Novel Process for Improved Long-Term Performance of DMFC Membrane-Electrode Assemblies

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Thanks to the liquid nature of the fuel and ensuing high system specific energy, the direct methanol fuel cell (DMFC) is a promising power source for portable electronics and other applications. In order to become fully commercially viable, DMFC not only needs to deliver high initial performance but also maintain that performance over long operating times, perhaps as long as thousands of hours.

There have been several routes of DMFC performance degradation identified to date, of which the main ones are: (a) Pt cathode catalyst oxidation, (b) gradual loss of the electrochemical surface area of electrodes, (c) ruthenium crossover from the anode to the cathode side of the cell, (d) loss of hydrophobic properties of the cathode, and (e) membrane degradation. In spite of the generally agreed upon importance of performance durability for the commercialization of DMFCs, little has been reported on long-term performance of DMFCs and methods for reducing the impact of various degradation mechanisms. The objective of this work has been to minimize uncorrectable performance loss of Nafion®-based DMFCs by optimizing the membrane-electrode assembly (MEA) fabrication process.

The reference (standard) MEAs in this work were obtained using catalyst inks prepared by suspending unsupported metal nanoparticles in a mixture of recast Nafion® colloidal solution and water. The anode and cathode inks were directly applied to two sides of a Nafion® 117 membrane. Such prepared MEA was placed in a 22-cm² fuel cell without further processing. Novel MEAs were made using recently developed alternative catalyst/ionomer suspensions and high-temperature processing routes, which included an acid boil. The results presented here refer to novel MEAs with “semi-optimized” catalyst inks and processing conditions.

As shown in Figure 1, the new fabrication process results in improved long-term MEA stability. At life-test times longer than 1400 hours, performance of the novel MEA is up to 20% higher than that of the standard MEA. After 3000 hours of the life test (the end of the longest novel MEA life test), the uncorrectable performance loss of the novel MEA is only 15 mA cm⁻² at 0.5 V, whereas that of a standard LANL MEA is 37 mA cm⁻² after merely 1000 hours.

Different rates of performance degradation are accompanied by different changes in the high frequency resistance (HFR) of the MEAs (Figure 2). The HFR gain is much higher for the standard MEA than for the MEA obtained by the new process. Since under well-controlled humidification conditions changes to membrane conductivity over time are expected to be very small, the HFR increase is likely to be caused by rising resistance at the membrane/electrode(s) interface(s) – much faster for the standard MEA than the novel one. This process appears to occur much faster for the standard MEA, suggesting significantly more robust membrane-electrode interface of the novel MEA.

Electrochemically active surface area of the anode and the cathode was determined at various life test times using carbon monoxide stripping charge. Loss in that charge was found to be much lower for the novel than standard MEA. This may be due to improved networking of the Nafion® polymer within the electrode, leading to better catalyst layer integrity.

Further analysis of CO stripping voltammetry for the two MEAs revealed the impact of high-temperature and pre-leaching of the Pt-Ru anode catalyst in acid boil on ruthenium crossover and subsequent contamination of the cathode by Ru. As observed earlier with other systems, the high-temperature treatment and pre-leaching involved in the novel fabrication process help to greatly reduce ruthenium crossover.

![Figure 1. Long-term performance of two 22-cm² MEAs at a constant voltage of 0.5 V. Cell operating temperature 80°C, ambient cathode pressure.](image1)

![Figure 2. Gain in the high-frequency resistance of two differently prepared MEAs during life-test. Cell operating temperature 80°C, ambient cathode pressure.](image2)

References