In Situ PEMFC Fuel Crossover & Electrical Short Circuit Measurement

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The concept of reactant crossover and a simple *in situ* method for its measurement in polymer electrolyte membrane (PEM) fuel cells is introduced. The method is also useful for determination of the presence of an electrical short in the PEMFC.

Fuel Crossover

Permeation of reactant from one electrode to the other through the PEM is referred to as *crossover*. Although crossover of both fuel (*e.g.*, hydrogen or methanol) and oxidant (oxygen) occurs, the latter generally occurs at a lower rate and thus most often *fuel crossover* is the property of interest.

Reactant crossover is important because it degrades fuel cell performance, efficiency and durability. Direct reaction of hydrogen with oxygen at the fuel cell cathode decreases the cell's open circuit voltage through generation of a mixed potential. Fuel efficiency is also lowered because although the reactant is consumed, the electrical work is not captured. In addition, severe crossover autocatalytically accelerates membrane degradation and pinhole formation via locally generated heat leading to proximate membrane thinning, which further accelerates the crossover process.

The rate of crossover is determined by the reactant's permeability through the membrane. For a given reactant, it is a function of the membrane composition, microstructure and thickness, as well as environmental parameters. Permeability is the product of diffusivity and solubility and therefore factors impacting these properties influence crossover rate. For example, the crossover rate increases at elevated temperature in part because diffusivity increases with temperature. All else being equal, a fuel cell with a thin membrane will exhibit higher crossover than one with a thick membrane because the concentration gradient of the reactant across the membrane that is the driving force for diffusion is larger.
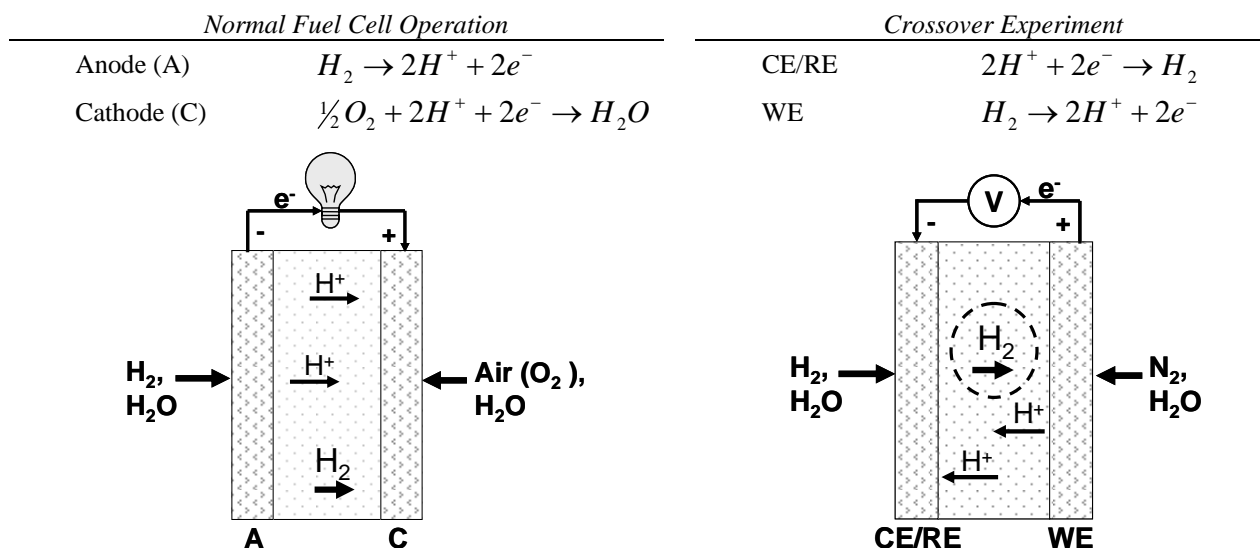
Similarly, direct conduction of electrons between the electrodes through the electrolyte is also a source of loss within a fuel cell. Although the electrolyte is designed to be an ionic but not electronic conductor, finite electrical shorts between the electrodes may occur as a result of electrolyte thinning (cell electrical resistance typically decreases with age) or as a result of pinhole formation. As with crossover, excessive electronic conduction through the electrolyte results in degradation of cell performance.

Fuel crossover and internal short circuits are essentially equivalent in terms of impact on efficiency. The crossover of one hydrogen molecule resulting in the loss of 2 electrons is the same as the loss occurring from the conduction of 2 electrons from the anode to the cathode. Fuel crossover of 1 mA/cm^2 equates to a loss in current efficiency of 0.25% at an operating current density of 400 mA/cm^2.

In Situ *Fuel Crossover Measurement*

To experimentally determine the fuel crossover, a suitable inert gas such as nitrogen is used to purge the fuel cell cathode while hydrogen is passed through the fuel cell anode. The potential of the fuel cell cathode (*i.e.*, the working electrode, WE) is swept by means of a linear potential scan to potentials at which any hydrogen gas present at the fuel cell cathode is instantaneously oxidized under mass transfer limited conditions. Such experiments are referred to as linear sweep voltammetry (LSV) [Bard 2001].

Normal Fuel Cell Operation		*Crossover Experiment*	
Anode (A)	$H_2 \rightarrow 2H^+ + 2e^-$	CE/RE	$2H^+ + 2e^- \rightarrow H_2$
Cathode (C)	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	WE	$H_2 \rightarrow 2H^+ + 2e^-$

WE = working electrode, CE = counter electrode, RE = reference electrode.

The conditions and electrode reactions during normal hydrogen fuel cell operation as compared to a hydrogen crossover experiment are shown below. A fuel cell is a driving system whereas the electrochemical crossover measurement is a driven system requiring the use of a potentiostat or other controllable power supply.

The working electrode is scanned at 1 to 4 mV/sec from the open circuit potential (~ 0.1 V) to ~ 0.8 V *vs.* CE/RE. Polarization to anodic potentials > 1.0 V can lead to irreversible damage of the fuel cell electrode resulting from carbon corrosion and catalyst oxidation. Fully or super-saturated (≥ 100% RH) conditions are generally used for both the fuel and inert gas.

Methanol crossover can also be determined using this basic voltammetric method, with the hydrogen being replaced by the liquid fuel [Ren 2000].

The output of working electrode current density (current normalized by the active area of the working electrode) *vs.* potential is used to determine the hydrogen crossover flux J_{x-over,H_2} (mole/cm^2/s) from Faraday's law,

$$J_{x-over,H_2} = \frac{i_{lim}}{n \cdot F} \qquad (1)$$

where i_{lim} is the transport limiting current density (A/cm^2), n is the number of electrons taking part in the reaction (electron-mole/mole), and F is Faraday constant (96,485 C/electron-mole).

The current typically attains either a constant or linearly increasing value with increasing electrode potential. A constant, electrode potential-independent current is indicative of a fuel cell with a very high (infinite) electrical resistance (*i.e.*, no internal shorting) whereas a linearly increasing current indicates that the cell has a finite resistance due to internal shorting. The electrical resistance of the cell can be estimated from the slope of the voltage *vs.* current plot.
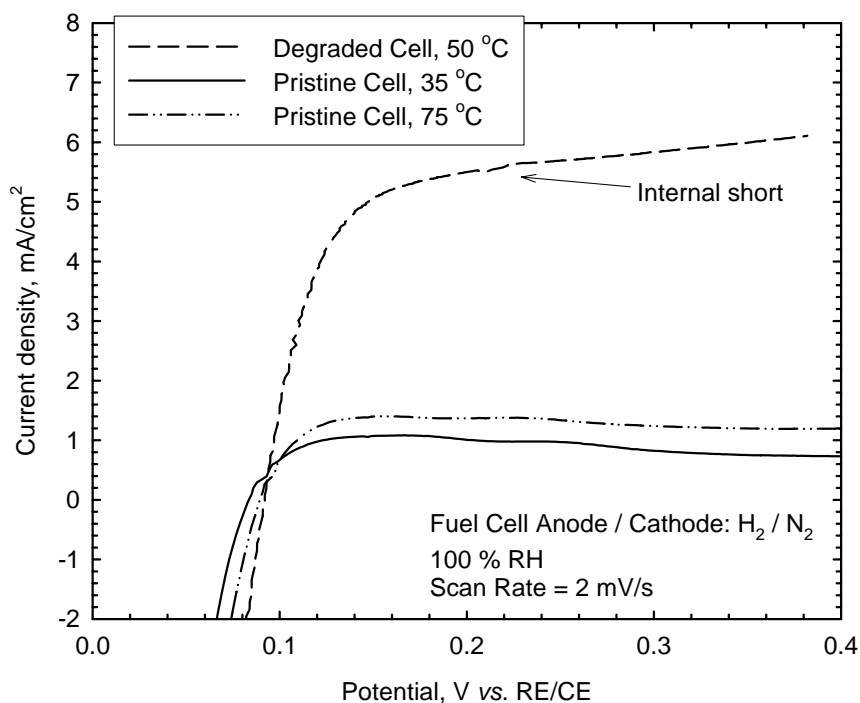

FIGURE 1. Linear sweep voltammograms for hydrogen crossover in a PEMFC.

As an example, Fig. 1 compares the H$_2$ crossover characteristics of a high-quality pristine cell to that of degraded cell. The pristine cell exhibited a limiting current density (i_{lim}) of 1.1 mA/cm^2 and 1.4 mA/cm^2 at 35 °C and 75 °C, respectively, demonstrating the temperature-dependent hydrogen permeability.

The mass transfer limited current density is proportional to the rate of H$_2$ crossover from the anode to the cathode through the membrane. Applying Faraday's law (1) with $n = 2$ for the hydrogen oxidation reaction, the crossover flux at 35 °C was 5.7×10^{-9} mole/cm^2/s.

In contrast, the degraded cell exhibited significant hydrogen crossover ($i_{lim} = 5.5$ mA/cm^2 or 2.9×10^{-8} mole/cm^2/s) and a significant internal electronic short-circuit between the two electrodes. The resistance of the electrical short was estimated to be 330 Ω-cm^2.

Crossover experiments an important diagnostic for membrane and membrane electrode assembly (MEA) developers, manufacturers, and integrators, and should be conducted whenever a new cell is assembled and periodically during testing. A crossover threshold is often used as end-of-life criteria in membrane durability testing.

ACKNOWLEDGEMENT

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