NEW PATENTS

ELECTROCHEMISTRY

Insoluble Anode

TOBATA SEISAKUSHO K.K. *Japanese Appl.* 10/72,690

An insoluble anode has an electrode substrate with at least one of Ti, Ta, Nb, Zr, and an electrode active layer of Pt group metal, such as Ru, Rh, Pd, Os, Ir or Pt, supported on the electrode substrate through a diffusion layer. The anode is used in electrolytic surface treatment, including electroplating. The anode displays superior durability at high current densities and during electrolysis.

ELECTRODEPOSITION AND SURFACE COATINGS

Activation Bath

METAL ARTS CO. INC. *U.S. Patent* 5,753,304

An activation bath comprises 0.1–2 g of a Pd salt, 20–250 g of an alkali metal fluoride or hydrofluoric acid, 0.05–0.5 l of carboxylic acid as a complexing agent, 1–3 g of an alkali metal salt of gluconic acid, 1–5 g of an Fe salt, 10–30 g of a Ni salt and sufficient deionised H_2O to make 1 gallon. The bath is used for the electroless plating of Ni onto Al-containing substrates, such as automobile wheels and computer discs. The process is efficient and requires fewer steps.

Oxidation Resistant Coatings

GENERAL ELECTRIC CO. *U.S. Patent* 5,759,380

A protective CrRuAl-based coating is formed on a shaped substrate by electrodeposition of Ru and Cr, followed by aluminising by heating in a powder pack to form the final coating. The Cr is 55–70 vol.% of the Cr and Ru layers. The coating may be formed on internal surfaces, especially on Nb-based substrates in jet engine components.

Glossy Palladium Plating Bath

OKUNO PHARM. IND. K.K. *Japanese Appl.* 9/235,691

A plating bath contains 1–40 g l^{-1} of Pd, 0.04–6 mol l^{-1} of an NH_4 compound and aromatic sulfonamide or sulfobenzoic acid imides. The pH of the H_2O-soluble Pd salt mixture is > 10. The plating is performed at 20–50°C with a current density of 0.1–10 A dm^{-2}. The plating has superior corrosion resistance, antiwear and electrical properties. It is used for electric contact points and connector circuit substrates.

Thin Platinum Films

TONG YANG CEMENT CORP. *Japanese Appl.* 10/84,086

A thin Pt film is formed on a substrate used in electronic components by depositing Pt on an insulated oxide layer on a substrate under an oxidising atmosphere, followed by heating to form an O_2-free Pt layer with a specified orientation, preferably (200). This method forms pure Pt thin films positively oriented in the polarisation direction. The electronic component has greatly enhanced performance and an improved fatigue effect.

APPARATUS AND TECHNIQUE

Electric Connection for Oxygen Detection

ROBERT BOSCH G.m.b.H. *European Appl.* 831,565A

A high melting point electrically conductive connection for I.C.E. lambda probes, used for detecting the O_2 content in exhaust gas, connects a contact point with a contact member. These are separated by a diffusion active layer of a Pd-Ni alloy, 2–20 μm thick. The contact member is heated to a welding temperature at the contact point. The contacts have high temperature and mechanical stability with relatively large surface area electric contact.

Electrode for Detection of Nitric Oxide

UNIV. DUKE *World Appl.* 98/14,639A

An electrode for detecting NO, especially in biological samples, has a surface, preferably comprising Ru and/or Ru oxide, which forms a complex, preferably a nitrosyl complex, with NO. A specific electrode is formed by conditioning such an electrode in saline at +675 mV for 2 hours. The electrode has a sensitivity for NO in the nM range, a response time of a few seconds, and is stable in biological fluids and tissue.

Exhaust Gas Sensor

GENERAL MOTORS CORP. *U.S. Patent* 5,733,504

An exhaust gas sensor for I.C.E. comprises inner and outer electrodes separated by a solid, porous electrolyte. A porous protective coating which covers the outer electrode is coated with a microporous composite layer made of 80–99.998 wt.% ceramic and the remaining 0.002–20 wt.% is a catalyst material selected from Pt, Pd, Rh or other transition metals. This layer is 10–500 μm thick to reduce H_2 induced lean shift.

Nitrogen Dioxide Sensor

SHIMADZU CORP. *Japanese Appl.* 10/90,221

A controlled potential electrolysis type NO_2 sensor has a metal layer and a Pt layer formed on a gas permeable diaphragm, which is in the contact surface of an electrolyte and a tested gas. A counter electrode and a reference pole are formed on a detection pole on the diaphragm. The concentration of NO_2 detected is based on the current between the counter electrode and the detection pole.

HETEROGENEOUS CATALYSIS

Palladium Composite Catalyst

AISIN AW CO. LTD. *European Appl.* 826,419A

A composite ZnO-Pd catalyst is prepared by dispersing and fixing Pd on the surface of a ZnO (1) substrate, by adsorption of Pd^{2+} ions from an acid solution, followed by reduction of the adsorbed Pd ions to metallic Pd. Active C fibres and/or TiO_2 are additionally integrated in, and deposited on, the surface of (1). The catalyst is used in the elimination of hazardous components, such as CO and NOx, from automobile exhaust gases.

Solid Bed Catalyst

BASF A.G. *European Appl.* 841,090A

Solid bed catalysts containing either Pd and Se and/or Te on a SiO_2 carrier have a BET surface area of 80–380 $m^2 g^{-1}$, a pore volume of 0.6–0.95 $cm^3 g^{-1}$ and a pore diameter of 3 nm–300 μm. They are used as isomerisation catalysts, especially for 3-buten-1-ol compounds. The process gives fewer hydrogenation reaction by-products or low boiling point compounds.

Diesel Engine Catalyst

CATALER IND. CO. LTD. *European Appl.* 842,692A

A catalyst for purifying diesel engine exhaust gas comprises SiO_2 and Al_2O_3 supports in a mixing weight ratio of 98:2–72:28, and 0.01–0.55 g Pd per litre of support. The catalyst can oxidise SO_2 in the exhaust gas at higher temperatures, so it can effectively inhibit the formation of sulfates, as well as simultaneously control the emission of particulates.

Purification of Exhaust Gases

INST. FRANCAIS DU PETROLE *European Appl.* 842,693A

A process for the low temperature purification of exhaust gases from I.C.E. comprises the incorporation of a Pd-based catalyst or an absorbent up-stream of the conventional three-way catalyst to eliminate alkynes, particularly acetylene, at 220–250°C. The system eliminates hydrocarbon pollution from cold start either by hydrogenation or absorption of the acetylene using the Pd-based compound. The process should meet the envisaged EC legislation for levels of CO, HCs and NOx in the years 2000 and 2005.

Nitrogen Oxide Trap for I.C.E.

FORD GLOBAL TECHNOLOGIES INC. *European Appl.* 845,289A

A NOx trap for I.C.E. exhaust gases comprises a porous support loaded with (in wt.%): 6–15 Sr oxide; 0.5–5 Pt, Pd and/or Rh; 3.5–15 Zr and 15–30 sulfate. It traps NOx during lean burn operation and releases absorbed NOx when the O_2 concentration falls; the desorbed NOx is converted to N_2 and O_2.

Noble Metal Support

ASAHI KASEI KOGYO K.K. *World Appl.* 98/26,867A

A noble metal support comprises a Pd-free layer inside the support, and a layer where Pd is supported in a region > 100 μm deep from the outer surface of the support. It has high activity and resistance to wear and is useful as a catalyst for oxidation, reduction and hydrogenation, esterification of acrolein and/or methacrolein, or as a catalytic converter for car exhausts.

Preparation of High Octane Paraffin

TEXACO INC. *U.S. Patent* 5,744,667

A high octane paraffin for use as a blending component in gasoline is prepared by reacting a 5–10 C acceptor olefin and a 3–10 C donor paraffin (1), with different backbone structures, in the presence of a Pt catalyst supported on a Li neutralised large pore B β-zeolite. The catalyst contains 0.1–2 wt.% Pt and 0.05–2 wt.% B, to dehydrogenate a portion of (1).

Catalytic Reforming of Hydrocarbons

UOP *U.S. Patent* 5,755,956

Reforming a gasoline-range hydrocarbon feedstock to an aromatics-rich effluent stream, involves contacting it with a catalyst comprising a multigradient noble metal of Pt and surface-layer Ru, a non-acidic large-pore molecular sieve, and an inorganic oxide binder. The process has increased selectivity for the conversion of paraffins to aromatics and improved catalyst stability, particularly in the presence of S.

Hydrogenation Catalyst

MITSUBISHI CHEM. CORP. *Japanese Appl.* 10/71,332

A hydrogenation catalyst comprises a C support and Ru, Sn and optionally another Group VIII metal, uniformly distributed inside the support. The catalyst is used for the catalytic hydrogenation of carboxylic acids giving high yields of 1,4-butanediol and/or tetrahydrofuran, from maleic anhydride, maleic acid, etc., under relatively mild conditions.

Diesel Engine Catalyst

HINO MOTORS LTD. *Japanese Appl.* 10/76,159

A purification catalyst has a fine particle-like carrier comprising Rh, Pt, Ir, Pd, Au, Ag or Ru, with a grain size of 0.1–50 μm; a metallic oxide fine particle, such as Al_2O_3, TiO_2 or SiO_2; and an inorganic binder, such as sols of SiO_2 or Al_2O_3, etc. The rate of NOx reduction of exhaust gas from a diesel engine is improved.

Diesel Exhaust Purification Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appls.* 10/76,162–3

A catalyst for exhaust gas purification for diesel and lean burn engines, has a catalyst layer chosen from Rh, Pd and Pt, and a ceramic component selected from Si carbide, Si nitride and B nitride along with at least one rare earth element selected from lanthanum, neodymium, etc. The catalyst shows high temperature durability and excellent purification capacity for hydrocarbons, CO and NOx.

Exhaust Gas Purification from I.C.E.

TOYOTA CHUO KENKYUSHO K.K. *Japanese Appl.* 10/85,600

A catalyst, for the oxidation and purification of hydrocarbons contained in exhaust gas from I.C.E. comprises Zr oxide particles and a catalytic noble metal, with ≥ 50% of the latter being in a high oxidation state. Pt carrying hydroxide, obtained by adding Pt to Zr hydroxide, is also included. The purification capacity of SOF in a low temperature region is good and the oxidation of SO_2 and the formation of sulfates is suppressed.

Removal of NOx

KYOCERA CORP. *Japanese Appl.* 10/85,602

An oxide catalyst material for removal of NOx from exhaust gas contains 0.5–20 wt.% Pd oxide and oxides of Ga and Ni. The NOx contained in the exhaust gas is directly decomposed into N_2 and O_2 without the use of a reducer. The catalyst is used for the removal of NOx from exhaust gas from factories, power stations and motor vehicles.

Purification of Exhaust Gas

DENKI KAGAKU KOGYO K.K. *Japanese Appl.* 10/85,604

A catalyst, for purifying exhaust gas from I.C.E., comprises a catalyst component containing Si nitride and/or B nitride, Si carbide, Rh and Pt and/or Pd. The Si nitride and/or B nitride are in the Pt- and/or Pd-containing layer while the Si carbide is in the Rh-containing layer. The catalyst improves exhaust gas purification. Catalytic activity and endurance under a stoichiometric environment are also improved.

Hydrogenation of Aromatic Amines

BAYER A.G. *German Appl.* 1/96/41,688

A catalyst for the hydrogenation of aromatic amines to cycloaliphatic amines comprises an alkalised support impregnated with 0.05–10 wt.% Ru and Pd in a weight ratio of Ru:Pd of (1:30)–(30:1), and contains no halogen. Aromatic amines can be completely converted even at high catalyst loadings, with a high selectivity for primary cycloaliphatic amines, without addition of NH_3 and with no hydrogenolysis or methanation.

Hydrogen Peroxide Production

BASF A.G. *German Appl.* 1/96/42,770

The production of H_2O_2 solutions containing ≥ 2.5 wt.% H_2O_2 involves continuously reacting H_2 and O_2 on catalysts containing Pd as an active component. The reaction takes place in H_2O or 1–3 C alkanol on moulded catalyst bodies. The catalysts used have a long service life.

HOMOGENEOUS CATALYSIS

Aromatic Haloamino Compounds

NOVARTIS A.G. *European Appl.* 842,920A

A catalyst is comprised of a Rh, Ru, Ir, Pt or Pd catalyst modified with an inorganic or organic P compound with an oxidation state < 5, and a V compound. The catalyst is used in the preparation of aromatic haloamino compounds by hydrogenation of the corresponding halonitro compounds. Haloaminos are intermediates in the production of dyestuffs and pesticides. The reaction gives very high selectivity with few side products, high yields and short reaction times, at low pressures (5 bar) and temperatures (100°C).

Supported Phase Chiral Catalyst

CALIFORNIA INST. OF TECHNOLOGY *U.S. Patent* 5,736,480

A supported phase catalyst, with a metal selected from Rh, Ru, Ir, Pd, Pt, V, Pb, Sn and Ni, comprises an organometallic compound of chiral 2,2′-*bis*(diphenyl phosphino)-1,1′-binaphthyl (BINAP) solubilised in a solvent having two alcohol groups. Each phenyl group is at least monosulfonated. Also claimed is the use of the above catalyst in the asymmetric hydrogenation of 2-arylacrylic acids, especially dehydronaproxen. The catalyst system is soluble in highly polar solvents but not in non-polar solvents so the catalyst may be solvated on a solid catalyst support, facilitating easy separation from the product after synthesis.

Hydrosilation of Unsaturated Compounds

DOW CORNING CORP. *U.S. Patent* 5,756,795

The hydrosilation of unsaturated organic and Si compounds, such as Si hydrides, in the presence of a Pt compound or Pt complex catalyst, and a specific accelerator, such as 1,7-octadiyne or maleic anhydride, is described. The accelerators improve yields in the presence or absence of O_2 and are very effective in the hydrosilation of internal unsaturated bonds.

Platinum Complex Catalysts

RHONE-POULENC CHIM. *French Appl.* 2,750,349

Pt complexes with various olefin ligands are claimed for use as homogeneous and thermo-activatable catalysts in hydrosilylation reactions between silanes or siloxanes, and compounds with reactive unsaturated aliphatic and/or polar functional groups. The catalyst is stable at 30–40°C for long periods. The Si oil product is used for anti-adhesive coatings on fibres, taking dental impressions, adhesives, etc.

Selective Chlorine Component Removal

GES BESEITIGUNG VON UMWELTSCHAEDEN *German Appl.* 2/97/22,331

A catalyst for the selective hydrogenative removal of fluorochlorohydrocarbons and halones from gases comprises a carrier with a fixed active component of $Os_aRu_bX_cY_d$ (where X = Group VIII metal; Y = Group III or IV metal or rare earth metal; and a, b, c and d = 0–100, with $a + b \neq 0$). The catalyst is used for the removal of ozone-damaging Cl-containing components, such as FCHCs from gases evolved in FHC production. The catalyst has higher activity and longer life than the Pd/AlF_3 previously reported.

FUEL CELLS

Platinum Electrocatalyst for Fuel Cells

NE CHEMCAT CORP. *European Appl.* 827,225A

An electrocatalyst (1) comprises a skeleton alloy of Pt with Ga, V, Cr, Mn, Fe, Co, Ni or Cu. Also claimed is an electrode and its production comprising the electrocatalyst and a H_2O repellent binder, bound to a conductive and gas permeable support substrate. (1) is a cathode for proton exchange membrane or phosphoric acid type fuel cells and may also be a gas button cell diffusion electrode, etc. It has high activity and long term stability for O_2 reduction compared to conventional electrocatalysts.

Catalyst for Use in Fuel Cells

JOHNSON MATTHEY PLC *European Appl.* 838,872A

A catalyst, for use in gas diffusion electrodes for fuel cells, particularly PEMFCs, comprises a Pt-M alloy in intimate contact with Y, where M is one or more transition metal, Group IIIA or Group IVA metal, and Y is a bronze-forming element or oxide (M is not Ru if Y is WO_3; M is optionally two or more metals where one metal is Ru). A catalyst comprising Pt-Ru alloy alloyed with W is also claimed. The catalyst is tolerant of poisons and can be used as the electrocatalyst on the anode and the cathode.

Electrocatalyst Particles

UNIV. MASSACHUSETTS *U.S. Patent* 5,702,836

Particles for a fuel cell electrocatalyst for oxidising alcohols comprise an Fe oxide core with an outer Pt oxide shell. The electrocatalyst is colloidal, lightweight and cheaper to manufacture due to the non-Pt core.

Anode Catalyst for Fuel Battery

TOSHIBA K.K. *Japanese Appl.* 10/74,523

A catalyst for a fuel battery has Pt or fine Pt alloy particles for H_2 storage distributed on the surface of a conductive C powder carrier. A highly active anode is obtained and battery durability is improved.

Hydrogen Fuel Cell Accumulator

R. WOLLHERR *German Appl.* 1/96/44,864

A hydrogen fuel cell accumulator, for use in electric vehicles, comprises a polymer electrolyte membrane cell with a Ru catalyst, an air filter, a metal hydride storage unit, a small compressor and a thermoelectric heat exchanger. The H_2 from the hydride storage unit is converted electrochemically with O_2 from the air. The air is cleansed by passing through a filter. The accumulator is economical to produce.

ELECTRICAL AND ELECTRONIC ENGINEERING

Glass Circuit Substrate

CANON K.K. *European Appl.* 838,980A

A glass circuit substrate comprises a layer of Pd nuclei carrying a Pd-P plating layer. Also claimed is the production of a semiconductor device, by fabricating the above substrate, patterning the plating layers to define wiring and electrodes, and bonding IC chips to the electrodes. A wiring pattern can be formed by wet plating, without degrading the smoothness of the glass surface or the adhesion against external thermal effects. Adhesion to the substrate is enhanced, thus resistance to peeling is improved.

Magnetic Recording Medium

SHOWA DENKO K.K. *U.S. Patent* 5,731,070

A magnetic recording medium comprises a Si layer on a non-magnetic substrate and a layer comprising at least one Pt group metal or alloy, or C, with the Pt being partly silicified and the C being partly amorphous, both due to Si diffusion. An undercoat is formed over the Pt/C layer, followed by a magnetic layer and a protective overcoat. The medium, used for magnetic recording disks, has a high coercive force and squareness ratio which increases the magnetic recording density.

Palladium-Containing Thin Bonding Wire

NIPPON STEEL CORP. *Japanese Appl.* 10/83,716

A thin Au alloy wire for bonding the electrode of a semiconductor device and an external lead includes 0.005–1 wt.% Pd and 0.005–0.3 wt.% Mn, the remainder being impure Au. The wire improves corrosion resistance, ensures long-term reliability, improves junction properties and allows high density mounting.

Electrically Conducting Body

FURUKAWA ELECTRIC CO. LTD. *Japanese Appl.* 10/84,065

The body comprises an electrically conductive base carrying a Ni or Ni alloy foundation layer on its surface. Upon this is an interface layer of Pd or Pd alloy, 0.005–0.1 μm thick, carrying a monoatomic layer of Au or Au alloy. The member has excellent soldering properties and oxidation of the interface layer is prevented. It is used in diodes, transistors, etc.

TEMPERATURE MEASUREMENT

Temperature Sensor

HONEYWELL INC. *U.S. Patent* 5,726,624

A tubular temperature sensor for use in ovens at ~ 1000°F, has conductive strips of Pt-Ag alloy deposited on a rigid Al oxide substrate, with insulating glass layers over and between the conductive strips. A resistive temperature detector (RTD) is placed on one end region of the substrate and attached electrically to the conductive strips. Fibreglass sleeved wires are not needed and electrical connections can be made to the RTD in parts where the sensor is at high temperatures.

MEDICAL USES

Crosslinkable Silicone Dental Compound

ZHERMACK S.p.A. *European Appl.* 822,233A

A crosslinkable Si compound for use in dentistry comprises a crosslinkable Si polymer, a crosslinking agent, a Pt catalyst and a Na-Al zeolite. The composition remains stable under storage conditions, even at temperatures higher than those normally recommended. The Pt catalyst is protected by the zeolite against the action of potential contaminants.

Precious Metal Dental Alloy

BEGO BREMER GOLDSCHLAEGEREI *German Appl.* 1/97/19,677

A precious metal dental alloy contains Au, Ag, Pt, Pd and Mn, with the Ag, and preferably the Mn, content higher than the Pt content. The alloy is free from Cu, Sn, In, Mg and Ca. The use of the above Cu-free precious metal alloy is claimed as material for false teeth, bridges, crowns, etc., which may be covered with ceramic and supported by implants, etc. The alloy has high hardness (250 HV5) and strength, resists corrosion and tarnishing, and is free from toxic Cu.

Dental Palladium-Based Alloy

SUPERMETALL RES. PRODN. COMPLEX *Russian Patent* 2,092,603

An alloy for use in dentistry contains in wt.%: 45–70 Pd, 10–25 Au, 10–15 Cu and 10–15 Sn, at a Cu:Sn ratio of 1:1. The alloy is non-toxic, strong, has good flowability for casting complex dental prostheses, and good adhesion to a wide range of ceramic coatings.

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