Effects of Possible Contaminants in Hydrogen Fuel for Mobile Vehicles with Fuel Cells

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Introduction

The most likely type of fuel cell for automotive applications today is the Proton Exchange Membrane Fuel Cell (PEMFC). Distinguishing features are lower operating temperature (60-80 °C) and pressure ranges, a special polymer electrolyte membrane (Nafion) and compact packaging, compared with other fuel cell types. The catalysts in use today are primarily platinum or platinum alloys, deposited on a carbon support. The surface area of a typical carbon-supported platinum catalyst is about 250 cm² of catalyst per 1 cm² of geometric area. A typical vehicle will have several hundred cells in the range of 300 cm² to generate 90-120 kW. The membrane, usually made of Nafion polymer, allows protons to migrate to the cathode, but diverts the electrons generated to the vehicle drive motors.

The chemical reactions are:

At the anode.
\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad E^0 = 0 \text{ volts} \]

At the cathode.
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.229 \text{ volts} \]

The quality of hydrogen fuel is critical for proper operations of fuel cells. The first line of defense against fuel cell contamination is prevention. At sufficiently low contaminant concentrations, the cell performance is unaffected. However, its purity must be monitored to ensure that consumers receive product that has not been adulterated and the fuel is free of critical contaminants that can corrupt performance, effect serious degradation of the life of fuel cells, or generate unintended pollutants. In 2005, California enacted legislation (Senate Bill 76, 2005) to mandate monitoring of trace impurities in hydrogen fuel that is commercially sold in California for vehicle use. The allowable contaminant levels are listed by SAE International J2719 “Hydrogen Fuel Quality for Fuel Cell Vehicles”, finalized in September 2011 and are listed in Table I. These standards were developed by the Hydrogen Quality Task Force of the Interface Working Group of the SAE Fuel Cell Standards Committee. Some of the target analytes can have severe impact on performance of fuel cells used to power vehicles. Other gases are included to ensure the fuel has not been diluted with air or other gases.
<table>
<thead>
<tr>
<th>Fuel Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Fuel Index (minimum, mol%)</td>
<td>99.97</td>
</tr>
<tr>
<td>Total Trace Gases (maximum, µmol/mol)</td>
<td>300</td>
</tr>
<tr>
<td>Water (maximum, µmol/mol)</td>
<td>5</td>
</tr>
<tr>
<td>Total Hydrocarbons (maximum, µmol/mol)</td>
<td>2</td>
</tr>
<tr>
<td>Oxygen (maximum, µmol/mol)</td>
<td>5</td>
</tr>
<tr>
<td>Helium (maximum, µmol/mol)</td>
<td>300</td>
</tr>
<tr>
<td>Nitrogen and Argon (maximum, µmol/mol)</td>
<td>100</td>
</tr>
<tr>
<td>Carbon Dioxide (maximum, µmol/mol)</td>
<td>2</td>
</tr>
<tr>
<td>Carbon Monoxide (maximum, µmol/mol)</td>
<td>0.2</td>
</tr>
<tr>
<td>Total Sulfur (maximum, µmol/mol)</td>
<td>0.004</td>
</tr>
<tr>
<td>Formaldehyde (maximum, µmol/mol)</td>
<td>0.01</td>
</tr>
<tr>
<td>Formic Acid (maximum, µmol/mol)</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammonia (maximum, µmol/mol)</td>
<td>0.1</td>
</tr>
<tr>
<td>Total Halogenated Compounds (maximum, µmol/mol)</td>
<td>0.05</td>
</tr>
<tr>
<td>Particulates Size (maximum, µm)</td>
<td>10</td>
</tr>
<tr>
<td>Particulate Concentration (maximum, µg/L @ NTP)</td>
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</tr>
</tbody>
</table>

**Effects of Various Contaminants on Hydrogen Fuel Cells:**

These impurities can be grouped into two categories - Catalyst Poisons/Inhibitors, and Diluents/Adulterants

**Catalyst Poisons/Inhibitors**

- **Water (5 ppmV)** - Presence of water at the anode can cause the formation of ice and may affect storage medium, like metal hydrides. In addition, other impurities (acid gases) may react with water and ruin internal materials. The cell is recoverable when water in the fuel is removed, except for degradation by acids.

- **Total Hydrocarbons - THC - (2 ppmV)** - hydrocarbons in a reducing atmosphere of hydrogen can readily convert to free carbon. This coking action can coat the catalyst obscure reaction sites and cell recovery is not likely.

- **Oxygen (5 ppmV)** – The anode of the fuel cell must be in a reducing atmosphere to properly generate protons. Presence of oxygen here will change this dynamic. The cell is recoverable when oxygen in the fuel is removed.

- **Carbon Monoxide (0.2 ppmV)** - Carbon monoxide potential relative to the hydrogen electrode is much lower than the air side electrode. This results in adsorption of carbon monoxide on the catalyst surface, reducing the catalysts activity. After exposure, recovery may not always be successful.

- **Carbon Dioxide (2 ppmV)** - Carbon dioxide has much smaller poisoning effect on catalysts than carbon monoxide. Carbon dioxide can be reduced to carbon
monoxide by hydrogen adsorbed on the catalyst surface by reverse gas shift reaction \( \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \), with the effects listed for carbon monoxide.

- **Total Sulfur (0.004 ppmV)** - Organosulfur compounds can cause significant and permanent deactivation of the catalyst, even at very low concentrations due to formation of strong metal-S bonds. Sulfur absorbs chemically onto the surface and reacts with the active catalysts, preventing reactant access, and can lead to non-selective side reactions which modify the surface chemistry of the anode. This degradation is accumulative.

- **Formaldehyde (0.01 ppmV)** - Formaldehyde, in contact with a platinum surface, can readily decompose with release of hydrogen and carbon monoxide. Formaldehyde has the propensity to stick to metal surfaces. This degradation is accumulative.

- **Formic Acid (0.2 ppmV)** - Formic acid has the susceptibility to stick to metal surfaces. When present in hydrogen feeding a fuel cell, formic acid will tie up reaction sites on the metal catalyst and thus reduce the output of the fuel cell. This degradation is accumulative.

- **Ammonia (0.1 ppmV)** - Ammonia in hydrogen will readily form ammonium (\( \text{NH}_4^+ \)) at the anode and reduce the production of protons. Recovery after exposure is not likely. This degradation is accumulative.

- **Total Halogenated Compounds (0.05 ppmV total)** - Organochlorines and organofluorines are very susceptible to holding on to free electrons, and thus can reduce the current generated at the anode of the fuel cell. The cell is recoverable when halogenates in the fuel are removed.

- **Particulate Concentration (1 µg/L)** – Small particles in the fuel can impact pneumatic controls, such as valves, and also generate a coat on active sites on the catalyst, thus impacting the generation of protons. After exposure, recovery may not always be successful. This degradation is accumulative.

### Diluents/Adulterants

- **Nitrogen/Argon (100 ppmV)** - Adulterant, most probably from ambient air contamination. These dramatically reduce the effectiveness of the hydrogen fuel. Also, nitrogen in the presence of protons may form ammonium, with resulting degradation of cell performance.
  
  \[
  \text{N}_2 + 4\text{H}^+ \rightarrow 2\text{NH}_4^+
  \]

- **Helium (300 ppmV)** - Adulterant, primarily from hydrogen sourced from natural gas. Natural gas can comprise as much as 7% helium, thus reduce the effectiveness of the hydrogen fuel.
Sources of Hydrogen

- Steam Reforming of Methane - Natural Gas
  Possible H₂ Contaminants - sulfur, helium (up to 7%), carbon monoxide, carbon dioxide, hydrocarbons, water vapor, formic acid, formaldehyde
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

- Dry CO₂ Reforming with Methane - landfills, sewage digester gas.
  Possible H₂ Contaminants - sulfur, halogenates, hydrocarbons, water vapor, carbon monoxide, carbon dioxide, ammonia, formic acid, formaldehyde.
  \[ \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2 + 2\text{CO} \]

- Hydrolysis - solar, hydroelectric, nuclear.
  Possible H₂ Contaminants - Oxygen, Water.
  \[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]

Contamination in Distribution/Transport of Hydrogen

- Possible contaminants - Oxygen, Nitrogen.

- Unswept tubing/holding tanks - 8% of ambient air in a given dead volume (such as a holding tank) at 1 atm, then compressed to 10,000 psiG, becomes 5 ppmV in Hydrogen at delivery pressure.

Adulteration of Hydrogen

- Possible contaminants - Oxygen, Nitrogen, ambient air.

- Retail Cost/liter of Hydrogen at 10,000 psiG - $1.36/m³. ($15/kg)

- Cost/20 liters of Liquid Nitrogen (equivalent to 1 m³ H₂ at 10,000 psi) - $2,500

- Cost/liter of ambient air - free