

# NEW PATENTS

## ELECTROCHEMISTRY

### Oxygen Reduction Electrode

UNIV. CASE WESTERN RESERVE *World Appl.* 99/46,429

An O<sub>2</sub> reduction electrode (1) has a Pt substrate and its surface is modified by S, Se or Te or their compounds, which renders it highly selective for the conversion of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> (~100%). An electrochemical device is also claimed with the electrode as cathode, preferably with an acidic electrolyte, for concentrating O<sub>2</sub> in a feed gas. (1) can function in acidic electrolytes and may be used in electrochemistry.

### Electrode for Nitrate Reduction

UPSCALE WATER TECHNOL. INC. *U.S. Patent* 5,935,392

An electrode (1) for the removal of nitrates from H<sub>2</sub>O or seawater, comprises a polyacrylonitrile-based C fibre electrode (2) coated with Ir oxide. The electrode is made by dipping (2) in an Ir chloride solution, and heating at 225–350°C for 1.5–1.75 h. An apparatus for reducing nitrates in an aqueous solution which includes a cathode, a reference electrode and (1) as an anode, is also claimed. The cell operates at higher anodic voltages without Cl or O evolution.

### Electrode for Hypochlorite Production Cell

ELTECH SYSTEMS CORP. *U.S. Patent* 5,989,396

An electrode for electrolytic cells used for hypochlorite production in desalinators, comprises a sheet metal plate with an anodic coating of oxides of Ir, Sn, Sb and Ti, and a cathode coating containing the oxides of one or more of Ru, Ir and/or Ti. The coatings are dried at 90–120°C and cured at 450–650°C. Improved disinfection efficiency is obtained at lower cost, without any safety risks.

### Electrode for Electrolysis of Dilute Salts

TANAKA KIKINZOKU KOGYO K.K.

*Japanese Appl.* 11/269,687–88

An electrode (1), used as an anode for electrolysis of dilute salt solutions for production of acidic H<sub>2</sub>O with a high sterilisation effect and for treating waste H<sub>2</sub>O containing organic matter, has Pt, Ir and Ir oxide layers sequentially coated on its base material containing Ti, Nb and/or Ta. (1) with Pt and Ir layers has a long life and can be maintained easily. Exhaustion of (1) under high current density conditions is restrained.

### Catalyst Electrode Used in Electrolysis

SHINKO PANTEC CO. LTD. *Japanese Appl.* 11/279,784

A catalyst electrode (1), used in electrolysis cells, is formed by adhering a Pt group metal from a cathode on a solid polymer electrolyte film in the presence of a magnetic field in an inert gas atmosphere. A predetermined voltage is impressed to the magnetic field which is formed parallel to the cathode surface, along the orthogonal direction, so the coated film becomes the anode. (1) has favourable adhesion and can be prepared easily and quickly at low energy.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electroless Plating of Specific Parts

K. TAKAGI

*European Appl.* 967,299

An efficient process (1) for partial electroless plating deposits film only to specific parts of a substrate, without requiring the conventional etching step. Plating comprises forming and activating the resin film, imparting and activating a catalyst onto the film with an acidic solution containing Pd ions, and then reducing the Pd ions to metallic Pd. (1) is used for metal plating of plastic substrates, such as epoxy and polyimide, especially for printed circuit boards.

### Electroless Palladium Plating

ISHIHARA YAKUHIN K.K.

*Japanese Appl.* 11/269,658

An electroless Pd plating composition includes aqueous solution containing an organic compound with bivalent S, a Pd compound, aminocarboxylic acid and formic acid. Pd film of suitable thickness, high purity and catalytic activity is obtained. The plated layer has excellent soldering property, corrosion resistance and long life span. Generation of cracks is prevented, and as there is no P present, waste H<sub>2</sub>O treatment is easy.

## APPARATUS AND TECHNIQUE

### Hydrogen Permeable Film

TOKYO GAS CO. LTD.

*Japanese Appl.* 11/286,785

Hydrogen permeable film (1) for oxy-hydrogen burners and fuel batteries contains multilayers of Pd and Pd alloy which are alternately plated by electroless or ionic plating on the surface of the porous support body, followed by heating to form H<sub>2</sub> permeable film. (1) can be efficiently obtained without pinholes and can be easily reproduced.

### Hydrogen Gas Permeable Membrane

OPTONICS SEIMITSU K.K.

*Japanese Appl.* 11/314,902

H<sub>2</sub> gas permeable film used for H<sub>2</sub> refiners contains heat treated Pd alloy laminated with Ag film. A laminated structure of repeated Pd and Ag layers is formed by electroplating on a conductive board and a lattice-like photoresist pattern is formed by photolithography. The in-plane thickness can be controlled and H<sub>2</sub> permeability efficiency is greatly increased.

### Photocatalyst Module for Purifiers

TOSHIBA K.K.

*Japanese Appl.* 11/335,187

A photocatalyst module (1) for air or H<sub>2</sub>O purifiers has a base material made of a ceramic porous substance with a specific blow hole rate, containing Pt or Au alloy or transition elements, dispersed on its surface. (1) has a large catalyst area, thus giving high catalytic activity, optical attainment property, photocatalyst efficiency, corrosion resistance and reduced power consumption. (1) can also be used for exhaust purifiers, antifouling sterilisation, deodorising, etc.

## HETEROGENEOUS CATALYSIS

### Fluid Bed Palladium-Promoted Catalyst

STANDARD OIL CO. OHIO *European Appl.* 949,000

A fluid bed catalyst (1) for vinyl acetate manufacture is produced by impregnating an inert microspheroidal support ( $\geq 50\%$  of particles  $< 100 \mu\text{m}$ ) with a solution comprising a halide-free salt of Pd and M (M = Ba, Au, La, Nb, Ce, Zn, Pb, Ca, Sr, Sb or their mixtures) and reducing the metal salts to form a deposit of Pd and M on the support. (1) gives a high performance and attrition resistance in vinyl acetate production, giving ethylene conversion rates of  $\leq 18.2\%$  and selectivity of  $\leq 87.8\%$ .

### Gas Particle Filter for Diesel Engines

FEDERAL-MOGUL SINTER PROD. *European Appl.* 951,931

A filter, for inserting into diesel engine exhaust pipes to trap particulates, is in the shape of a tube with its wall made from fritted metal grains, covered with a layer of felted metal fibres, both the grains and fibres being of stainless steel. The tube is filled with grains of Al coated with a combustion catalyst, such as Pt. The filter traps the finest particles and has a long operating life.

### Production of Acetaldehyde

EASTMAN CHEM. CO. *European Appl.* 953,560

Acetaldehyde (1) is produced by hydrogenation of acetic acid in the presence of a Fe oxide catalyst with a specific surface area containing 2.5–90 wt.% Pd at  $\sim 250\text{--}400^\circ\text{C}$ .  $\text{H}_2$  and acetic acid are fed to a reactor in a ratio of 2:1–25:1. High acetaldehyde selectivity of 84% is achieved by recovering volatile (1). (1) is used as a starting material in the manufacture of acetic anhydride, acetate esters, vinyl acetate resins, etc.

### Waste Gases Purification Catalyst

ALSI-PENTA ZEOLITHE G.m.b.H. *European Appl.* 955,080

A catalyst material (1), used for purifying gases containing  $\text{N}_2\text{O}$  and  $\text{NO}_x$ , is prepared by dry mixing  $\text{NH}_3$  salts,  $\text{NH}_3/\text{NH}_4$ -zeolites or N-containing compounds; high silicate zeolite structures with a Si:Al ratio of  $> 5$ ; and Pd, Rh, Mn, Cu, Fe, Co and/or Pt as active component, in a mill under normal pressure and temperature. The material is further tempered at  $\geq 300^\circ\text{C}$  until complete ion exchange has occurred. (1) has high catalytic activity at low reaction temperatures and also in steam and  $\text{SO}_2$ .

### Exhaust Gas Clean-up Catalyst

JOHNSON MATTHEY JAPAN LTD. *European Appl.* 960,649

A catalyst (1), especially useful for cleaning up hydrocarbons in exhaust gases in I.C.E., contains Pd, Pt, Rh, Ru, Ir, Os and/or other noble metals; and W, Nb and/or Mo metals or oxides; and can also contain  $\text{CeO}_2$  and/or  $\text{ZrO}_2$ . (1) has low-temperature activity to clean up exhaust gas directly after start-up. A method of clean-up in which the gas is treated in the channel through which the gas is discharged from the engine is also claimed. The composition of (1) is converted to an oxide only by calcination in air.

### Catalytic Hydrogenation of Aromatic Amines

BAYER A.G. *European Appl.* 965,579

Hydrogenation of aromatic amines to cycloaliphatic amines is performed at low pressure (0.5–40 bar) on supported Rh metal catalysts (1), which may also contain Ir, Ru, Os, Pd or Pt, or their mixtures, with a support base coated with salts of Cr, Mo, W, Mn and/or Re. The conversion of aniline increases with increasing Rh content but the selectivity to cyclohexylamine decreases to 20% at 40% conversion. (1) have high selectivity  $> 97\%$  for cyclohexylamine from aniline.

### Palladium-Gold Catalyst for Vinyl Acetate

CELANESE INT. CORP. *World Appl.* 99/42,212

A Pd-Au catalyst (1) is prepared by separately impregnating and fixing the Pd and Au water-soluble compounds, followed by reduction of the fixed solids to free metals on a suitable support. (1) has smaller variation in the Au:Pd ratio than products made by the double fix method, and exhibits high activity, good selectivity and long life. (1) are used for the production of unsaturated esters from olefins,  $\text{O}_2$  and organic acids, particularly in the manufacture of vinyl acetate from ethylene,  $\text{O}_2$  and acetic acid.

### Exhaust Gas Purification Catalyst

DAIHATSU MOTOR CO. LTD. *Japanese Appl.* 11/138,001

A catalyst for exhaust gas purification is produced by depositing both Pt and Rh on a granular Zr composite oxide (1),  $\text{Zr}_{1-x-y}\text{Ce}_x\text{R}_y\text{O}_{2-z}$ , where R is at least one rare earth element and Al, except Ce; z expresses O deficiency,  $x+y = 0.1\text{--}0.5$ ;  $x = 0.1\text{--}0.5$ ; and  $y = 0\text{--}0.2$ . Suppression of the growth of crystal particles of (1) and of Pt particles after high temperature runs results in high cleaning efficiency. Catalytic activity does not deteriorate even under severe conditions of  $\geq 900^\circ\text{C}$ .

## HOMOGENEOUS CATALYSIS

### Production of Arylalkenes and Conjugated Dienes

AVENTIS RES. & TECHNOL. G.m.b.H. & CO. K.G.

*European Appl.* 962,434

Production of arylalkene or conjugated diene compounds (1) by Heck reaction comprises reacting an aryl or vinyl halide or sulfonate with an olefin in the presence of a catalyst comprising a Pd(0) complex or a Pd(II) salt and a phosphite ligand which has better oxidative stability than conventional phosphine ligands. (1) are useful as ultraviolet absorbers, intermediates for pharmaceuticals and agrochemicals, etc.

### Production of Stanol Compounds

COGNIS DEUT. G.m.b.H. *World Appl.* 99/48,907

Stanols are produced by hydrogenating sterols (1) in the presence of a Pd catalyst in an organic solution using much reduced amounts of solvent. Alcohol, paraffin carbohydrates and mixtures of alcohol and carbohydrates can be used as solvents. The method is used for large-scale production due to its reduced consumption of solvent and good stanol yield.

## FUEL CELLS

### Fuel Cell Catalyst

DEGUSSA-HUELS A.G.

*European Appl.* 951,084

A fuel cell anode for the electrocatalytic MeOH oxidation contains a Pt metal or a Pt metal alloy as a primary catalytic component (1) and a transition metal complex cocatalyst of an optionally substituted phthalocyanine to reinforce the catalytic effect of (1). This anode is claimed to have a comparable or better performance than one containing a Pt catalyst with a Ru cocatalyst. (1) is not poisoned by the phthalocyanine complex.

### Platinum-Ruthenium Electrocatalyst

NE CHEMCAT CORP.

*European Appl.* 952,241

An electrocatalyst (1) comprises a cubic Pt-Ru solid solution alloy and a hexagonal Ru alloy, each having a crystalline diameter of 10–100 Å, supported on a conductive C carrier. The total amount of the combined alloys is 10–80 wt.%, based on the electrocatalyst. (1) has excellent poisoning resistance to CO, thus allowing the use of a small, simplified fuel reformer. (1) is used in SPEFCs as a propulsion power source for transportation means.

### CO-Tolerant Fuel Cell Oxidation Catalysts

DE NORA S.p.A.

*World Appl.* 99/53,557

A selective oxidation catalyst for fuel cells or oxidation of H<sub>2</sub> in the presence of CO comprises a C black-supported catalyst having an atomic composition Pt<sub>x</sub>:Mo<sub>y</sub>, where x is 0.5–0.9 and y is 0.5–0.1. Also claimed is a gas diffusion electrode having a web and the above catalyst layer and an ion exchange membrane coated on one side with the catalyst. Activity of the catalyst is high and controllable, and H<sub>2</sub> can be oxidised in the presence of CO without adversely affecting the Pt.

### Fuel Cell Electrodes

UNITED TECHNOLOGIES CORP.

*U.S. Patent* 4,613,582

A ternary metal alloy catalyst (1) is made by intimately contacting a finely divided noble metal, preferably Pt, supported on an electrically conductive C black with a solution of a compound of a Group IV, V, VI or VII transition metal, preferably Cr, and a Co compound, then heating and reducing in N<sub>2</sub>. Its catalytic activity for the electrochemical reduction of O<sub>2</sub> is > 2.5 times that of the supported unalloyed noble metal alone. (1) is used for the electrochemical reduction of O<sub>2</sub>, as a cathode in acid fuel cells.

### Direct Liquid-Feed Organic Fuel Cell

CALIFORNIA INST. OF TECHNOL.

*U.S. Patent* 5,945,231

A fuel cell for generating electrical power by electrochemical reactions of a liquid organic fuel comprises a solid electrolyte membrane, directly supporting anode and cathode catalyst (1) layers, each containing 7–10% Pt and Ru catalyst, 60–70% of perfluorovinyl ether sulfonic acid and 15–20% of PTFE. Efficiency is increased, permeation of (1) into backing layers is minimised and fuel crossover is reduced.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Magnetic Head Elements

TDK CORP.

*Japanese Appl.* 11/273,036

A spin type magneto resistance effective element for a magnetic head (1) has an antiferromagnetic layer made of Pt<sub>1-x</sub>R<sub>x</sub>Mn<sub>100-y</sub> alloy, specifically Pt<sub>25</sub>Rh<sub>25</sub>Mn<sub>50</sub>, where R is Rh, Ir or Ru with x = 5–30% and y = 40–60%. (1) has increased magnetic exchange energy.

### Magnetic Alloy Film

SHOWA DENKO K.K.

*Japanese Appl.* 11/273,947

A non-magnetic substrate carries a non-magnetic foundation film, a magnetic film and a protective film. The magnetic film contains in at.%, 1–7 Pt, 10–26 Cr, 0.5–4 Cu, Re or V, ~ 1–16 Ta, and remainder Co. The composition is used in floppy disks for a magnetic disk drive and has excellent coercive force and noise characteristics.

### Semiconductor for Light Emitting Diode

TOSHIBA K.K.

*Japanese Appl.* 11/274,562

A nitride compound semiconductor composition comprises a metal layer (1) formed from one of Pd, Rh, Ir, Sc, V, Zr, Hf, Ta, Co and Cu; and a second metal layer of Ti, Ni, Mo or W, deposited on (1). The Pd, etc., has favourable ohmic characteristics so sheet- and contact-resistance are greatly reduced, and thus wire bonding is easily performed. Light emitting devices of high brightness can be obtained at low cost.

### Ceramic Circuit Board

MIYOSHI DENSHI K.K.

*Japanese Appl.* 11/274,696

The heat release structure of a ceramic circuit board used in portable electronic devices has a heat release hole filled with 0.5–20 wt.% of Ag, Pd, Ru and/or Rh. Excellent heat release properties and size reduction of the ceramic substrate are obtained as the heat release hole is present at the bottom of the device.

### Processing PCB Substrate

HITACHI CHEM. CO. LTD.

*Japanese Appl.* 11/279,766

Processing a substrate of a printed circuit board involves sensitising and heat treatment by a Pd complex on the board surface prior to electroless plating. The electroless plating is used to make multilayered printed circuit board with fewer plating blisters.

### Metallisation of Polymeric Substrates

BLASBERG ETHONE-OMI

*German Appl.* 1/98/22,075

Metallisation of polymeric substrates for the production of printed circuit boards, preferably with micro-holes and fine structure, comprises doping an electrically conductive polymer layer with a Sn containing colloidal Pd solution, prior to contact with a Cu salt solution. This process allows more rapid metallisation and a faster lateral growth rate.

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