Effects of propylene, methyl methacrylate and isopropanol poisoning on spatial performance of a proton exchange membrane fuel cell

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HIGHLIGHTS

- Effects of organic contaminants in air on PEMFC were studied with a segmented cell.
- Cathode exposure to 100 ppm C_3H_6 resulted in performance loss of 130 mV at 1.0 A cm^{-2}
- PEMFC poisoning by 20 ppm methyl methacrylate led to a voltage loss of 80 mV.
- A moderate performance decline of 60 mV was caused by $5.3 \cdot 10^3$ ppm IPA in air.
- Performance loss is due to the contaminants chemisorption and oxidation on Pt.

ARTICLE INFO

ABSTRACT

This paper studies the effects of propylene, methyl methacrylate (MMA) and isopropanol (IPA) in air on the spatial performance of proton exchange membrane fuel cells (PEMFCs). The introduction of 100 ppm C_3H_6 into the oxidant stream resulted in a performance decrease of 130 mV at 1.0 A cm^{-2}, whereas 20 ppm MMA caused a voltage loss of 80 mV. A moderate performance decline of 60 mV was detected in the presence of $5.3 \cdot 10^3$ ppm IPA in air. Spatial electrochemical impedance spectroscopy (EIS) data showed an increase in charge and mass transfer resistances under exposure to C_3H_6 and MMA, although IPA did not affect the impedance. The observed PEMFC performances, local current redistributions and EIS data can be explained by the adsorption of contaminants on the Pt surface, their subsequent transformations, and their impacts on the electrochemical surface area and oxygen reduction mechanism. It was assumed that the studied contaminants were oxidized mainly to CO_2 via electrochemical and chemical pathways under the operating conditions and at the cathode potential. Self-recovery of PEMFC performance was observed for each contaminant after halting its introduction into the air. Possible contaminant oxidation/reduction mechanisms and their correlations with spatial performance and EIS are presented and discussed.

1. Introduction

Electrochemical energy conversion systems have attracted attention and been a focus of research for several decades, which has led to the commercialization of proton exchange membrane fuel cell (PEMFC) vehicles and residential power supply units. The first results of the early commercialization stage clearly indicated the need for further improvements in durability, reliability, environmental adaptability and cost reduction of fuel cell-powered systems. To produce electricity, the PEMFC requires hydrogen as a fuel and air as an oxidant. Air is an abundant and freely available reagent for fuel cell operations, but its availability varies in the presence of different air impurities, such as SO_2, NO_2, CO, O_3, particulates and volatile organic compounds (VOCs).

Inorganic (SO_2, H_2S, NH_3, NO_2) and organic (C_6H_6, 1,3-butadiene, toluene and warfare agents) air pollutants negatively affect PEMFC performance [1–15]. The performance decline is primarily due to chemisorption of contaminants on the catalyst (Pt) surface, followed by a decrease in the electrochemical surface area (ECSA) and a change in the oxygen reduction reaction (ORR) pathway from a 4-electron mechanism to a less efficient combination of 4- and 2-electron mechanisms [8,11,12,15]. Other contamination effects might include a decrease in ionomer proton conductivity and alterations in the hydrophilic/hydrophobic properties of membrane electrode assembly (MEA) components, which contribute to the observed PEMFC performance drop [12].

In a continuing effort to systematically evaluate PEMFC performance under exposure to VOCs, several air contaminants have been

Table 1
Global productions, typical applications, concentrations in air and exposure limits for selected contaminants.

Impurity	Worldwide production [10^6 tons]	Application	Air concent-ration (rural sites)	Air concent-ration (industrial sites)	US health ex-posure limits
C_3H_6	100	Production of polypropylene, acrylonitrile, propylene oxide, isopropanol, cumene	0.07–7 ppb [21–23]	100-260 ppb [22,24]	ACGIH: 500 ppm, 8 h TWA
MMA	3.15	Production of PMMA, paints and coatings, plastic material, medical equipment	0.06 ppm [27,28]	0.5–167 ppm [25–27]	NIOSH REL: 100 ppm TWA; OSHA PEL: 100 ppm TWA
IPA	1.8–2	Solvent, defroster, heat-exchange medium, application in chemical, cosmetic and pharma-ceutical industries	0.2–16 ppb [29,30]	–	NIOSH REL: 400 ppm TWA; OSHA PEL: 400 ppm TWA

identified for detailed investigation [14]. Selected VOCs include C_2H_2 (alkynes), C_6H_6 and $C_{10}H_8$ (arenes), CH_3CN (nitriles), CH_3Br (alkyl halides), C_3H_6 (alkenes), i-C_3H_7OH (alcohols) and methyl methacrylate ($CH_2=C(CH_3)COOCH_3$, esters). These chemical compounds are widely used in the chemical industry and in household chemical goods, and thus they might be present in ambient air. Our earlier publications offer incontestable evidence that all of these compounds cause serious damage to fuel cell performance [13,14,16–20]. The work is important for understanding the environmental adaptability and tolerance of PEMFCs to contaminants under field conditions, which is very valuable to fuel cell manufacturers because fuel cell vehicles are being commercially deployed (Toyota Mirai, Honda Clarity, Hyundai Tucson in the United States). Car manufacturers urgently need to obtain as much information as possible to minimize failure risks (warranty liabilities), diagnose and service vehicles affected by contamination and prevent failures.

The current work focuses on propylene, methyl methacrylate (MMA) and isopropanol (IPA) as potential air contaminants (Table 1). The annual production of propylene is approximately 100 million tons worldwide through petroleum refining, natural gas processing and ethylene production via steam/catalytic cracking of hydrocarbon feedstock. Additionally, C_3H_6 is a major chemical intermediate for manufacturing of polypropylene, acrylonitrile, propylene oxide, isopropanol and cumene. The propylene concentration measured in ambient air at rural and remote sites worldwide ranges from 0.01 to 7 ppb, and in urban and polluted air, its concentration varies from 0.3 to 32 ppb [21–23]. Suburban locations near industrial complexes or petrochemical plants might have C_3H_6 air concentrations of 100–260 ppb [22,24]. Propylene is expected to be released to the environment primarily from industrial manufacturing and use operations. Although C_3H_6 is not a gasoline component, it is present in motor vehicle exhaust as a result of fuel-rich combustion of hydrocarbon fuels. Thus, burning of hydrocarbon fuels, wood, cigarettes and synthetic polymers all release propylene to the atmosphere.

Methyl methacrylate is another airborne contaminant and was chosen in this study as a model ester to represent this class of organic compounds due to its wide application in production of polymethyl methacrylate (PMMA) plastics and co-polymer methyl methacrylate-butadiene-styrene. Acrylic sheets made by casting, molding or extruding of polymethyl methacrylate are used in safety glazing, panels and manufacturing products that require good optical clarity and stability, such as lighting. Methyl methacrylate polymers and copolymers are widely used in paint and surface coatings. Other applications of methacrylate polymers include dental prostheses, surgical bone cements and leaded acrylic radiation shields. The main source of MMA release to the atmosphere is the chemical industry, and its concentration in air ranges from undetected to 11.5 ppm during the manufacturing process. An exposure of 0.5–165 ppm was reported for polymethyl methacrylate production [25–27]. The average air MMA concentration estimated based on the fugacity model is ~ 0.244 mg m^{-3} (~ 0.06 ppm) [27,28], and thus its presence in regular indoor and outdoor environments is low.

The third potential contaminant is isopropanol, which is widely used as a solvent, heat-exchange media, intermediate in the chemical industry and defroster (for car windows). Isopropanol also has

applications in the cosmetic and pharmaceutical industries. The IPA concentration in air varies in the range of 0.2–16 ppb [29,30], and the maximum indoor concentration was found to be 90 ppb [31]. It is expected that the isopropanol concentration near industrial sites could be significantly higher, and its permissible exposure limit is 400 ppm according to the US Occupational Safety Health Administration [32].

Experimental data on fuel cell performance under cathode exposure to these contaminants are quite limited, and the observations are not explained in full volume [13,14,16]. It was reported that 100 ppm of C_3H_6 caused a performance loss of 120–130 mV at 80 °C and a constant current hold of 1.0 A cm^{-2} for single-cell operation [13]. Additionally, the average cell voltage of a 36-cell stack operated at 55 °C decreased from 0.630 to 0.380 V under injection of 50 ppm C_3H_6 [16]. PEMFC cathode poisoning with 20 ppm of methyl methacrylate and isopropanol in the air stream led to performance losses of 450 and 10 mV, respectively, at 45 °C and 1.0 A cm^{-2} [14]. All of these results were obtained using unaltered single-cell designs, which do not reveal the localized PEMFC behavior over the MEA active area, whereas a segmented cell system ensures simultaneous spatial monitoring of voltage, current and impedance and demonstrates excellent results for studying the effects of operating conditions and fuel and air contaminants on fuel cell performance [17–20,33–45]. Application of the segmented cell system for studying localized PEMFC behavior in the presence of contamination has seldom been completed for MEAs with active areas and conditions of commercial relevance (> 50 cm^2). Our previous detailed studies of spatial PEMFC behavior under cathode poisoning by C_2H_2, CH_3CN, arenes and CH_3Br demonstrated a non-uniform performance distribution over the MEA active area, which could lead to inhomogeneous degradation and premature failure [17–20]. Moreover, the chemical and electrochemical properties of air contaminants and their interactions with the catalyst strongly determine the localized fuel cell performance. This paper is a continuation of our publications (C_2H_2, CH_3CN, C_6H_6, $C_{10}H_8$ and CH_3Br [17–20]) and presents the spatial fuel cell phenomena that occur during cathode poisoning by propylene, methyl methacrylate and isopropanol. The results offer insights for comprehension of fuel cell contamination and environmental tolerance as well as suggestions for PEMFC durability improvement. In this work the chosen concentrations of pollutants in the air stream are higher than those observed in typical environmental conditions to accelerate contamination effects on fuel cell performance.

2. Experimental

All experimental work was performed using a fuel cell test station modified in-house to the required specifications, a Solartron SI 1287/ electrochemical interface and a segmented cell system developed at the Hawaii Natural Energy Institute and based on previous studies [46–49]. The segmented cell system allows simultaneous measurements of spatial impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The segmented cell hardware was based on 100 cm^2 cell design and contained a standard non-segmented flow field and a segmented flow field plates. The segmented flow field plate consisted of ten electrically insulated and consecutive segments embedded in a polymer frame along the path of the 10 serpentine