Short communication

The ionic conductivity and catalyst activity effects of acetonitrile on proton exchange membrane fuel cells

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ABSTRACT

The effect of trace levels of acetonitrile, an airborne pollutant, on proton exchange membrane fuel cells (PEMFCs) membrane/electrode assemblies (MEAs) was investigated in situ and ex situ using electrochemical impedance spectroscopy, cyclic voltammetry and polarization with a fuel cell and a membrane conductivity cell. In situ test results indicate that acetonitrile depresses electrode activity and decreases MEA ionic conductivity. Ex situ tests demonstrate that acetonitrile does not affect the membrane ionic conductivity, indicating the role for an acetonitrile reduction product (ammonium cation).

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1. Introduction

Fuel cell vehicles are currently being deployed (Toyota Mirai, etc). However, the risks associated with air pollution have not yet been eliminated or minimized. Pollutants adversely impact cell performance and durability. Most of the 200 airborne pollutants that have been identified are volatile organic compounds (VOCs), and most have not been characterized [1,2] for their effect on air filter effectiveness and cell performance. Such conditions extend to real-life operations. The effects of duty cycling and contaminant mixtures [3] on fuel cell stacks [4] have barely been explored if at all. Thus, car manufacturers urgently need to obtain as much information as possible to diagnose and service vehicles affected by contamination and prevent failures.

Acetonitrile is a model nitrile VOC with the highest concentration in air at up to 3 ppm among the 21 contaminants that were previously selected for screening [2]. Single cell tests revealed a relatively dramatic and rapid effect on cell performance, which prompted mechanistic studies that are, in part, reported here. Acetonitrile is an aprotic solvent used for electrical double layer studies on electrodes or organic molecule oxidation and reduction behavior. Acetonitrile adsorption behavior and stability on Pt has been widely studied in various solutions using a variety of electrochemical and spectroscopic techniques [511]. In acid solution, acetonitrile is chemisorbed on Pt over a wide potential range and inhibits both hydrogen adsorption and Pt oxidation [713]. Several

reversible acetonitrile reduction/oxidation reactions occur on Pt. Within 0.15–0.9 V vs SHE, intermediates are absent from the bulk solution. For higher and lower potentials, irreversible oxidation/reduction reactions occur with corresponding products that can subsequently desorb. Below 0.15 V vs SHE, the potential reduction products include ethane, ethanol, ammonium ions, amines, and CN^- [912]. Above 0.9 V vs SHE, the potential oxidation products comprise NO_2 and CO_2 [11]. The different CH_3CN products and intermediates on Pt may exert different effects on oxygen reduction reactions (ORR). Ex situ rotating ring/disk electrode (RRDE) analyses showed that acetonitrile adsorption on Pt/C impacted the oxygen reduction mechanism and increased the overpotential and H_2O_2 production [12]. These results provide a background for developing an acetonitrile contamination mechanism. However, the effect of acetonitrile on an operating PEMFC has not been reported; this is especially important considering that the acetonitrile products in a fuel cell are not necessarily predictable [15].

Ex situ and in situ methods, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), polarization (VI) and membrane conductivity were used to investigate the impact of acetonitrile.

2. Experimental

The single cell, operating conditions and experimental procedures were previously described and are summarized [14]. The MEAs were activated to obtain steady cell performance. Diagnostics before and after contamination testing include CV (electrochemical active surface area), linear sweep voltammetry (H_2 crossover), VI and high frequency resistance (HFR) [14].

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The single cell cathode was exposed to 20 ppm CH_3CN in N_2 for different durations [14]. The anode was fed with H_2. 400 ppm CH_3CN in an N_2 mixture (certified plus grade, Matheson Tri-Gas Inc.) was diluted with N_2. The MEA through-plane conductivity was measured using EIS at different times within a frequency range of 10 kHz to 0.1 Hz (ZPlot® software from Scribner Associates, Solartron SI1260 analyzer). A 0 V DC voltage with a 5 mV AC perturbation was applied between the cathode (working and sense) and anode (counter and reference) electrodes. Immediately after acetonitrile injection was interrupted, three CV scans were conducted under similar conditions. Subsequently, VI curves with H_2/air were obtained.

Ex situ tests were completed using a Nafion® XL membrane in a single chamber conductivity cell fed a CH_3CN–N_2–H_2 mixture for 30 min (25% N_2, 75% H_2 with 50 or 100 ppm CH_3CN). The in-plane proton conductivity of a $0.00275 * 1 * 3$ cm^3 sample was measured in a BekkTech cell at 80 °C with 50% relative humidity (RH). A 20 kHz to 1 Hz range was used for EIS, and 1 V DC voltage with 20 mV AC perturbation was applied between the Pt mesh working and counter electrodes. Two Pt wires separated by 0.425 cm and located between the Pt mesh electrodes served as sense and reference electrodes. The in-plane conductivity was calculated from the measured proton resistance and Ohm's law.

3. Results and discussion

3.1. MEA EIS and CV analyses

Fig. 1 shows EIS spectra. The intercept with the real impedance axis is the ohmic resistance for proton transport through the catalyst layer and membrane. Before exposure, the proton resistance was 0.058 Ω cm^2, which is consistent with previous results [14]. The resistance gradually increases to 0.066, 0.082 and 0.088 Ω cm^2 for a 25, 50 and 60 min exposure, respectively (a ~51% increase).

The CV profiles are in Fig. 2. Before exposure, the CV curve shows typical Pt/C features [14]. After a 1-h exposure, the anodic scan for the first cycle shows a depressed peak at 0.15 V vs HRE, whereas the 0.22 V peak increased. Above 0.4 V vs HRE, the oxidation current formed a shoulder at 0.58 V as well as peaks at 0.78 and 1.14 V. The cathodic scan shows a smaller PtO_x reduction peak at 0.78 V vs HRE but larger reduction currents between 0.3 and 0.6 V and above 1.0 V. For the second and third cycles, anodic scans show smaller oxidation currents than the first cycle, especially for the 0.22 V vs HRE peak. Cathodic curves were superimposed onto the first cycle results. The changes are consistent with acetonitrile adsorption on a Pt surface in an acid solution [7,13]. After a 3-h exposure, the acetonitrile coverage is more extensive, which further decreases the H_2- and Pt-related peaks. Additionally,
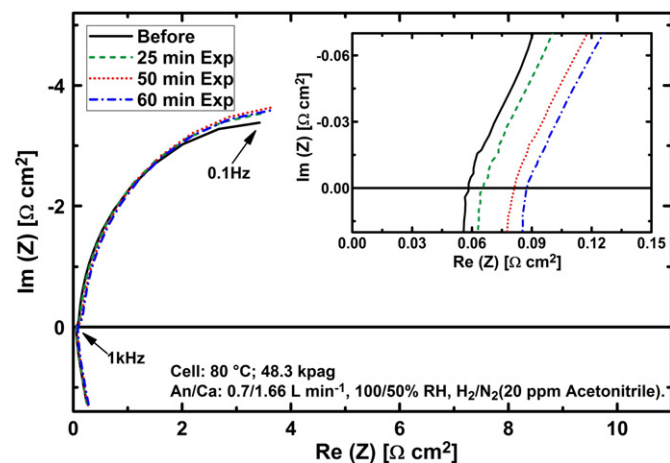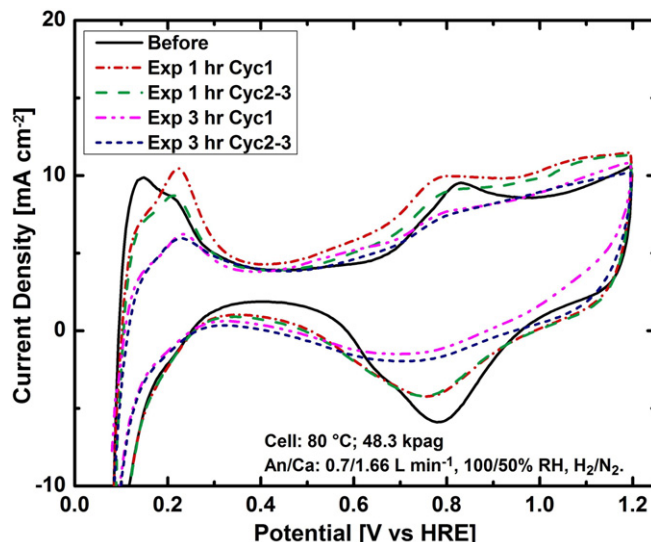

Fig. 2. CV responses to acetonitrile adsorption on Pt. "Exp 1 h Cyc1" refers to the first CV cycle after 1 h exposure, and "Cyc2–3" refers to second and third cycles.

current profiles for all 3 cycles overlap, except for smaller PtO_x reduction currents in the first cathodic scan.

The MEA results show clearer features than those obtained with a rotating disc electrode or RRDE in acid solutions [8,13]. At a lower potential than 0.15 V vs SHE or within 0.05–0.2 V vs SHE, acetonitrile is irreversibly reduced to CH_3–CH=NH through a two-electron process with a slow second step [8,9]. Above 0.36 V vs SHE, acetonitrile non-dissociatively adsorbs, and subsequent reactions are reversible. During exposure, acetonitrile adsorbs, displaces H species, and is reduced to CH_3–CH=NH. The CH_3–CH=NH species is oxidized to CH_3CN at 0.22 V vs SHE on Pt edge sites during the first anodic CV scan. A larger oxidation current at 0.22 V vs SHE is absent during the second and third anodic scans due to slow CH_3–CH=NH formation. Oxidation peaks at 0.58, 0.78 and 1.14 V vs SHE (positive scan) and the corresponding excess reduction current between 1.2–0.9 and 0.68–0.25 V vs SHE (negative scan) are attributed to reversible, non-dissociative CH_3CN reactions.

3.2. Single cell performance

Fig. 3 shows VI curves and HFR values. Cell performance decreases with an increase in exposure. After 1 and 3 h, the open circuit voltage
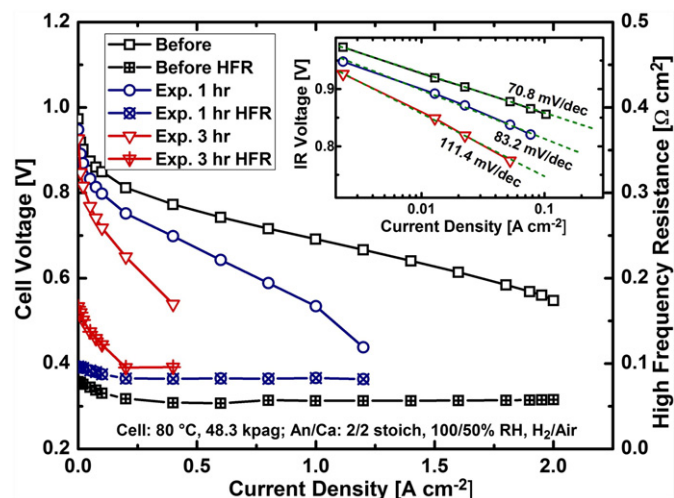

Fig. 1. EIS spectra before and after MEA exposure to humidified H_2 in the anode and N_2 with 20 ppm acetonitrile in the cathode.

Fig. 3. VI curves before and after MEA cathode exposure to 20 ppm acetonitrile.