Degradation of Membranes for PEMFC

1) Mechanical Degradation

Mechanical degradation is often the cause of early life failures, especially for very thin membranes. Mechanical degradation occurs in many forms including cracks, tears, punctures or pinhole blisters. Care must be taken in the preparation of the membranes, as foreign particles from fabrication can cause perforations, which may also occur at reactant inlets, seals or edges: any areas where the membrane is subjected to increased stress. Non-uniform pressure between the membrane electrode assembly (MEA) and the bipolar plates during fuel cell operation or during manufacture can accelerate membrane degradation. Inadequate humidification is detrimental to the membrane, as lack of water makes the membrane brittle and fragile [1]. Penetration of the catalyst particles into the membrane can cause local high stress areas [1,2]. These stress points can also be caused by a manufacturing imperfection or the misalignment of the catalyst transfer decal [1,3]. Cell reversal (for example, caused by fuel starvation) causes O2 to form at the anode through the electrolysis of water (instead of hydrogen oxidation). There is evidence that this formation of O2 causes localized heat evolution, resulting in holes in the membrane, perforations or stress points [4]. When a perforation or pinhole in the membrane occurs, the reactant gases crossover and react on the catalyst surface. This counterbalances the electrochemical reaction of the cell, and a drop in cell voltage is observed. The heat of this reaction may cause the membrane to soften or even melt, furthering the degradation, which then allows increased gas crossover, and a destructive cycle will occur [1,5]. Gas crossover also lowers both fuel efficiency and thermodynamic efficiency. Pinhole formation and the prevention of this degradation are recognized to be vitally important to the lifetime of the membrane.
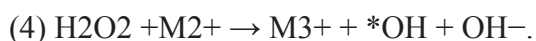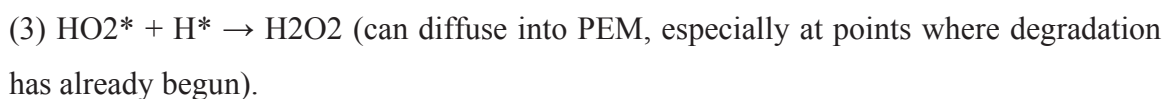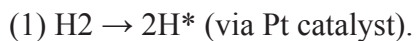
2) Thermal Degradation

High temperatures have several advantages for PEMFC. These conditions would reduce cooling requirements, allow co-generation of electricity and higher value heat, increase electrochemical kinetics and decrease the tendency of contamination. Unfortunately, the

degradation of the polymer membrane (along with other parts of the cell) increases with the temperature [6]. The main impact of a temperature increase on the membrane is the reduction in water content, leading eventually to irreversible dryness. For perfluorocarbon ionomer membranes (i.e., Nafion_) the temperature must reach 150 ∘C before their chemical structure is noticeably affected. This thermal stability is due to the C–F bond strength and the shielding effect of fluorines. Above 200 ∘C, the loss of sulfonate groups begins to occur [1].

Membranes' stability in changing temperatures is vital to their performance in the automotive industry. They must be able to withstand cold temperatures as well as hot, and tolerate cycling between these temperatures. A problem with these temperature fluctuations is that water within the fuel cell may freeze, thus expanding its volume, which would then decrease again upon melting. These volume changes could have a detrimental effect on the membrane's lifetime. A recent publication studied the effectiveness of gaspurging and solution-purging (antifreeze solutions) to remove residual water and prevent any damage caused by volume changes during temperature cycling [34].

3) Chemical and Electrochemical Degradation

The membrane is subjected to both a harsh chemically oxidizing environment on the cathode side and chemically reducing environment on the anode side. In addition to this, peroxy and hydroperoxy radicals formed in the fuel cell attack the membrane. The chemical degradation of PEM membranes is mainly attributed to these attacks. There are two proposed mechanisms for the formation of these radicals. General Electric proposed the following [1]:

(1) $H_2 \rightarrow 2H^*$ (via Pt catalyst).
(2) $H^* + O_2$ (diffused through PEM to anode$) \rightarrow HO_2^*$
(3) $HO_2^* + H^* \rightarrow H_2O_2$ (can diffuse into PEM, especially at points where degradation has already begun).
(4) $H_2O_2 + M^{2+} \rightarrow M^{3+} + {}^*OH + OH^-$.

(5) $*OH + H_2O_2 \rightarrow H_2O + HO_2*$ (hydrogen peroxide radical attacks PEM).

LaConti and coworkers [1] also found severe degradation of the polystyrene sulfonic acid (PSSA) solution in the presence of a platinum catalyst when it was in an atmosphere of H_2 and a small amount of O_2. They also confirmed the formation of H_2O_2 under these conditions. When the same solution was subjected to an atmosphere of pure hydrogen or pure oxygen (in the presence of platinum) only a small amount of degradation occurred. Without the platinum catalyst, no degradation occurred, even in combinations of the two gases. These results support the suggestion that diffusion through the membrane and the mixing of gases at the catalyst surface accelerate degradation.

Using electrochemical rotating disk and ring techniques, the reduction of both O_2 and H_2O_2 to water was found to be inhibited on platinum at low electrode potentials in acidic solution. A monolayer of hydrogen on the platinum surface inhibits the reduction. Therefore, some reduction of O_2 to H_2O_2 occurs, and it is more difficult to further reduce the peroxide to water, causing an accumulation of H_2O_2. In recent works, the yield of H_2O_2 from O_2 reduction was shown to be 2% at 0.050V (RHE), but in the presence of a chloride ion, the yield increases to 20%. In the presence of carbon monoxide, this yield drastically increases to 80% [1] H_2O_2 has also been identified in fuel cell product water [8] and the OH* radical has been identified on the cathode side of a PEM fuel, using a spin trap method combined with electron paramagnetic resonance (EPR) spectroscopy [9].

The peroxide radicals formed in the MEA are generally accepted to be the cause of membrane degradation. Depending on the type of membrane, radical attack can occur at the α-carbon of an aromatic group, at ether links, or at branching points of the polymer. Hydrogen abstraction can also occur. Any H-containing terminal bonds present in the polymer can be attacked by radicals, especially at low relative humidity conditions and temperatures above 90 ∘C.

4) Prevention of Degradation

From the information currently available about the degradation of PEMFC membranes, several steps can be taken to slow the process. Some possible prevention methods include avoiding/reducing metal contamination from all possible sources (end plates, reactant gas flows and stack components); decreasing gas permeability across the membrane, optimizing the membrane water content (increasing water content lowers the concentration of H2O2, however, it allows increased gas crossover at the same time). Radical inhibitors or peroxide-decomposition catalysts deposited within membrane could decrease the severity of radical attacks or a sacrificial material could be included to prevent direct attack on the membrane. There is evidence that pure H2SO4 may reverse the effects of impurity contamination of the membrane [10]. In situ temperature mapping would detect hotspots, identifying problem areas which could lead to pinholes/perforations. Humidity mapping would be equally important.

References

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