

Platinum Electrocatalysts for Phosphoric Acid Fuel Cells

At the Spring Meeting of the Electrochemical Society, held in Montreal, Canada during May, twenty-three papers were presented on a variety of topics concerned with fuel cell development. The trend in electrocatalysts for this application is clearly towards platinum alloys rather than to alternative metals.

Most of the emphasis at this symposium was on the more efficient use of platinum electrocatalysts particularly when used in oxygen electrodes for aqueous electrolyte fuel cells either of the acid or alkaline type. The alternative catalyst systems discussed were either considerably inferior in performance to those based on platinum or at a very early stage of development.

P. N. Ross Jr. of the Lawrence Berkeley Laboratory, University of California summarised the improvements made in platinum catalysed fuel cell electrodes over the last fifteen years. Most notable of these were: [i] A 40-fold reduction in the overall platinum loading in a phosphoric acid fuel cell had been achieved initially by moving from platinum black to catalysts dispersed on conductive carbon supports, and subsequently by improving the supported catalyst technology. [ii] An extension of electrode and consequently cell stack life by more than an order of magnitude. [iii] A four-fold reduction in voltage losses due to cell resistance and diffusion polarisation.

Typical platinum loadings for electrodes based on platinum on carbon black type supports are now $0.25\text{mg}/\text{cm}^2$ on the anode and $0.5\text{mg}/\text{cm}^2$ on the cathode. Cell performance with these electrodes at 177°C is about 0.65V at $220\text{mA}/\text{cm}^2$ at 80 per cent hydrogen utilisation and 2.5 times stoichiometric air at the beginning of life. Decay rates are typically 10mV per 10^3 hours under constant load. Studies indicate that voltage losses in the air cathode are due to gas phase and ionic diffusion and not the liquid phase diffusion of dissolved oxygen. There is a negative platinum crystallite size effect for

oxygen reduction with carbon supported platinum in phosphoric acid at elevated temperatures indicating that there is little benefit to dispersion of platinum below about 20\AA crystallites. The degree of wetting of the catalyst in electrodes which have small liquid diffusion losses is typically around 80 per cent.

Platinum Alloy Catalysts

Ross concluded that there was at most 20 to 30mV to be gained by refinement in air electrode structures using the platinum supported catalyst. However alloy supported catalysts, particularly platinum-vanadium and platinum-tantalum are more active by a factor of four to five than those with platinum alone. Initial results show a 20 to 30mV improvement in air cathode potential at $200\text{mA}/\text{cm}^2$. The gain in catalytic activity may eventually lead to a factor of two reduction in catalyst loading at the cathode.

Further information on these new platinum alloy catalysts, which seem likely to form the next generation of fuel cell electrocatalysts, was provided by V. Jalan (Giner, Inc.) although only in abstract form as the paper was not presented. These alloy systems are prepared by soaking a carbon supported platinum catalyst in either a colloidal dispersion of the base metal oxide or in a base metal salt solution, which subsequently reacts to deposit highly dispersed metal oxide/hydroxide onto the support. In either case the mixture of supported platinum and metal oxide is heated to about 900°C in an inert atmosphere.

Alloy catalysts comprising platinum with each of aluminium, cerium, silicon, strontium, titanium, tungsten and vanadium were reported.

All have greater activity for oxygen reduction in phosphoric acid than the platinum only system, with platinum-vanadium being the most active. Furthermore this superior activity was maintained over 10,000 hours testing. This improved stability appears to be related to a lower rate of loss of metal area for platinum alloy catalysts.

A subsequent paper by P. J. Hyde, C. J. Maggiore and S. Srinivasan at the Los Alamos National Laboratory, however, described the use of Ion Beam Analysis to study both new and aged electrode systems, and showed that the vast majority of the vanadium migrated from the cathode to the anode over 3000 hours. Thus platinum-vanadium is unlikely to be the optimum alloy system.

Another unrepresented paper by V. Jalan discussed the deposition of a thin carbon layer on and around carbon supported platinum particles which is achieved by heating a platinum on carbon catalyst at 360°C under a carbon monoxide atmosphere. This inhibits migration of platinum particles and improves electrode stability. It should be noted that all of Jalan's work quoted for the symposium is the subject of patents held by United Technologies Corporation. M. F. Weber, M. J. Dignam and R. D. Venter, of the University of Toronto, presented a paper on preliminary work aimed at catalyst preparation using sputtering techniques. Much development would be required to turn this into a practical production method.

Fuel Cell Electrolytes

A number of papers dealt with the interaction of oxygen with platinum at the cathode and the mechanisms involved for both acid and alkaline electrolytes. Despite some good physical and chemical properties, concentrated phosphoric acid is an indifferent fuel cell electrolyte due to the marked irreversibility of the dioxygen reduction reaction in this medium even at 200°C. E. Yeager, J. C. Huang and S. J. Clouser of the Case Western Reserve University examined the dioxygen reduction mechanism in purified phosphoric acid at various temperatures from 25 to 250°C. Direct reduc-

tion to water is the predominant path with only 5 per cent proceeding via hydrogen peroxide production at room temperature with virtually no peroxide detected at the high temperatures. Absorbed impurities tend to increase the hydrogen peroxide yield while slowing down the overall reduction. Studies at high polarisation suggest that a first electron transfer step is rate controlling.

Yeager and E. J. M. O'Sullivan (Case Western Reserve University) reported results of preliminary studies on alternative electrolytes, namely fluorinated acids. Most of the results reported were for monofluorophosphoric acid which is the most stable of the fluorophosphoric acids, although not sufficiently stable to hydrolysis for high temperature application. It is a stronger acid than phosphoric acid and less likely to be strongly adsorbed. The fluoro system gave high dioxygen diffusion limiting currents, more than an order of magnitude greater than for phosphoric acid. The authors concluded that the apparently high overall catalytic activity in monofluorophosphoric acid was caused by a higher dioxygen solubility. These results give impetus to the search for a stable pure fluoro acid electrolyte.

Papers by S. Sarangapani and L. G. Edwards of the Union Carbide Corporation and J. Molla and E. Yeager (Case Western Reserve University) considered the reduction of dioxygen on various carbon surfaces in alkaline electrolytes. In the absence of a catalytic metal the reaction proceeds largely through a peroxide intermediate. The first mentioned authors described a model for estimating the surface concentration of peroxides when using different carbons at the cathode. The second paper compared results for a carbon (Kettenblack) with and without platinum, and showed that the platinum was catalysing the direct reduction to water as well as catalysing the reduction and decomposition of peroxide. The nature of the carbon affected the ability of peroxide to escape from the pore structure prior to electrochemical or heterogeneous catalytic decomposition.

Relatively few alternatives to platinum

electrocatalysis were discussed. R. R. Durand Jr. and F. C. Anson of the California Institute of Technology, Pasadena, presented studies on co-facial dimeric cobalt porphyrins. These have the advantage of catalysing the four-electron reduction of dioxygen to water without peroxide formation while the reaction proceeds at unusually positive potentials in acidic electrolytes. However, dimers in the correct orientation are difficult to make and the chemical stability needs to be greatly improved before use at 180°C could be contemplated.

In situ Mössbauer spectroscopy studies of iron phthalocyanine (FePc) adsorbed on high surface area carbon electrodes were presented by D. A. Scherson, S. B. Yao, E. Yeager, J. Eldridge, M. E. Kordesch and R. W. Hoffman (Case Western Reserve University). The aim of the work was to gain insight into the stability problems of metal macrocyclics. The preliminary conclusion is that electrodes with polycrystalline FePc show superior activity to adsorbed species in monolayer form.

B. C. H. Steele, W. J. Albery and E. J. Calvo of the Imperial College of Science and Technology, London presented studies on lanthanum-nickel perovskites as potential oxygen electrocatalysts. Steady state oxygen reduction curves for LaNiO_3 , La_2NiO_4 and La_3NiO_7 enriched phases show comparable activity to platinum but with low limiting currents. Rotating ring disc electrode studies confirm that this is due to the oxygen adsorption step being rate limiting. This appears to be a general feature for perovskite oxides which are therefore unlikely to be viable alternatives to platinum for this application.

Novel Solar and Fuel Cell System

A different application area for fuel cells and platinum catalysts was described in a paper by G. G. Barna, S. N. Frank and T. H. Teherani of Texas Instruments Inc. This involves domestic heat and power generation using a novel solar pulsar system. Generator panels comprise silica semiconductor spheres which electrolyse HBr using solar energy to produce hydrogen and bromine which are stored and fed to a H_2/Br_2

fuel cell when electricity is required. The oxidation of hydrogen on platinum, in 48 per cent HBr is kinetically controlled and carbon supported platinum catalysts are required for optimum platinum usage. Optimisation of the fabrication process has led to small scale platinum/carbon anodes with limiting currents approaching the calculated kinetic limits. However a major problem is the lack of scaling of these limiting currents as the hydrogen partial pressure is increased to 100 per cent. Current studies are aimed at altering the nature of agglomerated catalyst by varying the colloid chemistry of the catalyst suspension and the type of carbon support. The development of this novel combination of solar energy and fuel cells will be followed with great interest.

Platinum Availability

M. J. Cleare of Johnson Matthey reassured the meeting as to the availability of platinum for use in electrocatalytic systems in general and fuel cells in particular. Reserves in active mines comprise 13,000 tonnes while a further 20 to 30,000 tonnes are estimated to be in presently unexplored deposits. The installation of 30,000 MW of phosphoric acid fuel cell capacity in the U.S.A. during the decade 1990 to 2000 would represent a requirement of around 15 tonnes of platinum per annum. This represents 15 per cent of world production and 28 per cent of predicted U.S. platinum usage in 1988. This should be compared with current platinum usage in automobile catalysts which is in excess of 50 per cent of U.S. consumption. Lead times of 18 to 24 months are required to establish new supply capacity and should present no problems in fulfilling requirements in advanced technology areas, which can be monitored during the many years they take to develop.

The symposium was well attended considering it was one of fifteen symposia taking place in parallel. There continues to be great interest in the theory and practice of phosphoric acid fuel cells. The trend in electrocatalysts for these is undoubtedly towards platinum alloys rather than alternative metals.

M.J.C.