Proton exchange membrane fuel cell cathode contamination — Acetylene

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HIGHLIGHTS

- Adsorbed acetylene is reduced at OCP of H_2/N_2 and oxidized at high potentials.
- 300 ppm acetylene in PEMFC cathode caused 88% cell performance loss.
- Acetylene affects oxygen reduction reaction and shifted ORR pathway.
- Potential-dependent processes and acetylene oxidation intermediates accumulation.
- Cell performance completely recovered with neat air operation.

ABSTRACT

Acetylene adsorption on PEMFC electrodes and contamination in single cells are investigated with 300 ppm acetylene at a cathode held at 80 °C. The results of adsorption experiments suggest that acetylene adsorbs readily on electrodes and is reduced to ethylene and ethane under an open circuit potential of H_2/N_2, as the adsorbates can be electro-oxidized at high potentials. The cell voltage response shows that 300 ppm acetylene results in a cell performance loss of approximately 88%. The voltage degradation curve is divided into two stages by an inflection point, which suggests that potential-dependent processes are involved in acetylene poisoning. These potential-dependent processes may include acetylene oxidation and reduction as well as accumulation of intermediates on the electrode surface. Electrochemical impedance spectroscopy analysis suggests that acetylene affects the oxygen reduction reaction and may also affect mass transport processes. Acetylene also may be reduced in the steady poisoning state of the operating cell. After neat air operation, the cyclic voltammetry results imply that the cathode catalyst surface is almost completely restored, with no contaminant residues remaining in the MEA. Linear scanning voltammetry measurements show no change in hydrogen crossover caused by contamination, and polarization curves confirm complete recovery of cell performance.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most promising clean energy conversion technologies. Currently, platinum (Pt) is the only commercially available as well as the most effective electrochemical catalyst for the oxygen reduction reaction (ORR), the key reaction of fuel cell processes [1,2]. The Pt ORR catalyst is also active towards most organic compounds. These compounds can adsorb and react on the Pt surface and compete with the ORR [3]. Unfortunately, there are

over 200 airborne pollutants, most of which are volatile organic compounds (VOCs) that can be introduced into the PEMFC cathode during air feeding [4–8]. In the past few decades, only a few organic air pollutants have been investigated as contaminants in PEMFCs [9–11], and the results have shown that these contaminants have a significant effect on performance. Recently, our group 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, twenty-one contaminants were selected from more than 150 airborne and indoor pollutants detected by Environmental Protection Agency (EPA) monitoring [8,12]. The single cell performance response to each of these 21 contaminants was investigated preliminarily under operating conditions that

accelerated contamination [13]. Acetylene, C_2H_2, one of the most critical contaminants, was found to degrade cell performance by more than 50%.

Acetylene, typically used as a welding fuel and as a precursor molecule in chemical synthesis, is representative of alkyne airborne contaminants. Acetylene in the atmosphere originates almost exclusively from anthropogenic sources, including manufacturing and end-use plant emissions, fossil and biofuel combustion exhausts, and biomass burning [14]. The acetylene concentration in an urban atmosphere is typically up to 0.1 part per million by volume (ppmv) [8]. A diffusion model predicts acetylene concentrations up to 5.5 (1 h average) and 3 ppmv (24 h average) near an acetylene plant [14]. The chemical/electrochemical adsorption/reactions of C_2H_2 on Pt have been studied extensively for the removal of unburned hydrocarbons from exhaust streams [15–20]. The adsorption of acetylene on a Pt surface can block 2.1 Pt sites per adsorbed species [19]. The conversion of acetylene on Pt surfaces depends on the potential and temperature: at a potential lower than 0.2 V vs reversible hydrogen electrode (RHE), acetylene is reduced to ethylene and ethane on a Pt surface in a sulfuric acid solution; at a potential higher than 0.70 V vs RHE, acetylene is oxidized to CO_2 [19]. Acetylene reactions also compete with the adsorption of oxygen: in the presence of oxygen, acetylene on Pt (111) reacts with surface oxygen to form CO, which subsequently either desorbs or is further oxidized to CO_2, the main oxidation product in the 330–420 K temperature range [15]. A polymeric surface species may also form on the electrode: for example, the cyclotrimerization or polymerization of acetylene on Pt/Al_2O_3 leads to benzene [17,19]. An ex-situ rotating ring disk electrode (RRDE) study showed that acetylene adsorption inhibited the ORR and assisted the ORR reaction pathway, resulting in a shift to 2-electron series reactions from a 4-electron direct reaction [21]. These results provide insight into the probable effect of acetylene contamination on PEMFCs. However, PEMFC contamination tests have not been reported.

In this study, the adsorption of acetylene on MEA electrodes was studied by exposure to acetylene in N_2 and cyclic voltammetry (CV). Accelerated acetylene contamination in a single cell was investigated under constant current operation with acetylene in the cathode. Electrochemical impedance spectroscopy (EIS), H_2 crossover measurements by liner sweep voltammetry (LSV) and polarization (VI) curve measurements were performed to obtain an understanding of the effects of acetylene contamination on PEMFCs. The electrochemical characterization results are analyzed and discussed in detail.

2. Experimental

Experiments were conducted at FCATS™ G050 series test stations (Green Light Power Technologies Inc.) with a custom-made 50 cm^2 single cell. The anode flow-field was a double channel serpentine, and the cathode flow-field was a triple channel serpentine. MEAs used for acetylene contamination tests were purchased from Gore (GORE® PRIMEA® M715 catalyst coated membrane) 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 operating conditions at the anode/cathode were as follows: 100/50% relative humidity (RH) and a flow rate of 0.697/1.659 L min^{-1}, which is a 2/2 stoichiometry of 1 A cm^{-2} under H_2/Air operation. The outlet backpressure was 48.3/48.3 kPa, which corresponds to the pressure of the dry reactants in the cell chamber at 1 atm for a cell temperature of 80 °C. The acetylene source was 4040 ppm acetylene in N_2 or 4030 ppm acetylene in Air (Matheson Tri-Gas Inc.).

Before the tests, MEAs were activated to obtain steady cell

performance. Diagnostics before contamination testing (B0T) included measuring the electrochemical active surface area (ECA) of the electrodes by CV, measuring the H_2 crossover of the MEA by LSV, and measuring the cell performance by VI. CV scanning was conducted with H_2/N_2 at 35 °C with fully humidified hydrogen or nitrogen at each side, with flow rates of 0.466 L min^{-1}. The hydrogen and nitrogen were supplied to the reference and working electrodes, respectively. A total of 3 scans were performed with a scan rate of 20 mV s^{-1}. The potential range was 0.08–1.20 V vs the hydrogen reference electrode (HRE). The LSV was obtained from 0.08 to 0.40 V vs HRE with a scan rate of 0.1 mV s^{-1} under the same conditions used for CV. VI curves with high frequency resistance (HFR, 1 kHz) were measured from the high current to the open circuit voltage (OCV) with a stabilizing time of 15 min at each current set point under the operating conditions described above with a 2/2 stoichiometry. This activation and diagnostic process ensured comparability and repeatability between the MEAs.

Acetylene adsorption tests were conducted with 300 ppm acetylene in N_2 at the cathode side. The MEA was held at the open circuit potential (OCP) of H_2/N_2 cell under the conditions described above. Acetylene was injected at approximately 6 min and stopped at 16, 36 and 66 min. A 0.5, 2, 10 or 30 min pure N_2 purge was applied to the contaminated cathode exposed to acetylene for 60 min. Three cycle CV curves between 0.08 and 1.20 V were obtained before testing as well as before and after the pure N_2 purges with a scan rate of 20 mV s^{-1}.

The acetylene contamination was investigated by applying 300 ppm acetylene in air at the cathode side with a constant current density of 1 A cm^{-2}. The three phases of operation included 5 h pre-poisoning with neat air, 5 h poisoning with acetylene at the cathode, and 10 h self-induced performance recovery with neat air. When the cells were exposed to acetylene, a mixture of acetylene in air was injected into the humidified feed stream of the cathode; the humidity of the gas was maintained at a constant level by increasing the temperature setting of the humidifier unit. During constant current testing, AC impedance data from 0.1 Hz to 10 kHz (10 points per decade) were obtained using a Solartron SI1260 Impedance/Gain-Phase Analyzer and Stanford Research SR560 Low Noise Preamplifiers with ZPlot® (Scribner Associates) software. An AC current perturbation of 0.75 A, resulting in a voltage change of approximately 5 mV, was applied to the single cell at a DC current of 50 A. The load bank cables on the positive and negative sides were equal in length and twisted to reduce system inductance and
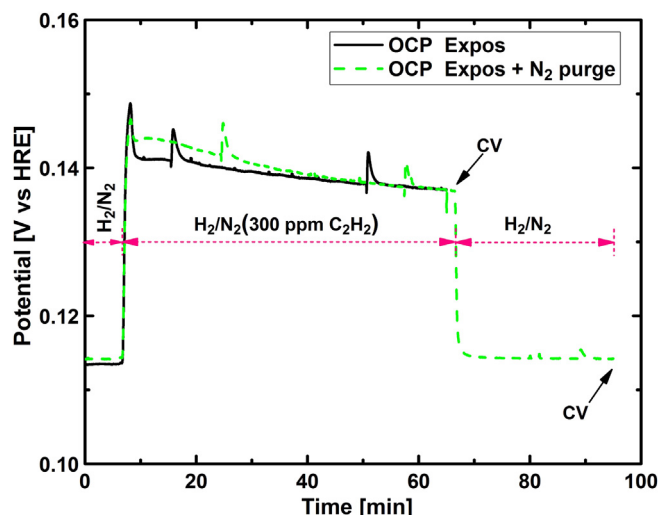

Fig. 1. OCP response to acetylene adsorption on an MEA electrode in the H_2/N_2 mode.