## Characteristics Of Small Formic Acid Fuel Cells Cynthia Rice, Su Ha, Rich Masel, Piotr Waszczuk, Thomas Barnard, Andrzej Wieckowski School of Chemical Sciences, University of Illinois 600 S. Mathews Ave., Urbana, IL 61801

The purpose of the work reported here is to determine whether direct formic acid fuel cells (DFAFC) are viable alternatives to direct methanol fuel cells (DMFC) in micropower applications. Formic acid is a liquid fuel. It has a lower energy content than methanol, but a higher theoretical reversible open circuit voltage (EMF) than methanol, 1.45 V vs. 1.18 V, respectively.

Formic acid electrooxidation occurs via two reaction pathways. One of the pathways is vary similar to methanol electrooxidation, forming CO as a reaction intermediate. Formic acid electrooxidation reaction pathway #1:

$$HCOOH + M^{+} \rightarrow M-CO + H_{2}$$
(1)  
$$H_{2}O + M^{0} \rightarrow M-OH + H^{+} + e^{-}$$
(2)

$$M-CO + M-OH \to 2M^0 + CO_2 + H^+ + e^-$$
 (3)

The sluggish rate of step (3) slows down the overall reaction rate, by blocking the surface sites to further formic acid adsorption. The second reaction pathway does not form CO as a reaction intermediate. Formic acid electrooxidation reaction pathway #2:

HCOOH +  $M^+ \rightarrow CO_2 + M^0 + 2H^+ + 2e^-$  (4) The product  $CO_2$  is formed directly thru step (4), circumventing the M-CO poisoning step. The key feature in formic acid fuel cells is the ability to preferentially oxidizing formic acid through reaction pathway #2, by selective catalyst modifications. Catalyst type can aid in forcing formic acid to oxidize thru reaction pathway #2. We have designed a new catalyst (UIUC-B) to enhance formic acid oxidation thru reaction pathway #2.

Methanol crossover is a major limitation for direct methanol fuel cells. Both methanol and water are transported across the proton conducting membrane, due to electro osmotic drag, from the anode side to the cathode side of the membrane electrode assembly (MEA). The methanol that reaches the cathode side adsorbs onto the cathode catalyst, blocking reaction sites and lowering the cell potential, thereby decreasing the overall cell efficiency. The phenomenon of fuel crossover is significantly decreased for formic acid, due to anionic repulsive forces. Formic acid dissociates when dissolved in water, forming an anion (HCOO<sup>-</sup>) that is repelled by the anionic sulfate groups  $(SO_4^{-2})$  within the solid polymer electrolyte membrane. Thereby, hindering osmotic drag of formic acid through the membrane to the cathode.

A standard 5 cm<sup>2</sup> MEA was prepared in house. The MEA consisted of a Pt black (Johnson Matthey) cathode catalyst (7 mg/cm<sup>2</sup>), a propriety anode catalyst UIUC-B (4 mg/cm<sup>2</sup>), and a Nafion<sup>®</sup> 117 membrane. Compared to direct methanol fuel cells (on Pt-Ru catalyst), the on-set of formic acid oxidation (on the UIUC-B catalyst) is decreased by approximately 0.1 V vs. DHE. A power density of 50 mW/cm<sup>2</sup> is attained at 60°C with formic acid on the anode and O<sub>2</sub> on the cathode. Formic acid oxidation is much more efficient than methanol in the complete conversion to the CO<sub>2</sub> end product. At 0.3 V vs. DHE formic acid current densities on the UIUC-B catalyst are close to 8 times greater than those for methanol on Pt-Ru catalyst. These results show formic acid as an attractive fuel for portable power applications.

Overall, we find that formic acid is a viable alternative to methanol for micropower applications. Direct formic acid fuel cells show eight times higher currents than direct methanol fuel cells, lower fuel crossover, and much simpler water management.