Improved Anode for a Direct Methanol Fuel Cell

Electrical resistance is decreased and utilization of catalyst is increased.

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A modified chemical composition has been devised to improve the performance of the anode of a direct methanol fuel cell. The main feature of the modified composition is the incorporation of hydrous ruthenium oxide into the anode structure. This modification can reduce the internal electrical resistance of the cell and increase the degree of utilization of the anode catalyst. As a result, a higher anode current density can be sustained with a smaller amount of anode catalyst. These improvements can translate into a smaller fuel-cell system and higher efficiency of conversion.

Some background information is helpful for understanding the benefit afforded by the addition of hydrous ruthenium oxide. The anode of a direct methanol fuel cell sustains the electro-oxidation of methanol to carbon dioxide in the reaction \( 	ext{CH}_3	ext{OH} + 	ext{H}_2	ext{O} \rightarrow 	ext{CO}_2 + 6	ext{H}^+ + 6e^- \). An electrocatalyst is needed to enable this reaction to occur. The catalyst that offers the highest activity is an alloy of approximately equal numbers of atoms of the noble metals platinum and ruthenium. The anode is made of a composite material that includes high-surface-area Pt/Ru alloy particles and a proton-conducting ionomeric material. This composite is usually deposited onto a polymer-electrolyte membrane and onto an anode gas-diffusion/current-collector sheet that is subsequently bonded to the proton-conducting membrane by hot pressed.

Heretofore, the areal density of noble-metal catalyst typically needed for high performance has been about 8 mg/cm\(^2\). However, not all of the catalyst has been utilized in the catalyzed electro-oxidation reaction. Increasing the degree of utilization of the catalyst would make it possible to improve the performance of the cell for a given catalyst loading and/or reduce the catalyst loading (thereby reducing the cost of the cell).

The use of carbon and possibly other electronic conductors in the catalyst layer has been proposed for increasing the utilization of the catalyst by increasing electrical connectivity between catalyst particles. However, the relatively low density of carbon results in thick catalyst layers that impede the mass transport of methanol to the catalytic sites. Also, the electrical conductivity of carbon is less than 1/300th of typical metals. Furthermore, the polymer-electrolyte membrane material is acidic and most metals are not chemically stable in contact with it. Finally, a material that conducts electrons (but not protons) does not contribute to the needed transport of protons produced in the electro-oxidation reaction.

Hence, what is needed is an additive that is stable in contact with the polymer-electrolyte membrane and that conducts both electrons and protons. Hydrous
ruthenium oxide has these properties. Its density is comparable to that of the platinum-ruthenium catalyst.

A membrane/electrode assembly that had an electrode area of 25 cm² and that included hydrous ruthenium oxide as an anode additive was fabricated to test this concept. An ink having a consistency suitable for painting was prepared by sonicating a mixture of 0.14 g of ruthenium oxide, 0.72 g of Nafion® ionomer solution, and 0.40 g of water. A layer of the ink was applied to a polymer-electrolyte membrane. A layer containing the Pt/Ru catalyst at a density of 4 mg/cm² was applied to the gas-diffusion/current-collector sheet. The membrane and the sheet were bonded in a hot press.

A fuel cell containing this membrane/electrode assembly containing the hydrous ruthenium oxide additive was fabricated and tested. Also fabricated and tested were two fuel cells not containing the additive — one having a catalyst loading of 4 mg/cm², the other having a catalyst loading of 8 mg/cm². Some results of the tests are plotted in the figure. These results show that at current densities up to a few hundred mA/cm², the polarization of the anode containing the additive was low — comparable to that of the anode that contained twice as much catalyst without the additive. In effect, these results can be interpreted as signifying that the degree of utilization of the anode catalyst was approximately doubled. The overall internal resistance of the cell containing the additive was 4.6 mW, which is among the lowest values yet observed for cells of the same size; this attests to the high protonic and electronic conductivity of hydrous ruthenium oxide.

This work was done by Thomas Valdez and Sekharipuram Narayanan of Caltech for NASA’s Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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