NEW PATENTS

ELECTROCHEMISTRY

Water Electrolysis Cell

SHINKO PANTEC CO. LTD. *Japanese Appl.* 2000/026,986

A solid electrolyte type H_2O electrolysis cell has a porous metal film, comprising Ir or Ru metal or their oxides with lower anode overvoltage than Pt, placed on both sides of a solid electrolyte film. Electrolysis of H_2O is performed at 60–120°C. No increase in electrolytic voltage occurs even at low voltage or high current density, so the running cost for the H_2O electrolysis is greatly reduced.

Water Electrolysis Apparatus

TOTO LTD. *Japanese Appl.* 2000/042,551

A H_2O electrolysis tank has an electrode with a catalyst layer of Pt group metals or their oxides. Reverse electrical washing of the electrode is performed and the electric charge of the electrode is dissipated using an electric charge diffusion unit. Electrolysis and charge diffusion times are shortened. The catalyst layer is reliably maintained, as diffusion of the oxidation potential is prevented.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrolytic Plating Cell for X-Ray Mask Production

INT. BUSINESS MACHINES CORP. *U.S. Patent* 6,039,858

An electrolytic plating cell contains an electrolyte, flowing around the cell, a Pt anode and a B doped Si substrate, which acts as the cathode. A Pt plating inhibitor electrode is also connected as a cathode and acts as a scavenger during plating when an electrolytic current is generated in the cell. Only one side of the substrate is plated and enhanced accuracy of the produced X-ray mask is achieved.

Electroless Metal Plating

LEARONAL JAPAN INC. *Japanese Appl.* 2000/017,448

An electroless plating solution, for printed circuit boards in electronic components, includes a compound with a pH of ≤ 10 to provide cations. The compound comprises a complexing agent that does not dissolve Pd, Co or Ni on the surface of the object to be plated, and a reducer which is oxidised by Pd, Co or Ni. Etching or corrosion of the metal is thus prevented, and the destruction of organic resist is avoided. Long-term stability is obtained.

Electroless Plating Solution

DAIWA KASEI KENKYUSHO K.K. *Japanese Appl.* 2000/026,977

An aqueous solution used in electroless plating contains one or more H_2O soluble complexes of Pd, Au and Ag as the source for precipitation and a specified mercapto- or sulfide compound (or their salts), which have reducing and complex-forming characteristics. Easy control of the rate of precipitation is possible.

Processing of Waste Plating Solution

TOKYO TO. *Japanese Appl.* 2000/033,269

An apparatus for processing organic substances in waste electroplating solutions, has a quartz glass pipe with 1–10 wt.% Pd precipitated on a TiO_2 layer. Pd is precipitated by immersing the pipe in $PdCl_2$ solution (1) and irradiating with UV. The pH of (1) is adjusted to 4 by Na acetate. The amount of sludge is reduced and no oxidative chemicals are needed. O_2 or air can be blown smoothly on the catalyst surface, thus increasing the oxidation/reduction reaction rate.

APPARATUS AND TECHNIQUE

Measuring NOx Concentration

NGK SPARK PLUG CO. LTD. *European Appl.* 987,547

A gas sensor for measuring NOx concentration in I.C.E. has two pump cells (1) and (2), each with internal and external electrodes which directly face two flow passages (1a) and (2a), linked by a diffusion resistance. O_2 is pumped through (1a). Part of the internal electrode of (1) contains a Pt group element and Cu. The gas to be measured reacts inside (2a) and current, corresponding to concentration, flows between the electrodes of (2) through the O ion conductor.

Low Temperature Oxygen Sensor

PURDUE RES. FOUNDATION *World Appl.* 00/07,001

A highly sensitive O_2 sensor for I.C.E., which operates at < 300 K, comprises non-stoichiometric metal oxides, such as ferroelectric PZT materials, between two electrodes of Pt, Ag, Au, metal phthalocyanine or a conductive metal oxide. When an electric field is applied, an offset d.c. voltage (1) develops between the electrodes. The magnitude and direction of (1) depends on variations in O_2 concentration or partial pressure at one of the device electrodes.

Generator Plate for Ozone Production

QUANTUM ELECTRONICS CORP. *U.S. Patent* 6,024,930

An O_3 generator plate (1) of dielectric material (Al_2O_3 or SiO_2) is coated on one side with an electrode with a starburst pattern (a central stem with radiating arms) and on the other side with a second, larger, electrode. The electrodes of Ni-Cr are coated with Pd and a Pb-Sn alloy, and overcoated with Cu and Au or Ag. (1) can produce O_3 at h.f. (~ 40 kHz) low alternating voltages (< 2 kV).

Hydrocarbon Gas Sensor for Motor Vehicle Exhaust

RIKEN CORP. *Japanese Appl.* 2000/028,573

A gas sensor (1) for detecting hydrocarbon gas in motor vehicle exhaust or exhaust from combustion apparatus, even at high temperature, has a cermet hydrocarbon gas detection electrode (2) of Pt and Rh alloy and an O-ion conducting counter electrode of Pt configured in ZrO_2 solid electrolyte. (1) measures the electrical potential difference between (2) and the Pt counter electrode, or a Pt reference pole.

Gas Sensor for I.C.E.

ROBERT BOSCH G.m.b.H. *German Appl.* 1/98/33,087

A gas sensor (1) comprises a measuring electrode with an electrically-conducting Pt base layer, such as Pt cermet, covered by a sintered porous layer containing a noble metal in the pores. The base layer is applied in a galvanic bath. (1) is a modified Nernst-type lambda-probe which can be used in the gas stream of I.C.E. and can function at 1200±100°C.

Gaseous Oxygen Sensor for an Exhaust Duct

HONDA GIKEN KOGYO K.K. *German Appl.* 1/99/35,301

A gaseous O_2 sensor has electrodes of porous, gas permeable Pt, arranged eccentrically within housing. One side of the plate sensor has a detection surface receptive to O_2, and a cylindrical shield surrounds the sensor. The gas flow path is improved, with better resistance to oscillation and shockwaves in the exhaust duct. The sensor is used in industrial ovens, process vessels, fossil burning appliances, and particularly in I.C.E.

HETEROGENEOUS CATALYSIS

Alkenyl Acetates Synthesis

DAIREN CHEM. CORP. *European Appl.* 976,713

A catalyst, for the production of alkenyl acetates from olefins, acetic acid and O_2, is prepared by impregnating a support with a solution containing Pd in an oxidative state and another metal, such as Au, Cu, etc., also in an oxidative state. The metals are reduced to the metallic state by a gaseous reducing agent and impregnated with an alkali or alkaline earth metal solution, followed by drying. The catalyst has a highly active metal surface, with longer life.

Hydrogen Peroxide Synthesis

ENICHEM S.p.A. *European Appl.* 978,316

A catalyst for the direct synthesis of H_2O_2 from H_2 and O_2 comprises Pd, Pt, Ru, Ir and/or Rh, supported on an acid-activated C, functionalised with sulfonic groups. The acid function is directly bound to the catalyst surface and is not released into the reaction medium, which allows use of extremely low quantities of halides, operation without free acids and Pt group metal amounts < 3 ppb in the solution. The catalyst is stable, producing highly concentrated H_2O_2. The possible introduction of salts or acidity in downstream processes is minimised.

Acetal or Ketal Content Reduction

DEGUSSA-HUELS A.G. *European Appl.* 983,985

The content of acetal or ketal in a high alcohol reaction mixture, obtained by the hydrogenation of aldehydes or ketones to alcohols, is reduced by catalytic hydrogenation in the presence of a Pd or Ru catalyst supported on active C at 80–250°C in 0.5–30 MPa of H_2. The acetal or ketal content can be reduced, without alcohol decomposition, in acidic or neutral aqueous reaction mixtures, even those having high alcohol content and low acetal/ketal content.

Removal of Gaseous Sulfur Compounds

GOAL LINE ENVIRONMENTAL TECHNOLOGIES *World Appl.* 00/02,645

Gaseous S compounds (1) are removed from gaseous streams by contacting with a catalyst/sorber comprising a noble metal, such as Pt, and a metal oxide sorber selected from Ti, Zr, Hf, Ce, Al, Si or their mixtures, and optionally a modifier of an oxide of Ag, Cu, Bi, Sb, Sn, As, In, Pb, Au or their mixtures. (1) are captured at > 99.75% efficiency and with a very low pressure drop. (1) are mainly H_2S and SO_2 from flue gas desulfurisation. CO is also oxidised to CO_2.

Benzene Hydrogenation

PHILLIPS PETROLEUM CO. *U.S. Patent* 6,013,847

Benzene in a feedstock is hydrogenated using a Pt-containing hydrogenation catalyst in the presence of a small quantity of H_2O and an organic chloride to alleviate, or eliminate, catalyst deactivation due to the H_2O. The reaction zone may contain 20 wt.% benzene, H_2 and ≤ 30 ppm H_2O in the feedstream. The catalyst functions at 100–300°F.

Isomerisation of Naphtha Feedstock

UOP L.L.C. *U.S. Patent* 6,015,932

Isomerisation of a naphtha feedstock (1) to an isoparaffin-rich product is performed at 40–250°C in the presence of a solid strong-acid catalyst comprising an anion-modified metal oxide and a Pt(0) group metal component. The deactivated catalyst can be reactivated, by contact with a liquid-phase hydrocarbon stream containing dissolved H_2 at a temperature at least 20°C lower than the isomerisation temperature. (1) can be selectively upgraded to high octane gasoline components.

Waste Gas Purification Catalyst

CATALER IND. CO. LTD. *Japanese Appl.* 2000/015,101

A catalyst for the removal of NOx, CO and HC from waste gas and for the purification of waste gas in I.C.E. contains a NOx occlusion material (1) of a porous oxide carrier, of alkali, alkaline earth and/or rare earth metals. It carries a Rh/ZrO_2 catalyst on the upstream side of the emission. A second catalyst carrying noble metals is downstream of the emission. High NOx purification occurs at the first stage and S poisoning of (1) is suppressed. A high purification rate and high endurance can be obtained.

Purification of Crude Aromatic Dicarboxylic Acids

COSMO SOGO KENKYUSHO K.K. *Japanese Appl.* 2000/037,633

A catalyst (1) is claimed for the purification of crude aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, etc. It comprises Pt group metals supported on activated C, which has surface area of ≥ 800 $m^2 g^{-1}$, S content of ≤ 1000 ppm, total pore volume of ≥ 0.6 ml g^{-1} and macropores of pore volume of ≥ 0.2 ml g^{-1}. The poisoning of (1) by metals is prevented and its life span is extended. (1) is used in the manufacture of polyester resins.

Nitrogen Dioxide Selective Absorbent

KOBE STEEL LTD. *Japanese Appl.* 2000/051,654

A selective absorbent for removing NO_2 in controlled atmospheres such as residential areas, road tunnels and underground car parks, comprises a ruthenate on a carrier of non-basic metallic oxide. Selective absorption and NO_2 removal is carried out efficiently at high levels for a long period of time. NO and other oxides present in low concentration are not absorbed or oxidised.

Exhaust Gas Purification Catalyst

NISSAN MOTOR CO. LTD. *Japanese Appl.* 2000/051,700

A catalyst for purifying exhaust gas has an integrated structure with a layer supporting catalytic constituents including a perovskite compound oxide (1), Al_2O_3 and Pd. (1) has formula $A_xNi_yO_z$, where A = La, Ce and/or Ba; $y = 1.0$; $0.01 \leq x < 0.1$; z = number of O atoms needed to satisfy the valence of each constituent. The catalyst removes hydrocarbons, CO and NOx at low temperatures and has improved durability at high temperatures.

Catalyst Structure for Exhaust Gas Purification

NISSAN MOTOR CO. LTD. *Japanese Appl.* 2000/051,707

A catalyst structure for use in the exhaust gas purifier of an I.C.E. includes a monolith carrier containing a hydrocarbon-adsorbent zeolite layer, and a Pd, Pt and Rh catalyst layer on the carrier. The weight ratio of the adsorbent:catalyst on the carrier is 9:1–1:4. The Pd layer has excellent low temperature activity and purifies hydrocarbon desorbed from the zeolite. The Pt added to the catalyst is poison resistant and the Rh metal can suppress catalyst reduction.

Hydrodeazotisation of Aromatic Compounds

CENT. NAT. RECH. SCI. INST. RECH. SUR. CATALYSE *French Appl.* 2,783,252

The hydrodeazotisation and hydrogenation of petroleum aromatic cuts, of aromatic content 5–70%, boiling range 90–500°C, and with N and S contamination levels of 1–1000 ppm each, are claimed. This involves contacting with H_2 in the presence of a 0.1–2% Pt/ZrO_2 catalyst which contains compounds highly resistant to S and N. The process eliminates N compounds, particularly pyrrole derivatives, and improves the stability of petroleum cuts, such as diesel, petrol and kerosene.

Catalysts for Vinyl Acetate Production

CELANESE CHEM. EUROPE G.m.b.H. *German Appl.* 1/98/34,569

Pd-based catalysts for vinyl acetate monomer production from acetic acid, ethylene and O_2 are made by impregnating a support with a Pd salt and alkali metal compounds, and with Hf compound(s) at the same time as, or after, Pd-impregnation. This is followed by drying at ≤ 160°C without calcining. The method is simple, giving improved activity, selectivity and long-term stability. Hf doping improves Pd bonding to the support and makes calcination unnecessary.

HOMOGENEOUS CATALYSIS

Manufacture of Diene Compounds

TAKASAGO INT. CORP. *European Appl.* 982,286

Diene compounds (1) are prepared by reacting 2-substituted 1,3-butadienes with terminal olefins in a hydrophilic solvent in the presence of a Ru catalyst. A C=C double bond is catalytically formed in a regioselective manner and 4-methyl-5-hexan-1-al is produced by subsequent hydrolysis. (1) can be used to prepare terpenes which are useful intermediates for pharmaceuticals, or to produce aldehydes for perfumes. High yields of (1) at low cost are obtained.

Preparation of Carboxylic Acid Compounds

ALBEMARLE CORP. *World Appl.* 00/02,840

Pd-catalysed arylation of an olefin with aryl halide and/or substituted aryl halide is conducted in a specified media. After a special procedure for acid or base phase separation, Pd-catalysed carbonylation of the olefinically-substituted aromatic intermediate proceeds using CO and H_2O or an alcohol to form (substituted) arylalkylcarboxylic acids and esters, such as profen-type compounds. The process allows large-scale industrial production of automatically-substituted aliphatic carboxylic acids and their acid derivatives. High-yield, high purity products are obtained.

Catalyst Composition

IND. TECHNOLOGY RES. INST. *U.S. Patent* 6,010,975

A catalyst for preparing a 3-pentenoic ester (1) from butadiene and an alcohol comprises one of: Pd acetate, Pd acetylacetonate or Pd hexafluoroacetyl acetonate; and cocatalysts of a bidentate phosphine and a bulky benzoic carboxylic acid. (1) is a starting material for preparing 5-formylvalerate esters, important intermediates for caprolactam production. High yield and selectivity are obtained without constant addition of cocatalyst, as esterification is avoided.

Modified Pyrimidine Nucleosides

NEXSTAR PHARM. INC. *U.S. Patent* 6,020,483

Preparation of a pyrimidine nucleoside modified at the 5- or 6-position of the pyrimidine ring comprises reacting a pyrimidine starting material with a functionalised alkene in the presence of a Pd catalyst, such as $Pd_2(dba)_3$ (dba = dibenzylideneacetone). The process is used to prepare modified nucleosides and nucleotides, used as antiviral, antibacterial, antifungal or antineoplastic agents.

Continuous Preparation of Diaryl Carbonates

GENERAL ELECTRIC CO. *U.S. Patent* 6,034,262

A continuous flow process for converting aromatic hydroxy compounds to diaryl carbonates involves reaction with O_2 and CO in the presence of a Group VIII metal (Pd) or compound catalyst, inorganic and organic cocatalysts, and a hexaalkylguanidinium bromide (1) or chloride, preferably bromide. Pb oxide and (1) are added separately into the reactor. Commercial scale production of diphenyl carbonates is allowed by direct carbonylation.

Preparation of Formyltriarylamines

TOSOH CORP. *Japanese Appl.* 2000/007,627

The preparation of formyltriarylamines comprises: acetalising a halogenated benzaldehyde with an alcohol in the presence of an acid catalyst; reacting the acetal compound obtained with a diarylamine in the presence of a Pd compound catalyst and a base; and then hydrolysing the acetal group of the compound obtained. Formyltriarylamines are raw materials for electrophotographic photoreceptors.

(Hetero)aryl-Substituted Olefins

STUDIENGESELLSCHAFT KOHLE m.b.H. *German Appl.* 1/98/43,012

(Hetero)aryl-substituted olefins are prepared by the Pd-catalysed reaction of a (hetero)aromatic halide, sulfonate or diazonium halide with an olefin at 60–180°C, in the presence of a solvent and a base, but in the absence of phosphonium salts (1) and phosphanes (2). The catalyst is a specific Pd(II) compound used in the presence of a N-containing additive. The process is simple, inexpensive, and the absence of (1) and (2) allows smooth Heck reactions with only small amounts of catalyst.

FUEL CELLS

Treating Feed Gas for Fuel Cells

GENERAL MOTORS CORP. *European Appl.* 987,054

A feed gas containing CO and H_2, is treated by reacting the CO with O_2 in the presence of an Ir catalyst dispersed on a refractory inorganic oxide carrier. A H_2-rich gas stream is produced with CO content reduced to a level suitable for use in a fuel cell. The catalyst is activated by contact with H_2 and MeOH gases at increased temperatures for a time sufficient to cause the dominant XPS peak of Ir to shift towards a value which corresponds to metallic Ir.

Bipolar Collector for a Fuel Cell

SORAPEC S.A. *World Appl.* 00/05,775

A bipolar collector for a SPEFC has metal cylinders which extend through a polymer plate into the electrodes. The cylinders are made of stainless steel which project by 0.1–0.3 mm from the polymer plate, and the projecting portions are covered with a cathodically deposited thin film of a Pt group metal or Au. The collector has excellent conductivity, which allows fuel cell operation at high current densities. It has low weight and low production costs.

Catalytic Ink for Fuel Cells

DEGUSSA-HUELS A.G. *German Appl.* 1/98/37,669

A catalytic ink, useful for the production of membrane electrode assemblies for fuel cells, comprises a dispersion of C particles and an organic Pt, Pd, Rh, Ru and/or Ir complex in a solution of a proton conducting polymer (ionomer). The coating is dried on a gas diffusion electrode for a PEFC, so the ionomer and substrate are not damaged and the complex is decomposed to form finely divided Pt group metal particles in a zero oxidation state.

ELECTRICAL AND ELECTRONIC ENGINEERING

Polymer Thick Film Conductor

E. I. DU PONT DE NEMOURS & CO. *European Appl.* 987,333

A polymer thick film conductor composition comprises conductive metal particles containing 0.1–5 wt.% of a finely divided powder of Pt group metals or their mixtures. Also included is a modified graphite (1), a thermoplastic polymer and optionally a surfactant. Graphite and/or metallised graphite combined with a surfactant may replace (1). The film is used in printing, sensing and in biosensors.

Soft Magnetic Films

MATSUSHITA ELECTRIC IND. CO. LTD. *European Appl.* 991,087

Soft magnetic thin and multilayered films (1) contain Fe, at least one element selected from Groups IVA, VA and VIA, and Pt and/or Pd. A multilayer film comprising soft magnetic films and double layered films of soft magnetic thin film and Si thin film are also claimed. (1) are used in TV antenna, cables with interference restrainers, noise filters, and magnetic heads, giving reduced noise in electronic equipment. The devices are smaller and thinner.

High Purity Ruthenium Sputtering Target

JAPAN ENERGY CORP. *World Appl.* 00/04,202

A high purity Ru sputtering target, suitable for forming semiconductor thin film, is prepared by adding a crude Ru powder to a NaOH solution, then bubbling Cl_2- and O_3-containing gases into the mixture to form RuO_4. The RuO_4 is then absorbed by a solution of HCl or HCl and NH_4Cl and evaporated to dryness. The resulting Ru salt is roasted in H_2 to give a high purity Ru powder, containing $\leq$ 100 ppm each of C, O and Cl. The targets are made by hot pressing.

p-Type Electronic Devices

FURUKAWA ELECTRIC CO. LTD. *Japanese Appl.* 2000/021,811

A *p*-type electrode (1) containing a Group III–V compound semiconductor has its surface sequentially laminated with Pt, Ni and Au layers. (1) has excellent adhesion and ohmic characteristics at high temperature. Contact resistance during connection with Au lead wire is reduced. (1) is used in electronic devices, such as LEDs, laser diodes, photodiodes, phototransistors, HBTs, FETs and HEMTs.

Cobalt-Platinum Sputtering Target

HITACHI METALS LTD. *Japanese Appl.* 2000/038,660

A Co-Pt sputtering target for manufacturing recording media such as hard disks for computers, also includes Ni or a Group IVA, VA or VIA element. The magnetic anisotropic and coercive force of the recording layer are increased, giving high density recording.

The New Patents abstracts have been prepared from material published by Derwent Information Limited.