

# World Hydrogen Energy Conference

## THE PLATINUM GROUP METALS IN HYDROGEN TECHNOLOGIES

The Tenth World Hydrogen Energy Conference held at Cocoa Beach, Florida, U.S.A. from 20th to 24th June 1994, was the latest in a bi-annual conference series begun in the mid 1970s. This meeting provided an opportunity to bring together a gathering of technical, political, industrial and economic interests with the common goal of promoting hydrogen as a clean, versatile fuel and as an increasingly important chemical commodity. Some 612 participants included energy planners, environmentalists, industrial gas manufacturers, process chemists, chemical engineers, metallurgists and materials scientists presenting papers on topics ranging from hydrogen safety, storage, production and utilisation. Some 40 papers attested to the continued importance of the platinum group and rare earth metals in hydrogen storage, separation, catalytic and fuel cell technologies, and those papers which were related to the use of the platinum group metals are selectively reviewed here.

### Hydrogen Sensors

The safe utilisation of hydrogen requires that proper account be taken of the potential hazards of an odourless, colourless and readily flammable gaseous element. During this conference assessments of some of these safety issues were presented. Clearly the detection and monitoring of hydrogen gas is an essential requirement for its safe handling in chemical, aerospace or other industry. Two papers focused on this need for cost effective and efficient methods of hydrogen detection.

A simple, low cost, hydrogen alarm system incorporating a palladium coated bimetallic coil was described by E. Szonntag, D. Woodbridge and T. Woodbridge of Aqua Magnetics Inc., Tampa, U.S.A. The device consists of two bimetallic temperature sensitive coils, one coated with finely dispersed palladium. With one end of both coils firmly fixed, exposure to hydrogen

produces a rapid rise in temperature as the palladium on the coated coil absorbs the gas. The exothermicity of the reaction is enough to close the gap between the free ends of the bimetallic coils. When suitably configured with an alarm buzzer, battery and arc suppression circuitry the sensor is capable of responding to hydrogen concentrations significantly below the lower flammability limit of hydrogen (LFL 4 per cent). The second bimetallic coil ensures that the device maintains a constant sensitivity to hydrogen regardless of ambient temperature conditions. A solid state electronic design incorporating palladium was also discussed.

A NASA sponsored programme to develop new hydrogen detection systems for use during Space Shuttle ground support operations was described in a paper by R. Barile of I-NET Space Services and D. Bardel of the Florida Institute of Technology. The large quantities of hydrogen fuel required by the shuttle mean that conventional hydrogen detection methods (including 60 platinum wire catalytic combustion sensors located close to fuelling lines and valves in the launch pad) are widely used at the Kennedy Space Centre. However, certain locations and situations in, or near to, the Space Shuttle cause existing systems severe difficulties in terms of repeatability, accuracy, drift, response time, convenience and durability. As part of their studies, the authors examined the factors influencing the response of a group of solid state hydrogen sensors in which a catalytic film, of palladium or a palladium alloy, was employed to absorb hydrogen preferentially from the local gas. The film may be configured as a resistor, capacitor, transistor or thermistor, depending on the type of sensor. The response time of such sensors depends critically on the transfer of hydrogen from the ambient atmosphere to the film and subsequent transfer of hydrogen within the film. Calculations and experimental observations confirmed that the

rate of transfer of hydrogen within the solid phase was extremely fast, and several orders of magnitude more rapid than the gas-solid mass transfer. The relatively slow convective transfer of hydrogen in the boundary layer above the solid surface was the rate determining step for many of this type of sensor. Response times can thus be improved by aiding the transfer of hydrogen to the solid-gas interface. Typically a simple sampling device, such as a fan or pump, is used.

## Photoelectrochemical Hydrogen Production

Over the past two decades a large body of work has been assembled on photoinduced hydrogen production. Whether the hydrogen is produced from water splitting or from a non-aqueous source the production mechanism is the same: light-driven electron transfer. Such systems rely on the use of a photosensitiser to effect the transformation of light energy into charge separation. One such group of photosensitisers, with particularly good properties, is the ruthenium polypyridinium complexes, such as  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ .

Photo-induced hydrogen production from aqueous solutions using a  $\text{Ru}(\text{bpy})_3^{2+}$  compound as a photosensitiser was described by C. Konigstein and R. Bauer, of Vienna University of Technology. The paper also dealt with the use of rhodium compounds,  $\text{Rh}(\text{I})\text{Cl}(\text{dpm})_3^-$  (Wilkinson's catalyst) and  $\text{Rh}(\text{bpy})_3^{3+}$  as electron relay/homogeneous catalysts in light induced hydrogen forming reactions.

The performance and characterisation of surface modified platinum-coated *p*-silicon electrodes, for photoelectrochemical hydrogen production from water was reported by C. Maier and G. Bilger, of Stuttgart University, and M. Specht of the Solar and Hydrogen Energy Research Centre, Stuttgart. Semiconductors with a suitable band-gap for direct water splitting are handicapped because of their tendency to corrode in aqueous environments. The prevention of corrosion by coating the semiconducting material with platinum or other metals has been found to be effective. In addition, the platinum coating also acts as an excellent catalyst for  $\text{H}^+$  reduction. In their study they

examined in some detail the role of different platinum surface morphologies in determining hydrogen evolution efficiencies and the long term stability of silicon-based photochemical devices. Platinum was deposited on single crystal silicon by three methods: electron beam evaporation, magnetron sputtering and photo-assisted electrochemical deposition from a  $\text{H}_2\text{PtCl}_6$  solution. While the physical vapour deposition techniques produced uniform and continuous platinum layers, the electrochemical procedure resulted in platinum island topographies which improved the photoelectrochemical properties. The electrochemical experiments showed that the platinum deposited via the electrochemical technique led to photocurrent-voltage characteristics capable of producing hydrogen at high conversion efficiencies (10 per cent in alkaline electrolytes).

Continuing the theme of photocatalytic hydrogen production using semiconductor technology, C. Linkous of the Florida Solar Energy Centre, Cape Canaveral, examined a platinum modified cadmium sulphide photocatalyst. Rather than deal with the aforementioned difficulties of aqueous electrolytes, Linkous chose to use hydrogen sulphide as a widely available hydrogen source. Platinisation of the cadmium sulphide particles was achieved by reduction of the chloroplatinate ion to the metallic state by photo irradiation in the presence of acetate ions. Photoreactor operation where hydrogen sulphide and light were the only inputs, and hydrogen and sulphur the only products, was demonstrated. The use of such a photoreactor system in the oil refinery industry was discussed.

Hydrogen photoproduction was demonstrated by K. Gurunathan, P. Maruthamuthu and M. Sastri, of the University of Madras, India, using a rarely studied wide band gap semiconductor,  $\text{SnO}_2$ , loaded with platinum and  $\text{RuO}_2$  and sensitised with  $\text{Ru}(\text{bpy})_3^{2+}$ . The maximum hydrogen production rate occurred at a  $[\text{Ru}(\text{bpy})_3^{2+}]$  concentration of  $3.75 \times 10^{-5}$  mol/l.

An alternative approach to the use of particulate systems for photoelectrochemical hydrogen generating processes was presented in two papers by S. Khare, N. Gontia and S. Nema,

of the University of Jabalpur, India. In the first paper, they examined photo-assisted hydrogen generation by an electroactive solid polymer electrolyte (SPE) membrane system. In this configuration  $\text{TiO}_2$  particles and a platinum catalyst were incorporated into a Nafion membrane from  $\text{TiCl}_4/\text{methanol}$  and  $\text{H}_2\text{PtCl}_6/\text{methanol}$  solutions. The platinum loading was  $0.05 \text{ mg/cm}^2$  of Nafion. A further preparative step involving the synthesis of an electroactive polymer: polypyrrole, within the Nafion membrane matrix was necessary to ensure that the membrane was both electronically and ionically conducting. Under irradiation the prepared membrane generated hydrogen at a level of 20 microlitres of hydrogen during a 10-hour period.

In the second paper, Khare, Gontia and Nema described the utilisation of a membrane system for hydrogen generation, this time with chlorophyll-platinum as the photoactive element. This was incorporated into a perfluoro-ionomer membrane matrix. A fine dispersion of platinum was prepared on a Nafion membrane prior to impregnation with chlorophyll derived from spinach. The light induced splitting of water by the platinised chlorophyll impregnated membrane was observed at a series of temperatures up to  $160^\circ\text{C}$ . Hydrogen generation continued for between 6 to 8 hours during photo irradiation with peak production at around 3 to 4 hours. The degradation in the water splitting ability of the membrane on prolonged irradiation was explained by the photolytic dissociation of the chlorophyll in the membrane.

A hydrogen generation system containing a platinum group metal was described by M. Gupta, M. Swarnkar and S. Nema also from the University of Jabalpur. In this system photo-induced water splitting was achieved by a 3-layer structure which utilised polyimide bound tris (2,2-bipyridine) ruthenium(II) complex and finely dispersed platinum.

### **Chemical/Fuel Applications for Hydrogen**

A paper describing chemical hydrogen storage by syngas production from electrolytically cogenerated hydrogen and carbon monoxide,

was presented by M. Specht, A. Bandi and E. Mennenkamp-Iwer, of the Solar Hydrogen Research Centre, Stuttgart. In this work the reduction of a steam and carbon dioxide mixture was performed by high temperature electrolysis at  $1000^\circ\text{C}$ . An oxygen conducting, high temperature, yttria-stabilised zirconia ceramic, equipped with platinum electrodes, facilitated the oxygen removal necessary for the reduction process. The product of the electrolysis reactions was a syngas (hydrogen, carbon monoxide and carbon dioxide), which is useful as the basis for the production of a variety of synthetic fuels.

A noble metal catalyst, incorporated into a catalytic burner was described in a paper presented by P. Brockerhoff and B. Emonts, from the Institut für Energieverfahrenstechnik Forschungszentrum, Jülich, Germany. The catalytic burner comprised a cylindrical porous ceramic fibre through which the natural gas, hydrogen and air mixture flowed. The outside of the porous tube was treated with an alumina washcoat and a finely divided platinum catalyst. The paper describes the optimisation of the noble metal catalyst system and the performance of the system particularly in terms of low carbon monoxide and nitrogen oxides emissions. Carbon monoxide emissions were always below  $100 \text{ mg/kWh}$  over a wide range of operating conditions and as low as  $3 \text{ mg/kWh}$  at a power density of  $120 \text{ kW/m}^2$ . Emissions of nitrogen oxides were below  $20 \text{ mg/kWh}$  and sometimes as low as  $6.7 \text{ mg/kWh}$  depending on operating conditions.

A palladium based catalyst was employed in tests on a Hythane (natural gas/hydrogen mixture) fuelled internal combustion engine by V. Raman and J. Hansel, of Air Products and Chemicals Inc., Pennsylvania, and J. Fulton and F. Lynch of Hydrogen Consultants Inc., Colorado, and D. Bruderly of Bruderly Engineering Associates, Florida. It was found that the post catalyst emissions from burning either natural gas or Hythane were so low (under steady state conditions) that the effect of the added hydrogen could not be detected. However, under transient operating conditions,

such as specified in the Federal Light Duty Vehicle Testing Procedure, significant differences between natural gas and Hythane emissions, post catalyst, were observed.

### **Platinum Group Metals in Heat Pump Systems**

A chemical heat pump system based on the reaction couple: 2-propanol dehydrogenation/acetone hydrogenation using ruthenium/carbon, ruthenium-platinum/carbon and ruthenium-palladium/carbon dehydrogenation catalysts was described by D. Taneda, I. Yasutomi, T. Imanishi, S. Shibata and T. Toida, of the JGC Corporation, Yokohama-shi, Japan. The heat pump system demonstrated an ability to upgrade low level heat at 353 K to temperatures of between 423 and 473 K. The effectiveness of the dehydrogenation catalyst was found to be highly significant in determining the efficiency of the overall system. The best catalyst was the ruthenium-palladium/carbon variant, with the pilot plant capable of giving coefficient of performance (COP) figures of 10 to 20. However the enthalpy efficiency remained low at only 10 per cent. The low efficiency was probably due to the limited dehydrogenation activity of the present catalyst. Improvements in the effectiveness of the dehydrogenation reaction would make the system a promising next generation heat pump.

A second paper, concerned with the chemical conversion of low quality heats via dehydrogenation using noble metal catalysts, was presented by Y. Saito and co-workers of the University of Tokyo. This group concentrated on the study of dehydrogenation catalysts for the 2-propanol-acetone and cyclohexane-benzene dehydrogenation reactions. Ruthenium, platinum, palladium and ruthenium-platinum composite catalyst systems were prepared for the dehydrogenation and dehydrogenation-dearomatization reactions with particular emphasis on the characterisation of particle size and metal composition.

A chemical heat pump, containing a platinum/alumina catalyst, which utilised the cyclohexane-benzene dehydrogenation reaction was

reported by K. Murata, K. Yamamoto and H. Kameyama from the Tokyo University of Agriculture and Technology. The platinum catalyst layer, of thickness around 270  $\mu\text{m}$ , was incorporated into the inner wall of a double pipe heat exchanger of 10 mm diameter. In order to compare the tube wall reactor with other catalyst configurations, a fixed bed reactor was also tested by filling the tubes with pelletised catalyst. The results showed that the catalyst volume was reduced 4 times and the pressure drop at the reactor by 100 times when using the tube wall reactor catalyst. The development and optimisation of the tube wall reactor system should therefore enable more compact heat pump systems to be designed.

### **Palladium Based Membranes**

A paper covering hydride phase miscibility gaps and inhomogeneities of hydrogen distribution within palladium based hydrogen diffusion membranes was presented by F. Lewis, R.-A. McNicholl and X. Tong, of Queen's University, Belfast. The paper discussed the form of hydrogen absorption isotherms in two types of hydrogen diffusion membrane alloy (palladium-platinum and palladium-silver). One of the interesting observations involved the possibility that the position of the critical temperature may not be fixed, as was previously supposed. Hydrogen concentration inhomogeneities arising from strain gradient and 'uphill diffusion effects' may have a role in shifting formally accepted phase boundaries. This suggests the need for caution with regard to the proper assessment of hydrogen permeation through metal membranes under different pressure and temperature conditions.

### **Proton Exchange Membrane Fuel Cells**

The development of a hybrid fuel cell battery powered electric vehicle, designated as the 'Green Car' was described by M. Nadal and F. Barbir of Energy Partners Inc., Florida, U.S.A. The 'Green Car' employs three platinum containing proton exchange membrane (PEM) fuel cell stacks, with each stack comprising 60 cells

with a total power output of 19.2 kW. Hydrogen fuelling was achieved using a composite high pressure container made of aluminium and glass/epoxy resin. The total volume of stored hydrogen was 11,700 litres of pure gas at a pressure of 3000 psi. The vehicle was capable of a top speed of 60 mph and a range of 70 miles, with refuelling times between runs of only 5 to 10 minutes.

A paper on the internal humidification of PEM fuel cells was presented by D. Staschewski of the Karlsruhe Nuclear Research Centre, Germany. Platinum-carbon electrodes were hot pressed onto Nafion resulting in a platinum concentration of 2.5 to 2.8 mg/cm<sup>3</sup>. In order to improve electrical conductivity some of the experiments were performed with gold plated components. The monocell tests showed that the internal humidification worked well, up to 200 A or 0.5 A/cm<sup>2</sup>.

The modification of electrocatalytic platinum bearing layers in solid polymer electrolyte systems was reported in a paper by V. Fateev, O. Archakov and E. Pivovarova, of the Kurchatov Institute, Moscow. Their study involved investigating the role of PTFE added to the catalyst layer in order to effect hydrophobisation.

The high parasitic power losses incurred by the use of compressors (particularly in vehicular applications) to provide pressurised gas to PEM fuel cells was the basis of work by C. Chamberlin, P. Lehman, R. Reid and T. Herron of Humboldt State University, California. Their work was directed to producing a hydrogen/air fuel cell which would be capable of operating at very low pressures (< 2 psig) and temperatures (41–42°C). To date this group have designed and fabricated 50 cm<sup>2</sup> and 150 cm<sup>2</sup> cells in 1, 2 and 4 cell stacks. The intention is to scale up to a 5 and 20 kW PEM fuel cell for incorporation into a vehicle.

A paper by N. Anand and co-workers of Texas A. & M. and H. Dhar of BCS Technologies Inc., Texas, described recent progress in PEM fuel cell technologies. In the last 6 years at Texas A. & M. platinum loadings have been reduced by a factor of 100. In addition, power density has tripled since the mid 1980s. A total plat-

inum loading of 0.5 g/kW (cathode loading of 0.05 mg/cm<sup>2</sup>) gives a nominal 0.74 V at 0.3 A/cm<sup>2</sup> on non-humidified air and hydrogen at 1 atmosphere. Projections from this performance baseline, and assumptions regarding future advances, and cost reductions from mass production, predicted a platinum demand of around 10 tons for 1 million compact new cars per year.

In addition to the work on PEM fuel cell systems themselves, future low and zero emission vehicles will require efficient and cost effective methods of supplying pure hydrogen to the fuel cell. In a paper on hydrogen production in fuel cell vehicles, B. Hohlein, G. Colman, R. Menzer, P. Brockerhoff, and E. Riedel, of Forschungszentrum Jülich G.m.b.H., Germany, and J. Hansen and I. Primdehl of H. Topsøe, Denmark, described the use of reformed methanol as a hydrogen energy carrier. The paper discussed the reforming process from the point of view of efficiency and balance of emissions. The paper concluded that the emissions of carbon monoxide, nitrogen oxides and volatile organic compounds would be very much less in a reformer/fuel cell than is possible with a conventional automobile drive system. The total emission balance for methanol produced from natural gas and consumed in a fuel cell vehicle will be 0.1 to 0.01 of the requirements for ULEV standards. This makes the indirect methanol fuelling approach for a fuel cell an attractive future option.

A paper covering on-board hydrogen purification for steam reformer/PEM fuel cell vehicles was presented by J. Amphlett, R. Mann and B. Peppley, of the Royal Military College of Canada, Ontario. This group examined various methods of hydrogen clean up, including pressure swing absorption, diffusion through metal membranes, polymer membranes, solvent absorption, low temperature shift, preferential oxidation (PROX) and internal oxidation within the anode compartment of the PEM fuel cell. Of these a PROX system based on a platinum catalyst and coupled with a shift reaction was preferred.

High temperature membrane separation of hydrogen using palladium membranes offers

the complete removal of all other contaminants, but suffers the drawback of excessive cost. It was concluded that the final choice of gas purification for a PEM fuel cell system working on reformed methanol may well depend on as yet unanswered questions regarding the possible secondary effects of impurities such as unreacted methanol and carbon dioxide. It is possible that these gases may react on the anode to form catalyst poisons, such as carbon monoxide or formic acid.

A concept hybrid vehicle, consisting of a battery recharged by a fuel cell, running on reformed compressed natural gas was described in a paper presented by K. Ledjeff, J. Gieshoff and G. Schaumberg, of the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany. The reforming reaction is promoted by a platinum catalyst operating at around 650°C. The experimental reformer was designed to produce hydrogen at a rate of 700 litres/hour which must then be purified by a medium and low tem-

perature shift, using iron and chromium oxide and copper and zinc oxide catalysts, respectively, before admission to the PEM fuel cell.

## Conclusions

The papers presented at the Tenth World Hydrogen Energy Conference reflect the general environmental thrust towards a more hydrogen-rich energy environment. Whether as a change to hydrogen combustion for automobiles or by the introduction of platinum containing fuel cells, hydrogen will clearly be an important element in a more environmentally sound future. The unusual hydrogen storage, hydrogen permeating and catalytic properties of the rare earth metals and platinum group metals ensure their role in a hydrogen-rich future.

The Conference proceedings, edited by D. L. Block and T. N. Veziroglu, have been published on behalf of the International Association for Hydrogen Energy. The next conference will be held in Stuttgart in 1996. M.L.D.

## High Temperature Platinum Selective Solar Surfaces

Spectrally selective coatings are used in solar collectors to concentrate the incident radiation. Their function is to enhance the operating efficiency of systems used for the production of electricity. These coatings have to be able to withstand high operating temperatures for long periods of time, and even higher temperatures for shorter times while the collectors are not in use.

Many materials and combinations of materials possess suitable optical properties and sufficient thermal stability for use at temperatures below 300°C. To improve the efficiencies of these systems, however, the coatings would be required to withstand significantly higher temperatures and few absorbers are stable in air at temperatures above 400°C.

For this reason researchers at the Universität Konstanz, Germany, have studied two systems, at temperatures up to 1000°C, for potential use as solar selective absorber surfaces, these being platinum on alumina and three molybdenum silicide modifications on alumina (J. H. Schön, G. Binder and E. Bucher, "Performance and Stability of Some New High-Temperature Selective Absorber Systems Based on Metal/Dielectric Multilayers", *Solar Energy Mater. Solar Cells*, 1994, 33, (4), 403-416).

The optical properties of thin sputtered films of platinum on alumina were evaluated and found to agree with existing data. Thermal stabilities were tested for up to 400 hours at temperatures of 550 to 825°C. Platinum/alumina multilayers on quartz were stable in air up to approximately 700°C. The solar absorptance changed during a 300 hour experiment from  $\alpha = 0.92$  to 0.90. On the actual metal used as a support in such collectors the coatings degraded faster, and at over 640°C the optical changes became more obvious.

Absorptances up to  $\alpha = 0.95$  and emittances of  $\epsilon \sim 0.1$  were achieved for platinum/alumina, and the coatings are thermally stable in air up to 600°C for a 400 hour testing period.

## Strain Gauge Materials

Please note that the following alterations should be made to one of the figures in the paper entitled "Noble Metals Alloys as Strain Gauge Materials", which appeared in *Platinum Metals Rev.*, 1994, 38, (3), 98-108.

On page 106, in Figure 7, the data points have been displaced one position to the left. The density of state peaks should be at (d + s) numbers of 3, 5, 7 and 10, that is for Sc, V, Mn and Ni, respectively. Any confusion caused is regretted.