

Increase Porosity of Anodes in Direct Formic Acid Fuel Cells

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Efficient direct electro-oxidation of liquid fuels, such as methanol and formic acid for portable fuel cell applications, remains a challenge limiting commercialization. The major performance detractors are (1) the formation of strongly adsorbed reaction intermediates, (2) fuel crossover through the membrane depolarizing the cathode, and (3) mass transport for fast fuel delivery into the anode catalyst layer and gaseous product removal.

Direct formic acid fuel cells (DFAFCs) have the advantage over direct methanol fuel cells in that it is possible for formic acid to be electro-oxidized via a direct non-strongly adsorbed reaction intermediate pathway.[1] In addition to being less susceptible to fuel crossover due to anionic repulsion of the polarized formic acid dipole by the anionically charged sulfonic groups in the proton exchange membrane (PEM).[2] However, catalyst selection is pivotal for enhanced performance; in the initial part of this study a commercial unsupported PtRu catalyst was used. This was done to ensure reproducible performance, although the indirect electro-oxidation pathway was the dominant mechanism.[3]

It has been shown that DFAFC performance is strongly impacted by catalyst layer porosity via either swelling of the catalyst layer[4] or using a pore former to create larger pore structures in the catalyst layer[3]. Fig 1 shows the impact of increased porosity on the onset of formic acid electro-oxidation in an anodic linear sweep voltammogram. The pore-forming templating agent selected for these initial studies was micron-sized lithium carbonate (Li_2CO_3), due to facile removal upon acid treatment. Topographic scanning electron microscopy showed a semi-uniformed distribution of pores ranging from 20 μm to 60 μm in diameter resulting in a 5% increase in the catalyst layer thickness. For a 17.5wt% increase in porosity a favorable 30 mV decrease in the overpotential was observed.

Thus far a method to reduce the average particles has been developed to selectively etch the commercial micron-sized particles to the nanometer size range. The next step will be to incorporate them into an anode catalyst layer. The structure and porosity of the catalyst layers will be probed with nano-computerized tomography (CT) and correlated to electrochemical performance and electrochemical impedance spectroscopy (EIS).

An important target for commercialization is the reduction of precious metal catalyst below 0.3 mg cm^{-2} . This should be attainable by utilizing supported catalyst materials as has been demonstrated in the literature.[5] Ex-situ studies in our laboratory have demonstrated superior performance by the decoration of Bismuth (Bi) onto carbon supported Palladium (Pd), due to improve activity and durability. At a Bi coverage of 40% the observed current density increased from 0.25 mA cm^{-2} for the Pd/C baseline to 0.55 mA cm^{-2} at 0.2 V vs. RHE.

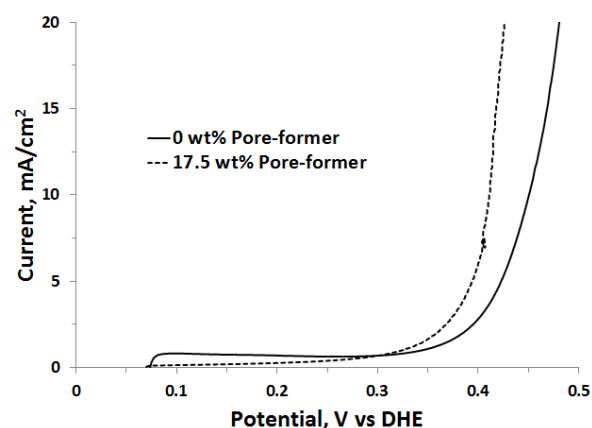


Fig 1. Anodic linear sweep voltammetry (40°C) as a function of porosity with 5M formic acid (2.5 ml min^{-1}) at 10 mV sec^{-1} . [Redraw from Ref [3] Fig 4]

The key directions within this investigation are to probe the impact of performance as a function of more active catalyst that promote the direct formic acid electro-oxidation reaction pathway and to reduce the size domains of the pore-formers from the micron-size to the nano-size. This is being done systematically using a suite of analytic tools, such as electrochemical impedance spectroscopy and nano-CT, to assess mass transport, proton conduction with the catalyst layer, charge transfer resistance of the reaction, and porosity.

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