

World Hydrogen Energy Conference

PLATINUM METALS IN DEVELOPING HYDROGEN TECHNOLOGIES

More than eight hundred participants attended the 11th World Hydrogen Energy Conference held in Stuttgart, Germany, from the 23rd to 28th June 1996, making it the largest in a series stretching back more than twenty years. From over 300 papers, some 40 to 50 involved various aspects of the platinum group metals, a selection of which are reported here.

Hydrogen Production

Water Electrolysis for Hydrogen Production

The efficient electrolysis of water is a key element in any future widespread use of hydrogen as a fuel, particularly if a proportion of the hydrogen is to be produced using renewable energy sources. However, hydrogen produced by water electrolysis is still very expensive compared with hydrogen produced from hydrocarbon feedstocks, such as natural gas.

Materials for alkaline and acidic water electrolysis were reviewed by O. Savadogo of the Ecole Polytechnique de Montreal, Canada, who reported on the properties of the platinum metals in a variety of electrolyser designs. Platinum and palladium are very effective cathode catalysts, while iridium, ruthenium, IrO₂ and RuO₂, with a combination of catalytic properties and high stability are excellent anode materials. In order to produce hydrogen at a cost competitive with coal gasification and gas reforming, the primary requirement is for the development of new, more economical materials. Lower loading platinum cathode materials and low cost corrosion-stable anodes are required.

The theme of materials development and the importance of ensuring the cost effective use of expensive metals was further developed in a paper by H. Mori, C. Inazumi, M. Kato and S. Maezawa of the Research Institute of Innovative Technology for the Earth, Osaka, K. Oguro and H. Takenaka of the Osaka National Research Institute and E. Torikai from Torikai Technical Engineering, Osaka, Japan. This group reported the development of membrane electrode

composites for solid polymer electrolyte (SPE) water electrolysis. A novel chemical plating technique was described for the deposition of iridium-platinum as the anode catalyst material. This technique was said to be advantageous in both controlling the iridium loading and minimising iridium losses. The complete system, consisting of a composite of platinum-iridium catalysed anode (iridium loading 0.5–2 mg/cm²), Nafion membrane and platinum catalysed cathode, operates at a lower cell voltage than a composite manufactured by a conventional method. Hydrogen was produced, containing 100–1000 ppm oxygen at a current efficiency of 97 per cent.

The same group, but also including N. Sawai of the Osaka National Research Institute, reported on the long term stability of a SPE electrolyser comprising platinum-iridium/membrane/platinum structures. As in the previous paper, the iridium or IrO₂ present on the anode was effective in lowering the cell overpotential. In addition, no iridium dissolution was observed during a 200 day test. Hydrogen gas purity from the electrolyser was seen to be constant; however the oxygen gas quality did change during the test with impurity levels increasing from 100 to 600 ppm. An accumulation of chromium, iron and nickel impurities was found in the electrolyte composite after test. These impurities, presumably from cell components, were thought to be responsible for the observed degradation.

As part of the giant Japanese We-Net project, M. Yamaguchi, K. Yagiuchi and K. Okisawa of Fuji Electric, Japan, presented work on high performance, SPE water electrolysers. They studied the effects of the preparation method of IrO₂ anode catalysts on cell performance, and determined a relationship between the pyrolysis temperature used for the IrO₂ production and the cell voltage of the resulting electrode assemblies. A pyrolysis temperature of 200°C gave the lowest cell voltage; higher pyrolysing

temperatures increased the voltage of the cell.

Another paper on SPE water electrolysis technology, also part of the We-Net project, was presented by M. Nagai, H. Tazima and A. Sakanishi of Mitsubishi Heavy Industries, Nagasaki; N. Histatome of the Nagasaki Shipyard and Engineering Works, and S. Ohkura of Power Systems, Yokohama, Japan. Tests were performed with iridium as the anode catalyst and platinum as the cathode catalyst. The anode support material was titanium in the form of expanded titanium mesh, sintered titanium fibre or titanium fibre, the latter being flame sprayed with titanium powder. The cells using platinum plated, flame sprayed titanium provided the best performance.

Chemical Production of Hydrogen

An overview of recently developed processes for hydrogen production based on catalytic pyrolysis of hydrocarbon feedstocks and partial oxidation of natural gas into syngas, was presented by V. N. Parmon, G. G. Kuvshinov and V. A. Sobyenin of the Federal Research Centre of the Russian Federation, Novosibirsk. The latter technique was demonstrated by the electrochemical oxidation of methane into hydrogen and carbon monoxide over a platinum electrode catalyst using an yttria stabilised zirconia, oxygen-conducting electrolyte. The electrochemical oxidation of methane to syngas avoids the costly air separation step, which is necessary for most oxidative conversions of methane.

An investigation into the possible use of the steam-iron process as a method of generating hydrogen was reported by V. Plzak, M. Weinberger, A. Eilers and J. Garche from the Center for Solar Energy and Hydrogen Research, Ulm, Germany. The process has the attraction of being 'carbon free' but the relatively high temperatures traditionally required for hydrogen production and the associated problems of low cycle stability are a disadvantage. Different iron sponges were treated with a range of metal (including platinum, palladium and ruthenium) and metal oxide dopants in order to investigate any possible catalytic and/or

sinter inhibiting effects. Redox cycling of the sponges showed that all metals less noble than iron had beneficial effects, reducing sintering and retaining activation. In particular, metals such as aluminium, which produce non-reducible oxides, appeared to have a particularly strong effect. None of the dopants had any beneficial catalytic effect in the oxidation side of the cycle, however, all the precious metals successfully catalysed the reduction step. The group concluded that the iron-steam process was feasible at temperatures around 300°C.

Photoproduction of Hydrogen

Work to develop a dual bed photocatalytic system for the solar driven splitting of water into hydrogen and oxygen was described by C. A. Linkous, D. K. Slattery, A. J. Ouellette, G. T. McKaige and B. C. Austin from the Florida Solar Energy Centre, Cocoa, U.S.A. The photocatalyst in the reductive water splitting bed was InP promoted with platinum, while the oxidative catalyst was TiO₂.

In a second paper D. K. Slattery and C. A. Linkous described an extension of the principle of combining a catalyst and semiconductor to utilise solar energy to split molecules other than water. A platinum catalysed CdS dispersion was shown to be effective in producing hydrogen from an alkaline H₂S solution at rates averaging 20 ml/hour when using a 1kW Xe lamp as an energy source.

Photoelectrochemical hydrogen production was also reported by C. U. Maier and M. Vetter of the University of Stuttgart, Germany. Investigations into platinum coated *p*-Si photocathodes showed that both the hydrogen evolution efficiency and the long term stability were strongly influenced by the surface morphology of the catalytic platinum layer. Platinum sub-monolayers between 0.1 and 0.2 nm thick were effective, but deposits of below 0.1 nm thick produced only a very weak catalytic effect and hence very low hydrogen evolution rates.

Joint work between N. Muradov and A. T. Raissi of the Florida Solar Energy Centre, Cocoa, U.S.A. and T. Doi of the Electrochemical Laboratory of Ibaraki, Japan, examined the

dehydrogenation of 2-propanol in a solar driven chemical heat pump application. A hydrogen production rate of 15 ml/hour was obtained from isopropyl alcohol-water solutions catalysed by a tungsten polyoxometallate photocatalyst promoted by colloidal platinum.

Hydrogen Processing and Storage Palladium-Based Diffusion Membranes

The successful development of a reconfigured palladium-silver hydrogen separator was reported by J. C. S. Booth, M. L. Doyle, S. M. Gee, J. Miller, L.-A. Scholtz and P. A. Walker of the Johnson Matthey Technology Centre. Ultrathin palladium-silver layers (7 μm thick) deposited onto a porous ceramic tubular support allow the production of substantially pure hydrogen while significantly minimising the amount of palladium required.

A paper reporting thin composite palladium membranes was given by G. Fu, X. Hong, D. Wu and O. Yuan of the Dalian Institute of Chemical Physics, China. This group described a membrane capable of producing 10 m^3/h hydrogen at a purity of 99.9995 per cent from a feedstream purity of 99.2 per cent. Hydrogen of purity 99.8 per cent was produced from a 70 per cent hydrogen-containing feedstream at a recovery rate of 72 per cent.

Palladium-based membranes for hydrogen separation and purification installations with capacities ranging from 500 to 2000 m^3/hour were described by V. M. Makarov, I. N. Veselov and I. N. Vandshev of the Russian Academy of Science, Ekaterinburg and N. I. Timofeev of the Ekaterinburg Non-ferrous Metals Processing Plant, Russia. They reported a palladium-based membrane capable of operation at temperatures exceeding 650°C, offering a useful increase in hydrogen productivity. Further work is being directed at developing alloys capable of operation at lower temperatures, in response to an increasing need by the semiconductor manufacturing industry for ultra pure hydrogen (99.999999 per cent).

The effect of hydrogen content, surface activation, strain gradients and phase transformations on the diffusion coefficient of hydrogen in

palladium and its alloys was discussed by F. A. Lewis, Queen's University, Belfast, Northern Ireland, R. V. Bucur of the University of Uppsala, Sweden, Y. Sakamoto of Nagasaki University, Japan, X. Q. Tong of the University of Southampton, England and K. Kandasamy of the University of Jaffna, Sri Lanka.

A 5 μm thick palladium membrane was investigated as an anode in a hydrogen/air fuel cell, suitable for operation in contaminated feed gas, by T. F. Otero and M. T. Bireben of the Universidad del Pais Vasco, San Sebastian, and J. Casado of the Carburos Metalicos, Barcelona, Spain. Experimental current densities were very low ($< 5 \text{ mA}/\text{cm}^2$) but the recognition of the central role of palladium oxides in promoting some of the slow processes of proton desorption indicate that higher current densities (target 150 mA/cm^2) may be possible in future.

Hydrogen Storage

Seasonal storage of hydrogen, using liquid organic hydrides, was reported by E. Newson, Th. Haueter, P. Hottinger, F. von Roth, G. W. Scherer and H. Th. Schucan of the Paul Scherrer Institute, Villigen, Switzerland. Hydrogen produced by water electrolysis was stored as methylcyclohexane which was then subsequently dehydrogenated to toluene to release the useful gas. Much of the work was directed towards improving the efficiency of the dehydrogenation reaction. Progress made between 1986 and 1994 increased toluene yields from 70 per cent to 99 per cent and reduced by-products from 15 to 0.5 per cent. Reaction engineering methods, including the use of hydrogen permeable palladium-silver membranes, have been applied in situ and outside the reaction chamber and this has allowed equilibrium conversions to be exceeded.

Hydrogen Utilisation in Fuel Cells

An analysis of energy consumption and emissions of proton exchange membrane fuel cell (PEMFC) and internal combustion engine (ICE) vehicles utilising different primary fuels was presented by P. Ekdunge and M. Raberg of Volvo, Gothenburg, Sweden. The analysis took

a global perspective encompassing the 'cradle to grave' total life cycle of the product and energy carrier. Thus, although a fuel cell vehicle running on hydrogen does not produce emissions, using this perspective, emissions are attributed to the fuel cell vehicle depending on how the hydrogen was produced. So, while the fuel consumption of the fuel cell vehicle is lower than the ICE vehicle, in a global perspective the ICE vehicle still shows a lower overall energy consumption. Advances in fuel cell technology may change this situation. Furthermore, the fuel cell vehicle does have a definite advantage over the ICE vehicle in terms of emissions from both a local and a global outlook.

A presentation focusing on recent developments in fuel cell technology for transport applications was given by W. Donitz of Daimler Benz, Friedrichshafen, Germany. The reduction of platinum loading of electrodes between 1990 and 1996 was presented as a demonstration of the promising trend in reducing system costs. The presentation was illustrated by reference to the Daimler Benz NE Car, a vehicle using a fuel cell power system with compressed hydrogen fuel. Donitz stated that current PEMFC technology is capable of meeting the demanding requirements expected with respect to functionality and compactness in a modern motor vehicle.

An overview of PEMFC development and of the external forces driving hydrogen into vehicular fuels was provided by G. E. Ballard of Ballard Power Systems, Vancouver, Canada. The critical nature of the Membrane Electrode Assembly (MEA) as the heart of the fuel cell – 'the MEA is the actual fuel cell' – was described. Current Ballard stacks are capable of 1000 watts per litre, making the PEMFC worthy of serious consideration for automotive propulsion.

MEA Materials and Preparation

The central importance of the MEA was demonstrated by a number of papers focusing on the preparation and optimisation of gas diffusion electrode structures. In particular, a number of workers discussed new methods of preparation and routes suitable for mass production.

PEMFC production methods were reported by A. Fischer, Z. Veziridis and H. Wendt of the Institut für Chemische Technologie, Darmstadt, Germany. Electrodes with a platinum loading of 0.2 mg/cm^2 were prepared by a variety of methods, including hot pressing and hot spraying of the electrocatalyst slurry. They concluded that even for very thin electrodes coarse porosity is required for optimum performance. Electrodes prepared by hot spraying showed a higher overall porosity and therefore exhibit better electrochemical performance.

The preparation of gas diffusion electrodes for PEMFCs using ion exchange and impregnation methods of dispersing the platinum catalyst were described by K. Yasuda, K. Amine, M. Mizuhata, K. Oguro and H. Takenada of the Osaka National Research Institute. Catalyst dispersions comprising 2 nm platinum particles were produced and subsequently used on electrodes capable of giving 6.7 W/mg platinum at 5.8 atm and 100°C.

The development of a process for the production of MEAs by a rolling process based on battery production techniques was described by D. Bevers, N. Wagner and M. von Bradke of the German Aerospace Research Establishment, Stuttgart. The work demonstrated the reactive mixing of the various components of the electrode (platinum catalyst, carbon) and continuous application onto an endless electrode belt. The rolled MEAs were tested alongside commercially available E-TeK electrodes (0.4 mg Pt/cm^2 , 20 per cent Pt/C) and were seen to perform at a level equal to or slightly better than the commercial material.

Another paper on the preparation and characterisation of PEM gas diffusion electrodes was presented by M. Vetter and H. D. Sommer of Stuttgart University. In this case the platinum was applied by DC sputtering rather than by a chemical route. The temperature of hot pressing was found to be crucial in determining the efficiency of the resulting electrode structures.

A paper from C. Mantegazza and A. Maggiore describing the De Nora S.p.A. fuel cell effort centred on the development of a mass producible fuel cell design capable of an average power

density of 0.1 kW/kg. The work concentrated on improving stack reliability and lowering manufacturing costs by dispensing with costly machined graphite parts. A power density target of 0.25 kW/kg by 1999 has been set.

A wide ranging paper by S. Cleghorn, X. Ren, T. Springer, M. Wilson, C. Zawodzinski, T. Zawodzinski and S. Gottesfeld of the Los Alamos National Laboratory, U.S.A., described work on PEMFC systems, focusing particularly on the automated fabrication of low loading platinum catalysed membranes (down to 0.14 mg/cm²) and low cost non-machined flow field and bipolar plates. In one promising configuration traditional complex machined flow plates were replaced with woven stainless steel screens. The performance of the unusual PEM fuel cells was said to be equal to or better than PEMs with machined metal flow fields.

Fuel Cell Fuelling Issues

The ongoing difficulty of the PEMFC's sensitivity to CO in the hydrogen feedstream was considered by a number of researchers including the Los Alamos group who discussed tackling the CO problem by using platinum-ruthenium electrode catalysts which are more CO tolerant than pure platinum. Another approach pursued by Los Alamos involved circumventing the CO problem by using a palladium-coated tantalum hydrogen diffusion membrane, which is completely selective for hydrogen and allows the hydrogen feed to the fuel cell to be 'dead ended'. This approach significantly simplifies the design and control of the complete system and adds only 1 mg of palladium per cm² of fuel cell membrane area. The experimental separator operated successfully in a simulated reformate (containing 74 per cent H₂, 24 per cent CO₂, 1 per cent CO) at 315°C and supplied a single cell PEMFC without any reduction in performance. A similar cell running without the separator in 100 ppm of CO suppressed the electrode output to one tenth of its pure hydrogen performance.

Los Alamos personnel also presented limited data on direct methanol fuel cells (DMFC) where the hydrogen clean up problem does not

exist. They claimed that recent advances in DMFC technology has brought their performance close to that of hydrogen-fuelled PEMFCs (DMFC power densities are only 2 to 3 times lower than a hydrogen-fuelled equivalent). In order to achieve this performance DMFC catalyst (Pt-Ru alloy) loadings are rather high and problems of durability remain.

The use of PEM fuel cells operating in gas containing CO was discussed by J. Garche, L. Jorissen and B. Rohland of the Centre for Solar Energy and Hydrogen Research, Baden-Wuttemberg, Germany. They proposed that the problem of CO deactivation of fuel cell electrodes could be resolved using a double layer electrode structure. In the first layer, chemical oxidation of the CO is catalysed while in the second layer an electrochemical catalyst (Pt-Ru or Pt-WO₃) which can tolerate 100 ppm of CO catalyses hydrogen oxidation.

Theoretical and practical aspects of coupling a 7.5 kW SPFC with a natural gas processor were described by K. Ladjeff-Hey, J. Gieshoff and B. Vogel of the Fraunhofer Institute for Solar Energy Systems, Freiburg, and V. Formanski of the Gerhard-Mercator University, Duisburg, Germany. The work focused on the selection of the most suitable gas clean-up system. Selective oxidation proved unsatisfactory due to a higher than acceptable hydrogen loss, and therefore a carbon dioxide scrubbing/methanation approach capable of reducing the CO content of the PEM anode gas to below 5 ppm was chosen. Further work incorporating a thin palladium-based membrane is in progress.

Summary

The 11th World Hydrogen Energy Conference highlighted progress in a range of technologies crucial to the introduction of a hydrogen based energy system. Platinum group metals appeared in a diverse range of applications reflecting the unique and desirable properties of this small family of materials in various hydrogen related technologies.

The fuel cell sessions were expanded compared to previous years and dominated by PEMFC contributions. Within this area the

emphasis appears to have moved from issues of stack technology to issues of cost and the development of processes that are suitable for mass production.

The full proceedings of this Conference, published by the International Hydrogen Energy Association, are currently available in three volumes. M.L.D.

Problems of the Palladium-Hydrogen System

An initiative by J. S. Cantrell and D. S. Sullinger produced a successful symposium on Metal-Hydrogen Systems as part of the American Chemical Society Central Section Meeting, held in Dayton, Ohio, from 10th to 11th June 1996. In a sub-section of the programme, of 26 presentations, particular focus was on recent progress in hydride battery developments, and over one-third of the contributions involved hydrogen systems of palladium and palladium alloys.

Three contributions from D. K. Ross and colleagues of the University of Salford, U.K., dealt with theoretical assessments of neutron scattering measurements for palladium and its alloys, and involved discussions of trapping processes of both protium and deuterium at dislocations, and of behavioural effects of positive muons. The effects of structural defects, due to hydride phase formations and decompositions, on the tensile properties of palladium-manganese alloys were considered in a poster by A. P. Croft, Lafayette College, Easton, U.S.A.

Solutions to detailed problems involved in the desorptive removal of various impurities from palladium powders were reported by G. L.

Powell, Lockheed-Martin Energy System, Oak Ridge, Tennessee and B. E. Mills, Sandia Laboratories, Livermore, California, while the involvement of thin films of palladium and palladium alloys in hydride battery developments was discussed by Y.-T. Cheng and Y. Li, General Motors Research Center, Warren, Michigan.

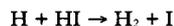
Various crystallographic problems associated with structural disorders produced on introducing high levels of protium, deuterium and tritium into palladium, were reported by J. S. Cantrell and T. A. Breiter of Miami University, Oxford, Ohio. Two contributions from F. A. Lewis, Queen's University, Belfast, in collaboration with R. V. Bucur, University of Uppsala, Sweden, K. Kandasamy, University of Jaffna, Sri Lanka, X. Q. Tong, Southampton University and Y. Sakamoto, University of Nagasaki, Japan, dealt with sequences of structural hydride changes related to pressure-composition-temperature relationships of the Pd-H and Pd-Pt-H systems. An associated review was presented of lattice expansion strain gradients in these systems responsible for Uphill Effects observed in hydrogen diffusion processes. F.A.L.

The 50 K Anomaly of the Palladium-Hydrogen System

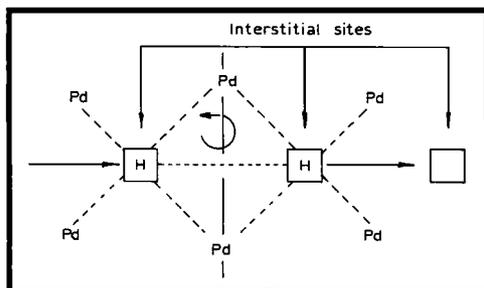
Various explanations have been advanced to identify the origin of the 50 K anomalies of the palladium-hydrogen system, that broadly characterise discontinuous regions near 50 K in plots of the temperature dependence of various experimental parameters, including the original observation of irregularities in specific heat plots (1). There is broad acceptance of proposed correlations between the 50 K anomalies and low temperature phase modifications and associated phase diagram alterations of the

palladium-hydrogen system. However, there have been puzzling absences of accompanying production of dislocation networks.

An earlier qualitative correlation of specific heat changes with ortho/para hydrogen gas interconversion equilibria gained little encouragement from findings of dissociated lattice hydrogen entities located in interstitial sites in the f.c.c. palladium lattice. However, by analogy with interpretations of transient bonding states in the reaction (2):



it is now suggested (1), that diffusing hydrogen atoms may be involved as specific-heat-contributing transient pairs during hydrogen diffusional transfers from occupied to vacant octahedral interstitial sites, as shown in the Scheme.



References

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