

# NEW PATENTS

## ELECTROCHEMISTRY

### Electrode for Water Purification

H. E. O'DONNELL *et al.* U.S. Appl. 2001/0,042,682

An electrode (1) for H<sub>2</sub>O purification, includes an intermediate layer and a protective pre-coat layer (containing a Pt group metal). The former decreases leakage of current from an electrolyte solution directly to the latter. A method to produce (1) is claimed. (1) has a longer service life and good current yield.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Chemical Vapour Deposition of Ruthenium Films

APPLIED MATERIALS INC European Appl. 1,178,131

Thin Ru films are deposited on a substrate by liquid source CVD using bis(ethylcyclopentadienyl)Ru, which is at room temperature. Deposition occurs in the kinetic-limited temperature regime. The bis(ethylcyclopentadienyl)Ru is vaporised at 100–300°C to form a CVD source material gas (1). Deposition onto the substrate is performed in a reaction chamber using (1) and O source reactant gas at ~ 100–500°C.

### High-Purity Bis(ethylcyclopentadienyl)ruthenium

TANAKA KIKINZOKU KOGYO KK World Appl. 01/42,261

High purity bis(ethylcyclopentadienyl)Ru is produced by hydrogenating bis(acetylcyclopentadienyl)Ru (1) without causing corrosion. (1) is prepared by reacting bis(cyclopentadienyl)Ru (2) with acetic anhydride and H<sub>3</sub>PO<sub>4</sub> as catalyst, while (2) is prepared by reacting cyclopentadiene with Ru chloride and Zn powder. CVD formation of thin Ru or Ru compound films is also claimed for use in capacitors for ICs.

### Fabrication of X-Ray Masks

INT BUSINESS MACHINES CORP U.S. Patent 6,287,434

An apparatus, for electroplating one side of a substrate for use in fabricating X-ray masks, has an anode positioned in an electrolyte. A Pt inhibitor electrode (1) is attached to the inner surface of the dielectric plate of the cathode. A Si substrate is attached to the inner surface of the cathode. (1) allows electroplating on one side of the substrate using a rack plating system.

### Palladium Plating Solution

KOJIMA KAGAKU YAKUHIN KK

Japanese Appl. 2001/192,885

A Pd plating solution (1), for decorative and electronic uses, comprises (in g l<sup>-1</sup>, as metal equiv. amount): 0.1–40 soluble Pd salt, 0.01–10 of pyridine carboxylic acid (PCA) and/or 0.002–1 of soluble salt of Fe, Zn, Tl, Se or Te, 0.005–10 of amine group derivative of PCA, and 0.001–1.2 of aldehyde benzoic acid derivative, and anionic or amphoteric group surfactant. (1) has stable properties and corrosion resistance and the Pd film has high purity, a mirror-like gloss and plasticity. Crack generation is suppressed.

## APPARATUS AND TECHNIQUE

### Water Denitrification

SUD CHEMIE MT Srl European Appl. 1,178,017

Nitrates are removed from H<sub>2</sub>O by making it flow over a transition metal catalyst, preferably 0.01–5 wt.% Pd, on a porous carrier which can activate applied H<sub>2</sub>, forming metallic hydrides (1). Denitrifying bacteria, which can survive in the presence of H<sub>2</sub>, adhere to (1). CO<sub>2</sub> is used to adjust the pH to 4.5–7.8. O<sub>3</sub> is fed into the tank to convert nitrites.

### Detecting Nitric Oxide

UNIV DUKE

U.S. Patent 6,280,604

An electrode (1) for rapid *in vivo* detection of NO in biological samples, such as blood, urine, synovial fluid, lymph, surgical drainage fluid, etc., has a surface made of material containing Ru and at least one oxide of Ru which complexes with NO when exposed to a NO-containing fluid. (1) exhibits maximal NO response after pre-conditioning. Direct response to NO has been observed for the Ru electrodes at potentials ≤ +675 mV vs. Ag/AgCl, while the paradoxical response of the Ru electrodes to NO occurs at potentials > +675 mV vs. Ag/AgCl.

### Material for a Deflecting Colour Filter

NATL INST ADV IND SCI TECHNOL

Japanese Appl. 2001/147,326

Material for a deflecting colour filter comprises a planar organic metal complex of Pd, Pt or Ni. Light transmittance can be changed, depending on the viewing angle. By gradually increasing the angle of incidence, light transmittance is decreased. For light hitting vertically to the film surface, transmittance is ~ 90%. Light transmittance at a specific wavelength depends on the incident angle of the light.

### Gas Sensor to Measure NOx Concentration

NGK SPARK PLUG CO LTD Japanese Appl. 2001/153,834

A gas sensor, for accurate measurement of NOx concentrations in ICEs, motor vehicles, aeroplanes and boilers, comprises an exterior electrode and an internal electrode formed on an O ion conducting layer. The internal electrode comprises (in wt.%): 0.1–25 Pd, 0.1–30 Au and remainder Pt. An O pump cell controls the O concentration in the sensor void. O pumping capability is maintained for a long time.

### Ozone Generator

KI SAN JET PLASMA CO LTD Korean Appl. 2001/007,966

An O<sub>3</sub> generator using low activity plasma ion discharge effects to produce purified O<sub>3</sub> has a discharge plate for low activity plasma ions. The discharge plate is prepared from a composite powder of Zr, Y, Ti, Al oxides and balance SiN. SiO<sub>2</sub> glass is added to form and sinter the synthetic ceramic sheets. Molten metal between the sheets contains 1.8–2.2 wt.% of Mo and 0.3–0.7 wt.% of Pt group elements.

## HETEROGENEOUS CATALYSIS

### Production of Epoxycyclododecane Compound

UBE IND LTD *European Appl.* 1,125,934

An epoxycyclododecane compound (1) for producing the resin component for paints and adhesives, is produced by hydrogenating 1,2-epoxy-5,9-cyclododecadiene with H<sub>2</sub> at 0.8–9 MPa pressure, in the presence of a long-life catalyst of Pt supported on activated C, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc. (1) are produced in high yield at a high reaction rate. (1) can also be used to produce a lactam compound which is an intermediate for polyamide 12 and polyesters, useful for producing synthetic resins and fibres.

### Purification of Naphthalenic Carboxylic Acid

BP CORP NORTH AMERICA INC *World Appl.* 01/56,967

A naphthalenic carboxylic acid, especially 2,6-naphthalene dicarboxylic acid (2,6-NDA), is purified by contacting with a purification solvent in the presence of H<sub>2</sub> and a Group VIII catalyst, such as Ru/C, at 520–575°F. 2,6-NDA is useful as a monomer in the production of dimethyl-2,6-naphthalene dicarboxylate-based polymers for use in films and food and beverage containers. Reduced amounts of organic impurities are obtained in the purified acid.

### Palladium Hydrogenation Catalyst

SUED-CHEMIE AG *World Appl.* 01/58,590

A catalyst for hydrogenation of unsaturated hydrocarbons, such as selective hydrogenation of diolefins to monoolefins or of acetylenes to olefins, contains a catalytically-effective amount of Pd and optionally Ag on a support. The support comprises a moulding of trilobal cross-section with holes through the lobes. Catalysts on a trilobal support have higher activity and selectivity than usual and can be used at gas hourly spatial velocities of ~ 12,000–15,000, compared with only 3000–8000 when beads, tablets or extrudates are used. The pressure drop is also lower.

### Production of Epoxide

ARCO CHEM TECHNOL LP *World Appl.* 01/62,380

An epoxide, such as propylene oxide, is produced by reacting an olefin, H<sub>2</sub> and O<sub>2</sub> in the presence of a catalyst of Ti zeolite, Pd and Au promoter. The Ti zeolite is impregnated with a solution of a Pd compound and Au compound in a solvent, followed by solvent removal and drying. Adding the Au promoter increases productivity and selectivity to epoxide.

### Jet Engine Catalytic Converter

P. BOURGON *Canadian Appl.* 2,299,746

A catalytic converter for a jet engine is built into the engine and uses Pt anodised onto all the metal parts of the combustion chamber and turbine, except for any bearings used in these stages. The anodised Pt catalyses some of the air/fuel mixture in the engine. The engine becomes more responsive, smoother, gains more thrust across the power band, and lasts longer as there are fewer contaminating byproducts. Fuel economy is increased.

### Hydrogenation Catalyst for Anthraquinones

ASAHI KASEI KOGYO KK *Japanese Appl.* 2001/170,485

A highly active hydrogenation catalyst (1) for anthraquinones is formed from a Pd component on support particles of diameter < 200 μm and bulk density 0.7–1.5 g ml<sup>-1</sup>. The support is a SiO<sub>2</sub>-based composition, with Al<sub>2</sub>O<sub>3</sub> and MgO in atomic ratio Mg:Al > 1/2. The Pd distribution is controlled and has surface area of 40–300 m<sup>2</sup> g<sup>-1</sup>. (1) is almost free from Pd loss and has excellent durability. The support has superior abrasion resistance.

### Hydrogenation of Carbonyl Compounds

BASF AG *German Appl.* 1/00/09,817

A catalyst (1) used in hydrogenation of carbonyl compounds to alcohols at relatively low temperature (< 140°C) contains (in part wt.): 0.0001–0.5 Re, 0.0001–0.5 Pt and 0–0.25 of Ru, Zn, Cu, Ag, Au, Ni, Fe, Mn, Cr, Mo, W and V on activated C, subjected to non-oxidative pretreatment. (1) has higher total selectivity for the hydrogenation of carbonyl compounds to alcohols, without ether formation.

### Catalyst Preparation by Chemical Vapour Deposition

HYOSUNG T & C CO LTD *Korean Appl.* 2001/046,425

A catalyst for the dehydration of hydrocarbons comprises (in wt.%): 0.1–2.0 Pt, 0.0–1.0 K, 0.1–1.0 Sn, and 0.0–1.0 Eu or Yb on an Al<sub>2</sub>O<sub>3</sub>-Al borate support. The support is prepared by mixing Al(NO<sub>3</sub>)<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> with NH<sub>3</sub> solution. The support has pore volume 0.4–1.0 cc g<sup>-1</sup>, mean pore size 200–3000 Å and surface area 25–150 m<sup>2</sup> g<sup>-1</sup>. CVD impregnates the catalyst active species onto the support by spray injection of the chemicals in the reactor at 800°C.

## HOMOGENEOUS CATALYSIS

### Carbonylation of Unsaturated Compounds

SHELL INT RES MIJ BV *World Appl.* 01/68,583

Carbonylation of 3C or more ethylenically unsaturated compounds used in the preparation of detergents, involves reacting CO and hydroxyl-group-containing compounds in the presence of a catalyst system (1) in an aprotic solvent. (1) comprises a source of Pd cations, bidentate diphosphine and a source of anions derived from an acid having pK<sub>a</sub> < 3 at 18°C in an aqueous solution. High regioselectivity towards a linear product is obtained.

### Manufacture of Cyclic Polyether Compounds

KAGAKU GIJUTSU SHINKO JIGYODAN *Japanese Appl.* 2001/199,987

The manufacture of a cyclic polyether compound used as starting material for the synthesis of natural substances, such as ciguatoxin, comprises cross-coupling an alkyl borane and cyclic enol phosphate, in the presence of a basic aqueous solution containing a Pd(0) compound which has a phosphine ligand, as the catalyst. The method can be used to manufacture cyclic polyether product, which is suitable for the synthesis of cyclic compounds larger than six-membered rings.

## FUEL CELLS

### Electrode Catalyst for Fuel Cells

NE CHEMCAT CORP

*European Appl.* 1,156,543

A highly active electrode catalyst (1) for a fuel cell electrode, such as for SPEFCs, comprises 20–70 wt.% Pt on conductive C, which has O chemically bonded to it, at an atomic ratio of 0.7–3 to the Pt. Also claimed is an alloy catalyst prepared by depositing a metal component which alloys with Pt in a Pt precursor, which is then reduced to form the alloy. (1) is also used in a membrane electrode assembly.

### Proton Conducting Polymer Membrane

JOHNSON MATTHEY PLC

*World Appl.* 01/69,706

A proton conducting polymer membrane of thickness < 100  $\mu\text{m}$ , for a membrane electrode assembly (MEA) and a fuel cell, comprises channels and/or capillaries (< 50  $\mu\text{m}$ ) arranged in the z-direction of the membrane. Tow or yarn or Pt or Nb wires are placed or inserted into the membrane during its formation. The tow or yarn is subsequently removed to form channels; and/or the Pt or Nb is left *in situ* to form capillaries. The membrane allows the supply of additional  $\text{H}_2\text{O}$  to the system to sustain  $\text{H}_2\text{O}$  electrolysis during cell reversal in a MEA or fuel cell. The MEA exhibits improved performance at low reactant gas pressure.

### Generation of a Hydrogen-Rich Fuel Gas Stream

UOP LLC

*U.S. Patent* 6,299,995

A H-rich fuel gas stream (1) is generated by passing a fuel stream over an O-containing preferential oxidation catalyst at 70–160°C. The catalyst comprises Ru metal dispersed on an  $\text{Al}_2\text{O}_3$  carrier with apparent bulk density of 0.2–0.4  $\text{g cm}^{-3}$  and high porosity (average pore size 800–1500 Å). (1) containing < 50 ppm of CO is passed to a fuel cell for electric power generation for a motor vehicle. CO is converted and high selectivity to  $\text{CO}_2$  is maintained.

### Platinum-Ruthenium Alloy Electrodes for Fuel Cells

ISHIFUKU KINZOKU KOGYO KK

*Japanese Appl.* 2001/205,086

Catalysts loaded with Pt-Ru alloys, for fuel cell electrodes, are prepared by reducing Pt ammine type complexes and Ru salts (not containing Cl) to a state where Ru bonds to C powder. Very fine Pt-Ru alloy particles are dispersed uniformly on the C powder support, and poisoning by CO is inhibited.

### Selective Oxidation Catalyst for Fuel Cell

MATSUSHITA ELECTRIC WORKS LTD

*Japanese Appl.* 2001/212,458

A selective oxidation catalyst (1) used for fuel cells, particularly SPFCs, contains Ru and Pt on a porous carrier, such as  $\alpha\text{-Al}_2\text{O}_3$ , at a Ru:Pt weight ratio of 0.1–9.5. The Ru and/or Pt are localised in a layer  $\leq 100 \mu\text{m}$  under the outer surface of the porous carrier. (1) selectively oxidises CO in a reformed gas, at low temperature, by an  $\text{O}_2$ -containing gas. Improved fuel and electricity generation efficiencies are obtained.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Ceramic Capacitor Electrode-Forming Paste

NGK INSULATORS LTD

*European Appl.* 1,178,493

A paste to form a ceramic capacitor electrode contains (in wt.%): 10–14 of an organic vehicle and 86–90 of Pt powder. The Pt powder contains powders of spherical, flaky and indefinitely-shaped particles. The electrode layer film formed with the paste has density of  $\geq 80\%$ , surface roughness of 0.4–0.6  $\mu\text{m}$  and adhesion strength of  $\geq 2 \text{ kg}$ . There is improved adhesion to the dielectric layer and small through-holes can be made in the electrode layer.

### Oxidation Stabilisation of Semiconductors

MICRON TECHNOLOGY INC

*U.S. Patent* 6,291,364

A catalyst matrix is used in high pressure, high temperature oxidation in  $\text{N}_2\text{O}$  of a gate dielectric layer or cell dielectric layer on Si to stabilise the semiconductor. Oxidation at 5–250 atm pressure and 600–750°C occurs in the presence of a catalyst selected from Pt, Ir, Pd, Rh, Pb, Ni or Ag and their oxides. The method and apparatus prevent  $\text{N}_2\text{O}$  from becoming supercritical; temperature and pressure spikes are prevented. The exposure of semiconducting wafers to high temperature is minimised and undesirable diffusion prevented.

### Chip-Type Multilayer Electronic Part

TDK CORP

*U.S. Patent* 6,342,732

A chip-type laminated electronic part, for a multilayered ceramic capacitor, comprises internal metal electrodes and terminal electrodes (1), which contain Ag and Pd as their main ingredients (Ag:Pd = 7:3 to 3:7 wt. ratio). (1) also contain 0.1–1.0 wt.% B. (1) are prevented from oxidising when the electrical part is joined to the substrate, so that improved electrical bonding to the internal electrodes is attained.

### High Output Piezoelectric Ceramic

NEC HYOGO LTD

*Japanese Appl.* 2001/146,470

A high output piezoelectric ceramic composition for oscillators, piezoelectric actuators, and ultrasonic motors, consists of ternary composite oxide system of Pb-Mn-Sb, Pb-Zr, and Pb-Ti. Piezoelectric ceramics with a high exothermic threshold of oscillating velocity can be manufactured by sintering at low temperature together with Ag-Pd electrodes.

### Reflecting Film for Liquid Crystal Display Elements

FURUYA KINZOKU KK

*Japanese Appl.* 2001/226,765

A heat-resistant reflecting film (1) for a LCD element, consists of Ag alloy material containing 0.1–3.0 wt.% Pd. Also claimed are: a laminate of one or more layers of (1); a LCD element using the laminate; and a portable device which can use the LCD element as reflector, reflecting film or building glass material. (1) has improved heat-resistance, reliability and optical reflecting rate. (1) has enhanced bonding with the substrate layer, glass substrate or resin substrate. Brightness is improved, due to reduced optical loss.