CIB on the Pt cathode should not vary substantially in the potential range of 0.7 – 0.4 V.²⁸ As the cell voltage decreases further with time, however, crossover H_2 begins to accumulate on the Pt surface, additional HOOH builds up, and the adsorbed CIB can be electro-reduced and/or hydrogenated²⁹. The cell performance degradation slows, but a cell voltage of 0.057 V is ultimately reached. The adsorbate coverage and the ORR apparently reach a steady state that leads to a stable cell voltage. After discontinuing the CIB injection, the desorption and hydrogenation of adsorbed CIB might continue simultaneously at the low potential; the hydrogenation product could be benzene, which adsorbs on Pt surface stronger than CIB,²⁷ but the CIB desorption could still release a portion of the Pt sites to the ORR reaction. This release corresponds to the first stage of voltage recovery. The cell voltage recovered slowly to 0.13 V within the first 1.5 hours of recovery. Subsequently, a relatively fast recovery appears when most of the adsorbed CIB apparently desorbs. The 5% irreversible cell voltage loss at the end of this self-recovery suggests that a certain amount of residuals remains on the cathode, perhaps at the corners/edges of the Pt nanoparticles where it might bind more strongly.

3.1.2 Electrochemical Impedance Spectroscopy Analysis—The AC impedance responses of the MEA were collected during the CIB contamination experiment to determine the impact of CIB on the electrochemical reactions in the MEA. Fig. 2 and the inset show a representative impedance spectrum in terms of a Nyquist plot for each phase of the contamination experiment. As shown in the inset, before exposure, the response of the MEA shows a typical EIS at high current densities characterized by three distinguishable depressed semicircles.⁴⁸ The value of approximately $0.064 \Omega \text{ cm}^2$ at the intersection of the EIS with the Re (Z) axis at high frequencies arises from the serial ohmic resistance of proton and electron transport in the bulk system. The high frequency (>1 kHz) response can be attributed to the hydrogen oxidation reaction (HOR), the midrange frequency (5 Hz – 1 kHz) response to the ORR (the diameter of the midrange frequency arc represents the ORR charge

transfer resistance), and the low frequency (0.1 Hz – 5 Hz) response to mass transport in the gas diffusion electrode (GDE) (the diameter of the low frequency arc is usually considered as the mass transport resistance of the oxygen in the GDE). During exposure, the mid- and low-frequency arcs in the EIS before and at the steady poisoning state (20 min and 2 hours exposures) merge together and are significantly expanded compared with the arcs prior to exposure. An additional inductive loop also appears at low frequencies, as shown in the fourth quadrant during the exposure, which is similar to the response of the HOR to CO contamination at the PEMFC anode.⁴⁹ Even after a 1.2 hours self-recovery, the EIS shows the largest arcs in the mid and low frequencies. After 8 hours of self-recovery, the EIS overlaps that before exposure, as shown in the inset. These results suggest the possible complete recovery of the MEA.

The expanded and merged arc in the mid frequency indicates that the ORR charge transfer resistance increased dramatically and dominated the ORR resistance. The significant ORR charge transfer effect suggests a severe loss of electrode ECSA due to poisoning of Pt by CIB and its intermediates. The inductive loop at low frequencies might be attributed to the impact of AC perturbations on the contaminant coverage on the Pt surface. When applying the AC perturbations on the CIB covered cathode, the slight potential changes could promote or inhibit the electrochemical oxidation or reduction of adsorbates on the Pt surfaces. If electrochemical oxidation of CIB intermediates occurs on the Pt surface, the effect of potential changes on these reactions would be directed in the direction opposite to that on the ORR. The effect would show an aggravated contamination response, i.e., a significantly expanded arc in the mid and low frequencies. In contrast, if the electrochemical reduction of CIB intermediates occurs on the Pt surfaces, the effect of potential changes on the adsorbate reaction is complementary to that on the ORR. The effect would show a mitigated contamination response, i.e., inductive behavior. Therefore, the conspicuous inductive behavior suggests that the CIB intermediates might be electrochemically reduced on the Pt surfaces on the cathode at steady state poisoning. Further, the reduction is rapid and sensitive to a slight potential change. The small perturbation could noticeably affect the coverage of the CIB intermediates on the Pt surface due to the rapid reduction. The reduction of CIB intermediates might continue throughout the 2-hour self-recovery, whereas the cell voltage is restored to 0.13 V, as indicated by the obvious inductive loop in the EIS obtained after 1.2 hours of self-recovery. This mechanism requires additional study and will be analyzed in future EIS work.

3.1.3 CV, LSV and VI characterizations—After the CIB contamination experiment (EOT), diagnostics were performed with a comparison to BOT to determine the permanent influence of CIB contamination on the MEAs. The CV scanning was used after self-recovery to detect the activity changes of the cathode, analyze possible intermediate residue on the Pt surfaces and attempt to obtain any additional recovery in the MEA performance. The CV profiles prior to the experiments show the typical features of Pt/C in a CCM. As shown in Fig. 3, after the CIB contamination experiment, the hydrogen oxidation/reduction current peaks (within a potential range of 0.10 – 0.40 V vs. HRE) were partially reduced during the first cycles, and the onset of the Pt oxidation current shifted positively. An obvious extra oxidation current was noted in the Pt oxidation potential range, whereas the Pt

oxide reduction current peaks obviously decreased. After 9 cycles of CV clean-up, the 10th CV curve shows a nearly restored H oxidation current and Pt oxidation current above 0.85 V, except in the region of approximately 0.2 V, which is normally attributed to adsorption on the particles/edges of the nanoparticles as opposed to the faces and gives rise to the feature closer to 0.1 V. However, the shift of the Pt oxidation onset, the decrease of the Pt-oxide reduction current, and the change of the hydrogen reduction current peaks still remain. The ECSA percentage changes were calculated by comparing the hydrogen oxidation current peak of each cycle to that from before the contamination experiment. The ECSA was improved from 88.6% to 96.8% from the first cycle to the sixth cycle and subsequently maintained a stable value.

The reduced hydrogen oxidation current in the first cycle is attributed to the residue of CIB intermediates remaining after self-recovery. The intermediate residue occupies the Pt active sites and causes the irreversible cell performance loss shown in Fig. 1. These residues could be electro-oxidized at potentials above 0.85 V and result in the extra oxidation current in the Pt oxidation potential range.^{21, 29} In CV scan up to 1.2 V, the residue is cleaned off after several cycles, and a certain amount of the Pt active sites are again available. The ECSA of the electrode is restored gradually during CV cycling, which further improves the cell performance, as shown in Fig. 1. However, the shift in the onset potential for Pt oxidation remains unchanged during the 10 CV scans. These results suggest that some electro-inactive species from the CIB remain on the Pt surfaces (most likely on the more active corner/edges of the Pt nanoparticles) and permanently alter the MEA. The remaining 3.3% irrecoverable ECSA loss should be accounted for by these electro inactive species, which result in the ~1% irrecoverable cell performance loss in Fig. 1.

Hydrogen crossover currents through the MEA membranes are also detected by LSV before and after the CIB contamination experiments. The oxidation current densities showed a similar value of ~1.1 mA cm⁻² before and after the contamination experiment tests. These results suggest that CIB contamination has no obvious effect on H₂ membrane permeability.

The MEA polarization curves were collected before and after the CIB contamination experiments as shown in Fig. 4. At current densities greater than 0.8 A cm⁻², the polarization curves almost overlap with each other, but at values less than 0.8 A cm⁻², the cell performance shows a slight difference. The inset shows the kinetic region of the polarization curves in the Tafel coordinates at current densities of 0.01 A cm⁻² to 0.1 A cm⁻². Both polarization curves show similar Tafel slopes of ~71 mV per decade, which confirms the absence of active adsorbates (as opposed to simple poisons) on the electrode surface. The 16±1 mV difference between the two curves could be attributed to the 3.2% irrecoverable ECSA loss and perhaps also to the adsorption of certain electro inactive species, such as Cl⁻ created during the CIB contamination. These results suggest that a permanent kinetic effect remains after neat air operation and CV scan recovery.

3.2 Chlorobenzene contamination reactions in PEMFC

3.2.1 Cell performance degradation and recovery under constant voltages—To better characterize the reactions of CIB in an operating PEMFC, CIB contamination was also investigated under different constant cell voltages using the same test procedure as in Fig. 1.

The GC-MS, GC and IC were used to identify and measure the products of the reactions. Fig. 5(a) illustrates the current density transients at cell voltages of 0.5 V, 0.65 V and 0.85 V and the OCV transient resulting from a temporary 10 ppm CIB exposure. Note: “0.5-0.49(IR:0.6-0.5) V” indicates the variation of the cell voltage (internal resistance corrected voltage) during the CIB exposure and after self-recovery. Before the CIB injection, the current was higher at a lower cell voltage, as expected. When the CIB injection was initiated, all of the current densities decreased rapidly within the first hour of exposure, and the rate of reduction subsequently slowed until the current densities reached stable values. After the CIB injection was interrupted, the current density was partially restored to a stable value within a certain time. The recovery rate varies with the different injection cell voltages. The details of the current density response at different voltages are listed in Table 1. For example, at 0.5 V, the current density decreased approximately 71.6% within 0.8 hour of exposure and reached a relatively stable value at 3.5 hours after the exposure with an 87.4% loss, whereas at the end of the 10-hour exposure, the total performance loss was approximately 91.8%. Within the first 6 hours of self-recovery, the current density at 0.5 V was restored to 78.2% of its value before the CIB exposure, and at approximately 10 hours, the current density increased to a stable value of approximately 90% of its initial performance before the CIB exposure. From Table 1, beginning at exposure, the current density decreases were inversely proportional to the cell voltages; however, during self-recovery, the cell at the highest performance level. At OCV, the voltage slowly decreased to 95.6% within the 10-hour exposure and restored to 96.3% during the self-recovery.

The constant voltage test could not be directly conducted at 0.3 V and 0.1 V because the cell current densities at 0.3 V and 0.1 V exceeded the load bank limit in the test station, and the mass transport limitation was reached, thus starving the cathode. Therefore, the CIB exposure at 0.3 V and 0.1 V was combined into one experiment and initiated in constant current mode with a current density of 1 A cm^{-2} , as shown in Fig. S2; when the cell voltage degraded to 0.3 V, the contamination test was switched to constant voltage mode (CC→CV) for GC and GC-MS analysis. Fig. 5(b) shows the constant voltage experiment portion of the cell current density response to CIB poisoning and recovery. The cell current density decreased from 1 A cm^{-2} to 0.23 A cm^{-2} within approximately 5 hours exposure at 0.3 V. When the cell voltage was switched to 0.1 V, the current density reached 0.88 A cm^{-2} , decreased slowly and stabilized at 0.78 A cm^{-2} within approximately 7 hours. While the cell voltage was switched back to 0.3 V, the current density dropped to 0.37 A cm^{-2} , and subsequently stabilized at 0.18 A cm^{-2} in 4 hours. The self-recovery was performed first at 0.1 V until the current reached the final limit (approximately 2.2 hours) and then at 0.3 V for approximately 1 hour. At the beginning of self-recovery, the CIB exposure was interrupted simultaneously with the voltage switching (from 0.3 V to 0.1 V); the current density jumped back to approximately 0.80 A cm^{-2} , which is similar to the current density at the steady poisoning state at 0.1 V. Next, the cell current density began recovery at 0.1 V and at 0.3 V. Comparison of the current density responses at constant voltage reveals that the CIB has a more severe effect on the MEA at 0.3 V than that at 0.1 V, where the IR voltage was 0.32 and 0.16 V, respectively; however, the self-recovery was easier at 0.1 V than at 0.3 V.

In summary, during the CIB contamination and self-recovery, both the degradation and recovery rates decrease with an increase in cell voltage when the cell voltage exceeds 0.3 V,

and a higher cell voltage resulted in a more irreversible cell performance loss. The cell performance also undergoes fast recovery below 0.16 V. These results are consistent with the cell performance response to CIB under constant current mode.

3.2.2 GC-MS and GC analysis of the reaction products at constant cell voltage

—During the CIB exposure under various constant voltages, the products of the CIB reactions in the PEMFC were analyzed by comparing the gas composition in the inlet and outlet of both the cathode and anode. A GC-MS was used to identify and measure the heavy molecular products, and a GC was used to analyze the light products. The original GC-MS graphs are provided in the supplemental information, i.e., Fig. S3, together with all of the MS results in Fig. S4. The results obtained above 0.3 V are similar to those at OCV: the cathode outlet gases show a slightly reduced CIB peak during poisoning and an obvious CIB peak during self-recovery. However, at 0.3 V and 0.1 V, the cathode outlet gases show a considerable benzene peak during poisoning, compared in Fig. S5a. All of the anode outlet gases show a clear cyclohexane peak during CIB poisoning, and the peak size increases with the cell voltage decrease, as shown in Fig. S5b. It should be noted that no other type of species was detected in the cathode or anode outlet gases in the GC (Fig. S6) and GC-MS analysis. These results demonstrate the adsorption/desorption and the reactions of CIB in the cell cathode as well as the anode during the poisoning/recovery. If the cell cathode potential is equal to or less than 0.32 V, the CIB is reduced to benzene in the cathode; above 0.32 V, only adsorption/desorption occur but no conversion of CIB occurs in the cathode. The formation of benzene and cyclohexane indicate that CIB can be reduced to benzene at and below 0.32 V on the cathode and that the CIB/benzene also can permeate through the membrane to the anode, where the potential is low, and become further reduced to cyclohexane.

A summary of the CIB conversion products under different cell voltages is given in Fig. 6. The conversion ratios were estimated by dividing the product amounts from the outlet by the CIB amount at the inlet with the GC-MS results. The cell internal resistance corrected voltage (IR-Voltage) was applied because the corrected voltage is close to the cathode potential, which is used to discuss the potential dependency of CIB adsorption and reactions. Fig. 6 shows a clear potential dependency of production ratio. On the cathode, the benzene production decreases with the increase in cathode potential, and above 0.32 V, no detectable benzene is observed in the outlet gases. On the anode, the amount of cyclohexane created decreases with the increase in the cell voltage; a trace (~0.05% of total CIB) of benzene also occurs in the anode outlet gases at the cathode potential of 0.16 V. The benzene might be a hydrogenation product of CIB due to the existence of hydrogen at low potential. On the cathode, at 0.16 V, approximately 5.7% of CIB was converted to benzene; above 0.4 V, as observed from the CV curve in Fig. 3, the hydrogen can be readily oxidized, and the lack of hydrogen minimizes the CIB hydrogenation. On the anode, where the potential is less than 0.05 V, a small amount of CIB permeates from the cathode and is reduced to cyclohexane. Detectable benzene is also noted when the cathode voltage is less than 0.3 V, which might come from the cathode side. In summary, above 0.32 V, only adsorption/desorption of CIB occurs; below 0.32 V, the adsorbed CIB is reduced to benzene; and below 0.1 V, the CIB and the created benzene are reduced to cyclohexane. These results support the hypothesis

that CIB adsorption/oxidation occurs at high potentials, adsorption/desorption occurs at middle potentials, and adsorption/reduction occurs at low potentials, as found during the analysis of the CV and EIS data in Section 3.1.

3.2.3 Cell effluent water analysis—During the constant voltage tests, the effluent water was also collected for IC analysis on the created Cl^- ions, and the results are shown in Fig. 7. It should be noted that the tests at 0.1 V and 0.3 V were combined together, and only a mixed result appears in Fig. 7. At 0.1 V and 0.3 V, there is a significant amount of Cl^- in the effluent water, but at higher voltage, the Cl^- concentration becomes negligible, especially at 0.65 V and 0.85 V. These results are consistent with the GC-MS analysis, which shows that the CIB is hydrogenated/reduced to benzene at the cathode and to cyclohexane at the anode at low cell voltage. The byproduct is HCl, which correlates with the ECSA loss of the CV analysis and the kinetic performance loss of the VI curves in Section 3.1.3.

3.3 Chlorobenzene adsorption on the Pt surface

X-ray adsorption spectroscopy was used to investigate the potential dependency of the CIB adsorption on the PEMFC cathode. Two different previously reported XAS analysis procedures were used to reveal the relative CIB coverage on the Pt surface: the μ XANES procedure that uses the first ~ 40 eV data above the Pt edge^{35–37} and the FT(μ) EXAFS analysis procedure that uses the data above 40 eV extending to ~ 800 eV⁵⁰. Both analysis procedures isolate the effect of the adsorbate by taking the difference,

$$\Delta\mu = \mu(V, \text{CIB}) - \mu(0.5\text{V}, \text{N}_2) \quad [2]$$

where the spectra at 0.5 V and the WE chamber purged with N_2 , is assumed to represent “clean” Pt. Of course, in an aqueous electrochemical environment, some water molecules are always in contact with the Pt surface, but it has been previously shown that these water molecules are not site specifically adsorbed such that they produce little or no scattering in the XAS spectra⁴¹. In contrast, it has been repeatedly shown that as the potential exceeds 0.6 V, the μ tracks the adsorption of O and OH, and below 0.3 V, it tracks the adsorption of H, both originating from water activation^{36–39, 51}. These O(H) or H adsorbates are adsorbed in particular Pt surface sites, e.g., H in either a 3-fold or a top site (often referred to as under- or over-potential deposited H, respectively), O in a bridged site, or OH in an atop site. These different adsorption sites produce characteristic μ signatures as confirmed by theoretical FEFF8 calculations⁵², thus enabling the μ XANES procedure to identify both the adsorbate and the adsorption site.

Fig. 8 shows the μ XANES data defined as in Eq. 2 at 5 different cell potentials after exposure to 500 ppm CIB in air. Full multiple scattering calculations were performed to obtain the theoretical X-ray absorption spectra μ_{theo} on a small Pt_6 cluster to model the Pt surface, as shown in Fig. 8. The difference, $\mu_{\text{theo}} = \mu_{\text{theo}}(\text{Cl}/\text{Pt}_6) - \mu_{\text{theo}}(\text{Pt}_6)$ was obtained with the Cl in either an atop, bridged, or 3-fold site, giving three significantly different μ signatures as previously reported⁴². The result that shows the best agreement is clearly that with Cl in the atop site as illustrated in Fig. 8. It should be noted that Cl and CIB could give a similar signature, assuming the Cl end of the CIB molecule is bound to the Pt because atoms not bound to the surface do not contribute significantly to the μ . As performed many

times previously^{16, 36–39}, we can also plot the magnitude of μ , $|\mu_{\max}|$ at the maximum of approximately 3 eV (as indicated by the double arrow in Fig. 8) to reflect the relative coverage of ClB (see Fig. 9).

Before discussing the relative ClB/Pt coverage indicated by $|\mu_{\max}|$, as shown in Fig. 9, we obtained the relative ClB/Pt coverage from the $|FT(k-\mu)|$. The large overlap between the Pt-ClB peak and the Pt-Pt peaks in the EXAFS spectrum (Fig. S7) makes this separation difficult, but we can isolate the Pt-Cl contribution by taking the difference μ , as defined by Eq. 2, and subsequently taking the Fourier Transform of this difference, $FT(k-\mu)$. Fig. 10(a) shows this difference for both ClB/Pt and “clean” Pt at 0.2 V. This difference for the “clean” Pt is within the noise level and the values for the ClB/Pt shows the difference due to the adsorbed ClB. Fig. 10(b) shows these data at five different cell potentials, which reveals a 2-peak contribution instead of one, apparently because of the varying Pt-Cl scattering cross section. We take the average intensity of these two peaks to represent the relative coverage of ClB/Pt, as shown in Fig. 9.

Fig. 9 shows that the relative coverage of ClB/Pt apparently peaks at approximately 0.2 V. One can better understand this result after comparison with the known coverage of such anions as $H_2PO_4^{-44}$, $HSO_4^{-16, 41}$, and the halides Cl^- , Br^- , and I^- in aqueous electrolytes^{42, 45}. Studies on adsorption of these anions on metals in the gas phase have been reported in the literature^{16, 41–45}, but more relevant for this work are those studies of the adsorption that occurs in an electrochemical environment on an electrified surface, where the anions must contend with the water double layer that also forms on Pt. Even more relevant are those studies that use the μ technique in situ, and therefore, we summarize only those results below. In all cases, the anion coverage generally goes to zero below 0.1 V and above 0.7 V because these weakly adsorbing anions are mostly “driven” off the surface by the more tightly adsorbing H below 0.2 V and O(H) above 0.7 V. Between these limiting potentials, the coverage is dictated by the competition between several competing forces: water double layer formation, the strength of the electrostatic interaction between the anion and the surface, and the lateral inter adsorbate interactions. Most critical is the relative size of the anion because all of the anions mentioned are singly charged (-1). As the anion spherical radius increases, the surface charge density decreases, and therefore the electrostatic interactions decrease (both with the surface and the lateral inter-adsorbate).

The Cl^- /Pt coverage peaks approximately at 0.7 V because the Pt surface becomes more electropositive with increasing potential, thus enabling the relatively small Cl^- to crowd onto the Pt surface just before it is driven off by the adsorbing O(H)⁴². At high coverage, the lateral inter-adsorbate interactions become important such that commensurate overlayers form when the Cl^- might not all exist in the same atop site but rather populate the atop, bridged, and 3-fold sites at high coverage to decrease the lateral interactions. In contrast, the Br^- /Pt coverage is relatively constant in the range of 0.2 – 0.7 V with an ordered adsorption layer of Br^- in the atop sites^{42, 45}. The I^- /Pt coverage decreases, peaking at approximately 0.2 V because the much larger I^- is not able to form compressed commensurate overlayers like the Cl^- , and the much lower surface charge density on the large I^- makes the electrostatic charge interaction less able to contend with the water double layer that also forms as 0.2 V is exceeded⁴⁵.

The coverage of bisulfate and biphosphate on Pt in an electrochemical environment, as exhibited by the μ , is also relevant in this work^{41, 44}. The bisulfate coverage on Pt reaches a peak at approximately 0.5 V, but it is invisible to the scattering process that produces the μ because bisulfate does not adsorb on specific sites⁴¹. Thus the bisulfate is invisible just as the water double layer is invisible. However, at the outer limits, where H begins to adsorb below 0.3 V and O(H) begins to adsorb above 0.65 V, bisulfate becomes visible in the μ because the H and O(H) adsorbed in site-specific sites forces the bisulfate into specific sites. Biphosphate, which binds more strongly to Pt, is visible in the μ at room temperature⁴⁴ but becomes invisible at higher temperature as the increased kinetic motion enables a higher mobility on the surface⁴⁶.

Not unexpectedly, the ClB/Pt coverage as shown in Fig. 9 does not behave like Cl^- , but more like the larger anions, e.g., I^- or Br^- . The ClB molecule is not charged, but most likely, the Cl end is somewhat negatively charged such that ClB behaves in a manner similar to that of I^- , which decreases (or at least becomes more invisible like bisulfate) on the Pt cluster planes when it cannot compete with the water double layer formation. However, at the Pt cluster corners/edges, when water double layer formation is hindered, it behaves more like Br^- (it remains constant). Thus, the μ visible coverage for ClB apparently does not continuously decrease or become invisible (similar to I^-); only that from the planes between 0.2 and 0.5 V becomes invisible and that on the corner/edges remains visible above 0.5 V.

The cause of the apparent difference between the two XAS results in Fig. 9 above 0.5 V is a relevant question. As the potential exceeds 0.5 V, the μ XANES suggests that the coverage decreases, but the FT(μ) EXAFS suggests that it increases slightly or remains constant. The actual coverage is likely best reflected in the FT(μ) EXAFS because the μ XANES magnitude (intensity/ClB adsorbate) might decrease because of the polarization of the weak Pt-ClB bond with increasing potential, as previously observed with Pt-I⁴⁵. The ClB molecule is certainly polarizable and as it binds on the Pt surface, the electrons are shifted within the molecule and perhaps even to the Pt as the Pt surface becomes more positively charged with potential. The XANES region will be affected to a greater extent by this electron redistribution than the EXAFS region, and the Ft(μ) EXAFS perhaps more faithfully reflects the actual ClB/Pt coverage.

From the above XAS analysis, the additional information from the literature, and the results obtained in this work, we can conclude that (see Fig. 11): ClB bonds relatively weakly (via van der Waals dispersion forces) in a nearly flat orientation on neutral Pt(111)⁴⁵ in the gas phase, but on steps or on small particles (as exists in these catalysts), it apparently bonds in more tilted positions or more vertically with the Cl down to decrease its footprint and better compete with the water double layer formation. Little information has been reported on the bonding of ClB on an “electrified” Pt surface, although certain references suggest atop bonding with Cl down⁵⁴ in an electron-deficient center (i.e., positively charged), as indicated by the μ XANES signature. When the potential exceeds 0.7 V, co-adsorbed O(H) oxidizes the ClB to produce a wealth of products, including CO_2 . Below 0.25 V, when co-adsorbed H/M exists with ClB/Pt (perhaps on top or possibly blocking certain Pt sites because H_{upd} is decreased in the presence of ClB), dissociation of ClB occurs, producing benzene and HCl. As the XAS data reveal, the ClB begins to desorb at 0.2 V when 3-fold H

begins to adsorb (also referred to as under potential deposited H), but significant hydrogenolysis of benzene to C_6H_{12} does not occur until below 0.1 V, when the more active atop H (also referred to as over potential deposited H) begins to adsorb.

4. Conclusions

The effects of ClB contamination in the PEMFC cathode were investigated, and ClB adsorption and reactions on the Pt surface were studied using XAS (XANES and EXAFS), GC, IC, and GC/MS. A 20 ppm ClB exposure caused a cell performance loss of greater than 90%; however, this loss was partially recovered (up to 94%) by neat air operation and up to 98% of the loss was recovered by CV cycling. The ClB adsorbate configurations and reactions depend on the electrode potential, as illustrated in Fig. 11. At low potential (<0.1 V vs. SHE), H adsorbs on the Pt surface; ClB deposits on top of the H and/or directly binds on the Pt surface via the benzene ring and is reduced to C_6H_{12} upon removal. Near the potential of zero charge, ClB adsorbs on Pt via van der Waals forces with a low coverage. Above 0.2 V, and beginning at 0.10 V, ClB binds to Pt via the Cl atom. The adsorbed ClB can be reduced to C_6H_6 if the electrode potential is less than 0.3 V or can desorb at higher potentials. The ClB adsorption causes significant increase in the ORR charge transfer resistance. At low potential, the reduction of ClB adsorbates showed inductive behavior in EIS. The CV results suggest that the cathode catalyst surface is partially restored by neat air operation, but there are still some contaminant residues in the MEA and on the Pt which can be mostly removed by CV cycling. The polarization curves show certain permanent performance losses that might be attributed to the effect of Cl^- , which was created during the ClB contamination and subsequent dissociation to benzene and Cl^- . The Cl^- binding to the Pt surface is much stronger than that of C_6H_6Cl . Fortunately, the Cl^- can be flushed out slowly by liquid water. The potential-dependent contamination mechanisms identified in this work might apply to other aromatic compounds, but further testing will be required to fully confirm this hypothesis. Furthermore, liquid water scavenging might offer a useful mitigation strategy for other halocarbon contaminants.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors are grateful to the United States Department of Energy (award DE-EE0000467) and the Office of Naval Research for financial support of this project. The authors are grateful to the Hawaiian Electric Company for ongoing support of the operations of the Hawaii Fuel Cell Test Facility. Operations of the NSLS beamline X3A were supported by the Center for Synchrotron Biosciences grant P30-EB-009998 and by the National Institute of Biomedical Imaging and Bioengineering. The authors also thank John Toomey for assistance with the XAS measurements.

References

1. Air Quality Statistics Report, United States Environmental Protection Agency. AirData Home page: Access to monitored air quality data from EPA's Air Quality System data Mart. <http://www.epa.gov/airquality/airdata/index.html> (accessed August 2015)

2. Borup R, Meyers J, Pivovar B, Kim Y, Mukundan R, Garland N, Myers D, Wilson M, Garzon F, Wood D, et al. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chem Rev.* 2007; 107:3904–3951. [PubMed: 17850115]
3. St-Pierre, J. *Polymer Electrolyte Fuel Cell Durability*. Springer; New York: 2009.
4. Cheng X, Shi Z, Glass N, Zhang L, Song D, Liu Z, Wang H, Shen J. A Review of PEM Hydrogen Fuel Cell Contamination: Impacts Mechanisms and Mitigation. *J Power Sources.* 2007; 165:739–756.
5. Moore J, Adcock P, Lakeman J, Mepsted G. The Effects of Battlefield Contaminants on PEMFC Performance. *J Power Sources.* 2000; 85:254–260.
6. Ma Z, Zaera F. Organic Chemistry on Solid Surfaces. *Surf Sci Rep.* 2006; 61:229–281.
7. Mohtadi R, Lee W, Van Zee JW. Assessing Durability of Cathodes Exposed to Common Air Impurities. *J Power Sources.* 2004; 138:216–225.
8. Li H, Zhang J, Shi Z, Song D, Fatih K, Wu Sh, Wang H, Zhang J, Jia N, Wessel S. PEM Fuel Cell Contamination: Effects of Operating Conditions on Toluene-Induced Cathode Degradation. *J Electrochem Soc.* 2009; 156:B252–B257.
9. Smith M, Myers D. The Effect of Hydrocarbon Contaminants on the Oxygen Reduction Activity of Pt/C Electrocatalysts: a Rotating Disk Electrode Study. 211th ECS meeting, Abs. :0214.
10. St-Pierre J, Angelo M, Zhai Y. Focusing Research by Developing Performance Related Selection Criteria for PEMFC Contaminants. *ECS Trans.* 2011; 41(1):279–286.
11. St-Pierre J, Zhai Y, Angelo M. Effect of Selected Airborne Contaminants on PEMFC Performance. *J Electrochem Soc.* 2014; 161:F280–290.
12. Gould B, Bender G, Bethune K, Dorn S, Baturina O, Rocheleau R, Swider-Lyons K. Operational Performance Recovery of SO₂-Contaminated Proton Exchange Membrane Fuel Cells. *J Electrochem Soc.* 2010; 157:B1569–B1577.
13. Baturina O, Swider-Lyons K. Effect of SO₂ on the Performance of the Cathode of a PEM Fuel Cell at 0.5–0.7 V. *J Electrochem Soc.* 2009; 156:B1423–B1430.
14. Baturina O, Epshteyn A, Northrup P, Swider-Lyons K. The Influence of Cell Voltage on the Performance of a PEM Fuel Cell in the Presence of HCl in Air. *J Electrochem Soc.* 2014; 164:F365–F372.
15. Baturina O, Epshteyn A, Northrup P, Swider-Lyons K. Insights into PEMFC Performance Degradation from HCl in Air. *J Electrochem Soc.* 2011; 158:B1198–B1205.
16. Ramaker D, Gatewood D, Korovina A, Garsany Y, Swider-Lyons K. Resolving Sulfur Oxidation Removal from Pt Pt₃Co Electrocatalysts Using in Situ X-ray Absorption Spectroscopy. *J Phys Chem C.* 2010; 114:11886–11897.
17. Long C, Li Q, Li Y, Liu Y, Li A, Zhang Q. Adsorption Characteristics of Benzene–Chlorobenzene Vapor on Hypercrosslinked Polystyrene Adsorbent a Pilot-Scale Application Study. *Chem Eng J.* 2010; 160:723–728.
18. Wang J, Mei Y, Liu Ch, Chen J. Chlorobenzene Degradation by Electro-heterogeneous Catalysis in Aqueous, Solution: Intermediates Reaction Mechanism. *J Environmental Sci.* 2008; 20:1306–1311.
19. Hsu, Ch; Jou, Ch. Catalytic Degradation of Chlorobenzene in Aqueous Solution with Microwave and Waste Metals. *Sustain Environ Res.* 2013; 23:49–52.
20. Liu M, Han M, Yu W. Hydrogenation of Chlorobenzene to Cyclohexane over Colloidal Pt Nanocatalysts under Ambient Conditions. *Environ Sci Technol.* 2009; 43:2519–2524. [PubMed: 19452910]
21. Hoshi N, Sasaki K, Hashimoto S, Hori Y. Electrochemical Dechlorination of Chlorobenzene with a Mediator on Various Metal Electrodes. *J Electroanal Chem.* 2004; 568:267–271.
22. Rodríguez J, Pastor E. A Comparative Study on the Adsorption of Benzyl Alcohol Toluene Benzene on Platinum. *Electrochim Acta.* 2000; 45:4279–4289.
23. Liu L, Zhao G, Wu M, Lei Y, Geng R. Electrochemical Degradation of Chlorobenzene on Boron-Doped Diamond Platinum Electrodes. *J Hazard Mater.* 2009; 168:179–186. [PubMed: 19264395]
24. Richardson N, Palmer N. A Comparison of Chlorobenzene Benzene Adsorption on Pt{001}. *Surf Sci.* 1982; 114:L1–L6.

25. Yoneda T, Takido T, Konuma K. Hydrodechlorination Reactivity of Para-Substituted Chlorobenzene over Platinum/Carbon Catalyst. *J Mol Catal A: Chem.* 2007; 265:80–89.
26. Haines B, Gland J. Deep Oxidation of Chlorobenzene on the Pt(111) Surface. *Surf Sci.* 2008; 602:1892–1897.
27. Naumov V, Tyurin Y. Effect of Substituents on the Adsorption of Aromatic Compounds on a Smooth Platinum Electrode at High Anode Potentials. *Elektrokhimiya.* 1974; 10(3):413–417.
28. Soriaga M, Hubbard A. Determination of the Orientation of Adsorbed Molecules at Solid-Liquid Interfaces by Thin-Layer Electrochemistry: Aromatic Compounds at Platinum Electrodes. *J Am Chem Soc.* 1982; 104:2735–2742.
29. Musilová-Kebrlová N, Janderka P, Trnková L. Electrochemical Processes of Adsorbed Chlorobenzene and Fluorobenzene on a Platinum Polycrystalline Electrode. *Collect Czech Chem Commun.* 2009; 74:611–625.
30. Kazarinov V, Maksimov K, Gorokhova L, Vasil'ev Y. Adsorption Electrochemical Behavior of Benzene and Its Chlorinated Derivatives on a Smooth Platinum Electrode. *Elektrokhimiya.* 1984; 20(6):782–789.
31. Ramaker D, Koningsberger D. The atomic AXAFS and DI XANES Techniques as Applied to Heterogeneous Catalysis Electrocatalysis. *Phys Chem Chem Phys.* 2010; 12:5514–5534. [PubMed: 20442940]
32. Croze V, Ettingshausen F, Melke J, Soehn M, Stuermer D, Roth C. The Use of in situ X-ray Absorption Spectroscopy in Applied Fuel Cell Research. *J Appl Electrochem.* 2010; 40:877–83.
33. Mukerjee S, Srinivasan S, Soriaga M. Role of Structural Electronic Properties of Pt and Pt Alloys on Electrocatalysis of Oxygen Reduction. *J Electrochem Soc.* 1995; 142:1409–1422.
34. Mukerjee S, Ziegelbauer J, Arruda T, Ramaker D, Shyam B. Understanding Electrocatalytic Pathways in Low and Medium Temperature Fuel Cells: Synchrotron-based In Situ X-Ray Absorption Spectroscopy. *Interface.* 2008; 17(4):46–52.
35. Teliska M, Murthi V, Mukerjee S, Ramaker D. Correlation of Water Activation Surface Properties, and Oxygen Reduction Reactivity of Supported Pt–M/C Bimetallic Electrocatalysts Using XAS. *J Electrochem Soc.* 2005; 152:A2159–A2169.
36. Teliska M, O'Grady W, Ramaker D. Determination of H Adsorption Sites on Pt/C Electrodes in HClO₄ from Pt L23 X-ray Absorption Spectroscopy. *J Phys Chem B.* 2004; 108:2333–2344.
37. Teliska M, O'Grady W, Ramaker D. Determination of O and OH Adsorption Sites and Coverage in situ on Pt Electrodes from Pt L23 X-ray Absorption Spectroscopy. *J Phys Chem B.* 2005; 109:8076–8084. [PubMed: 16851943]
38. Scott F, Roth C, Ramaker D. Kinetics of CO Poisoning in Simulated Reformate and Effect of Ru Island Morphology on PtRu Fuel Cell Catalysts as Determined by Operando X-ray Absorption Near Edge Spectroscopy. *J Phys Chem C.* 2007; 111:11403–11413.
39. Scott F, Mukerjee S, Ramaker D. CO Coverage/oxidation Correlated with PtRu Electrocatalyst Particle Morphology in 0.3 M Methanol by in situ XAS. *J Electrochem Soc.* 2007; 154:A396–A406.
40. Baturina O, Gould B, Korovina A, Garsany Y, Stroman R, Northrup P. Products of SO₂ Adsorption on Fuel Cell Electrocatalysts by Combination of Sulfur K-Edge XANES and Electrochemistry. *Langmuir.* 2011; 27:14930–14939. [PubMed: 22047613]
41. Teliska M, Murthi V, Mukerjee S, Ramaker D. Site specific vs Specific Adsorption of Anions on Pt and Pt-based alloys. *J Phys Chem C.* 2007; 111:9267–9274.
42. Arruda T, Shyam B, Ziegelbauer J, Mukerjee S, Ramaker D. Investigation into the Competitive and Site-specific Nature of Anion Adsorption on Pt Using in situ X-ray Absorption Spectroscopy. *J Phys Chem C.* 2008; 112:18087–18097.
43. Koningsberger D, Mojet B, Van Dorssen G, Ramaker D. XAFS Spectroscopy; Fundamental Principles and Data Analysis. *Top Catal.* 2000; 10:143–155.
44. He Q, Shyam B, Nishijima M, Ramaker D, Mukerjee S. Mitigating Phosphate Anion Poisoning of Cathodic Pt/C Catalysts in Phosphoric Acid Fuel Cells. *J Phys Chem C.* 2013; 117:4877–4887.
45. Farmand, M. PhD Thesis. The George Washington University; DC: 2013. X-ray Absorption Spectroscopy Characterization of Electrochemical Processes in Renewable Energy Storage and Conversion Devices. <http://gradworks.umi.com/35/57/3557518.html> (accessed August 2015)

46. Kaserer S, Caldwell K, Ramaker D, Roth C. Analyzing the Influence of H_3PO_4 as Catalyst Poison in High Temperature PEM Fuel Cells Using in operando X-ray Absorption Spectroscopy. *J Phys Chem C*. 2013; 117:6210–6217.
47. Ramaker D, Korovina A, Croze V, Melke J, Roth C. Following ORR intermediates adsorbed on a Pt cathode catalyst during break-in of a PEM fuel cell by in operando X-ray absorption spectroscopy. *Phys Chem Chem Phys*. 2014; 16:13645–13653. [PubMed: 24664398]
48. Zhai Y, Bethune K, Bender G, Rocheleau R. Analysis of the SO_2 Contamination Effect on the Oxygen Reduction Reaction in PEMFCs by Electrochemical Impedance Spectroscopy. *J Electrochem Soc*. 2012; 159:B524–B530.
49. Ciureanu M, Wang H, Qi Zh. Electrochemical Impedance Study of Membrane-Electrode Assemblies in PEM Fuel Cells. II. Electrooxidation of H_2 and H_2/CO Mixtures on Pt/Ru-Based Gas-Diffusion Electrodes. *J Phys Chem B*. 1999; 103:9645–9657.
50. Patridge C, Love C, Swider-Lyons K, Twigg M, Ramaker D. In-Situ X-ray Absorption Spectroscopy Analysis of Capacity Fade in Nanoscale- LiCoO_2 . *J Solid State Chem*. 2013; 203:134–144.
51. Scott F, Mukerjee S, Ramaker D. Contrast in Metal-Ligand Effects on Pt_nM Electrocatalysts with M Equal Ru vs Mo and Sn As Exhibited by in Situ XANES and EXAFS Measurements in Methanol. *J Phys Chem C*. 2010; 114:442–453.
52. Ankudinov A, Ravel B, Rehr J, Conradson S. Real-Space Multiple-Scattering Calculation and Interpretation of X-Ray-Absorption Near-Edge Structure. *Phys Rev B*. 1998; 58:7565–7576.
53. BruceRavel/Horae – IFEFFIT. [cited 2015 Jan 23] Available: <http://cars9.uchicago.edu/ifeffit/BruceRavel/Horae>
54. Eley, D.; Pines, H.; Weisz, P. *Advances in Catalysis*. Vol. 29. London: Academic Press; New York; 1980. [Internet][cited 2015 Jan 22] Available: <http://site.ebrary.com/id/10244312>

Fig. 1.
Cell voltage response to exposure by 20 ppm ClB in the cathode air stream under 1 A cm^{-2} and 45°C .

Fig. 2.

EIS before, during and after the MEA cathode was exposed to 20 ppm CIB under 1 A cm⁻² at 45 °C. Inset highlights the data of Re(Z) below 0.6 Ω cm².

Fig. 3. MEA CV profiles before (BOT), after the 20 ppm ClB contamination and neat air recovery (EOT-01) and after 9 CV cycles (EOT-10). The bar chart summarizes the % recovery after each cycle.

Fig. 4. MEA polarization curves before exposure (BOT) and after the 20 ppm CIB exposure followed by neat air recovery (EOT). Inset highlights the difference in the kinetic region.

Fig. 5.

(a) Cell OCV and current density response to 10 ppm CIB exposure at 0.85, 0.65 and 0.5 V;
 (b) Cell voltage at 1 A cm^{-2} and current density response to 10 ppm CIB exposure at 0.3 and 0.1 V.

Fig. 6. Reaction products of CIB in PEMFC during poisoning at different voltages, as shown in Fig. 2. Cell IR-Voltage: Ohmic resistance corrected cell voltage, which is closer to cathode potential than the measured cell voltage.

Fig. 7.

Cl^- concentration in the effluent water during constant potential contamination tests with 10 ppm ClB in cathode air.

Fig. 8.

μ as defined in Eq. 2 at five different cell potentials as noted. The double arrows defines the magnitude $|\mu_{\max}|$. The theoretical μ_{theo} as obtained from FEFF8 calculations on a Pt₆ cluster with Cl adsorbed in an atop site is also shown.

Fig. 9. Relative CIB/Pt coverage as obtained from both the μ XANES (left axis) and from the $FT(\mu)$ EXAFS data (right axis) as described in the text.

Fig. 10.

(a) $FT[k\Delta\mu]$ for clean Pt and ClB/Pt (at 0.2 V) where μ is defined as in eq. 2. And the original μ functions are shown in Fig. S7 in the Supplemental Information. (b) $FT(k\Delta\mu)$ data at 5 different cell potentials as indicated.

Fig. 11.

Schematic illustration of ClB adsorption and reactions on Pt in the different potential regions indicated, and summary of different products found in the exhaust gas. The water molecules that form the double layer are not shown here even though they are present. As indicated in the text, ClB adsorbs more strongly on the corners/edges of the Pt nanoparticles but also not shown here.

Table 1
Summary of cell performance losses before and after recovery under different voltages

Loss (%)	Recov (%)				
0.5 V	0.8 hr	3.5 hr	10 h	6 hr	10 hr
	71.6	87.4	91.8	78.2	90.0
0.65 V	0.5 hr	2.6 hr	10 h	15 hr	55 hr
	65.0	86.4	93.9	67.8	81.6
0.85 V	0.5 hr	2 hr	10 hr	2 hr	10 hr
	52.6	68.2	84.2	21.1	23.7
OCV	10 hr			5 hr	
	4.4			96.3	