NEW PATENTS

ELECTROCHEMISTRY

Water Electrolysis Cell

JAPAN ENERGY CORP. *Japanese Appl.* 10/273,791

A H_2O electrolysis cell consists of a solid polymer electrolyte, such as a fluororesin type cation exchange membrane, flanked on two sides by a catalyst coated anode and cathode. The catalytic layer of the anode contains a mixture of Ir and Ru oxides formed by hydroxide co-precipitation. The cell voltage is reduced, and an improved H_2O electrolysis cell is obtained.

Hydrophobic Electrode

PERMELEC ELECTRODE LTD. *Japanese Appl.* 10/280,183

A hydrophobic electrode for gas diffusion has a conductive base with a top composite plated layer, which consists of hydrophobic F compounds, such as fluororesin, fluoride pitch, etc., and Pt. The base is immersed in a plating bath containing a Pt compound, a hydrophobic F compound powder and a surface active agent. The electrode has high corrosion resistance and increased electrode efficiency.

APPARATUS AND TECHNIQUE

Electrolytic Ozone Generator

UNIV. WUHAN *World Appl.* 98/40,535A

An electrolytic ozone-generating apparatus comprises an ozoniser, anode and cathode H_2O boxes, an equilibrium device and circulating tubes. Cathodic catalyst sheet is made by moulding a paste of 5–15 wt.% Pt in Pt/C in PTFE and H_2O at 80°C, an anodic catalyst sheet is made from PbO_2 with PTFE, and a porous anode current-collecting sheet from Ti coated with Pt, Sn and Sb oxides. It gives stable operation with high ozone generation efficiency under pressure.

Two-Cycle I.C.E. Control System

SANSHIN KOGYO K.K. *U.S. Patent* 5,836,155

A two-cycle I.C.E. control system has a sensor which is placed inside the Pt-coated accumulator chamber of the engine. The catalytic layer of Pt acts as a catalyst to accelerate the oxidation of oil and exhaust gases to prevent contamination of the sensor. The sensor provides accurate signals of engine running conditions; the combustible gases are not diluted with fresh charge air but are able to purge cycle-to-cycle and to provide cycle-by-cycle information.

Electrode Wire for Ozonisers

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 10/251,003

Electrode lead wire for ozonisers is produced by electrodeposition of ceramic material on a Pt wire, followed by baking the coated wire. The wire can withstand high voltage. It has high dimensional accuracy and uniform coat thickness along peripheral and longitudinal directions. The film thickness of the ceramic is controlled and electrodeposition time is reduced.

Deodorising Apparatus

AIWA K.K. *Japanese Appl.* 10/263,367

A deodorising apparatus for semiconductor plant, motor vehicle interiors, etc., has an insulator provided with a Pt wire heater in holes through which surrounding gas passes and is oxidised by heating at 300–400°C. Gases, such as NH_3, H_2S, trimethylamine and methyl mercaptan, are efficiently deodorised at the high oxidation temperature. As a large thermal protection structure is not required (because of the insulator) the size of the apparatus is reduced.

Oxygen Sensor for Exhaust Gas Purification

TOYOTA CHUO KENKYUSHO K.K. *Japanese Appl.* 10/282,046

A solid electrolyte O_2 sensor for an exhaust gas purification system has a Pt electrode and an oxide ion conductive solid electrolyte. A sensor, chosen from Groups II, III, V, VI and VIII, is coupled with Pt on the surface exposed to gas for detection. This minimises variation in the electromotive force in the downstream side of the catalyst to allow control of the exhaust gas.

HETEROGENEOUS CATALYSIS

Exhaust Purification Catalyst

NISSAN MOTOR CO. LTD. *British Appl.* 2,322,309A

A catalyst comprises a substrate coated with porous carrier grains supporting Pd and/or Rh and grains including $(La_{1-x}A_x)_{1-a}BO_b$ containing Pt and/or Pd, where A is Ba, K and Cs; B is a transition element such as Fe, Co, Ni and/or Mn; $x = 0–1$, $a = 0–0.2$ and b is a number where the net electric charge of the double oxide becomes 0. The catalyst has good NOx absorption capacity and can purify NOx in O_2-rich exhaust at high temperature over a long period.

Nitrogen Oxide Trap

FORD GLOBAL TECHNOLOGIES INC. *European Appl.* 857,510A

NOx trap useful for trapping NOx present in exhaust gases generated during lean-burn operation of I.C.E. comprises: a porous support; a catalyst comprising ≥ 30 wt.% alkali metal selected from Na and/or K; and a 0.2–4 wt.% Pt catalyst, both relative to the porous support. The trap and its specific arrangement in the exhaust system are also claimed. S poisoning of the trap is greatly reduced, and the trap can sorb NOx without forming sulfates.

Tertiary Amine Preparation

BASF A.G. *European Appl.* 869,113A

Mono- or polyfunctional tertiary amines are prepared from nitriles by reaction with secondary amines and H_2 over a Pd-based catalyst, comprising 0.1–10 wt.% Pd and 0.01–10 wt.% of at least one other metal, selected from Groups IB and VIII, Ce and La, on a carrier. The catalyst has a longer working life and better long-term stability than prior catalysts and gives good conversion and selectivity.

High-Frequency Heating Catalyst

ZEXEL CORP. *European Appl.* 872,911A

A high-frequency heating catalyst, useful in cleaning exhaust gases of harmful substances at low temperatures at the start-up of an I.C.E., comprises a high-frequency absorbing layer and an insulating material on a high-frequency absorbing substrate with a Pd, Pd-Rh or Pt-Rh catalyst. The high-frequency absorbing layer is made of an electroconductive metal oxide and an insulating material with an impedance adjusted to the characteristic impedance of a medium through which a high-frequency wave is transmitted, such that reflection power ratio is ≥ 10 dB.

Palladium Nanoparticle Sol

HOECHST RES. & TECHN. DEUT. G.m.b.H. & CO. *European Appl.* 879,642A

Soluble nanoparticles containing Pd, optionally with Groups IB and VIIIB metals, are embedded in a protective colloid which contains a polymer with betaine groups. The resulting sol is applied to a catalyst support by dipping, spraying, immersion, impregnation, spray drying or spin coating. The nanoparticles have improved stability and the catalyst is used for the production of vinyl acetate.

Phenol Preparation

TOSOH CORP. *European Appl.* 885,865A

Phenol is prepared by oxidation of an aromatic compound with O_2 and H_2 in the liquid phase in the presence of a supported catalyst consisting of a Group VIII metal selected from Pt, Pd, Rh, Ru and/or Ir and of a V compound. The reaction is carried out further in the co-presence of a diketone compound. Phenol is produced without any by-products in high selectivity with high catalytic activity for extended duration.

Carboxylic Acid Production

BP CHEM. LTD. *European Appl.* 885,870A

A carboxylic acid and/or a carboxylic acid anhydride are produced by contacting a composition of an alcohol and/or a carboxylic acid ester, optionally H_2O, a first hydrocarbyl halide promoter and/or a hydrocarbyl ether reactant and a second hydrocarbyl halide promoter with CO in the presence of a catalyst comprising an insoluble imidazole-containing resin supporting a Group VIII metal species, such as Rh and Ir compounds. Acetic acid and acetic acid anhydride production is claimed.

Hydroxylammonium Salt Preparation

DSM N.V. *World Appl.* 98/18,717A

A process for preparing a hydroxylammonium salt (1) comprises catalytic reduction of nitrate ions in an acid medium with a supported Pd and/or Pt catalyst which includes ≥ 0.00025 mmol of halogen ions per m^2 of the catalyst metal surface area. A process where the catalyst is treated with I, Br, Cl, etc., and/or halogenated aliphatic, aromatic, etc., branched or linear hydrocarbons with 1–12C atoms, is also claimed. The catalysts retain enhanced selectivity towards hydroxylammonium salt after prolonged use. (1) are used for production of oximes from ketones or aldehydes.

Removal of Nitrogen Oxides in Exhaust Gas

EBARA CORP. *World Appl.* 98/46,334A

NOx is removed from an exhaust gas by adding NH_3, in an amount 0.5–3 times the total amount of the NO and NO_2 stoichiometric amounts, to an exhaust gas generated by chemical vapour deposition during semiconductor processing and containing N_2O, NO and NO_2. The mixed gas is brought into contact with a noble metal catalyst, such as Pd/Al_2O_3, at a temperature high enough to decompose NOx. The treatment of N_2O, NO and NO_2 can be carried out in one step and the method generates no newly produced N_2O.

Synthesis Gas Production

CHIYODA CORP. *World Appl.* 98/46,524A

Synthesis gas is produced by reacting a C-containing organic compound with CO_2 and/or steam in the presence of a catalyst comprising 0.0005–0.1 molar % Rh, Ru, Ir, Pd and/or Pt (metal equivalent with respect to metal oxide carrier) supported on an oxide carrier. The catalyst specific surface area is ≤ 25 $m^2 g^{-1}$ and the electronegativity of the metal ion in the carrier is ≤ 13.0. The catalyst C precipitation activity is regulated to a very low value, so that C precipitation is suppressed over long periods even under pressure and synthesis gas is continuously produced in high yield, using small-size equipment, at reduced cost.

Manufacturing Isobutanol

EXXON RES. & ENG. CO. *U.S. Patent* 5,811,602

Isobutanol for use in the production of potential high octane oxygenates for gasoline engines, is manufactured by contacting a catalyst, comprising Pt and/or Pd supported on three-phase mixed-oxide crystallites containing Zr, Mn and Zn, with MeOH feed containing ethanol, *n*-propanol, ethylene and/or propylene and synthetic gas. A method for incorporating a light olefin into alcohol to prevent MeOH decomposition with reactant steam is also claimed.

Diesel Engine Catalyst

TOYOTA JIDOSHA K.K. *Japanese Appl.* 10/202,103

A catalyst for oxidising exhaust gases for diesel engines contains Pt particles, 5–50 nm in grain size, carried by heat treatment carrier particles. Due to the large Pt particle size, SO_2 oxidation activity is lowered. The porous carrier absorbs hydrocarbons and the high hydrocarbon oxidation ability of the catalyst is maintained in the low temperature region. CO and soluble organic components are purified. Discharge of sulfate is reduced by suppressing sulfate oxidation activity over high temperature ranges.

Exhaust Gas Cleaning Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appl.* 10/286,462

An internally structured catalyst for I.C.E. comprises catalytic components of Nb-Ca-Zr composite oxide layers carrying Rh and X-Ce-Zr (X is Pr, Y, La and Nd) composite oxide layers carrying Pt. This gives a catalyst with improved high temperature durability, excellent low temperature activity and purifying performance, and a high resistance against catalytic poisons and sintering.

Vinyl Acetate Preparation

HOECHST A.G. *German Appl.* 1/97/21,368

A method for producing vinyl acetate involves the use of a novel shaped body for noble metal supported catalyst systems in gas phase oxidation of ethylene and acetic acid. The body consists of porous HiFlow® rings made from ceramic materials, such as SiO_2, Al_2O_3, TiO_2, ZrO_2 or their mixtures, covered with a layer of Pd/Au/K, Pd/Cd/K or Pd/Ba/K. The method gives increased catalyst usage and space-time yield.

HOMOGENEOUS CATALYSIS

Preparation of Azithromycin

HOVIONE INTER. LTD. *European Appl.* 879,823A

The azithromycin, a macrolide antibiotic, is prepared from an imino ether by reduction and reductive methylation carried out sequentially with a Pt group metal catalyst and H_2 in the presence of formaldehyde. Both reactions are carried out in the same reaction vessel. The Pt group metals are Pd, Pt, Rh or Ru and the process is conducted in the presence of acetic acid, formic acid or ethanol. The acidity is controlled using a buffer, such as Na acetate. The process requires milder conditions and a purer product at a higher yield is obtained. The catalyst can be recycled and reused several times.

Methylindoline Compounds

IHARA CHEM. IND. CO. LTD. *World Appl.* 98/45,261A

Preparation of 5-methylindolines (1) comprises hydrogenating a 5-formylindoline in the presence of a Pd catalyst in an inert solvent. (1) can be prepared simply in high yields and are intermediates for pharmaceuticals.

Heteroaromatic Olefins

DSM N.V. *Word Appl.* 98/49,128A

A heteroaromatic olefin is prepared by arylating an aliphatic unsaturated compound using an aromatic or heteroaromatic carbonyl compound as the arylating agent in the presence of $PdCl_2$, $PdBr_2$, PdI_2, Na_2PdCl_4, $Pd(OAc)_2$, etc., and a halide, preferably, NaBr. The process uses no surfactants and salt formation is prevented. It is used for preparing agrochemical and pharmacological intermediates, such as methyl cinnamate or 2-vinyl-6-methoxynaphthalene.

FUEL CELLS

Fuel Cell Electrodes

DE NORA S.p.A. *European Appl.* 872,906A

Anodes and cathodes for use in polymeric membrane fuel cells comprise an electroconductive porous and planar substrate with a pre-layer formed by C mixed with a first hydrophobic binder containing a catalytic layer formed by a catalyst mixed to a second hydrophobic binder. The catalyst is made of pure Pt or a Pt alloy dispersed on a high surface area C in the range 30–40 wt.% of noble metal and 10–20 wt.% binder. The hydrophobicity of the applied layers can be adjusted to improve the H_2O balance of the process.

Solid Polymer Type Fuel Cell Production

MATSUSHITA ELECTRIC IND. CO. LTD. *European Appl.* 874,413A

Electrodes are formed on both sides of a solid polymer electrolyte membrane by coating with a mixed liquid containing an organic solvent, a noble metal catalyst supporting C powder and a colloid of a solid polymer electrolyte, 1 to < 400 nm in size, adsorbed on the C powder. A gas diffusible layer is present between the membrane and the electrode. This assembly and the fuel cell produced are also claimed.

PEM Fuel Cell Catalyst

DEGUSSA A.G. *European Appl.* 880,188A

A CO tolerant anode catalyst for a PEM fuel cell, comprises a finely divided conductive support bearing Pt and Ru in a highly dispersed unalloyed form, the crystallite size of Pt being < 2 nm and that of Ru < 1 nm. Also claimed is production of the catalyst by suspending the support in H_2O, adding aqueous Pt and/or Ru compound solutions, adjusting the pH to 7–9, depositing the Pt and/or Ru using a reducing agent, followed by filtering and drying at ≤ 200°C. The catalyst allows the CO contents in the reformed gas supply of the fuel cell to be > 100 ppm, without significant fuel cell power losses. It is useful for traction batteries for vehicles.

Two-Part Catalyst for Fuel Cells

UNIV. CHICAGO *World Appl.* 98/55,227A

A two-part catalyst comprises a dehydrogenation portion selected from a Group VIII metal, especially Pd and/or Pt, and an oxide-ion conducting portion selected from a ceramic oxide crystallising with a fluorite or perovskite structure. The catalyst is used for forming a H_2-rich gas from a hydrocarbon fuel, especially in fuel cells, and fuel is used to contact the catalyst at ≥ 400°C for a time sufficient to generate the gas while maintaining the CO content to < 5 vol.%. The catalyst provides effective conversion to H_2 rich gas while minimising formation of CO_2.

Methanol Fuel Cell

ASAHI GLASS CO. LTD. *Japanese Appl.* 10/255,831

A methanol fuel cell, with high output, has an electrode composed of an intermetallic compound of a Pt group metal and a rare earth metal. The intermetallic compound for the electrode has a $-CF_2SO_3$- group and forms a Lewis acid which is present in effect in high dispersion on the catalyst. This results in an enhancement of the activity of the MeOH oxidation reaction.

Polymer Electrolyte Fuel Batteries

TOSHIBA K.K. *Japanese Appl.* 10/270,057

The fuel battery includes Pt-Ru catalyst layers between a polymer electrolyte film and a fuel pole. Two catalyst layers are produced, one in contact with the polymer electrolyte film contains ≤ 50 wt.% Ru, and the other, in contact with the fuel pole, contains ≥ 50 wt.% Ru. The pollution of the catalyst in the fuel pole by CO, present in the heating gas, is prevented. The battery has excellent voltage characteristics.

Palladium Alloy Membrane Foil

DBB FUEL CELL ENGINES G.m.b.H.

German Appl. 1/97/38,513

A Pd alloy membrane foil for H_2 separation is prepared by alternate electrodeposition of alloy component layers. The Pd alloy contains Groups VIII or IB metal. The membrane is especially used for high purity H_2 separation from MeOH reforming product gas for supplying fuel cell systems for motor vehicles. This method for production of foil results in thinner membranes which give better H_2 permeation rates.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ferroelectric Capacitor

SONY CORP. *European Appl.* 875,938A

An electronic material, $Pd_a(Rh_{100-x-y-z}Pt_xIr_yRu_z)_bO_c$, contains: a = 20–70; b = 10–40; c = 15–60; x, y and z and $x + y + z$ = 0–100 and a + b + c = 100, all in at.%. It is used as the lower electrode in dielectric capacitors, in memory cells and as diffusion-preventing layers. A semiconductor device, also claimed, allows greater choice of processing temperatures and high-temperature annealing so PZT and SBT may be used as dielectrics. Diffusion between semiconductor diffusion layers and overlying plugs is prevented.

Conductive Circuits on Glass

CANON K.K. *European Appl.* 884,934A

Conductive circuits have a substrate comprising a Ni layer (of Ni or Ni-P) and a Pd layer (of Pd or Pd-P) deposited on a glass substrate, both preferably by electroless plating, with an electroplated layer deposited on the Pd layer. The electroplated layer is Au, Ag, Cu, Ni, Pt, Pd, W or Mo. The circuitry is formed with good adhesion without requiring high temperature processing of the glass which can result in warp or strain within the glass.

High Coercivity Magnetic Recording Medium

UNIV. NEBRASKA-LINCOLN *U.S. Patent* 5,824,409

A magnetic recording medium has a coercivity of 3000–6300 Oe, and comprises a substrate and a magnetic recording layer composed of alternate thin film layers of Pt, Fe or Co, which are deposited by sputtering and then vacuum annealed. The recording layer has a high anisotropy ordered FePt or CoPt phase (CuAuI structure) film. The easy axis is in the film plane, and the grain size is ≤ 15 nm. The medium has high coercivity, an areal density of 10 Gb in^{-2}, and a fine grain size, which allows increased data storage.

Magnetic Recording Medium

TOSHIBA K.K. *U.S. Patent* 5,830,569

A magnetic recording medium (1) comprises a V-containing underlayer and a CoPtO-based alloy magnetic film, which has a crystalline phase and an amorphous phase with more O_2 in the crystalline phase. (1) has a large coercive force and an appropriate coercive force rectangularity ratio. It is suitable for high density recording even when the magnetic film is thin.

Electrically Conductive Film

ASAHI GLASS CO. LTD *Japanese Appl.* 10/237,665

An aqueous solution for forming electrically conductive coatings, for CRT tubes, contains dispersed fine alloy particles (≤ 100 nm in size) selected from at least two metal salts of Pt, Pd, Ru, Ag, Ni, Cu, and Au and necessary additives. The films formed have excellent electromagnetic wave shielding properties, coating durability and chemical resistance.

Thin Film Recording Medium

AKASHIC MEMORIES CORP. *Japanese Appl.* 10/269,550

A metallic thin film magnetic recording medium for HDD has a magnetic layer comprising (in at.%): 3–6 Ni, 10–15 Cr, 6–7 Ta, 2–3.5 Pt and balance Co. The medium reduces noise generation, has a high coercive force, and has improved data recording and regeneration characteristics.

MEDICAL USES

Dental Silicone Composition

JENERIC/PENTRON INC. *World Appl.* 98/40,043A

A room temperature curable dental Si composition for the manufacture of a dental impression material comprises a mixture of a polyorgano-hydrogen-siloxane, a silicone polymer, a vinyl siloxane/Pt/Pd catalyst complex, and inorganic fillers. The catalyst is a complex of 1,3-divinyltetramethyldisiloxane and H_2PtCl_6 doped with Pd, and contains 1.1–1.2% Pt and 500–600 ppm Pd. Outgassing of H_2 is prevented. The material can also be used for making other moulded articles, such as lithographic plates, release liner, reflecting sheeting, adhesives, etc.

Palladium Dental Alloy

DEGUSSA A.G. *World Appl.* 98/44,894A

Ag-Pd alloys consisting of (in wt.%): 45–60 Ag, 30–45 Pd, 0–5 Au, 0–5 Pt, 0–3 Ge, 0–3 Cu, 0–7 Ga, 0–5 Co, 0–1 Mo, 0–1 Ir, 0–1 Ru, 0–1 Re and 0–6 In, Sn or Zn. The alloy also contains 0–1 In with 1–6 Sn and 2–6 Zn or 3–6 In with 0–4 Sn and 4–6 Zn. The alloy is used in the production of low melting dental ceramic with a coefficient of expansion of ~ 16.5 μm $m^{-1}K^{-1}$. It is used as tooth replacement, being corrosion resistant and biocompatible.

Titanium-Nickel-Palladium Dental Alloy

FURUKAWA ELECTRIC CO. LTD.

Japanese Appl. 10/251,781

A cast clasp for denture bases or partial dentures consists of Ti-Ni-Pd series alloy and contains (in at.%): 49–52 Ti, 3–15 Pd and the remainder Ni with unavoidable impurity. The alloy shows super-elasticity at body temperature and below. The alloy preferably contains 5–10 at.% Pd in which the transformation temperature is low and stable super-elasticity can be obtained; at 7–8 at.% Pd, the super-elasticity is most stable.

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