

# NEW PATENTS

## ELECTROCHEMISTRY

### Rhodium Sulfide Electrocatalyst

DE NORA S.p.A. *U.S. Patent* 6,149,782

A catalyst for electroreduction of O<sub>2</sub> in industrial electrolyzers comprises Rh sulfide coated on one side of a gas diffusion electrode. The catalyst is highly resistant towards corrosion and poisoning by organic species. It is particularly suitable for use in aqueous HCl acid electrolysis, when technical grade acid containing organic contaminants is employed.

## PHOTOCONVERSION

### Tandem Cell for Photoelectrochemical Cleavage

ECOLE POLYTECHNIQUE FEDERALE LAUSANNE  
*World Appl.* 01/02,624

A highly efficient tandem cell for cleaving H<sub>2</sub>O or seawater to H<sub>2</sub> and O<sub>2</sub> by visible light comprises two superimposed electrically-connected photocells. The photoactive material in the top cell, in contact with aqueous electrolyte, absorbs blue and green light, generating O<sub>2</sub> and protons from the H<sub>2</sub>O. The bottom photocell contains a Ru polypyridyl sensitiser and converts yellow, red and near IR light (from the top cell) to reduce the protons to H<sub>2</sub>. The H<sub>2</sub> evolution is catalysed by a thin coating of Pt, Pd, Ru, Rh, Ir, Ni, a poly- or heteropolyacid of W, V, etc., on the cathode.

### Photobiomolecular Deposition of Metallic Particles

UT-BATTELLE LLC *U.S. Patent* 6,162,278

Photobiomolecular deposition of metal nanoparticles uses a sample comprising an electron donor (H<sub>2</sub>O), a protein-chlorophyll photosystem I unit (1) and a metal precursor, reducible by (1), selected from Pt, Pd, Ru, Os, Ir, Au, Ag, etc., preferably [PtCl<sub>6</sub>]<sup>2-</sup> or [OsCl<sub>6</sub>]<sup>2-</sup>. Light induces single electron emission in (1), reducing a single atom of the metal precursor to form a (1)/metal complex, which is then deposited on a substrate, such as Au, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, glass, etc.

### Photolytic Purification of Contaminated Gas

KSE INC. *Canadian Appl.* 2,307,271

A contaminated gas stream is purified by passing it through photolytic and photocatalytic stages, simultaneously irradiating it with UV. The photocatalyst contains 0.01–10 wt.% of Pt and/or Pd and oxides of Ti, Si, Zr, etc. Partially oxidised species and remaining contaminants are converted to less harmful products. A synergistic effect is obtained by the process.

### Photocatalyst Film for Purifying Water

OSAKA PREFECTURE *Japanese Appl.* 2001/038,217

A photocatalytic film for purifying H<sub>2</sub>O comprises W oxide with a Pt, Ru or Ru oxide coating. During H<sub>2</sub>O purification nitrogen oxide is removed and CO<sub>2</sub> decomposed. Acetic acid decomposition is possible. Catalyst activity is maintained; harmful byproducts are not formed. 'Natural' photoirradiation is sufficient.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Replenisher for Palladium Electroplating Baths

LUCENT TECHNOLOGIES INC. *European Appl.* 1,057,902

Pd tetraamine sulfate (1), used for replenishing Pd electroplating baths, is prepared by contacting Pd with excess nitrate solution, distilling the Pd nitrate solution produced at ≤ 115°C, followed by adding Pd sulfate and NH<sub>4</sub>OH. Pd concentrations in the plating bath within 5–10 wt.% of the recommended level is maintained. As (1) is electrochemically inert, corrosion and oxidation of bath components is minimised.

### Electroless Deposition of Conductive Material

INT. BUSINESS MACHINES CORP. *World Appl.* 00/79,023

Electroless deposition of a conductive material onto a substrate involves pressing the surface of a stamp wetted by ink containing a PdCl<sub>2</sub>-containing catalyst in polar and molecular form (in aqueous or ethanolic solution) onto the substrate. The substrate is preconditioned. On separation of stamp and substrate at least part of the catalyst layer is left on the substrate. The polar catalyst gives high resolution for printing.

### Black Ruthenium Plating Solution

NIKKO GOULD FOIL K.K. *World Appl.* 01/11,113

A black Ru plating solution contains Ru sulfate, sulfamic acid, a thio compound and a sacrificial oxidising agent to prevent the decomposition of the thio compound due to anodic oxidation. A stable black plating is obtained by inhibiting the decomposition of the thio compound (added as a colour former). The plating obtained can be easily controlled, has high gloss, good adhesion to a substrate, and excellent resistance to corrosion and abrasion.

### Palladium Alloy Plating Solution

NISSHIN KASEI K.K. *Japanese Appl.* 2000/303,199

A plating solution for electric and electronic components comprises (in g l<sup>-1</sup>): 1–50 Pd soluble salt, 0.01–50 Cu salt, 50–500 electroconductive compound, 0.01–40 pyridine compound and 0.001–2 soluble semimetal compound. The metal contents are 40–90 wt.% Pd and 1–60 wt.% Cu. The plated layer is uniform, has good corrosion resistance and good germicidal action. Crack formation is prevented.

### Electroless Pd-Mo Alloy Plating

NIPPON KOJUNDO KAGAKU K.K.

*Japanese Appl.* 2001/003,179

An electroless Pd-Mo alloy plating solution is made by adding a Mo compound to a Pd plating solution comprising a Pd compound; a reducer (acid or salts of formic or (hypo)phosphorous acids); B hydride and amine boranes; a complexing agent (NH<sub>3</sub> or amines); a buffer (carbonic acid or borates); and stabilisers (S or Pb compounds). The Pd-Mo layer has excellent wire bonding and ball solder bondability.

## APPARATUS AND TECHNIQUE

### Determining a Measurable Quantity by a Solar Cell

FRAUNHOFER GES. FOERDERUNG ANGEWANDTEN  
German Appl. 1/99/35,180

A measurable quantity (Q) is determined by a solar cell coated with an indicator, such as Ru and/or a phthalocyanine complex, the fluorescence or spectral response of which depends on (Q), in the presence of natural or artificial light. The method can be used to determine pH, pressure, temperature or humidity, or to determine the presence and/or concentration of a gaseous, liquid or solid substance, especially O<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, etc., in medicine, biotechnology, etc.

## HETEROGENEOUS CATALYSIS

### Converting Particulate Matter in Gasoline Exhaust

JOHNSON MATTHEY PLC  
European Appl. 1,077,078

Treatment for particulate matter (PM) trapped on a filter in the exhaust of a stoichiometrically operated gasoline engine is described. The method enables use of the continuously regenerating trap concept and high S content fuels. A plasma generator converts H<sub>2</sub>O in the exhaust into an oxidant to oxidise NO and/or N<sub>2</sub> in the exhaust to NO<sub>2</sub>. The NO<sub>2</sub> is then used to combust the PM. An oxidation catalyst of Pt, Pd or their mixture is present. NO oxidation to NO<sub>2</sub> by plasma occurs without SO<sub>2</sub> oxidation to SO<sub>3</sub>.

### Heterogeneous/Enantioselective Hydrogenation

SOLVIAS A.G.  
World Appl. 01/00,545

Heterogeneous/enantioselective hydrogenation of prochiral organic  $\alpha$ -keto compounds uses Pt as the catalyst in the presence of a soluble/immobilised chiral aromatic N base with N atom(s) adjacent to a stereogenic centre. The carbonyl group in the  $\alpha$ -ketoacetals is hydrogenated enantioselectively with high selectivity, yield and optical yield. The optically active  $\alpha$ -hydroxyacetals produced are intermediates of natural compounds, pharmaceuticals and pesticides.

### Hydrogenation Catalyst for Aromatics Feed Stream

UNITED CATALYSTS INC.  
World Appl. 01/09,268

A hydrogenation catalyst for use in aromatics feed streams which contain S comprises 100 ppm–5 wt.% each of Pt and Pd catalyst on an inert Al<sub>2</sub>O<sub>3</sub> carrier containing  $\geq 50\%$   $\theta$ - or  $\delta$ -Al<sub>2</sub>O<sub>3</sub>. The Pt and Pd is combined with the inert Al<sub>2</sub>O<sub>3</sub> followed by calcining and reduction. The catalyst has high activity and selectivity, and is tolerant of low to medium S levels.

### Hydrogenation Treatment of Gas Oil

COSMO OIL CO. LTD.  
World Appl. 01/15,805

A catalyst for hydrogenating gas oil, for production of straight-run gas oil and blends with hydrocarbon oils, is described. It comprises 0.1–10 mass% Pt, 0.1–20 mass% Pd and 0.05–1.2 mass% halogen supported on an inorganic oxide containing Al<sub>2</sub>O<sub>3</sub> of crystallite diameter 20–40 Å. A high-quality oil containing  $\leq 10$  ppm S with low aromatic content is obtained. The catalyst can be repeatedly regenerated.

### Regenerating Sulfur Poisoned Diesel Catalysts

JOHNSON MATTHEY PLC  
World Appl. 01/19,500

A diesel engine comprises a combustion management unit and an exhaust gas treatment system without a NO<sub>x</sub> trap. The system contains a Pt group metal catalyst. The combustion management unit can modulate the air:fuel ratio ( $\lambda$ ) to 0.90, or preferably to 0.95 or richer when release of significant quantities of S-containing species from the catalyst components occurs. The catalyst is thus regenerated.

### Preparation of 2-Phenyl Ethanol

COUNCIL SCI. IND. RES.  
U.S. Patent 6,166,269

The preparation of 2-phenyl ethanol, useful for perfumes, detergents, etc., and for industrial manufacture of styrene, phenylethyl ester, phenylacetaldehyde, etc., involves hydrogenating styrene oxide in an organic solvent over a supported pgm catalyst, such as 1% Pd/C, at pH 12–13 and temperature 40–120°C. NaOH is used as a promoter. This method avoids use of diethyl ether, ethylene oxide and AlCl<sub>3</sub>. After reaction the catalyst is separated. More than 99.5% of the styrene oxide is converted to 2-phenyl ethanol with 99.9% selectivity under milder conditions.

### Direct Catalytic Production of Hydrogen Peroxide

HYDROCARBON TECHNOL. INC.  
U.S. Patent 6,168,775

A supported noble metal catalyst (as an aqueous slurry) of Pd in combination with Pt, Au, Ir, Os, Rh and/or Ru is used for the direct catalytic production of H<sub>2</sub>O<sub>2</sub> from H- and O-containing feedstreams. The support (particulate), such as C black, total surface area 50–500 m<sup>2</sup> g<sup>-1</sup>, carries 0.1–10 wt.% noble metal crystals of sizes 1–100 nm. The metal crystals have a 110 and/or 220 phase exposition and the metal atoms (Pd) are in a linear alignment pattern on the metal crystals. H<sub>2</sub>O<sub>2</sub> is continuously removed. The used catalyst can be recycled. The catalyst permits the process to use lower safer H<sub>2</sub> concentrations in O<sub>2</sub>.

### Highly Loaded Palladium Three-Way Catalyst

FORD GLOBAL TECHNOL. INC.  
U.S. Patent 6,187,709

A lowered light-off temperature for a highly loaded Pd-containing three-way automotive catalyst during cold-start is claimed. The catalyst is subjected to a flow of an oxidising gas after engine shut down for a period of time while being held at  $\geq 450^\circ\text{C}$ . The oxidising gas contains  $\geq 0.85$  vol.% O<sub>2</sub>. The catalyst comprises  $\geq 100$  g Pd per ft<sup>3</sup> support material and is the only catalyst in the exhaust system of the vehicle.

### Catalyst for Butane Conversion

PHILLIPS PETROLEUM CO.  
U.S. Patent 6,191,064

A catalyst useful for the conversion of *n*-butane to butenes for producing BTX (benzene, toluene and xylene) is claimed. It is prepared by impregnating Al<sub>2</sub>O<sub>3</sub> with Sn, followed by steam treatment, impregnation with a Pt compound, treatment in air at a calcining temperature and finally chlorination. The catalyst increases the production of BTX and has a greater selectivity for the production of isobutylene.

## HOMOGENEOUS CATALYSIS

### Making Late Stage MRSA Carbapenem Intermediates

MERCK & CO. INC. *World Appl.* 01/00,624

A method for making late stage MRSA carbapenem intermediates via one-pot nitromethylation-allylation involves reacting a carbapenem with a C acid in the presence of a base. This is followed by Pd-catalysed substitution of the resulting allyl compound with a nucleophile in the presence of a phosphine or phosphite ligand. The intermediates are used as antibacterial agents against Gram positive and Gram negative bacteria. This method avoids disadvantages associated with the Stille coupling and Wittig methods.

### Catalysts for Asymmetric Synthesis

BOEHRINGER INGELHEIM PHARM. INC.

*World Appl.* 01/18,012

Triphenylphosphines and triphenylarsines having an *ortho*-amidine group (1) are useful as chiral bidentate ligands in catalysts for asymmetric syntheses, such as Heck reactions or hydroformylation. Specific enantiomers of compounds are synthesised by using Pt, Pd, Rh, Ru, Ir, etc., catalysts and a phosphino- or arsenoamidine ligand. The chiral ligands can be fine tuned for a particular asymmetric synthesis by replacing a single substituent. (1) gives higher optical purities than BINAP or dba.

### Bisalkoxycarbonylation of Olefins

DAICEL CHEM. IND. LTD.

*U.S. Patent* 6,159,891

A catalyst for efficient bisalkoxycarbonylation of olefins, comprises a Pd halide and a novel phosphine chalcogenide ligand. The corresponding succinate derivatives may be obtained from olefin in high yields under moderate conditions. The reaction may be performed in batch, semi-batch or continuous systems, and reaction products are readily isolated and purified.

### Organofunctional Alkyldialkoxysilane Preparation

CROMPTON CORP.

*U.S. Patent* 6,166,238

Organofunctional alkyldialkoxysilanes for use as coupling agents, adhesion promoters, organic polymers, etc., can be prepared by adding an olefin to a hydroalkyldialkoxysilane. The reaction is performed at elevated temperature in the presence of a Pt catalyst, such as H<sub>2</sub>PtCl<sub>6</sub> or a Pt vinylsiloxane. The formation of hydrosilation byproducts is minimised, and lower molar excesses of the olefinic reactant can be used, due to their reduced isomerisation.

### Production of Diaryl Carbonates

GENERAL ELECTRIC CO.

*U.S. Patent* 6,172,254

Diaryl carbonates are prepared by contacting a hydroxyaromatic compound(s), such as phenol, with O<sub>2</sub> and CO in the presence of a catalyst system. The catalyst comprises a Group VIII B metal (preferably Pd); an alkali metal or alkaline earth metal halide (preferably NaBr); and a promoter (at least one 2–8C aliphatic or 7–10C aromatic mono- or dinitrile, preferably acetonitrile or adiponitrile). The promoter maximises the effectiveness of the inexpensive halide.

## Preparation of Amines

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

*German Appl.* 1/99/33611

Amines are prepared by the reductive amination of aldehyde or ketone with a primary or secondary amine or NH<sub>3</sub> in the presence of H<sub>2</sub> and a homogeneous catalyst system. The catalyst system comprises metal atom-ligand complex(es) selected from Pt, Pd, Rh, Ru, Ir and Ni, and specific mono- or bidentate, achiral and/or chiral P-containing ligand(s). The aminations can take place under mild conditions giving amines in high yields at a high amine:alcohol ratio.

## FUEL CELLS

### Methanol Reforming Catalyst

DEGUSSA-HUELS A.G.

*European Appl.* 1,063,011

A catalyst for steam reforming MeOH for use in a vehicle fuel cell contains a Pd-Zn alloy and Zn oxide as the catalytically active component. These are deposited on a support of Al oxide, Al silicate, Ti oxide and/or zeolites. Also claimed is a process for the production of an alloyed catalyst. The catalyst has high selectivity and specific H<sub>2</sub> productivity.

### Electrocatalyst for Fuel Cells

DMC<sup>2</sup> DEGUSSA METALS CATALYSTS CERDEC A.G.

*European Appl.* 1,079,452

An electrocatalyst for use in the production of fuel cells comprises C black carrier containing > 4000 ppm H, and Pt or multimetallic doped or alloyed Pt as the catalytically active component. A gas diffusion electrode for the cathode or anode side of a membrane fuel cell contains both a porous catalyst layer on a hydrophobic conducting substrate material and the electrocatalyst. The catalyst has a high dispersion of metal particles on the carrier and high activity during testing the electrochemical system.

### Water Gas Shift Reaction Catalyst

MATSUSHITA ELECTRIC WORKS LTD.

*World Appl.* 01/03,828

A water gas shift reaction catalyst is formed by supporting at least Pt on a metal oxide support. The catalyst is used to remove CO from H<sub>2</sub> gas which is to be used in a fuel cell electricity-generating system. O<sub>2</sub> with the CO removed is then supplied to the fuel cell for electricity generation. The catalyst removes CO in H<sub>2</sub> gas with good efficiency over a wide temperature range.

### Platinum Films for Fuel Cell Electrodes

UT-BATTELLE LLC

*U.S. Patent* 6,136,704

A porous Pt metal film is formed by reactive sputtering of a PtO<sub>2</sub> layer in an O<sub>2</sub>/inert gas over at least part of a substrate to form a low density hexagonal PtO<sub>2</sub> crystalline phase. The PtO<sub>2</sub> film is then reduced to form a porous metal Pt film with a Pt metal density of 15–40%. The resulting films are used in making electrodes for fuel cells, batteries and sensors. The method involves few processing steps, thus reducing the manufacturing costs of the films.

## Carbon Monoxide Resistant SPEFC Catalysts

TANAKA KIKINZOKU KOGYO K.K.

*Japanese Appl.* 2001/015,121–122

Catalysts for a SPEFC contain Pt, Ru and Mo on C powder supports in molar ratio 1:(0.25–1):(0.2–0.5); Pt, Ru and W on C powder supports in molar ratio 1:(0.25–2):(0.25–0.5); and Pt and W on C powder supports in molar ratio (9–4):(1–4). The catalysts have high CO poisoning resistance properties and are excellent for use in electrode batteries.

## Solid Polymer Electrolyte Fuel Cell

AISIN SEIKI K.K.

*German Appl.* 1/00/36,981

A SPEFC comprises an electrode catalyst dispersed in a cellular dispersion layer, forming a gas diffusion layer. The catalyst comprises Pt, Pt alloy or C dispersed in the pores of a flat element of C fibre material, metal or sintered C. The design improves gas permeability and electrical conductivity, and provides a uniform distribution of catalyst over the gas diffusion layer.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Treatment for Glass Fibre-Braid Electrical Wire

DOW CORNING TORAY SILICONE

*European Appl.* 1,072,565

A treatment agent for a glass fibre-braid coated electrical wire comprises a diorganopolysiloxane (1) with a viscosity of 100–100,000 mPa·s at 25°C which contains at least two alkenyl groups per molecule. It also comprises an optional organopolysiloxane resin, a pgm catalyst (containing pgm in 0.1–500 wt. parts per 1,000,000 wt. parts of (1)), an inorganic filler and an organotitanium compound. The composition permeates into the glass fibre-braid, binding glass fibre-braid and glass fibres well without surface tackiness.

### Electrode for Storage Capacitor

INFINEON TECHNOLOGIES A.G. *World Appl.* 01/01,462

An electrode for a storage capacitor, useful for DRAM, is produced by forming catalytically active terminal areas (1) of noble metal or conductive noble metal oxide and catalytically inert insulation area(s). Organometallic noble metal compound(s) are applied selectively to the substrate at 0–120°C to form (1). In an example, Pt(PF<sub>3</sub>)<sub>4</sub> was deposited. The process avoids the need for direct structuring of electrode material, which is often difficult to etch.

### Use of Palladium in Integrated Circuits

MICRON TECHNOLOGY INC.

*U.S. Patent* 6,159,769

A semiconductor is formed by applying Pd layer(s) on electrical contact point(s) of a substrate and disposing an unset, conductive polymer bump on the Pd layer(s). The connections are flexible during thermal expansion and contraction, thus reducing failure rate of semiconductor assemblies during burn-in and use. Flip-chip type semiconductor dies, Si wafers and printed circuit boards can be made by this method.

## High Coercivity Iron Platinum-Silicon Nitrides

NAT. SCI. COUNCIL

*U.S. Patent* 6,183,606

A high coercivity FePt-Si<sub>3</sub>N<sub>4</sub> granular composite thin film, used as a magnetic recording media, is produced by magnetron co-sputtering of FePt and Si<sub>3</sub>N<sub>4</sub> targets on a low temperature substrate, followed by annealing in a vacuum. A post-annealed FePt-Si<sub>3</sub>N<sub>4</sub> film is granular, has saturation magnetisation (M<sub>s</sub>) > 375 emu cm<sup>-3</sup> and in-plane coercivity (H<sub>c</sub>) > 2000 Oe. The film has high coercivity, a magnetic easy-axis parallel to the film plane and improved resistances to oxidation, corrosion and wear.

## Dielectric Capacitor for Ferroelectric Memory

SONY CORP.

*Japanese Appl.* 2000/349,245

A dielectric capacitor, for nonvolatile ferroelectric memory, has an upper electrode with two metals M<sub>I</sub> and M<sub>II</sub> in an O-containing layer. The layer contains, as M<sub>I</sub>: Pt, Pd, Rh, Ru or Ir; as M<sub>II</sub>: transition metal of Hf, Ta, Zr, Nb, V, Mo, W or rare earth elements; and O expressed by M<sub>Ia</sub>M<sub>IIb</sub>O<sub>c</sub>, where 90 ≥ a ≥ 4, 15 ≥ b ≥ 2, c ≥ 4, such that a + b + c = 100 in at.%. Since the upper electrode has an O-containing layer of preset composition, its processing is simplified, which allows miniaturisation of the capacitor.

## High Density Laminated Printed Wiring Board

NEC TOYAMA LTD.

*Japanese Appl.* 2001/024,332

High density laminated printed wiring board is manufactured by forming a mask film on a photo-sensitive resin layer formed on board. A Pd layer formed upon the laminated resin layers is polished to predetermined height, so that part of the Pd layer is removed to form a Cu plating layer on which Cu can be plated. The mask film has different light transmissivities, corresponding to the position and depth of each part of the pattern. Insulation between circuits formed on board is reliably obtained by Pd removal.

## Electroconductive Film Formation

ISHIFUKU KINZOKU KOGYO K.K.

*Japanese Appl.* 2001/043,733

An electroconductive film for circuits and electrodes on ceramic bases is claimed. It includes: 0.1–1 wt.% Pd or Pt powder in Ag, with 1–3 wt.% Cu and Cu coprecipitation powder and a glass frit binder. Improved adhesion of the solder fixes film to base.

## Silver-Palladium Electrodes for Thermistor

MURATA MFG. CO. LTD.

*Japanese Appl.* 2001/044,007

A thermistor element with negative characteristic comprises Ag-Pd electrodes and Ag terminal electrodes at the centre of the surface of the Ag-Pd electrodes. The thermistor element is firmly clamped by springs to the Ag terminal centre, and the whole structure is packaged. The arrangement has good resistance to destruction when a heavy-duty solenoid is used.

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