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Study of the acetonitrile poisoning of platinum cathodes on proton exchange membrane fuel cell spatial performance using a segmented cell system

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HIGHLIGHTS

- Effects of CH_3CN on PEMFC performance were studied with a segmented cell and EIS.
- Cathode exposure to CH_3CN led to voltage loss and redistribution of local currents.
- PEMFC behavior is due to CH_3CN chemisorption and its reduction/oxidation reactions.
- Hydrolysis of CH_3CN and intermediate imine resulted in NH_3, an additional contaminant.
- PEMFC performance under CH_3CN exposure depended on current and H_2O production.

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ABSTRACT

Due to the wide applications of acetonitrile as a solvent in the chemical industry, acetonitrile can be present in the air and should be considered a possible pollutant. In this work, the spatial proton exchange membrane fuel cell performance exposed to air with 20 ppm CH_3CN was studied using a segmented cell system. The injection of CH_3CN led to performance losses of 380 mV at 0.2 A cm^{-2} and 290 mV at 1.0 A cm^{-2} accompanied by a significant change in the current density distribution. The observed local currents behavior is likely attributed to acetonitrile chemisorption and the subsequent two consecutive reduction/oxidation reactions. The hydrolysis of CH_3CN and its intermediate imine species resulted in NH_4^+ formation, which increased the high-frequency resistance of the cell and affected oxygen reduction and performance. Other products of hydrolysis can be oxidized to CO_2 under the operating conditions. The reintroduction of pure air completely recovered cell performance within 4 h at 1.0 A cm^{-2}, while at 0.2 A cm^{-2} the cell recovery was only partial. A detailed analysis of the current density distribution, its correlation with spatial electrochemical impedance spectroscopy data, possible CH_3CN oxidation/reduction mechanisms and mitigation strategies are presented and discussed.

1. Introduction

Forthcoming mass production of proton exchange membrane fuel cells (PEMFCs) as electrochemical replacements of internal combustion engines and portable power generation brings up questions regarding the durability, reliability and high performance of fuel cells under different environmental conditions. Air is the most practical and economic oxidant for fuel cell operations; however, air may contain inorganic and organic impurities. Industrial and automotive vehicle exhausts contain the major contaminants (SO_2, NO_x, NH_3 and H_2S). Additionally, a few natural processes, such as volcanic activity, negatively affect air quality. These inorganic air pollutants are known to cause significant PEMFC performance losses and even degradation.

The effects of major inorganic airborne contaminants have been intensively studied [1–11]. Sulfur dioxide and hydrogen sulfide have been shown to cause drastic decreases in PEMFC performance, which can only be partially recovered by reintroducing pure air into the cathode gas stream [1,2,5–15]. Sulfur-containing impurities easily adsorb onto the Pt cathode, significantly decreasing the Pt

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electrochemical area (ECA) and oxygen reduction activity and increasing H_2O_2 formation, which accelerates electrolyte degradation [7,12,13]. The effects of nitrogen-containing air contaminants (e.g., NO_x and NH_3) were found to be moderate and recoverable [1,2,6,7,9,10,16–23]. PEMFC exposure to NaCl solutions resulted in performance degradations due to the negative impact of Cl^- on the Pt ECA [24,25].

A few organic compounds were studied as possible airborne pollutants for PEMFCs. The chemical warfare agents (sarin, sulfur mustard, cyanogen chloride and hydrogen cyanide) seriously compromised PEMFC performances in irreversible manners [1]. Benzene, toluene and 1,3-butadien also caused performance decreases, but the losses were recovered [2,26]. To expand the list of studied airborne organic pollutants, seven compounds were chosen from 260 possible air contaminants suggested by the Environmental Protection Agency [27]. The list includes acetylene, propene, methyl methacrylate, 2-propanol, bromomethane, naphthalene and acetonitrile. These compounds are widely used as solvents (CH_3CN, i-C_3H_8OH), synthesis precursors in the chemical industry (C_2H_2, $CH_3C(CH_3)COOCH_3$, C_3H_6, CH_3CN), welding fuels (C_2H_2), and fumigants (CH_3Br, $C_{10}H_8$). All seven contaminants have been found to cause serious PEMFC performance losses and have significant impacts on ORR [28,29].

Acetonitrile is a volatile, highly polar solvent used to extract fatty acids, animal/vegetable oils and butadiene. It is also a well-known solvent for spinning synthetic fibers and in casting and molding plastics. It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. In laboratories acetonitrile is applied in high-performance liquid chromatography, as a solvent for electrochemistry, DNA synthesis and peptide sequencing. Based on the broad industrial applications for acetonitrile, it can be prevalent at industrial sites and should be considered as a possible air pollutant because it will affect the PEMFC.

The electrochemisorption and reactivity of acetonitrile at platinum electrodes have been of primary interest in the fundamental study of electrocatalysis [30–35]. The effects of acetonitrile on the co-adsorption of hydrogen and oxygen are important for understanding electrochemical hydrogenation and oxidation reactions. The study of the electrochemical behavior of nitriles (CH_3CN and C_6H_5CN) provides valuable information because of 1) the use of nitriles as electrochemically “inactive” aprotic solvents, 2) the involvement of nitriles in organic oxidation processes where nitrilium ions and amides can be formed, and 3) in reductive dimerization [31,36–43] Moreover, the ORR in acetonitrile solutions have been intensively studied using rotating disk electrode (RDE), rotating ring disk electrode (RRDE) and cyclic voltammetry (CV) techniques [44–47].

The evaluation of fuel cell performance with a single cell does not reveal the spatial behavior of a PEMFC. In contrast, a segmented cell system provides locally resolved voltage, current and impedance data. It is a powerful tool for understanding the details of fuel cell operations under different conditions [48–55], the detection of membrane electrode assembly (MEA) defects [56,57], hydrogen recirculation [58], and hydrogen stream CO poisoning [59–65]. Information about the current distribution when exposed to organic airborne pollutants is crucial to understanding the poisoning mechanism, improving the PEMFC environmental adaptability and developing useful mitigation strategies. This paper focuses on the detailed spatial performance studies of a fuel cell exposed to 20 ppm CH_3CN and operated at different current densities. Additionally, spatial electrochemical impedance spectroscopy (EIS) was employed to understand and characterize the local PEMFC response under exposure to acetonitrile.

2. Experimental

The experiments were conducted at a Grandalytics single fuel cell test station using a segmented cell system [54]. This diagnostic tool continues the previous works [49,50,66,67] and allows simultaneous rather than sequential measurements of spatial EIS, spatial linear sweep voltammetry (LSV) and CV to be performed. The system has ten current channels in a high (standard) current mode and ten channels in a low current mode. The standard current mode enables the measurement of segment currents up to 15 A. The low current mode yields current measurement up to 375 mA, which is typical for CV and LSV experiments.

The segmented cell hardware was based on 100 cm^2 cell design. The hardware contained a segmented flow field, which consisted of ten cell segments forming a continuous path along ten parallel serpentine channels. Each segment had an area of 7.6 cm^2 and had its own distinct current collector and gas diffusion layers (GDL). The same channel designs were used for the segmented cathode and standard anode flow fields (the reactant streams were arranged in a co-flow configuration). The segmented cell hardware was applicable to either the anode or the cathode.

The segmented cell was operated with a commercially available 100 cm^2 MEA provided by Gore. The anode and cathode were made of Pt/C catalysts with a loading of 0.4 $mg_{Pt}\ cm^{-2}$. Sigracet 25 BC was used as the anode and cathode GDLs. The cathode used a segmented GDL and gasket configuration, whereas a single GDL was applied at the anode, and the total active area of the MEA was 76 cm^2. The gasket material was made of Teflon, with thicknesses of 125 μm for the anode and the cathode.

During CH_3CN exposure, the dry contaminant gas was injected into a humidified air stream, which was maintained at a constant level by increasing the temperature setting of the humidifier unit. The anode/cathode testing conditions for the contamination experiments were H_2/air, at a 2/2 stoichiometry, a 100/50% relative humidity and a 48.3/48.3 kPa_g backpressure. The cell temperature was 80 °C. The MEA was operated under galvanostatic control of the whole cell current in the range of 0.1–1.6 A cm^{-2} (based on the 76 cm^2 of the active MEA area).

The polarization curves (VI curves) in the H_2/air gas configuration were measured under the same conditions as the contamination experiment. VI curve measurements were also performed in the $H_2/He + O_2$ (21 vol.%) and H_2/O_2 gas configurations and under galvanostatic control of the total cell current. To maintain a constant water transport in the cell for any given total cell current density, the flow rates of $H_2/He + O_2$ and H_2/O_2 were identical to those used during the H_2/air operation with a stoichiometry of 2. Consequently, the stoichiometry of $He + O_2$ remained at 2, whereas the stoichiometry of O_2 increased to 9.5. The resulting three different VI curves (H_2/air, $H_2/He + O_2$ and H_2/O_2) were used for the determination of the activation, ohmic and mass transfer (permeability and diffusion) overpotentials, as previously described [54].

The VI curve measurements and contamination experiments were combined with EIS to determine the high-frequency resistances (HFR) of the cell and segments and to record the impedance spectra for all ten segments and the overall cell. The selected frequency range for the EIS experiments was 0.05 Hz–10,000 Hz, and the amplitude of the sinusoidal current signal perturbation was 2 A, which resulted in a cell voltage response of 10 mV or lower. The HFR was determined from the intercept of the EIS with the x-axis at higher frequencies of the Nyquist plot.

CV experiments were conducted for the determination of the ECA using a Solartron SI 1287/electrochemical interface. The CV experiments were performed at a cell temperature of 35 °C with a