



Impact of operating conditions on the acetylene contamination in the cathode of proton exchange membrane fuel cells



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HIGHLIGHTS

- Higher acetylene concentration decrease cell performance more.
- Acetylene contamination at higher current density decrease cell performance more.
- Acetylene contamination at lower cell temperature decreases cell performance more.
- Concentration/potential barriers exist, determine tolerance of PEMFC to acetylene.
- Adjusting operation parameters may mitigate acetylene contamination effects.

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ABSTRACT

Realistically, proton exchange membrane fuel cells (PEMFCs) are operated under varying operating conditions that potentially impact the acetylene contamination reactions. In this paper, the effects of the cell operating conditions on the acetylene contamination in PEMFCs are investigated under different current densities and temperatures with different acetylene concentrations in the cathode. Electrochemical impedance spectroscopy is applied during the constant-current operation to analyze the impacts of the operating conditions on the acetylene electrochemical reactions. The experimental results indicate that higher acetylene concentrations, higher current densities and lower cell temperatures decrease the cell performance more. In particular, cathode poisoning becomes more severe at medium cell current densities. The cell cathode potentials at such current densities are not sufficient to completely oxidize the intermediate or sufficiently low to completely reduce the adsorbed acetylene. Based on these investigations, the possible condition-dependent limitations of the acetylene concentration and cell operating voltage are proposed for insight into the acetylene contamination mitigation stratagem. Regarding the barrier conditions, the acetylene reactions change abruptly, and adjusting the cell operation parameters to change the acetylene adsorbate and intermediate accumulation conditions to induce complete oxidation or reduction conditions may mitigate the severe acetylene contamination effects on PEMFCs.

1. Introduction

In the past few decades, PEMFCs have been considered as one of the most promising clean energy technologies and suitable primary power sources [1,2]. Unfortunately, there are over 200 airborne pollutants that can be introduced into the cathodes of the cells during air feeding. The Pt cathode catalyst for the oxygen reduction reaction (ORR) is sensitive to most of these pollutants, which can adsorb and react on the Pt surface and inhibit the ORRs [3–5]. In other words, most airborne pollutants are potential contaminants for PEMFCs and bring considerable challenges for fuel cell applications.

Recently, a few toxic pollutants, such as NO_x, SO₂, halogens and

certain volatile organic compounds (VOCs), have been investigated as cathode contaminants in PEMFCs. The results have disclosed the negative impacts of these pollutants on the performance and durability of PEMFCs [6–19]. Since 2010, twenty-one potential contaminants were selected in our group for a PEMFC accelerated contamination study [3,20]. Most of the selected contaminants significantly impacted the cell performance [20]. Acetylene, representing the alkyne airborne contaminants, is one of the critical contaminants that causes more than 50% loss in the cell performance at 45 °C with a concentration of 20 ppm [20]. Acetylene is a widely used welding fuel and chemical synthesis reagent. The acetylene concentration near a production plant estimated by a diffusion model is 5.5 (1 h average) and 3 (24 h average)

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ppm by volume [21].

Acetylene contamination mechanisms in PEMFCs have been developed using in situ and ex situ gases and electrochemical analyses [22–24]. Acetylene adsorbs on PEMFC electrodes and inhibits ORRs in the cathode. At cathode potentials above 0.65 V, adsorbed acetylene is electro-oxidized into carbon dioxide and desorbs easily [24]. At potentials below 0.3 V, adsorbed acetylene is reduced to ethylene, ethane and methane, and the reduction products desorb even more rapidly. However, when cells are operated with cathode potentials between 0.65 V and 0.3 V, the electro-oxidation intermediate CO (or COH-type species) forms above 0.5 V, and the electroreduction intermediates vinylidene and ethylidyne form below 0.3 V. Those intermediates are stable during electro-oxidation, especially vinylidene and ethylidyne, and accumulate on the cathode, significantly depressing ORRs. These reaction mechanisms suggest that the acetylene contamination process in PEMFCs probably strongly depends on the operating conditions.

As a candidate power source, PEMFCs have been operated at varying operating conditions. From a previous investigation of SO₂ contamination in PEMFCs, the concentrations of the contaminants, cell current density and temperature were determined to be important operating parameters that can affect SO₂ contamination significantly [25]. Therefore, in this paper, the cell performance responses to acetylene exposure were investigated under different cell current densities and temperatures with different acetylene concentrations. Electrochemical impedance spectroscopy (EIS) and Polarization (VI) curves were analyzed to understand the effects of the operating conditions on the acetylene contamination in the PEMFCs. Furthermore, the cell performance recovery and mitigation strategies were proposed for various cell operation conditions.

2. Experimental

The acetylene contamination experiments were conducted on an FCATS™ G050 series test station (Green Light Power Technologies Inc.) with an internal 50 cm² single cell and an anode/cathode flow field with double/triple serpentine channels [22,24]. Gore PRIMEA M715 catalyst-coated membranes (MEAs) were used for all acetylene contamination tests. The catalysts were 50% Pt/C, with a Pt loading of 0.4 mg Pt cm⁻² on each side of the MEA. The MEAs were assembled between the two flow fields with 25 BC gas diffusion layers (GDL, SGL Tech.).

After the full activation and diagnostics procedures were conducted before contamination testing (BOT) with a new MEA [22], an acetylene contamination experiment was conducted under the operating conditions listed in Table 1. The operating conditions at the anode/cathode

Table 1

The operating conditions matrix for the constant-current contamination experiments with acetylene in the PEMFC cathode.

Test ID	Acetylene Concentration [ppm]	Current Density [A cm ⁻²]	Temperature [°C]
1	20	1	80
2	50	1	80
3	100	1	80
4	200	1	80
5	300	1	80
6	400	1	80
7	500	1	80
8	5	1	45
9	20	1	45
10	100	1	45
11	100	0.2	80
12	100	0.6	80
13	200	1.5	80
14	300	0.2	80
15	300	0.6	80
16	100	1	10

were as follows: 100/50% relative humidity (RH) and a 2/2 flow stoichiometry; and the outlet back pressures were 48.3/48.3, 10/10, and 5/5 kPa g for cell temperatures of 80 °C, 45 °C, and 10 °C, respectively, which corresponded to the pressure of the dry reactants in the cell chamber at 1 atm. Acetylene concentrations were larger than in ambient air to accelerate tests and facilitate the separation of degradation effects. Each contamination experiment included three phases of constant-current operation (CCO): (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. The gas mixtures were supplied by Matheson Tri-Gas Inc. and contained 20, 100, 400 or 4000 ppm acetylene by volume in air. Before and after the CCO procedure, the VI curves 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 operating conditions similar to those of the constant-current (CCO) operation.

During CCO procedure, AC impedance data were obtained from 0.1 Hz to 10 kHz (10 points per decade) using a Solartron SI1260 Impedance/Gain-Phase Analyzer and Stanford Research SR560 Low Noise Preamplifiers with ZPlot® (Scribner Associates) software. An AC current perturbation resulting in a voltage change of approximately 5 mV, was applied on the single cell during CCO at a DC current of 75, 50, 30 or 10 A.

3. Results and discussion

3.1. Cell performance degradation and recovery

3.1.1. Acetylene concentration effect

The concentration effect on the acetylene contamination in PEMFCs was investigated using three-phase constant-current experiments with a current density of 1 A cm⁻². Fig. 1 a) and b) show the cell voltage response to acetylene with different concentrations at 80 and 45 °C, respectively. It should be noted that the cell voltage responses to 20, 50 and 100 ppm acetylene were similar, and those to 400 and 500 ppm acetylene were similar. Therefore, the results of tests 1, 2 and 6 in Table 1 are not shown in Fig. 1 a). It can be seen that all cell voltages dropped immediately within the first several minutes of acetylene exposure. However, the following responses were significantly different for each concentration, especially the cell operated at 45 °C, though all MEAs reached stable performance during the first 5 h of operation with neat H₂/Air.

For the cells tested at 80 °C, when the acetylene concentration was lower than a certain value, the cell voltage degradation showed similar behaviors. The exposure to 100 ppm acetylene is discussed as an example. The cell voltage dropped ~40 mV, from 0.672 V to 0.635 V, during the first minute, increased ~20 mV up to 0.653 V within the second minute, then reached to a stable voltage of 0.663 V during the following 30 min. At the poisoning equilibrium state, the 100 ppm acetylene caused a total loss of ~10 mV in the cell voltage. Within ~3 min after the acetylene injection was stopped, the cell voltage of both cells recovered to its initial value before exposure. When the acetylene concentration was higher than 300 ppm, the cell voltage degradation showed different behaviors from those observed at a low concentration. For the exposure to 300 ppm acetylene, two stages were involved in the degradation of the cell voltage. At the beginning of the exposure, the cell voltage dropped approximately 20 mV, from 0.677 to 0.653 V within 2 min. Next, slow transient degradation was observed, followed by a second rapid decrease. After approximately 30 min of exposure, the cell voltage decreased to 0.110 V, and the degradation slowed down again. At approximately 1 h of acetylene exposure (6 h into the experiment), the cell voltage reached a steady value of approximately 0.082 V. This final poisoned state represented an approximately 88% loss in the cell performance. When the acetylene injection was stopped, the cell voltage increased immediately. The cell voltage recovery also included two stages, and these two stages of

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