

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Tin-Rich Part of the Au–Pt–Sn System

A. N. TORGERSEN, L. OFFERNES, A. KJEKSHUS and A. OLSEN, *J. Alloys Compd.*, 2001, 314, (1–2), 92–95

Condensed phases, tie-lines and tie-triangles for an isothermal section of the Sn-rich part (≥ 50 at.%) of the Au–Pt–Sn phase diagram at 400°C are presented. There is a limited solid-solubility exchange between Au and Pt in most of the binary phases; however, for AuSn and Pt₂Sn₃ the ranges of homogeneity are appreciable. AuPt₂Sn₄ was also found.

Grain-Boundary Segregation of Impurities in Iridium and Effects on Mechanical Properties

L. HEATHERLY and E. P. GEORGE, *Acta Mater.*, 2001, 49, (2), 289–298

Impurities of Fe, Ni, Cr, Al and Si (50–5000 ppm) were added to Ir-0.3 W-0.006 Th-0.005 Al to examine their effects. Fe, Ni, Cr and Al do not segregate to the grain boundaries of Ir, even when present at bulk levels of 3000–5000 ppm. Very low levels of Si (50 ppm) in the bulk segregate to Ir grain boundaries and at bulk levels of Si (< 200 ppm), both Th and Si segregate to the Ir grain boundaries. Fe, Ni, Cr, Al (and Si at low levels) do not embrittle Ir, whereas high levels of Si cause severe embrittlement.

CHEMICAL COMPOUNDS

Peculiarities of K₂PdCl₄ and K₂PtCl₄ Complexation with Polymer-Supported Dibenzo-18-crown-6

G. G. TALANOVA, K. B. YATSIMIRSKII and O. V. KRAVCHENKO, *Ind. Eng. Chem. Res.*, 2000, 39, (10), 3611–3615

Dibenzo-18-crown-6 supported on a styrene-divinylbenzene copolymer matrix (PDB18C6) is an efficient sorbent of Pt(II) and Pd(II) from aqueous K₂PtCl₄ and K₂PdCl₄ solutions, respectively. The sorption proceeds via coordination of K⁺ with the crown ether O atoms accompanied by the complex cation association with [PtCl₄]²⁻ and [Pd_nCl_{2n+2}]²⁻. PDB18C6 shows stronger binding of Pt than of Pd.

Determination of Absolute Configuration of (π -Allyl)Palladium Complexes by NMR

Spectroscopy and Stereoselective Complexation

A. GOGOLL, C. JOHANSSON, A. AXÉN and H. GRENNBERG, *Chem. Eur. J.*, 2001, 7, (2), 396–403

The (*S,S*)- and (*R,R*)-enantiomers of the chiral chelating ligand *N,N'*-bis(phenylethyl)bispidine form complexes with (π -allyl)Pd species with high stereoselectivity. In the ¹H NMR spectra of the resulting complexes, signals of “antenna” protons were easily identified. Interligand nuclear Overhauser effects involving these protons enabled the absolute stereochemistry of the (π -allyl)Pd complex to be determined.

Characterization of the Inorganic/Organometallic Osmium(IV) Compound [Cp*₂Os^{IV}Cl]₂[Os^{IV}Cl₆] as Formed by the Reaction of OsCl₃ with Pentamethylcyclopentadiene in Air

T. SIXT, W. KAIM and W. PREETZ, *Z. Naturforsch.*, 2000, 55b, (3/4), 235–237

OsCl₃ was reacted with pentamethylcyclopentadiene in EtOH in air to give the ionic Os(IV) compound [Cp*₂OsCl]₂[OsCl₆], which contains two Os(IV) ions. Under similar conditions the RuCl₃ homologue gave the Ru(III) compound [Cp*₂RuCl]₂, confirming the more facile oxidation of trivalent Os to the tetravalent state.

Ruthenium Terpyridine Complexes with Mono- and Bi-Dentate Dithiolene Ligands

H. SUGIMOTO, K. TSUGE and K. TANAKA, *J. Chem. Soc., Dalton Trans.*, 2001, (1), 57–63

[Ru(CO)₂Cl(terpy)]PF₆ (1) (terpy = 2,2':6,2''-terpyridine) reacts with Na₂mnt (mnt = S₂C₂(CN)₂) to give initially [Ru(CO)₂(mnt- κ S)(terpy- κ^3 NN'N'')] which then rearranges to [Ru(CO)₂(mnt- κ^2 SS')(terpy- κ^2 NN')] in solution. (1) reacts with 3,4-toluenedithiol (H₂tdt) to give [Ru(CO)₂(tdt- κ^2 SS')(terpy- κ^2 NN')].

ELECTROCHEMISTRY

Analysis of the Activation Mechanism of Hydrogen Storage Alloy Negative Electrodes Containing Palladium Ion-Adsorbed Carbon Powder

S. MORISHITA, K. FUJITA, K. ITOH, S. TOWATA and K. ABE, *Nippon Kagaku Kaishi*, 2000, (11), 773–778

Pd²⁺/C powder (1) has been used to promote the initial activation of the H₂ storage alloy negative electrodes in Ni–MH batteries. Electrode impedance values, and TEM and XRD of (1) were taken after cathodic polarisation. A mechanism is proposed: Pd²⁺ is reduced to fine Pd particles during the first charge. The fine Pd particles act as active sites for charge/discharge reactions. The alloy particles are pulverised due to volume expansion on H₂ absorption; new active sites are formed on the fresh alloy surface.

Zeolitic Inorganic–Organic Polymer Electrolyte Based on Oligo(ethylene glycol) 600 K₂PdCl₄ and K₃Co(CN)₆

V. DI NOTO, *J. Phys. Chem. B*, 2000, 104, (44), 10116–10125

Aqueous solutions of K₂PdCl₄ and K₃Co(CN)₆ were combined separately with poly(ethylene glycol) 600 and then reacted together to give a zeolitic polymer electrolyte, [Co₃Pd₃(CN)₆Cl₃(CH₂_{2n}H_{4n+2}O_{n+1})K]₃ (1). (1) conducts ionically by two distinct conductivity regions which follow Arrhenius-type equations. At 25°C (1) has conductivity $\sim 3 \times 10^{-5}$ S cm⁻¹.

PHOTOCONVERSION

Low-Lying Electronic States and Photophysical Properties of Organometallic Pd(II) and Pt(II) Compounds. Modern Research Trends Presented in Detailed Case Studies

H. YERSIN and D. DONGES, *Top. Curr. Chem.*, 2001, 214, 81–186

A review of photophysical research is presented, using two homologous organometallic compounds Pd(2-thpy)₂ (1) and Pt(2-thpy)₂ (2) (2-thpy⁻ = 2-(2-thienyl)-pyridinate) as representative compounds. The triplets of (1) and (2) are marked by differences of nearly two orders of magnitude in metal/MLCT character. Highly resolved spectra are obtained in *n*-octane, at low temperature (1.3 K) and by laser spectroscopy, allowing detailed analysis. (191 Refs.)

New Luminescent and Redox-Active Homometallic Dinuclear Iridium(III), Ruthenium(II) and Osmium(II) Complexes Prepared by Metal-Catalyzed Coupling Reactions

P. M. GRIFFITHS, F. LOISEAU, F. PUNTORIERO, S. SERRONI and S. CAMPAGNA, *Chem. Commun.*, 2000, (23), 2297–2298

Complexes [(ppy)₂Ir(phen-phen)Ir(ppy)₂]²⁺ (ppy = monoanion of 2-phenylpyridine; phen-phen = 5,5'-bis(1,10-phenanthroline)), [(bpy)₂Ru(phen-phen)-Ru(bpy)₂]⁴⁺, [(bpy)₂Os(phen-phen)Os(bpy)₂]⁴⁺ and [(Me₂bpy)₂Os(phen-phen)Os(Me₂bpy)₂]⁴⁺ (Me₂bpy = 4,4'-dimethyl-2,2'-bipyridine) were prepared. They exhibit relatively intense room temperature luminescence which can be attributed to ³MLCT levels.

Rapid Synthesis of New Emitting Ir(III) Polypyridine Complexes

N. YOSHIKAWA, Y. MASUDA and T. MATSUMURA-INOUE, *Chem. Lett. Jpn.*, 2000, (10), 1206–1207

Microwave-assisted synthesis of Ir(III) polypyridine complexes, such as [Ir(bpy)₃](PF₆)₃, has been achieved in ethylene glycol in a 500 W microwave oven of frequency 2450 MHz. The OH group of ethylene glycol was activated. These complexes were characterised by intense phosphorescence emission (505–630 nm).

On the Photochemical Behavior of the [Ru(NH₃)₄(NO)nicotinamide]³⁺ Cation and the Relative Stability of Light-Induced Metastable Isonitrosyl Isomers of Ru Complexes

C. KIM, I. NOVOZHLOVA, M. S. GOODMAN, K. A. BAGLEY and P. COPPENS, *Inorg. Chem.*, 2000, 39, (25), 5791–5795

Low-temperature IR experiments on crystalline samples of *trans*-[Ru(NH₃)₄(NO)nicotinamide]³⁺ salts (1) show a light-induced absorption band typical for isonitrosyl MS1 NO linkage isomers upon exposure to 300–500 nm light from a Xe source. The formation of a metastable species was confirmed by DSC measurement on (1) irradiated at low temperature with 457 nm light from an Ar⁺ laser. The light-induced species decays at 250–260 K.

APPARATUS AND TECHNIQUE

Electrochemical Sensing of Glucose at a Platinum Electrode with a Chitin/Glucose Oxidase Film

K. SUGAWARA, H. FUKUSHI, S. HOSHI and K. AKATSUKA, *Anal. Sci.*, 2000, 16, (11), 1139–1143

An electrochemical glucose sensor, which can detect glucose in liquids, uses a Pt electrode covered with a chitin/glucose oxidase film. Glucose oxidase having a negative charge was immobilised on a protonated chitin film in 0.1 mol dm⁻³ acetate buffer (pH 5.0) via an electrostatic interaction. An oxidation peak of H₂O₂ from the enzyme reaction occurs at +0.5 V (vs. Ag/AgCl) in 0.1 mol dm⁻³ acetate buffer (pH 6.2). The calibration curve of glucose was linear from 5 × 10⁻⁷–3 × 10⁻⁵ mol dm⁻³.

Reagentless Biosensor for Isocitrate Using One Step Modified Pt-Ir Microelectrode

A. C. PEREIRA, F. L. FERTONANI, G. DE OLIVEIRA NETO, L. T. KUBOTA and H. YAMANAKA, *Talanta*, 2001, 53, (4), 801–806

An isocitrate biosensor (1) had the isocitrate-dehydrogenase-ICDH enzyme, the NADP⁺ coenzyme and Meldola's Blue mediator immobilised on the surface of a Pt-Ir microelectrode. Catalytic currents were proportional to isocitrate concentrations: 7.7 × 10⁻⁶–1.04 × 10⁻⁴ mol l⁻¹. The detection limit of (1) was 3.50 × 10⁻⁶ mol l⁻¹. The response time < 20 s, the lifetime ~ 30 determinations and no significant interference was noticed from sugars or citric acid.

Sensing Properties of Palladium-Gate MOS (Pd-MOS) Hydrogen Sensor-Based on Plasma Grown Silicon Dioxide

D. DWIVEDI, R. DWIVEDI and S. K. SRIVASTAVA, *Sens. Actuators B, Chem.*, 2000, 71, (3), 161–168

A Pd-gate MOS H₂ sensor (1) was fabricated on a *n*-type <100> Si wafer having resistivity of 1–6 Ω cm using plasma technology. The response-recovery time and sensitivity of (1) were studied for H₂ concentrations of 1480–11,840 ppm at signal frequencies of 500 Hz, 10 and 100 kHz at room temperature. H₂-induced interface-trapped density was evaluated as a function of gas concentration using a bias scan conductance method. (1) has improved performance: high sensitivity and low response recovery time.

Gas-Sensing Properties of PdO-Modified SnO₂-Fe₂O₃ Double-Layer Thin-Film Sensor Prepared by PECVD Technique

M. S. TONG, G. R. DAI and D. S. GAO, *Vacuum*, 2000, 59, (4), 877–884

SnO₂-Fe₂O₃ double-layer thin films were fabricated onto Si and ceramic substrates by using the plasma-enhanced CVD technique. The SnO₂ surface was then coated with PdO and CO sensing properties were tested. Pd was deposited onto the films by dipping them into a solution of PdCl₂, followed by reducing the Pd²⁺ with formaldehyde and SnCl₂. The films have high sensitivity and selectivity to CO.

HETEROGENEOUS CATALYSIS

Heterogeneous Catalysis on the Atomic Scale

G. ERTL, *Chem. Rev.*, 2001, 1, (1), 33–45

The progress of catalytic reactions on an atomic scale was observed using NH_3 oxidation and other reactions as examples and by utilising scanning tunnelling microscopy and other surface techniques. CO oxidation on a Pt(111) surface proceeds preferentially along the boundaries between adsorbed O and CO patches. Ru is practically inactive for the same reaction under lower pressures but is transformed into RuO_2 at atmospheric pressure, where some of the surface Ru atoms function as coordinatively unsaturated sites. In the H_2 oxidation reaction on Pt(111), an autocatalytic reaction step occurs.

Investigation of the Operation Time Dependence of the Yield of Ammonia Conversion to Nitrogen(II) Oxide by Platinum Catalyst Sets

P. A. KOZUB, N. V. TRUSOV, G. I. GRYN and V. V. PREZHDO, *J. Chem. Technol. Biotechnol.*, 2001, 76, (2), 147–152

The origins of changes in the catalytic activity of Pt catalysts used for the NH_3 oxidation reaction were studied. A general mathematical model for the dependence of the catalyst activity upon the operation time of a single Pt gauze is proposed. The model can be used to determine the gauze operating times, to calculate the average product yields for various types of operating conditions, and to select the optimal gauze rotation procedure.

Heterogeneous Enantioselective Hydrogenation of Ethyl Pyruvate Catalyzed by Cinchona-Modified Pt Catalysts: Effect of Modifier Structure

H. U. BLASER, H. P. JALET, W. LOTTENBACH and M. STUDER, *J. Am. Chem. Soc.*, 2000, 122, (51), 12675–12682

The effect of the structure of chiral modifiers derived from natural cinchona alkaloids on the enantioselectivity and rate of the Pt/ Al_2O_3 -catalysed hydrogenation of ethyl pyruvate is reported. The strongest effects on ee, but somewhat less on rate, were observed for changes in the O–C₉–C₈–N part of the cinchona alkaloid and for partial or total hydrogenation of the quinoline rings.

Pt/CeO₂ Catalysts in Selective Hydrogenation of Crotonaldehyde: High Performance of Chlorine-Free Catalysts

M. ABID and R. TOUROUDE, *Catal. Lett.*, 2000, 69, (3, 4), 139–144

The hydrogenation of crotonaldehyde was conducted in the gaseous phase at atmospheric pressure, on Pt/CeO₂ catalysts (1) prepared from metal precursors, some containing Cl. (1), prepared from $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, led to 5–20% crotyl alcohol selectivity when (1) was reduced at 473–673 K. When the reduction temperature was increased up to 973 K, the crotyl alcohol selectivity reached > 80%. When (1) contained Cl, crotyl alcohol selectivity was < 30%.

The Removal of Ammonia from Water by a Hydrophobic Catalyst

T.-L. HUANG, K. R. CLIFFE and J. M. MACINNES, *Environ. Sci. Technol.*, 2000, 34, (22), 4804–4809

A process for removing NH_3 from H_2O involves stripping NH_3 from the aqueous phase followed by gas-phase oxidation of NH_3 over a Pt/styrene divinyl benzene copolymer hydrophobic catalyst (1) at 90–125°C. The stripping and catalytic oxidation were carried out simultaneously in a continuous trickle-bed reactor, where the packing material was a mixture of (1) and $\gamma\text{-Al}_2\text{O}_3$ spheres. The NH_3 concentration in the inlet gas was 500–1500 ppmv.

Formation of Platinum Silicide on a Platinum Nanoparticle Array Model Catalyst Deposited on Silica during Chemical Reaction

J. ZHU and G. A. SOMORJAI, *Nano Lett.*, 2001, 1, (1), 8–13

Pt nanoparticle model catalysts with 28 ± 2 nm diameters and 100 ± 2 nm square periodicity have been fabricated with electron beam lithography on SiO_2 substrates. The reactivity and selectivity of the Pt/ SiO_2 array favour dehydrogenation for a cyclohexene and H_2 mixture, not hydrogenation, at 100°C. Experiments with Si deposited on Pt foil show that Pt silicide could form at the Pt/ SiO_2 interface.

The Mechanism of Palladium-Catalyzed Decomposition of Ethanol – A Comparison of Chemical Kinetic and Surface Science Studies

J. M. DAVIDSON, C. M. MCGREGOR and L. K. DORAISWAMY, *Ind. Eng. Chem. Res.*, 2001, 40, (1), 108–113

The decompositions of EtOH and acetaldehyde over Pd/ Al_2O_3 were studied in pulse reaction mode at 200°C in flowing He and with added H_2 , CO and H_2O . Acetaldehyde decomposes to CH_4 and CO with progressive coking that can be suppressed by H_2 . The response times, as monitored by MS peaks for CH_4 and CO, were very similar. EtOH decomposed to $\text{CH}_4/\text{CO}/\text{H}_2$, the corresponding traces being either broad and unsymmetrical or resolved into two peaks. In H_2/He , the slower set of responses is suppressed, and those from CH_4 and CO appear sharp and similar in shape to those observed from acetaldehyde.

Environmentally Benign Oxidation Using a Palladium Catalyst System

M. HAYASHI, K. YAMADA, S. NAKAYAMA, H. HAYASHI and S. YAMAZAKI, *Green Chem.*, 2000, 2, (6), 257–260

Benzyllic and allylic alcohols were converted into the corresponding carbonyl compounds in the presence of 20–50 wt.% of 10% Pd/C, with 3 equiv. of vinyl acetate or under a C_2H_4 atmosphere in MeCN, at 50–80°C. The product distribution of the reaction of 2-cyclohexen-1-ol with 5 mol% of $\text{Pd}(\text{OAc})_2$ under a C_2H_4 atmosphere was 68% phenol, 28% cyclohexanone and 4% cyclohexanol. In the oxidation of D-glucal to 1,5-anhydrohex-1-en-3-ulose using $\text{Pd}(\text{OAc})_2$ and vinyl acetate, the Pd catalyst can be reused without a decrease of catalytic activity.

HOMOGENEOUS CATALYSIS

Ionic Liquids in Regioselective Platinum-Catalysed Hydroformylation

P. WASSERSCHIED and H. WAFFENSCHMIDT, *J. Mol. Catal. A: Chem.*, 2000, 164, (1–2), 61–67

Room temperature liquid chlorostannate ionic liquids (1) have been used as solvents for the catalyst $(\text{PPh}_3)_2\text{PtCl}_2$ (2). (1) were prepared by the reaction of 1-butyl-3-methylimidazolium chloride or 1-butyl-4-methylpyridinium chloride with SnCl_4 . (2) dissolved in (1) has enhanced stability and selectivity in the hydroformylation of methyl-3-pentenoate compared to the identical reaction in conventional organic solvents. In the case of 1-octene hydroformylation, a biphasic reaction occurs when using (1) as the catalyst solvent for (2).

Salt-Free C-C Coupling Reactions of Arenes:

Palladium-Catalyzed Telomerization of Phenols

A. KROTZ, F. VOLLMÜLLER, G. STARK and M. BELLER, *Chem. Commun.*, 2001, (2), 195–196

Electron-rich phenols were reacted with 2 molecules of 1,3-dienes (butadiene, isoprene) in the presence of $\text{Pd}(\text{OAc})_2\text{-PR}_3$ catalysts ($\text{R} = \text{Cy}, \text{Ph}, (\text{OC}_6\text{H}_5)(\text{C}_6\text{H}_5)_2$) to give C-allylated phenols. After reduction with H_2 and Pd/C the corresponding alkylated products were obtained in high yields. This telomerisation of phenols with dienes constitutes a salt-free functionalisation of the aromatic nucleus and has remarkable catalyst turnover numbers.

A New Efficient Palladium Catalyst for Heck Reactions of Deactivated Aryl Chlorides

A. EHRENTAUF, A. ZAPF and M. BELLER, *Synlett*, 2000, (11), 1589–1592

A new Pd catalyst consisting of $\text{Pd}(\text{dba})_2$ and di-1-adamantyl-*n*-butylphosphine (1) has been developed for the Heck reaction of non-activated and deactivated aryl chlorides. (1) gives improved results for the Heck reactions of non-activated aryl chlorides than previously known catalyst systems.

Rhodium Catalyzed Hydroformylation of 1,1-Bis(*p*-fluorophenyl)allyl or Propargyl Alcohol: A Key Step in the Synthesis of Fluspirilen and Penfluridol

C. BOTTEGHI, M. MARCHETTI, S. PAGANELLI and F. PERSI-PAOLI, *Tetrahedron*, 2001, 57, (8), 1631–1637

A key intermediate, 4,4-bis(*p*-fluorophenyl)butylbromide, in the synthesis of the neuroleptic agents, Fluspirilen and Penfluridol, has been prepared starting from commercially available 4,4'-difluorobenzophenone (1). The preparation of (1) involved the Rh catalysed hydroformylation, in toluene or in the biphasic system toluene/ H_2O or cyclohexane/ H_2O , of 1,1-bis(*p*-fluorophenyl)-2-propenol (2) and/or 1,1-bis(*p*-fluorophenyl)-2-propynol. For (2), the H_2O soluble catalytic systems $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{TPPTS}$ and $\text{Rh}(\text{CO})_2\text{acac}/2,7\text{-bis}(\text{SO}_3\text{Na})_2\text{Xantphos}$ were used.

Selectivity of the $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ Catalyzed Hydrogenation of Nitrile-Butadiene Rubber

J. S. PARENT, N. T. MCMANUS and G. L. REMPEL, *J. Appl. Polym. Sci.*, 2001, 79, (9), 1618–1626

$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ (1) is an efficient catalyst precursor for the hydrogenation of olefin within acrylonitrile-butadiene copolymers. The nitrile unsaturation of the copolymer remains intact. However, (1) catalyses an undesirable crosslinking reaction, which is not produced by the commercial Rh-based systems. Further research of (1) may overcome this.

The Development of $\text{L}_2\text{X}_2\text{Ru}=\text{CHR}$ Olefin Metathesis Catalysts: An Organometallic Success Story

T. M. TRNKA and R. H. GRUBBS, *Acc. Chem. Res.*, 2001, 34, (1), 18–29

The evolution of Ru-based olefin metathesis catalysts from simple salts to highly tuned alkylidene complexes is described. Particular emphasis on $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$ and its derivatives is given. Trends in catalyst activity are analysed and catalysts coordinated with *N*-heterocyclic carbene ligands are described. Ongoing work to improve the activity, stability and selectivity of this family of $\text{L}_2\text{X}_2\text{Ru}=\text{CHR}$ complexes is overviewed. (85 Refs.)

FUEL CELLS

Fuel Cells: Principles, Types, Fuels, and Applications

L. CARRETTE, K. A. FRIEDRICH and U. STIMMING, *ChemPhysChem*, 2000, 1, (4), 162–193

In this review, the main reactions responsible for the conversion of chemical into electrical energy in fuel cells are given and the thermodynamic and kinetic fundamentals are stated. The theoretical and real efficiencies of fuel cells are also compared to those of the I.C.E. The different types of fuel cells and their main components are explained and related material issues are discussed. A section is devoted to fuel generation and storage. Attention is also given to the integration of fuel cells into complete systems. (191 Refs.)

Electrooxidation of H_2 on Pt/C Pt-Ru/C and Pt-Mo/C Anodes for Polymer Electrolyte Fuel Cell

A. POZIO, L. GIORGI, E. ANTOLINI and E. PASSALACQUA, *Electrochim. Acta*, 2000, 46, (4), 555–561

A semi-empirical equation that fits experimental electrode potential vs. current density data for gas diffusion anodes using Pt/C, Pt-Ru/C and Pt-Mo/C electrocatalysts is reported. A physico-chemical interpretation of all parameters used in the equation is given. The presence of a strong kinetic limitation on Pt-M/C ($\text{M} = \text{Ru}, \text{Mo}$) electrodes was demonstrated. A Heyrovsky-Volmer mechanism for the H_2 oxidation reaction is proposed on Pt-M/C ($\text{M} = \text{Ru}, \text{Mo}$). Some Pt-Mo anodes showed performances comparable to the Pt-Ru (1:1) anode.

Effect of Structure of Carbon-Supported PtRu Electrocatalysts on the Electrochemical Oxidation of Methanol

Y. TAKASU, T. FUJIWARA, Y. MURAKAMI, K. SASAKI, M. OGURI, T. ASAKI and W. SUGIMOTO, *J. Electrochem. Soc.*, 2000, 147, (12), 4421–4427

Pt-Ru/C electrocatalysts (1) were prepared from EtOH solutions of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, $\text{Ru}_3(\text{CO})_{12}$, $\text{RuNO}(\text{NO}_3)_x$ and RuCl_3 , and C black. The Cl-free $\text{Ru}_3(\text{CO})_{12}$ and $\text{RuNO}(\text{NO}_3)_x$ gave highly dispersed and uniform PtRu nanoparticles. $\text{Ru}_3(\text{CO})_{12}$ yielded high surface area catalysts. (1) from EtOH solutions of $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ - $\text{Ru}_3(\text{CO})_{12}$ had high mass-specific activity toward MeOH oxidation.

Electrocatalysis in Direct Methanol Fuel Cells: In-Situ Probing of PtRu Anode Catalyst Surfaces

H. N. DINH, X. REN, F. H. GARZON, P. ZELENAY and S. GOTTESFELD, *J. Electroanal. Chem.*, 2000, 491, (1–2), 222–233

Stripping voltammetry of CO adsorbed at unsupported, highly dispersed PtRu anode DMFC catalysts was used as an *in situ* probe of surface composition. CO stripping data for three dispersed, unsupported PtRu catalyst samples indicates that surface metal alloy domains of atomic ratio Ru:Pt near 1:1 are the key for higher DMFC anode activity. Catalyst free of blocking by oxide components gives highest activity.

ELECTRICAL AND ELECTRONIC ENGINEERING

Growth-Induced Perpendicular Magnetic Anisotropy and Clustering in $\text{Ni}_x\text{Pt}_{1-x}$ Alloys

D. VASUMATHI, A. L. SHAPIRO, B. B. MARANVILLE and F. HELLMAN, *J. Magn. Magn. Mater.*, 2001, 223, (3), 221–232

Polycrystalline and epitaxial (100), (110) and (111)-oriented Ni_3Pt , NiPt and NiPt_3 films were vapour deposited at 80–700°C. At moderate growth temperatures (200–400°C), the films exhibit growth-induced properties similar to those of Co-Pt alloys: enhanced and broadened Curie temperature, perpendicular magnetic anisotropy and large coercivity. Unlike Co-Pt, NiPt films exhibit a strong orientational dependence of anisotropy and enhanced Curie temperature.

Low Temperature Synthesis of Silver-Palladium Alloy Powders Internal Electrodes for Multilayer Ceramic Devices

R. UEYAMA, K. KAMADA, M. HARADA, T. UEYAMA, T. YAMAMOTO, K. KURIBAYASHI, K. KOUMOTO and T. SHIOSAKI, *J. Mater. Sci.*, 2001, 36, (2), 371–379

Ag-Pd pastes were prepared from: (a) coprecipitated powder, (b) agglomerated alloy powder made by heat treatment, and (c) pulverised alloy powder produced by an improved pulverisation method. Paste from (c) showed a higher film packing density (6.3 g cm^{-3}) than those from (a) and (b). The film consisting of (c) had a lower expansion at $\sim 500^\circ\text{C}$, a lower shrinkage at 700–1100°C and a lower electric resistivity.

Correlation between Magnetic and Transport Properties of Co/Ir/Co Sandwiches and Surface Roughness

S. COLIS, G. SCHMERBER and A. DINIA, *Thin Solid Films*, 2000, 380, (1–2), 137–141

$\text{Co}_{3\text{nm}}/\text{Ir}_x/\text{Co}_{3\text{nm}}$ sandwiches with 0.5, 1 and 1.5 nm thickness of Ir were deposited on glass substrates covered by a $\text{Fe}_{5\text{nm}}/\text{Co}_{0.5\text{nm}}/\text{Cu}_{3\text{nm}}$ layer, using the ion beam sputtering technique. The maximum giant magnetoresistance and coupling strength were 2% and $-0.55 \text{ erg cm}^{-2}$, respectively. The average surface roughness was $\sim 0.3 \text{ nm}$, allowing antiferromagnetic exchange coupling to be seen in the sandwich stack.

Anisotropic Etching of RuO_2 and Ru with High Aspect Ratio for Gigabit Dynamic Random Access Memory

T. YUNOGAMI and K. NOJIRI, *J. Vac. Sci. Technol. B*, 2000, 18, (4), 1911–1914

Anisotropic RuO_2 and Ru etching technology for gigabit DRAM has been developed using high density $\text{O}_2 + 10\% \text{ Cl}_2$ plasma in an inductively coupled plasma etching system. The taper angle for RuO_2/Ru increased with decreasing pressure, with increasing $\text{O}_2 + 10\% \text{ Cl}_2$ flow rate and with increasing overetch time. Under conditions of low pressure, high gas flow rate and 100% overetch time, a $0.3 \mu\text{m}$ thick RuO_2/Ru pattern having $0.2 \mu\text{m}$ critical dimension and a taper angle of 89° was obtained.

MEDICAL USES

Carboplatin Decomposition in Aqueous Solution with Chloride Ions Monitored by X-Ray Absorption Spectroscopy

E. CURIS, K. PROVOST, I. NICOLIS, D. BOUVET, S. BÉNAZETH, S. CRAUSTE-MANCIET, F. BRION and D. BROSSARD, *New J. Chem.*, 2000, 24, (12), 1003–1008

X-Ray absorption spectroscopy has been used to study carboplatin (1) in H_2O , with Cl^- at different concentrations. (1) is the major compound present in solution, even after 15 days, in neutral solutions with Cl^- concentrations $< 9\%$, exposed to light or not. With high Cl^- concentrations (18%) or in acidic solutions (0.1 M HCl), (1) is chlorolysed and cisplatin formation as the decomposition product is observed.

Ruthenium(II) Complexes Containing Bidentate Schiff Bases and Their Antifungal Activity

N. DHARMARAJ, P. VISWANATHAMURTHI and K. NATARAJAN, *Transition Met. Chem.*, 2001, 26, (1–2), 105–109

$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{B})]$ complexes (B = PPh_3 , pyridine (py) or piperidine (pip)) were reacted with bidentate Schiff base ligands (from condensations of salicylaldehyde with aniline, *o*-, *m*- or *p*-toluidine) to give $[\text{RuCl}(\text{CO})(\text{L})(\text{PPh}_3)_2(\text{B})]$ (1) (L = Schiff base anion). *In vitro* activity against fungus *Aspergillus flavus* was: $[\text{RuCl}(\text{CO})(\text{sal-}p\text{-toluidine})(\text{PPh}_3)_2(\text{py})] > [\text{RuCl}(\text{CO})(\text{sal-}p\text{-toluidine})(\text{PPh}_3)_2] > [\text{RuCl}(\text{CO})(\text{sal-aniline})(\text{PPh}_3)_2(\text{py})] > [\text{RuCl}(\text{CO})(\text{sal-aniline})(\text{PPh}_3)_2] > \text{sal-}p\text{-toluidine} > \text{sal-aniline}$.