

## State of the DMFC Cathode During Prolonged Cell Operation

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Thanks to inherent system simplicity, high energy density of methanol and no need for fuel reforming, the direct methanol fuel cell (DMFC) has long been considered a promising source of electricity for both portable (mobile phones, laptops, etc.) and higher power applications, including transportation<sup>1</sup>. Although direct combustion of methanol at the fuel cell anode is not a new concept, progress in DMFC research and technology has not been accomplished until this decade<sup>2-4</sup>.

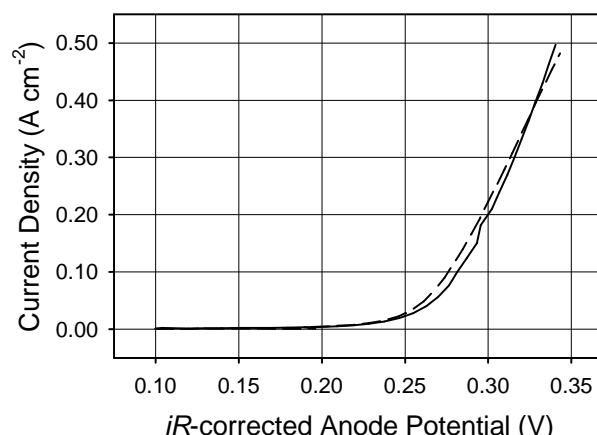
The most important factors determining the performance of the DMFC are electrocatalytic activity of the methanol anode, methanol crossover through the polymer electrolyte membrane, ionic membrane conductivity, and water management at the cathode. It has been shown that careful optimization of the electrode structure and composition and selection of right DMFC operating conditions can help accomplish respectable power density and good fuel utilization even with “leaky” membranes, such as Nafion<sup>®</sup> 117<sup>3,5</sup>.

With significant progress in anode electrocatalysis and fuel utilization in recent years, the cathode is becoming the performance-limiting component of the DMFC, especially at longer cell operating times<sup>6</sup>. Among factors already identified as impeding DMFC cathode performance the two most important are: (i) depolarization of the cathode potential due to methanol crossover (mixed-potential case), (ii) catalyst “flooding” with the excessive water either generated in the electrode process itself or delivered to the catalyst layer by diffusion and electro-osmotic drag across the membrane. In addition to these generally agreed upon phenomena, we report here on some additional effects, directly impacting electrocatalytic properties of the DMFC cathode at prolonged operation of the fuel cell.

Constant voltage life tests at 0.55 V indicate a substantial loss in the DMFC current over an initial time period of 50 to 70 hours of continuous cell operation. Since the anode does not usually undergo any degradation during that time (cf. anode polarization plots recorded at the beginning and at the end of a 200-hour uninterrupted life test, Figure 1), the observed current drop must be due to cathode performance loss. In order to identify the nature of that loss the electrocatalytic state of the cathode was probed using CO stripping<sup>7</sup> and through cathode polarization ( $H_2$ /Air polarization curves) at different times during the life test. The final state of the cathode was additionally characterized with XRD and ICP analysis.

The cathode performance degradation observed by us has to be considered an intrinsic feature of the catalytic materials used and of the electrochemical conditions present in the DMFC. In order for the catalysts to be sufficiently electroactive, they are prepared in a form, which is far from thermodynamic equilibrium. This makes them prone to transformations, particularly under the conditions of fuel cell operation. The nature of these transformations will be addressed in the talk, as will

possible approaches to stabilizing the DMFC cathode operation, even at an expense of initial catalyst activity.



**Figure 1.** Steady-state anode polarization plots before (solid line) and after (dashed line) 200-hour, continuous operation life test. Experimental conditions: cell working area 22 cm<sup>2</sup>; membrane Nafion<sup>®</sup> 117; anode feed 1.0 M methanol, 3 mL min<sup>-1</sup>; cathode feed H<sub>2</sub> at 200 mL min<sup>-1</sup>, 1 atm backpressure, externally humidified at 95°C (driven cell operation); cell temperature 80°C.

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