

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Palladium Nanoparticles Stabilised by Polyfluorinated Chains

M. MORENO-MAÑAS, R. PLEIXATS and S. VILLARROYA, *Chem. Commun.*, 2002, (1), 60–61

Pd nanoparticles can be prepared by reduction of $\text{Na}_2(\text{Pd}_2\text{Cl}_6)$ in the presence of compounds having long perfluorinated C chains (1) such as 1,5-bis(4,4'-bis(perfluorooctyl)-1,4-pentadien-3-one). The reduction is performed in MeOH at 60°C. (1) is the only constituent of the stabilising layer.

Influence of the Thermal Annealing on the Electrical Resistivity and Thermal Diffusivity of Pd:Ag Nanocomposites

C. A. S. LIMA, R. OLIVA, G. CARDENAS T., E. N. SILVA and L. C. M. MIRANDA, *Mater. Lett.*, 2001, 51, (4), 357–362

Nanocrystalline Pd:Ag powder was formed by solvent evaporation of metal colloids. The obtained Pd:Ag powder was then compressed into compacts of ~250 μm thick, 10 mm diameter wafers, and annealed at different temperatures for ~1 h. The electrical resistivity exhibited a sharp exponential decrease with increasing annealing temperature $\leq 400^\circ\text{C}$. At $> 400^\circ\text{C}$, electrical resistivity remained almost constant. The dependence of thermal diffusivity on increasing annealing temperature is complex.

CHEMICAL COMPOUNDS

Oxidation of $[\text{Pt}^{\text{II}}\text{Cl}_2(\text{ethane-1,2-diamine-}N,N'\text{-dicarboxylic Acid})]$ and Ligand Ring Closure in the Platinum(IV) Oxidation State

P. N. WONG, M. S. DAVIES and T. W. HAMBLEY, *Aust. J. Chem.*, 2001, 54, (5), 303–306

Oxidation of $[\text{Pt}^{\text{II}}\text{Cl}_2(\text{H}_2\text{enda})]$ using H_2O_2 gives rise to a variety of products, including three crystal and two isomeric forms. The major product is the ring closed $[\text{Pt}^{\text{IV}}\text{Cl}_2(\text{enda})]$ and if the solution is heated under reflux for 24 h, this is the only product.

Kinetics of Substitution of Aqua Ligands from *cis*-Diaqua(ethylenediamine)platinum(II) Perchlorate by DL-Penicillamine in Aqueous Medium

P. S. SENGUPTA, R. SINHA and G. S. DE, *Transition Met. Chem.*, 2001, 26, (6), 638–643

The kinetics of the interaction of DL-penicillamine with $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ were studied spectrophotometrically at pH 4.0. The reaction proceeds via rapid outer-sphere-association complex (1) formation, followed by two slow steps. The first is the conversion of (1) into the inner-sphere complex, independent of ligand concentration, and the second is a slower chelation step, where another aqua ligand is replaced.

Tris(pyrazolyl)methanesulfonate (Tpms) – A Versatile Alternative to Tris(pyrazolyl)borate in Rhodium(I) Chemistry

W. KLÄUI, D. SCHRAMM, W. PETERS, G. RHEINWALD and H. LANG, *Eur. J. Inorg. Chem.*, 2001, (6), 1415–1424

TiTpms (Tpms = tris(pyrazol-1-yl)methanesulfonate) reacts with $[\text{Rh}(\text{LL})\text{Cl}]_2$ (LL = $(\text{CO})_2$, cod and nbd) to give $\text{TpmsRh}(\text{LL})$ complex. In solution, $\text{TpmsRh}(\text{CO})_2$ (1) reversibly forms $\text{TpmsRh}(\mu\text{-CO})_3\text{-RhTpms}$. $\text{TpmsRh}(\text{CO})(\text{PR}_3)$ ($\text{PR}_3 = \text{PPh}_3, \text{PMe}_3, \text{PCy}_3, \text{P}(\text{Ph})_2(\text{PhSO}_3\text{K})$) were obtained by reaction of (1) with the corresponding phosphanes. IR studies indicate that Tpms is a weakly donating ligand.

Synthesis of Chloro(2-methylimidazole)ruthenium(III) Complexes and Their Aqueous Solution Chemistry, and the Crystal Structure of $[\text{2-MelmH}]_2[\text{RuCl}_5\text{-2-Melm}]$

C. ANDERSON, *Can. J. Chem.*, 2001, 79, (10), 1477–1482

2-Methylimidazole reacts with RuCl_3 in $\text{HCl-H}_2\text{O-EtOH}$ to give $(\text{2-MelmH})_2[\text{RuCl}_5(\text{2-Melm})]$ and $(\text{2-MelmH})[\text{RuCl}_4(\text{2-Melm})_2]$ (2-MelmH = protonated 2-methylimidazole). The ratio of the products depends on the reaction conditions employed.

ELECTROCHEMISTRY

Temperature-Dependent Surface Electrochemistry on Pt Single Crystals in Alkaline Electrolyte:

Part 1: CO Oxidation

T. J. SCHMIDT, P. N. ROSS and N. M. MARKOVIC, *J. Phys. Chem. B*, 2001, 105, (48), 12082–12086

The continuous electrooxidation of CO in 0.1 M KOH electrolyte (CO_b) on $\text{Pt}(hkl)$ at 275 and 333 K was investigated. Significant reaction rates were observed even in the potential region for H underpotential deposition (H_{upd}). The CO_b oxidation on $\text{Pt}(hkl)$ involves a Langmuir-Hinshelwood type reaction between the adsorbed states of CO and OH_{ad} .

Electrochemical Properties of Pt-Modified Nano-Honeycomb Diamond Electrodes

K. HONDA, M. YOSHIMURA, T. N. RAO, D. A. TRYK, A. FUJISHIMA, K. YASUI, Y. SAKAMOTO, K. NISHIO and H. MASUDA, *J. Electroanal. Chem.*, 2001, 514, (1–2), 35–50

B-doped nanoporous honeycomb diamond films modified with Pt nanoparticles (10–150 nm) were studied with CV and electrochemical impedance spectroscopy in acid solution. These electrodes showed high electroactivity for H adsorption and oxidation of MeOH, EtOH and 2-propanol. The current density (geometric basis) in the CV for MeOH oxidation at a Pt-modified porous film of pore diameter 400 nm and pore depth 3 μm was enhanced by a factor of 16 compared to values obtained with a bulk Pt electrode.

An Electrochemical Impedance Study of the Electrochemical Doping Process of Platinum Phthalocyanine Microcrystals in Non-Aqueous Electrolytes

J. JIANG and A. KUCERNAK, *J. Electroanal. Chem.*, 2001, 514, (1–2), 1–15

The electrochemical doping process (1) of Pt phthalocyanine microcrystalline film (2) in MeCN was studied using electrochemical impedance spectroscopy. At low doping levels of (1), the rate of the first electrochemical step is slow and determined by the conductivity of (2). Once (2) becomes conductive, the electrochemical reaction is accelerated abruptly. Further increases in doping potential trigger another slow oxidation process.

Formation of Palladium Complex at Carbon Paste Surface in Chloride Solution as Studied by Cyclic Voltammetry

K.-H. LUBERT, M. GUTTMANN and L. BEYER, *Collect. Czech. Chem. Commun.*, 2001, 66, (10), 1457–1472

The deposition and dissolution of Pd at a non-modified C paste electrode was studied by CV in Cl⁻ solutions (≥ 0.5 M KCl and pH 3–6). Pd⁰ was deposited from [Pd^{II}Cl]²⁻ solution by potential cycling from E ≥ 0 V (vs. Ag/AgCl) or application of positive potentials or by potentiostatic treatment at E ≤ 0 V. [Pd^{II}Cl₄] was formed on applying anodic potentials.

PHOTOCONVERSION

Photochemistry of μ -Hydrido-tetrakis(tertiary phosphine)diplatinum Complexes

R. BOARETTO, S. SOSTERO and O. TRAVERSO, *J. Photochem. Photobiol. A: Chem.*, 2001, 144, (2–3), 101–106

The primary photoprocesses of *trans-trans* monohydrido-bridged [(PEt₃)₂HPt(μ -H)PtH(PEt₃)₂][BPh₄] and *trans-cis* dihydrido-bridged [(PEt₃)₂HPt(μ -H₂)Pt(PEt₃)₂][BPh₄] are homolyses of their Pt–Pt bonds. The Pt–Pt bond dissociation leads to cleavage of Pt(μ -H)Pt and Pt(μ -H₂)Pt yielding the reactive complexes [(PEt₃)₂PtH₂] and [(PEt₃)₂PtH(S)][BPh₄] (S = solvent).

Dendrimers Based on Ruthenium(II) and Osmium(II) Polypyridine Complexes and the Approach of Using Complexes as Ligands and Complexes as Metals

S. SERRONI, S. CAMPAGNA, F. PUNTORIERO, C. DI PIETRO, N. D. McCLENAGHAN and F. LOISEAU, *Chem. Soc. Rev.*, 2001, 30, (6), 367–375

The use of the 'complexes as ligands and complexes as metals' synthetic strategy for the preparation of luminescent and redox-active Os(II) and Ru(II) dendrimers is reviewed. The photophysical and redox properties of such dendrimers containing 2,3-dpp (2,3-bis(2-pyridyl)pyrazine) bridges are included. Alternative approaches to polypyridine dendrimers are briefly discussed. (27 Refs.)

Photochromic Atropisomer Generation and Conformation Determination in a Ruthenium Bis(bipyridine) Phosphonite γ -Cyclodextrin System

D. HESEK, G. A. HEMBURY, M. G. B. DREW, V. V. BOROVKOV and Y. INOUE, *J. Am. Chem. Soc.*, 2001, 123, (49), 12232–12237

Irradiation of *rac*-[Ru(bpy)₂(PhP(OMe)₂(Cl))Cl] (1) at $\lambda > 460$ nm results in the photochromic generation of a new atropisomer and chirality inversion, via rotation of PhP(OMe)₂ around the Ru–P bond. The formation of a supramolecular complex between (1) and γ -cyclodextrin allows the stabilisation of the new atropisomeric conformation.

Ruthenium Polypyridine Complexes. On the Route to Biomimetic Assemblies as Models for the Photosynthetic Reaction Center

H. DÜRR and S. BOSSMANN, *Acc. Chem. Res.*, 2001, 34, (11), 905–917

Photophysical data and the preparation of RuL₃ complexes (1) from simple or more complicated bipyridine ligands, L, are reported. (1) with polyether bipyridines as building blocks, such as in Ru podates and coronates, were shown to be among the most photostable Ru complexes. Two-shell biomimetic model systems have more efficient electron transfer than one-shell systems. Covalently linked assemblies are more efficient in electron transfer. (41 Refs.)

ELECTRODEPOSITION AND SURFACE COATINGS

Nanostructured Pt-Doped Tin Oxide Films: Sol–Gel Preparation, Spectroscopic and Electrical Characterization

F. MORAZZONI, C. CANEVALI, N. CHIODINI, C. MARI, R. RUFFO, R. SCOTTI, L. ARMELAO, E. TONDELLO, L. E. DEPERO and E. BONTEMPI, *Chem. Mater.*, 2001, 13, (11), 4355–4361

Nanostructured (3–6 nm) thin films (80 nm) of SnO₂ and Pt-doped SnO₂ (1) were obtained by a sol–gel route using [Sn(OBu')₄] and [Pt(acac)₂] precursors. Glancing incidence X-ray diffraction measurements showed that Pt(IV) substituted for Sn(IV) in the lattice of the air annealed films. XPS established that the reaction of (1) with CO reduces Pt(IV) to Pt(II) at 373 K and to Pt(0) at 673 K.

Computed Depth Profile Method of X-Ray Diffraction and Its Application to Ni/Pd Films

H. WU, B. LI, W. MIAO, X. LIU and K. TAO, *Surf. Coat. Technol.*, 2002, 149, (2–3), 198–205

A method based on parallel beam XRD for profiling structure and phase distributions along with depth was used to characterise Ni/Pd thin films (1) and to obtain their phase depth profile. (1) were annealed at 380°C for 30 min. In the data analysis procession, the non-negative least squares algorithm was employed to resolve the ill-posed inverse problem that emerged in the solving procession.

APPARATUS AND TECHNIQUE

Glucose Sensor Based on Au-Pt Black Electrode-Preparation of Functionally Different Sites on Electrode Surface

O. TAKEI, S. TOYAMA, M. SOMEYA, T. KUROKAWA, R. USAMI, K. HORIKOSI and Y. IKARIYAMA, *Electrochemistry (Jpn.)*, 2001, 69, (12), 956–958

A glucose sensor has been developed based on a composite metal (Au and Pt) black electrode, fabricated by simultaneous codeposition of Au and Pt. Enzyme was immobilised at Au sites on the electrode surface, while enzymatic product was oxidised at Pt sites. 40:60 mol% Au:Pt gave the largest response.

Sputtered, Electroless, and Rolled Platinum–Ceramic Membranes

S. TOSTI, L. BETTINALLI, S. CASTELLI, F. SARTO, S. SCAGLIONE and V. VIOLANTE, *J. Membrane Sci.*, 2002, 196, (2), 241–249

Sputtering, electroless deposition and rolling of thin Pd-Ag alloy films over ceramic porous tubes were used to produce Pd-ceramic composite membranes for H₂ separation and production. In the sputtered (0.5–5 μm) and electroless (2.5–20 μm) membranes, thermal cycling of the hydrogenated metallic layer produces membrane failures. Rolled (50–70 μm) membranes, however, have a complete H₂ selectivity and good chemical and physical stability.

HETEROGENEOUS CATALYSIS

The Effect of Metal Order on the Oxidation of a Hydrocarbon Mixture over Alumina-Supported Combined Platinum/Rhodium Catalysts

M. J. PATTERSON, D. E. ANGOVE and N. W. CANT, *Appl. Catal. B: Environ.*, 2001, 35, (1), 53–58

The oxidation of a mixture of benzene, toluene, 1-hexene and isooctane in the absence and presence of CO was investigated over Pt/Al₂O₃ and Rh/Al₂O₃ monolith catalysts arranged singly and in various 1:1 and 4:1 combinations. Physical mixtures of the Pt and Rh are more active than the individual metals for complete removal of hydrocarbons when CO is present. Without CO, Pt is more active than Rh for aromatic and isooctane oxidation. Removing CO on Rh facilitates oxidation of benzene and isooctane on Pt. If Rh is put ahead of Pt in a sequential bed arrangement, the effect is maximised.

Adsorption and Decomposition of NO on Carbon and Carbon-Supported Catalysts

J. ZAWADZKI and M. WIŚNIEWSKI, *Carbon*, 2002, 40, (1), 119–124

The interactions of NO with C and C-supported catalysts have been studied by means FTIR spectroscopy. Direct decomposition of NO over C-supported catalysts (Pt, Cu) was investigated at 473–623 K. NO conversion increased with increasing reaction temperature. Pt/C has a very high activity for NO decomposition, even in the absence of O₂.

Electrochemical Evaluation of the Morphology and Enantioselectivity of Pt/Graphite

G. A. ATTARD, J. E. GILLIES, C. A. HARRIS, D. J. JENKINS, P. JOHNSTON, M. A. PRICE, D. J. WATSON and P. B. WELLS, *Appl. Catal. A: Gen.*, 2001, 222, (1–2), 393–405

Cinchona-modified Pt/graphite (1) is enantioselective for the hydrogenation of ethyl pyruvate to ethyl lactate at 1 bar pressure and 293 K. CV was used to investigate surface morphology, alkaloid adsorption and morphology change on sintering. CVs of (1) were interpreted using literature data for Pt single crystals. O-induced surface reconstruction is lifted by reduction. Adsorption rates for cinchona alkaloids on (1) are: cinchonine > cinchonidine > dihydrocinchonidine. Cinchonidine adsorption is site selective during uptake from the acidic electrolyte solution. Sintering increases particle size.

Kinetics of Hydrogenation of 4-Chloro-2-nitrophenol Catalyzed by Pt/Carbon Catalyst

S. B. HALLIGUDI and S. S. KHAIRE, *J. Chem. Technol. Biotechnol.*, 2002, 77, (1), 25–28

Hydrogenation of 4-chloro-2-nitrophenol (CNP) catalysed by 1% Pt/C at 300 K and 21.3 atm H₂ in a stirred pressure reactor gave 4-chloro-2-aminophenol (CAP) exclusively. Pd/γ-Al₂O₃ is also active in the hydrogenation; however, dechlorination of CNP or CAP occurs forming 2-nitrophenol and 2-aminophenol, respectively. From an Arrhenius plot of ln rate vs. 1000/T for the Pt/C reaction an apparent activation energy of 22 kJ mol⁻¹ was estimated.

Molecular Weight Effects in the Hydrogenation of Model Polystyrenes Using Platinum Supported on Wide-Pore Silica

J. S. NESS, J. C. BRODIL, F. S. BATES, S. F. HAHN, D. A. HUCUL and M. A. HILLMYER, *Macromolecules*, 2002, 35, (3), 602–609

A kinetic study of the hydrogenation of model polystyrenes (PS) (molecular weight (MW) = 1.5–276 kg mol⁻¹) using Pt/wide-pore SiO₂ catalyst was carried out. The initial rate of hydrogenation, r_0 , was found to be inversely proportional to the PS MW. For MW ≤ 102 kg mol⁻¹, r_0 scaled with the number-average degree of polymerisation, X_n , to the -0.15 power. The two highest MW samples, 190 and 276 kg mol⁻¹, had significantly slower initial rates of hydrogenation and did not follow this trend.

Effect of Transition Metals on Catalytic Performance of Ru/Sepiolite Catalyst for Methanation of Carbon Dioxide

L. LUO, S. LI and J. GUO, *Chin. J. Catal.*, 2002, 23, (1), 85–87

The effects of adding Mo, Mn and Zr to Ru/sepiolite (1) catalyst was investigated for methanation of CO₂. The activity of (1) is closely associated with the electronic state on the Ru surface. Mo increases the active surface area, Ru dispersity, number of active sites, and poisoning resistance. When $T \leq 674$ K, the energy factor predominates and results in $S(\text{CH}_4)/S(\text{CO})$ decreasing. Otherwise steric factors dominate.

HOMOGENEOUS CATALYSIS

Stability and Thermodynamics of the PtCl₂ Type Catalyst for Activating Methane to Methanol: A Computational Study

J. KUA, X. XU, R. A. PERIANA and W. A. GODDARD, *Organometallics*, 2002, 21, (3), 511–525

The relative stability and reaction mechanism of Pt(NH₃)₂Cl₂ and Pt(bpym)Cl₂ (bpym = bipyrimidine) in concentrated H₂SO₄ were studied. The mechanism was found to involve a series of steps beginning with C–H activation to form an intermediate ion-pair Pt(II)–CH₃ complex prior to forming a Pt(II)–CH₃ complex. The calculated relative activation barriers for C–H activation are in good agreement with experimentally observed H/D ratios. Subsequent oxidation to a Pt(IV) complex can occur with reduction of SO₃. Release of methyl bisulfate regenerates the Pt(II) catalyst.

Microwave Promoted Palladium-Catalyzed Phenylation of Aryl Chlorides and Sodium Tetraphenylborate

J.-X. WANG, B. WEI, Y. HU, Z. LIU and Y. YANG, *Synth. Commun.*, 2001, 31, (24), 3885–3890

Unsymmetrical ketones (1) can be synthesised from sodium tetraphenylborate and aryl chlorides using Pd(PPh₃)₂Cl₂ as the catalyst under microwave irradiation. KF was the best base for the reaction. This method is simple, fast and affords good yield (87–98%) of (1). The results show that the synthesis of (1) under microwave irradiation was 133 times faster than with conventional heating.

Synthetic Process Development and Scale Up of Palladium-Catalyzed Alkoxy-carbonylation of Chloropyridines

R. CRETAAZ, J. WASER and Y. BESSARD, *Org. Process Res. Dev.*, 2001, 5, (6), 572–574

Mono- or dicarbonylation of 2,3-dichloropyridines in the presence of CO, EtOH and Pd(OAc)₂/dppf or PdCl₂(Ph₃P)₂/dppb catalyst, gives selectively either alkyl 3-chloropyridine-2-carboxylates or dialkyl pyridine-2,3-dicarboxylates in good yields, depending on the reaction conditions. The process was used for the scale up of the monoalkoxy-carbonylation of 2,3-dichloro-5-(trifluoromethyl)pyridine, giving ethyl 3-chloro-5-(trifluoromethyl)pyridine-2-carboxylate with high selectivity and yield.

Palladium-Catalyzed Intramolecular α -Arylation of α -Amino Acid Esters

O. GAERTZEN and S. L. BUCHWALD, *J. Org. Chem.*, 2002, 67, (2), 465–475

A simple route to dihydroisindole and tetrahydroisindole carboxylic acid derivatives involves the use of Pd-catalysed intramolecular α -arylation of α -amino acid esters. The best results in the cyclisation reactions used a slight excess of biphenyl-based, sterically hindered phosphines together with Pd₂(dba)₃.

Rhodium-Catalyzed Conjugate Addition of Aryl- and Alkenyl-Stannanes to α,β -Unsaturated Carbonyl Compounds

S. OI, M. MORO, H. ITO, Y. HONMA, S. MIYANO and Y. INOUE, *Tetrahedron*, 2002, 58, (1), 91–97

Addition of aryl- or alkenyl-trimethylstannanes to α,β -unsaturated carbonyl compounds in the presence of a catalytic amount of [Rh(cod)(MeCN)₂]BF₄ and H₂O affords the conjugate addition products in good yields. The use of H₂O allowed the reaction to proceed smoothly. The aryl- or alkenyl-Rh complex, which is generated by the transmetalation from the organo-Sn compound, is proposed as the active catalytic species.

Catalyst Screening by Electrospray Ionization Tandem Mass Spectrometry: Hofmann Carbenes for Olefin Metathesis

M. A. O. VOLLAND, C. ADLHART, C. A. KIENER, P. CHEN and P. HOFMANN, *Chem. Eur. J.*, 2001, 7, (21), 4621–4632

In situ synthesis of complexes combined with an assay by electrospray ionisation tandem mass spectrometry has been employed to investigate [{R₂P(CH₂)_nPR₂- κ^2 P}XRu=CHR]⁺ in ring-opening metathesis polymerisation. The most reactive complex for acyclic olefin metathesis utilised chloride as the anionic ligand X, had a small chelating angle ($n = 1$), and reduced steric demand of the substituents R (Cy vs. *t*-Bu). Variation of the carbene moiety CHR' had little influence.

Ring-Closing Metathesis, Kharasch Addition and Enol Ester Synthesis Catalysed by a Novel Class of Ruthenium(II) Complexes

B. DE CLERCQ and F. VERPOORT, *Tetrahedron Lett.*, 2001, 42, (51), 8959–8963

Ru Schiff base complexes were shown to be good catalysts for the Kharasch addition of CCl₄ across olefins. The yields depended on the catalyst and the substrate used. Also, ring-closing metathesis of diolefins was achieved. The best catalytic system was able to form tri- and tetrasubstituted double bond products. Stereoselective formation of enol esters or enynes in excellent yields was also achieved.

Highly Efficient Use of NaOCl in the Ru-Catalysed Oxidation of Aliphatic Ethers to Esters

L. GONSALVI, I. W. C. E. ARENDS and R. A. SHELDON, *Chem. Commun.*, 2002, (3), 202–203

Ru-catalysed bleach α -oxidation of ethers was achieved without the need of an excess of oxidant by careful pH control during the reaction. Fast complete conversions (as short as 3 h) and high yields in esters ($\leq 95\%$) were obtained by efficient reoxidation of Ru to the active catalytic species (RuO₄) by optimal use of the terminal oxidant, NaOCl. CH₂Cl₂ and EtOAc were employed as solvents. Using a stoichiometric amount of NaOCl, high substrate to catalyst ratios were possible in biphasic media at room temperature.

FUEL CELLS

Chemical and Electronic Effects of Ni in Pt/Ni and Pt/Ru/Ni Alloy Nanoparticles in Methanol Electrooxidation

K.-W. PARK, J.-H. CHOI, B.-K. KWON, S.-A. LEE, Y.-E. SUNG, H.-Y. HA, S.-A. HONG, H. KIM and A. WIECKOWSKI, *J. Phys. Chem. B*, 2002, 106, (8), 1869–1877

The electrooxidation of MeOH in H₂SO₄ was studied using Pt, Pt/Ni (1:1 and 3:1), Pt/Ru/Ni (5:4:1 and 6:3.5:0.5) and Pt/Ru (1:1) alloy nanoparticle catalysts, in relation to MeOH oxidation processes in a DMFC. Pt/Ni and Pt/Ru/Ni exhibited excellent catalytic activities compared to pure Pt and Pt/Ru.

Synthesis and Characterization of Osmium Carbonyl Cluster Compounds with Molecular Oxygen Electroreduction Capacity

R. H. CASTELLANOS, A. L. OCAMPO, J. MOREIRA-ACOSTA and P. J. SEBASTIAN, *Int. J. Hydrogen Energy*, 2001, 26, (12), 1301–1306

A cluster electrocatalyst (1) is based on Os_x(CO)_n (2) and Vulcan C; (2) was prepared by pyrolysis of Os₃(CO)₁₂ in 1,2-dichlorobenzene under N₂. The electrocatalytic parameters of the O reduction reaction for (1) were studied with a rotating disk electrode in 0.5 M H₂SO₄ electrolyte. (1) used in a H₂/O₂ PEMFC cathode is reported to perform nearly as well as a Pt one.

ELECTRICAL AND ELECTRONIC ENGINEERING

Impacts of Postannealing Ambient Atmospheres on Pt/SrBi₂Ta₂O₉/Pt Capacitors

A.-D. LI, T. YU, H.-Q. LING, D. WU, Z.-G. LIU and N.-B. MING, *J. Mater. Res.*, 2001, 16, (12), 3526–3535

Films of SrBi₂Ta₂O₉ (SBT) were formed on Pt/TiO₂/SiO₂/Si substrates at 750°C in O₂. SBT film capacitors were postannealed in Ar (N₂) at 350–750°C and then reannealed in O₂ at 750°C. Composition analyses show that Ar- or N₂-annealing at 750°C leads to Bi evaporation and O loss. After 550°C 100% Ar or N₂ postannealing, the remnant polarisation decreases and the coercive field increases significantly. The subsequent O₂ annealing can only partly restore the SBT phase; the ferroelectric properties cannot be rejuvenated.

Preparation of Pt-PtO_x Thin Films as Electrode for Memory Capacitors

K. KURIBAYASHI and S. KITAMURA, *Thin Solid Films*, 2001, 400, (1–2), 160–164

Pt-PtO_x thin films (1) were deposited on Si(100) at substrate temperatures of 30–700°C by reactive r.f. magnetron sputtering with a Pt target. (1) mainly consisted of amorphous PtO and Pt₃O₄ (or Pt₂O₃) at < 400°C. The amorphous Pt in (1) increased as deposition temperature increased to 600°C. Pure Pt films of (111) orientation were formed at 700°C. The electrical resistivity of (1) was of the order 10⁻¹–10⁻⁵ Ω cm.

The Influence of Surface Cleaning on the Stability of Pd/GaAs Contacts

P. MACHÁČ, A. KANTA and V. PEŘINA, *J. Mater. Sci.: Mater. Electron.*, 2001, 12, (11), 649–653

The thermal stability of Pd/n⁺-GaAs ohmic contacts with Ge and Sn layers was studied at 300 and 400°C. The Pd/Ge contact structures have better thermal stability than Pd/Sn. The Ge(20 nm)/Pd(10 nm) structure has two optimum annealing temperatures, the higher one producing ohmic contacts with slightly lower contact resistivity and better stability. Ge/Pd contact structures are based on solid phase regrowth mechanisms. The annealing mechanism is completely different in the Sn/Pd structures. Etching the GaAs wafers before metal deposition in H₂SO₄:H₂O₂:H₂O (1:8:500) followed by HCl:H₂O (1:1) or in concentrated HCl gives the best thermal stability.

Characterization of Hydrous Ruthenium Oxide/Carbon Nanocomposite Supercapacitors Prepared by a Colloidal Method

H. KIM and B. N. POPOV, *J. Power Sources*, 2002, 104, (1), 52–61

Amorphous nanostructured composite electrodes based on RuO₂ (1) were loaded on C using a colloidal method. The colloids were synthesised from solutions containing various amounts of RuCl₃·xH₂O adjusted with NaHCO₃ to pH 5. The electrochemical performance of the composite material depends on the annealing temperature and the particle size of (1).

MEDICAL USES

Voltammetric Studies of the Effect of Cisplatin-Liposome on HeLa Cells

Y.-X. CI, Q. ZHAI, S. WANG, W.-B. CHANG, C.-Y. ZHANG, H. MA, D.-Y. CHEN, M.-Z. ZHAO and S.-W. HU, *Talanta*, 2001, 55, (4), 693–698

The effect of cisplatin-liposome on HeLa cells was studied using a voltammetric method (1). The peak current decreased with both cisplatin-liposome concentration and increasing treatment time. The decrease of peak current was in accordance with damage to the nucleus and loss of mitochondrial membrane potential. (1) may be a useful way to study the electron-transfer mechanism in drug-treated cells.

Study on the Microstructure and the Phase Composition of Two Precious Metal Dental Casting Alloys

X. ZHAO, X. LAN and Z. SHANG, *Precious Met. (Chin.)*, 2001, 22, (4), 13–16

Dental alloys Ag-30Au-15Pd-11Cu (1) and Ag-11Au-23Pd-9Cu (2) in the as-cast conditions consist of two phases: Ag-Pd-rich f.c.c. solid solution (α₁) and Cu-rich f.c.c. solid solution (α₂). Au is evenly distributed throughout both phases. The as-cast microstructure of (1) consists of equiaxed grains of α₁ and a small amount of lamellar eutectic structure (α₁ + α₂). (2) consists mainly of lamellar eutectic structure (α₁ + α₂) and a small amount of (α₁).