PEMFC Cathode Contamination Mechanisms for several VOCs - Acetonitrile, Acetylene, Bromomethane, Iso-propanol, Methyl Methacrylate, Naphthalene and Propene

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Proton exchange membrane fuel cells (PEMFC) are currently being demonstrated and marketed as replacements for more established technologies such as the energy inefficient and unsustainably fueled internal combustion engine (1). However, a gap still exists between PEMFC durability targets and current system specifications. PEMFCs are fed with ambient air that contains the oxygen oxidant. The fuel cell exposure risk to a multitude of air contaminants is significant (2). Contamination mechanisms were only established for a few species but they are needed to devise robust prevention and recovery procedures.

Contaminants were selected using a two tiered approach that greatly decreased the number of species requiring an experimental evaluation (3,4). Seven organic contaminants with different functional groups were chosen for extensive characterization tests: acetonitrile (a nitrile, solvent and chemical intermediate), acetylene (an alkyne, welding fuel and chemical intermediate), bromomethane (an halocarbon and fumigant), iso-propanol (an alcohol, solvent, chemical intermediate and windshield de-icer), methyl methacrylate (an ester and synthesis precursor for poly(methyl methacrylate), a shatter-resistant alternative to glass), naphthalene (an aromatic, chemical intermediate and fumigant) and propene (an alkene and synthesis precursor for polypropylene used for films, packaging, etc). Impedance spectroscopy was first used to assess resistance loss types: kinetic, ohmic, mass transfer. All seven species led to changes in kinetic and mass transfer resistances. Only acetonitrile affected the ohmic resistance. Subsequently, additional tests were completed to resolve in more detail each resistance loss type. A rotating ring/disc electrode, a membrane conductivity cell, a segmented cell, a single fuel cell coupled with a gas chromatograph and a tracer based method able to measure the liquid water content in flow field channels and gas diffusion electrodes (5,6) were either used or planned to either localize more precisely or gain additional insight into each resistance loss type.

Acetylene experimental data were synthesized into a consistent and cohesive contamination mechanism (Fig. 1). As the acetylene moves along the flow field channels, it is not appreciably dissolved into liquid water droplets because its solubility is too low. In other words, the scavenging effect of liquid water is negligible (7). As the acetylene penetrates the gas diffusion layer, it may adsorb on the C fibers, sub-layer C particles and catalyst C support affecting its hydrophobic and liquid water management properties, and induce a change in mass transfer resistance. This hypothesis remains to be tested as the carbon surface area and acetylene adsorption energy are expected to be smaller than on Pt. Subsequently, the acetylene reaches the ionomer. However, acetylene does not impact catalyst layer ionomer conductivity. Further

along its transport path, the acetylene reaches the catalyst layer where it adsorbs on the Pt surface, reduces the active area and induces an oxygen reaction mechanism change which is detected by an increase in the fraction of peroxide produced from 3 to 14% at 30°C and 0.5 V vs RHE. The acetylene deleterious impact persists within an application relevant cell voltage range of 0.55 to 0.85 V despite a large change in acetylene conversion of respectively <1 to ~100% (mostly CO_2 with CO traces). Mass transfer in the ionomer layer is also affected by the presence of adsorbed acetylene on the catalyst surface (longer transport path) and is expected to be the major contributor in comparison to acetylene adsorption on C. Planned residence time distribution measurements (tracer based method) are expected to clarify the source of the mass transfer loss (C versus Pt adsorption) by quantifying the amount of liquid water in the gas diffusion electrode. The change in liquid water content indirectly provides an assessment of the C surface hydrophobic state. Finally, the acetylene reaches the membrane. However, acetylene does not impact the membrane conductivity.

Current distribution measurements indicate that a contamination front moves from the cell inlet to the outlet during the cell voltage transient, from the contaminant injection to the steady state. After a temporary acetylene exposure, the cell voltage recovers to almost its original value (>90% recovery). The small remaining loss in performance is ascribed to residues on the catalyst surface. A revised version of the acetylene mechanism will be presented as well as an experimental data summary for all other selected contaminants.

REFERENCES

1. *2011 Fuel Cell Technologies Market Report*, United States Department of Energy, Energy Efficiency and Renewable Energy (2012).
2. J. St-Pierre, in *Polymer Electrolyte Fuel Cell Durability*, F. N. Büchi, M. Inaba, and T. J. Schmidt, Editors, p. 289, Springer (2009).
3. J. St-Pierre, M. S. Angelo, and Y. Zhai, *Electrochem. Soc. Trans.*, **41**(1), 279 (2011).
4. J. St-Pierre, Y. Zhai, and M. Angelo, *Int. J. Hydrogen Energy*, **37**, 6784 (2012).
5. J. Diep, D. Kiel, J. St-Pierre, and A. Wong, *Chem. Eng. Sci.*, **62**, 846 (2007).
6. J. St-Pierre, A. Wong, J. Diep, and D. Kiel, *J. Power Sources*, **164**, 196 (2007).
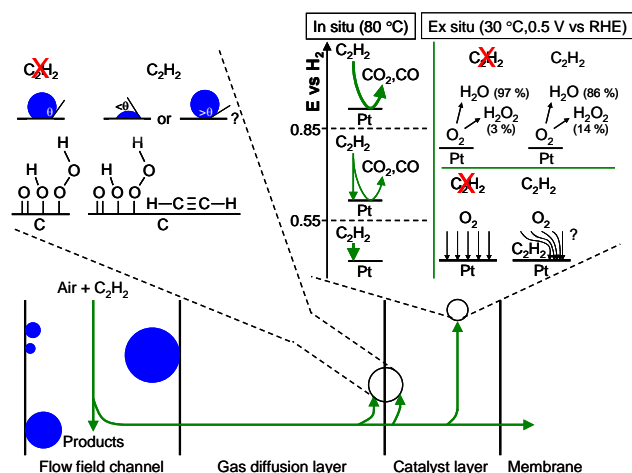7. B. Wetton and J. St-Pierre, *Electrochem. Soc. Trans.*, **50**(2), 649 (2012).

Fig. 1. Proposed acetylene contamination mechanism.