The Effect of Membrane Thickness on Short- and Long-Term Performance of a Direct Methanol Fuel Cell

Jeong Lee, R. Wycisk, Jun Lin and Peter N. Pintauro, Case Western Reserve University, Department of Chemical Engineering, Cleveland, OH 44106-7217

It is well known that the optimum proton-exchange membrane material for a direct methanol fuel cell (DMFC) should have a high proton conductivity and low methanol crossover. Such a combination of properties is difficult to achieve and, in general, membranes with low methanol permeability also exhibit sluggish proton conduction. Consequently, a major objective of DMFC development has been to maximize the conductance/permeability ratio of the polymeric membrane material.

Alternatively, attempts have been made to optimize both the MEA structure (MEA=membrane-electrode-assembly, composed of the membrane and attached catalyst layers) and the operational conditions of a DMFC in order to effectively utilize existing membrane materials. Some investigators employ thin membranes to decrease the ohmic resistance of an MEA and a dilute methanol feed to lower methanol crossover.

Membrane thickness, in particular, has a direct bearing on the primary processes that cause DMFC power losses, via ohmic losses (IR drop) and methanol crossover flux. It is, therefore, of prime importance to understand the interdependence of membrane thickness and DMFC operating conditions (e.g., methanol feed concentration, temperature and air/oxygen flow rate and pressure) on the short-term and long-term performance of a direct methanol fuel cell.

When methanol contacts the air cathode in a DMFC, it will be oxidize chemically (with oxygen from the cathode feed air) to form CO_2 and water. Methanol oxidation at the air cathode has a number of unwanted consequences: (1) There is cathode depolarization (a loss in voltage) due to a mixed potential phenomenon (where two reactions, the electrochemical reduction of O_2 and the chemical oxidation of methanol, occur on the same electrode), (2) CO, generated as an intermediate on the cathode during the oxidation of methanol, poisons the cathode catalyst, (3) oxygen is consumed during methanol oxidation and is not available for electrochemical reduction, (4) there is excess water generation at the cathode and flooding of the electrode occurs (which will lower O_2 access to catalytic sites), and (5) there is consumption of methanol without electricity generation, thus lowering the overall fuel efficiency of the fuel cell.

The effects of membrane thickness on the initial and long-term power output from a DMFC can be quantified using Nafion®-based MEAs (here, long-term is defined as a few days of fuel cell operation). In general, the power generated using a thin membrane is initially high (due to lower resistive losses) but falls rapidly (within a few hours) due to methanol crossover, whereas the initial performance with a thicker membrane is low (due to its high ohmic resistance) but is more stable during long-term operation because there is less methanol oxidation at the cathode. This situation is not the case for a proton-exchange membrane H_2/air fuel cell, where decreasing the membrane thickness improves fuel cell performance (until the membrane becomes so thin that H_2 and/or O_2 gas crossover becomes a concern). Figures 1 and 2 exemplify the fundamental difference in thickness behavior of a proton conducting membrane (commercial Nafion samples) in a H_2/air fuel cell and a DMFC. The voltage-current density plots in Figure 1 show an improvement in fuel cell performance when the thickness of Nafion is decreased from 175 μm (Nafion 117, dry) to 50 μm (Nafion 112, dry) due to a decrease in the areal resistance (defined as the membrane thickness divided by proton conductivity). Here better performance is quantified in terms of power density output (where the power density is defined as the product of voltage and current density). The situation is much different for a DMFC, as demonstrated in Figure 2, where the fuel cell voltage-current plot with Nafion 112 lies below that for Nafion 117. Now methanol crossover is the dominant factor in controlling fuel cell power, in which case a thicker membrane is a better methanol barrier, even though its areal resistance is greater than that of a thin film.

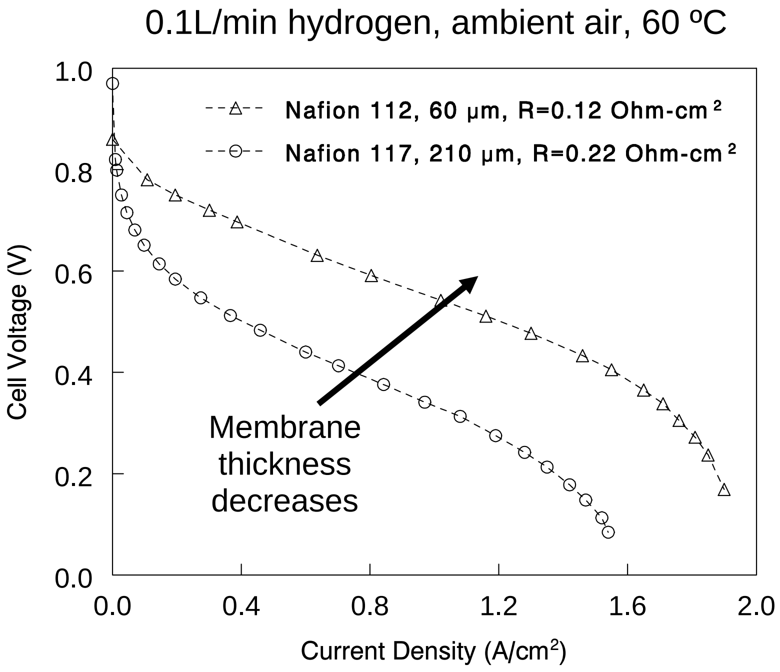

Figure 1 - Effect of membrane thickness on the performance of a H_2/air proton exchange membrane fuel cell with two commercial Nafion membranes, where R denotes the membrane areal resistance.

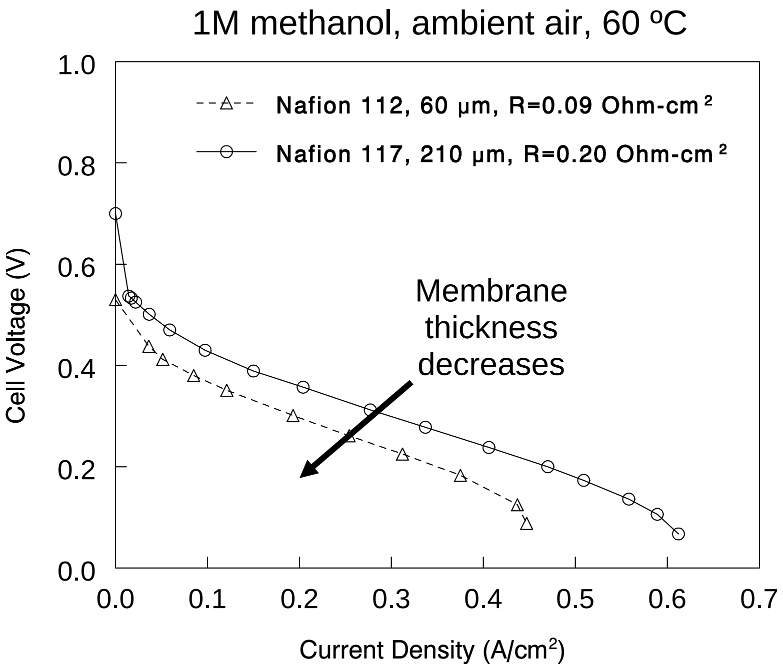

Figure 2 - The effect of membrane thickness on DMFC performance for two commercial Nafion membranes, where R denotes the membrane areal resistance.

Examples of Nafion 117 and Nafion 112 performance in a direct methanol fuel cell for continuous operation up to 47 hours are shown in Figures 3 and 4. Data was collected under the following fuel cell operating conditions: 80^{o}C, 0.5 M methanol feed concentration, and ambient pressure air at 500 sccm. The MEA prepared with Nafion 117 exhibits very stable performance over 21 hours of operation. The initial voltage-current density plot with Nafion 112 is better than that with Nafion 117, due to its reduced thickness and lower resistance, but the power output begins to drop after one hour. For Nafion 112, the deleterious effects of methanol crossover dominate the power output and there is a steady degradation of the voltage-current density plots. The low open circuit voltage for the Nafion 112 MEA, as compared to that for Nafion 117, is another indication that methanol crossover is a problem.

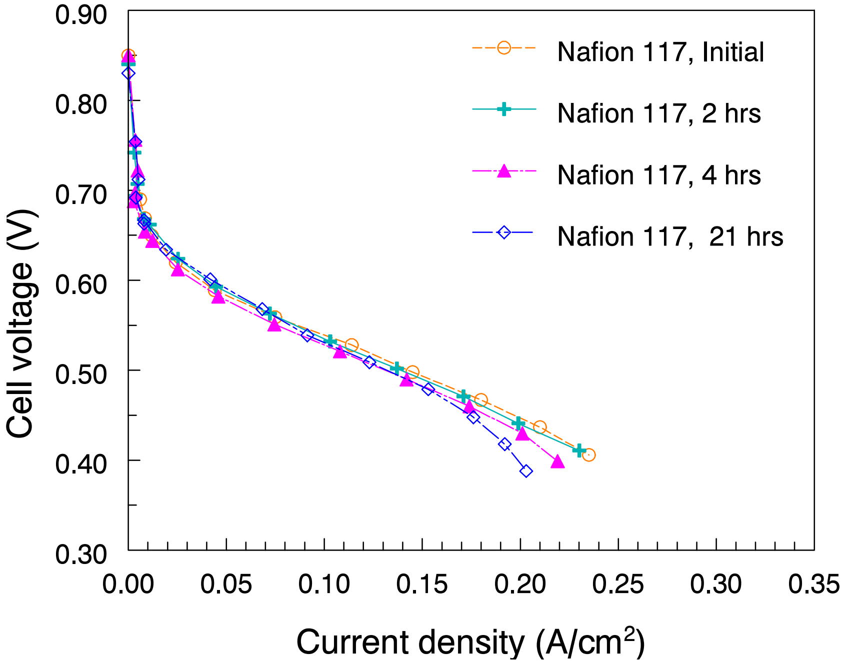

Figure 3 - Performance of a direct methanol fuel cell with a Nafion 117 membrane-electrode-assembly (MEA). 80^{o}C, 0.5 M methanol, air at 1 atm.

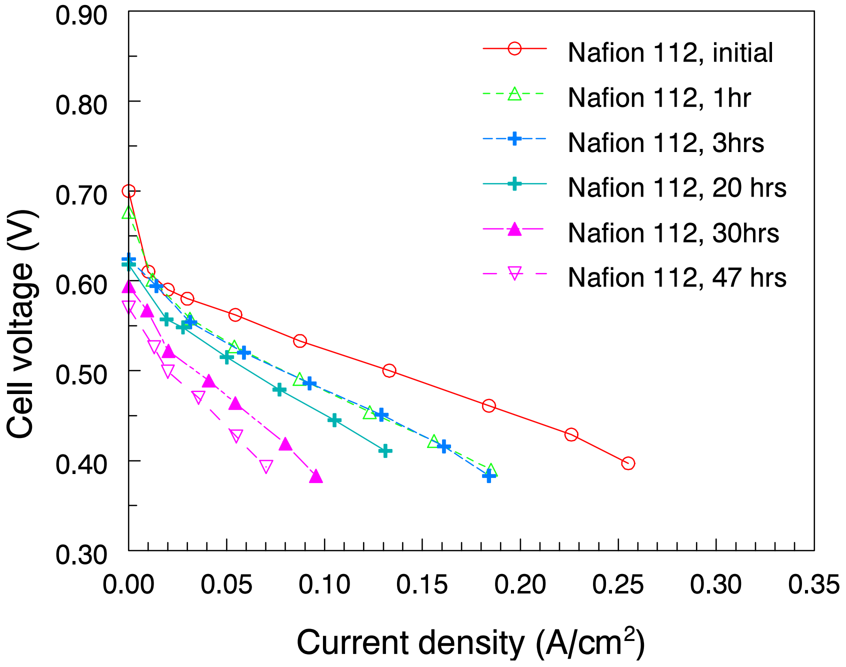

Figure 4 – Performance of a direct methanol fuel cell with a Nafion 112 membrane-electrode-assembly (MEA). 80^{o}C, 0.5 M methanol, air at 1 atm.

Conclusions:

1. The decline in MEA performance during the operation of a direct methanol fuel cell is due to methanol crossover, where the production of CO and excess water at the cathode affects the oxygen reduction reaction.

2. Membranes that are too thick work poorly in a DMFC due to the high ohmic resistance of the MEA, whereas membranes that are too thin work poorly due to methanol crossover. Only thin membranes show long-term performance degradation because the deleterious effects of methanol crossover accumulate over time.

3. Preconditioning the MEA as a hydrogen fuel cell before DMFC testing produces a more rapid decline in DMFC performance, as compared to preconditioning with methanol.

4. Load cycling during long-time DMFC tests improves MEA performance. During the current-off phase of each cycle, CO and/or water is removed from the cathode. Unfortunately, little is known regarding the optimum load cycling conditions that will minimize MEA performance degradation of a DMFC.