ELECTROCHEMISTRY OF HYDROGEN AND METHANOL OXIDATION AT CARBIDE ELECTRODES

G T Burstein, D R McIntyre and A Vossen

Department of Materials Science and Metallurgy
University of Cambridge
Pembroke Street
Cambridge CB2 3QZ
United Kingdom

One of the large costs of materials in low temperature fuel cells is the cost of the noble metal catalysts which are used as anode and cathode. Despite the large volume of work that has been expended in optimizing these electrocatalysts, the amount of platinum-based metal which is required for high-power fuel cells remains large. Such high-power fuel cell systems would be necessary for vehicle power were such vehicles to be driven by electric motors alone. Two main sources of fuel for this exist. Hydrogen is the fuel of choice since its anodic oxidation is easy and well characterized. The alternative to this gaseous system is the direct methanol fuel cell, in which the fuel can in principle be carried as a liquid. Methanol has the big advantage over hydrogen by being liquid, since its energy density is very much larger than that of hydrogen, even when the gas is at high pressure. Methanol has the disadvantage however, of being a relatively poor electrochemical fuel. Methanol requires a large overpotential to drive its anodic oxidation at a significant rate. A high overpotential for oxidation reduces the voltage, and therefore also the power, of a fuel cell powered in this way. Several reasons for this sluggish reaction have been proposed. The best electrocatalyst for methanol oxidation so far used is a platinum-ruthenium alloy. Although the optimum ratio of these elements is under some dispute, the dominant element is platinum, and these catalysts are expensive. For hydrogen oxidation, the anodic process is very much easier, but platinum catalysts are very susceptible to poisoning by carbon oxides, particularly carbon monoxide. To operate successfully, the hydrogen needs to be free of carbon oxides, posing a restraint on hydrogen generated from reforming reactions of hydrocarbons.

One potential approach to these matters is to attempt to develop electrocatalysts which are not base on the platinum group metals. Electrocatalysts synthesized from base components require properties additional properties. Whereas platinum is sufficiently noble that its corrosion in the normally acidic electrolytes is not normally possible, electrocatalysts synthesized from base components requires a state of passivity towards corrosion. It is the passive surface that must provide the electrocatalytic characteristics for the fuel oxidation reaction.

This paper presents results of research into synthesis and analysis of metal carbides as potential sources for electrocatalytic materials. There is some previous work which has been carried out using carbides (eg. refs 1,2). Several carbides have been synthesized and examined. Experiments consist of fabricating electrodes from these which were tested for passivity towards corrosion in sulfuric acid at 70˚C. Many of these materials passivate readily, but some require passage of considerable charge. This charge can represent growth of an oxide film, or it can represent dissolution of the metal component of the carbide accompanied by surface enrichment with carbon. Following the tests for passivity, the electrodes were tested for activity towards the methanol and/or hydrogen, also at 70˚C in sulfuric acid. Some physical characteristics of these materials are presented. These include analysis of particle size, surface area determination through BET adsorption isotherms, structure determined by x-ray diffraction, and energy dispersion x-ray analysis to determined the overall compositions. Although they can be made quite passive towards corrosion, these materials are not powerful electrocatalysts. However, the observations presented are quite unique, and are worth consideration mechanistically.

We show in this paper that it is possible to develop electrocatalysts which are relatively immune to poisoning by carbon monoxide when the anode is fed with appropriately contaminated hydrogen. This is to our knowledge a new observation, and shows that the mechanism of action of these complex electrocatalysts is different from that of platinum based electrocatalysts. We also show that electrocatalysts can be made in this fashion which are more anodically reactive towards methanol than towards hydrogen under otherwise identical experimental conditions. This observation is unusual since the methanol oxidation is inherently more difficult, requiring a six electron transfer, and also necessitating more than one reaction product. A mechanism for this process is proposed, involving activated surface carbon atoms. It is proposed that these surface carbon atoms, activated by the underlying metal, act as adsorption sites for the methanol which the undergoes progressive oxidation through a surface cyclization and ring-opening sequence. We show some changes that occur in the electrochemistry when the surface has been treated so as to enrich it with one component of the carbide. This has been done to enrich with the metal component by selective carbon removal, or alternatively, by enrichment in the carbon component by selective removal of the metal component. Discussion of the results is presented.

References:

1. L. Baudendistel, L.H. Bohm, J. Heffler, G. Louis and F.A. Pohl, *Proc. 7th Internat. Energy Conversion Conf.*, paper 729004, ACS, Washington DC (1972).

2. G. Bronoel, S. Besse and N. Tassin, *Electrochim. Acta*, **37**, 1351 (1992).