

ABSTRACTS

of current literature on the platinum metals and their alloys

CHEMICAL COMPOUNDS

Theoretical Study of Methyl-Pd^{II} N-Heterocyclic Silylene and Germylene Complexes: Comparisons to N-Heterocyclic Carbene Reactivity

D. S. MCGUINNESS, B. F. YATES and K. J. CAVELL, *Organometallics*, 2002, 21, (24), 5408–5414

A density functional analysis of the title complexes revealed a very low activation barrier for methyl migration to the silylene or germylene ligand. In the absence of solvent or counterion effects, reductive elimination of silicenium or germacenium cations is less likely. The activation barrier for coupling of the methyl group was in the order: Si < Ge < C.

Cyclooctadienemethylpalladium Complexes: Synthesis, Structures and Reactivity

A. KLEIN, A. DOGAN, M. FETH and H. BERTAGNOLLI, *Inorg. Chim. Acta*, 2003, 343, 189–201

$[(\text{COD})\text{PdMe}(\text{L})]^n$ ($n = 0$, L = Cl, OH, OMe, OEt, O*i*Pr, OPh, OTol, OMe; $n = 1$, L = H₂O, PPh₃, pyridine, collidine; $n = 2$, L = *N*-methyl-pyrazinium) undergo fast ligand exchange reactions in solution to give new mono or binuclear Pd complexes. Neutral complexes with oxo-ligands OR are highly reactive towards oxo-nucleophiles, including H₂O. $[(\text{COD})\text{PdMe}(\text{OH})]$ and $[(\mu\text{-OH})\{(\text{COD})\text{PdMe}\}_2]^+$ seem to play an important role in hydrolysis reactions.

Crystal Structure and Gas Adsorption Property of Rhodium(II) Benzoate Pyrazine

S. TAKAMIZAWA, T. HIROKI, E. NAKATA, K. MOCHIZUKI and W. MORI, *Chem. Lett.*, 2002, 31, (12), 1208–1209

$[\text{Rh}_2(\text{O}_2\text{CPh})_4(\text{pyz})_\infty$ (1) has perfect linear geometry with the chain skeleton bridged by pyrazine in the axial direction of the lantern-like Rh benzoate. (1) indicated N₂ adsorption on a microporous medium although it probably does not have a microporous structure. The structure of (1) may open the crystal packing for gas molecules.

Mass Spectrometry of Polystyrene and Polypropene Ruthenium Complexes. A New Tool for Polymer Characterization

E. ROYO and H.-H. BRINTZINGER, *J. Organomet. Chem.*, 2002, 663, (1–2), 213–220

Reaction of $[\text{Ru}(\text{C}_5\text{H}_5)(\text{NCCH}_3)_3][\text{PF}_6]$ with polystyrene (PS) of numerical mass average (M_n) 1430–135,000 in a ratio $[\text{Ru}]/[\text{PS}] = 1:1$ to 3:1 favours effective ionisation of the polymer by MALDI-MS techniques. An increase in signal intensity is achieved over that obtained with Ag⁺ salts. Polypropylene (PP) salts of M_n 2700 and 6100 are ionised after reaction with $(\text{RuC}_5\text{Me}_5)_3\text{H}_5$. This is the first observation of MALDI-MS signals for PP.

ELECTROCHEMISTRY

Specificity of Electrochemical Reactivity of Small Aliphatic Oximes to Geometries of Pt(111) and (100) Surfaces

B. PIEROZYNSKI and B. E. CONWAY, *J. Electroanal. Chem.*, 2002, 538–539, 87–97

Electrochemical CV experiments on the reactivity of formamidoxime and acetaldehyde oxime on Pt(111) and (100) single crystal surfaces revealed remarkable specificity to surface geometry upon adsorption. The roles of Faradaic reduction coupled with electrosorption, including participation of diffusion control, were clearly distinguishable.

Microstructure, Electrochemical Surface and Electrocatalytic Properties of IrO₂+Ta₂O₅ Oxide Electrodes

J.-M. HU, J.-Q. ZHANG, H.-M. MENG and C.-N. CAO, *J. Mater. Sci.*, 2003, 38, (4), 705–712

Surface electrochemical properties of Ti/IrO₂-Ta₂O₅ electrodes indicate a 'double-layer' electrochemical structure containing the 'inner' and 'outer' layers. The voltammetric charge declines with the decrease of grain size of the oxide coatings due to surface tension.

Electrochemical Behavior of Dopamine and Ascorbic Acid at Osmium(II) Complex Cationic Monolayer Modified Gold Electrodes

J. ZHANG and I. C. JEON, *Anal. Sci.*, 2002, 18, (10), 1085–1088

At an $[\text{Os}(\text{bpy})_2(\text{bpy}(\text{CH}_2)_{13}\text{SH})]^{2+}/\text{Au}$ electrode, the oxidation peak of dopamine (DA) shifted to a much more positive potential as compared with that of a bare Au electrode, but the oxidation peak potential of ascorbic acid (AA) exhibited a slightly negative shift. When $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ was mixed into the cationic monolayer, the enhanced packing of the mixed monolayer blocked the access of DA or AA to the electrode, resulting in further positive shifts for both oxidation peak potentials.

Synthesis and Electrochemical Behavior of $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ and Its Oxo-Bridged Dimeric Complex $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}\text{ORu}^{\text{III}}\text{SiW}_{11}\text{O}_{39}]^{11-}$

M. SADAKANE and M. HIGASHIJIMA, *Dalton Trans.*, 2003, (4), 659–664

CV showed that $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{III}}(\text{H}_2\text{O})]^{5-}$ was reversibly reduced to the aquaRu(II) derivative, oxidised to the aquaRu(IV), hydroxyRu(IV) and oxoRu(IV) complexes depending on the pH, and could be further oxidised to the oxoRu(V) complex. $[\text{SiW}_{11}\text{O}_{39}\text{Ru}^{\text{IV}}\text{ORu}^{\text{III}}\text{SiW}_{11}\text{O}_{39}]^{11-}$ was reversibly oxidised/reduced to the $\text{Ru}^{\text{IV}}\text{ORu}^{\text{IV}}/\text{Ru}^{\text{III}}\text{ORu}^{\text{III}}$ complex.

PHOTOCONVERSION

Luminescence of the Nonclassical Homoleptic Metal Carbonyl Complex $[\text{Rh}(\text{CO})_4]^+$

T. W. BITNER, J. I. ZINK, M. D. HAVIGHURST and S. H. STRAUSS, *Inorg. Chem.*, 2002, 41, (24), 6187–6189

$[\text{Rh}(\text{CO})_4]^+$ (1) is luminescent at low temperature with a peak maximum at $19,640\text{ cm}^{-1}$ and a full-width at half-maximum of 2900 cm^{-1} . The solution absorption and low temperature solid state luminescence spectra of $[\text{Rh}(\text{CO})_4](1\text{-Et-CB}_{11}\text{F}_{11})$ are reported. Rh–C bond length changes of $\sim 0.07\text{ \AA}$ in the excited state are calculated. The calculated bond length changes in (1) are similar to those in classical metal carbonyls.

Synthesis of New Iridium Complexes and Their Electrophosphorescent Properties in Polymer Light-Emitting Diodes

W. ZHU, C. LIU, L. SU, W. YANG, M. YUAN and Y. CAO, *J. Mater. Chem.*, 2003, 13, (1), 50–55

Ir complexes with *p*-substituted 2-phenylpyridine ligands were incorporated into PLEDs using poly[1,4-bis(6'-cyano-6'-methylheptyloxy)phenylene] (CNPPP) as the host and these materials were compared with *fac*-tris(2-phenylpyridinato)Ir-doped devices. Green electrophosphorescence was observed, with peak emissions at ~ 495 and 515 nm . *fac*-Tris[2-(4-*tert*-butylphenyl)pyridinato]Ir-doped CNPPP gave an external quantum efficiency of 4.4% (photoluminescence/electroluminescence) and a luminous efficiency of 10 cd A^{-1} at 120 cd m^{-2} . These values are 4.2% and 10 cd A^{-1} , respectively, at 2500 cd m^{-2} .

Flow Injection Chemiluminescent Method for the Successive Determination of L-Cysteine and L-Cystine Using Photogenerated Tris(2,2'-Bipyridyl) Ruthenium (III)

T. PÉREZ-RUIZ, C. MARTÍNEZ-LOZANO, V. TOMÁS and J. MARTÍN, *Talanta*, 2002, 58, (5), 987–994

The title method is based on the reaction of L-cysteine with $\text{Ru}(\text{bipy})_3^{2+}$ and peroxydisulfate under UV irradiation to produce chemiluminescence. Cystine is determined after reduction to cysteine in a Cu-coated Cd reductor mini-column in the flow system. The inclusion of a selection valve allows the successive determination of the two analytes.

Light-Induced Metastable Linkage Isomers of Ruthenium Sulfur Dioxide Complexes

A. YU. KOVALEVSKY, K. A. BAGLEY, J. M. COLE and P. COPPENS, *Inorg. Chem.*, 2003, 42, (1), 140–147

The irradiation of *trans*- $[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{SO}_2)\text{X}]\text{Y}$ (1) ($\text{X} = \text{Cl}^-, \text{H}_2\text{O}, \text{CF}_3\text{COO}^-$; $\text{Y} = \text{Cl}^-, \text{C}_6\text{H}_5\text{SO}_3^-, \text{Tos}^-, \text{CF}_3\text{COO}^-$) with laser light at low temperatures caused linkage isomerisation of SO_2 , starting with η^1 -planar *S*-bound to η^2 -side *S,O*-bound SO_2 . The stability of the MS2 metastable state correlates with increasing σ -donating ability of the *trans* ligand and the size of the counterion.

ELECTRODEPOSITION AND SURFACE COATINGS

Morphology and Luminescence of Porous GaN

Generated via Pt-Assisted Electroless Etching

D. J. DÍAZ, T. L. WILLIAMSON, I. ADESIDA, P. W. BOHN and R. J. MOLNAR, *J. Vac. Sci. Technol. B*, 2002, 20, (6), 2375–2383

Ultrathin Pt films were sputtered onto the surface of GaN and then etched with a 1:2:1 or 1:2:2 solution of $\text{CH}_3\text{OH}:\text{HF}:\text{H}_2\text{O}_2$. Etching proceeded by first forming a network of small pores, after which ridge structures formed, with the porous network in trenches between the ridges. As etching progressed further, the sidewalls of the ridges became steeper, and then the ridges started to disappear. The light emission properties of the etched porous GaN varied depending on the original, nonporous GaN.

Studies of Codeposited Hydrogen in Palladium

Electrodeposition

C.-H. HUANG and I.-Y. WEI, *Plat. Surf. Finish.*, 2002, 89, (12), 60–63

The tensile stress of Pd electrodeposits (1) on Ni cathodes is influenced by the amount and nature of codeposited H. The escape-state of codeposited H in (1) was identified. A softer escape-state was predicted when the Pd bath contained an optimum amount of wetter at lower current densities (CDs). This gave less codeposited H during plating and less deposit cracking. A wetter concentration of 2.0 g l^{-1} and a CD of 0.1 A dm^{-2} gave crack-free (1).

APPARATUS AND TECHNIQUE

Design and Performance of a Microcantilever-Based Hydrogen Sensor

D. R. BASELT, B. FRUHBERGER, E. KLAASSEN, S. CEMALOVIC, C. L. BRITTON, S. V. PATEL, T. E. MLSNA, D. MCCORKLE and B. WARMACK, *Sens. Actuators B, Chem.*, 2003, 88, (2), 120–131

The title sensor (1) contains an array of 10 micro-machined cantilever beams. Each cantilever is $500\text{ }\mu\text{m}$ wide \times $267\text{ }\mu\text{m}$ long \times $2\text{ }\mu\text{m}$ thick and has a capacitance readout capable of measuring cantilever deflection to within 1 nm . A 20 nm thick coating of 90% Pd-10% Ni bends some of the cantilevers in the presence of H_2 . The Pd-Ni coatings are deposited in UHV. (1) can detect H concentrations of 0.1–100% with \sim linear response at 10–90% H. Humidity, temperature and O concentration affect its operation.

Gas Sensor Activity of ArgoGel Resin-Supported Pentaruthenium Clusters

C. M. G. JUDKINS, K. A. KNIGHTS, B. F. G. JOHNSON and Y. R. DE MIGUEL, *Polyhedron*, 2003, 22, (1), 3–7

$[\text{Ru}_5\text{C}(\text{CO})_{15}]$ (1) clusters have been attached to phosphine ligands supported on ArgoGel amine resin. These cluster-containing beads exhibit a characteristic colour change and FTIR shift when treated with H_2S , SO_2 or CO. The reactions probably involve the polyhedral rearrangement of (1) from its original square pyramid to a bridged-butterfly metal core.

HETEROGENEOUS CATALYSIS

Steady-State Multiplicity and Superadiabatic Extinction Waves in the Oxidation of CO/H₂

Mixtures over a Pt/Al₂O₃-Coated Monolith

M. SUN, E. B. CROISSET, R. R. HUDGINS, P. L. SILVESTON and M. MENZINGER, *Ind. Eng. Chem. Res.*, 2003, 42, (1), 37–45

Under experimental conditions, steady-state multiplicity phenomena exist in a certain range of CO and H₂ concentrations for the catalytic oxidation of CO/H₂ over a cordierite monolith washcoated with Pt/Al₂O₃. CO inhibits the ignition of H₂, whereas H₂ assists the ignition of CO. Extinction of the reaction due to a step increase of CO or a step decrease of H₂ occurred in the form of a downstream-moving wave accompanied by a sharply localised superadiabatic temperature excursion.

Hydrodechlorination of CCl₄ over Pt/Al₂O₃: Effects of Platinum Particle Size on Product Distribution

J. W. BAE, I. G. KIM, J. S. LEE, K. H. LEE and E. J. JANG, *Appl. Catal. A: Gen.*, 2003, 240, (1–2), 129–142

Impregnated Pt/Al₂O₃ catalysts had different Pt particle sizes depending on the Pt precursor (Pt(NH₃)₂(NO₂)₂ or H₂PtCl₆) and on the pH of the Al₂O₃ suspension. The average Pt particle size increased with decrease in pH for the Pt(NH₃)₂(NO₂)₂-based Al₂O₃ suspension, but this trend was reversed for H₂PtCl₆. In the hydrodechlorination of CCl₄, the larger the Pt particle size, the higher the selectivity to CHCl₃. On small Pt particles, strong chemisorption of CCl₄ occurs and formation of completely dechlorinated CH₄ was favoured.

The Drastic Effect of Platinum on Carbon-Supported Ruthenium-Tin Catalysts Used for Hydrogenation Reactions of Carboxylic Acids

Y. HARA and K. ENDOU, *Appl. Catal. A: Gen.*, 2003, 239, (1–2), 181–195

When Pt was incorporated on Ru-Sn/active C, the reaction rate was almost tripled for the hydrogenation of 1,4-cyclohexanedicarboxylic acid. The Pt also prevented the Sn from dissolving into the reaction mixture, whereas for bimetallic Ru-Sn/active C dissolved Sn was detected during hydrogenation. The durability of the Pt-Ru-Sn/active C was verified by carrying out a catalyst recycling test up to 7 cycles. For Pt-Ru-Sn/active C, Sn(0) was the major Sn species.

Hydrogenation of Alkenes over Palladium and Platinum Metals Supported on a Variety of Metal(IV) Phosphates

R. A. W. JOHNSTONE, J.-Y. LIU, L. LU and D. WHITTAKER, *J. Mol. Catal. A: Chem.*, 2003, 191, (2), 289–294

A substantial variation in relative rates of hydrogenation of 1-octene and 4-methylcyclohexene over platinumised and palladised metal(IV) phosphates has been found; some being more effective than a standard Pd/C. Steric effects due to substrate/support interactions affected selectivity to hydrogenation.

Catalytic Combustion of Methane over Palladium-Based Catalysts

D. CIUPARU, M. R. LYUBOVSKY, E. ALTMAN, L. D. PFEFFERLE and A. DATYE, *Catal. Rev.*, 2002, 44, (4), 593–649

The literature on supported Pd catalysts for combustion of CH₄ is reviewed. The oxidation/reduction mechanisms for supported Pd, the poisoning, restructuring, the form of oxygen on the surface, CH₄ activation over Pd and PdO phases, and transient behaviour are all discussed. The relevance for practical catalytic combustors is included. (131 Refs.)

Palladium-Containing Zeolite Beta Macrostructures Prepared by Resin Macrotemplating

V. NAYDENOV, L. TOSHEVA and J. STERTE, *Chem. Mater.*, 2002, 14, (12), 4881–4885

Self-bonded Pd-containing zeolite beta spheres (1) were prepared by a multistep procedure using a macroporous anion exchange resin as a macrotemplate. Pd is homogeneously distributed within the zeolite spheres as PdO. The Pd dispersions decreased with an increase in Pd content. The pore structure of (1) consisted of both micropores (from the zeolite) and meso/macropores (from the resin removal). (1) may be directly used as catalysts (in fixed bed reactors) thus excluding further processing to form macroparticles and avoiding deterioration effects due to the addition of binders in conventionally prepared zeolite-supported catalysts.

HOMOGENEOUS CATALYSIS

Total Synthesis of Deoxymannojirimycin and D-Mannolactam via Carbonylation of 5-Vinyloxazolidin-2-ones

J. G. KNIGHT and K. TCHABANENKO, *Tetrahedron*, 2003, 59, (3), 281–286

The Pd-catalysed decarboxylative carbonylation of a serine-derived 5-vinyloxazolidinone (1) has been successfully applied to the stereoselective total synthesis of the polyhydroxylated piperidine alkaloids: deoxymannojirimycin and D-mannolactam. Heating a solution of (1) in EtOH at 60°C under pressure of CO (65 atm) in the presence of PdCl₂(PPh₃)₂ (10 mol%) for 32 h gave a δ-lactam intermediate in 81% yield, which was subsequently converted.

Development of the Suzuki–Miyaura Cross-Coupling Reaction: Use of Air-Stable Potassium Alkynyltrifluoroborates in Aryl Alkynylations

G. A. MOLANDER, B. W. KATONA and F. MACHROUHI, *J. Org. Chem.*, 2002, 67, (24), 8416–8423

The Pd-catalysed cross-coupling reactions of K alkynyltrifluoroborates with aryl halides or triflates gave moderate to excellent yields. PdCl₂(dppf)-CH₂Cl₂ with Cs₂CO₃ in THF-H₂O or THF were the most effective systems. Air-stable, highly functionalised alkynyltrifluoroborates can be simply prepared and stored indefinitely. This provides an advantage in combinatorial chemistry applications.

A Novel and Efficient Method for the Pd-Catalysed Oxidative Carbonylation of Amines to Symmetrically and Unsymmetrically Substituted Ureas

B. GABRIELE, R. MANCUSO, G. SALERNO and M. COSTA, *Chem. Commun.*, 2003, (4), 486–487

A new method for the PdI₂ with KI catalysed oxidative carbonylation of amines to symmetrically and unsymmetrically substituted ureas has been developed. Unprecedented catalytic efficiencies for this kind of reaction were obtained. The use of a coordinating aprotic solvent of low polarity, such as 1,2-dimethoxyethane, was essential for the success of the reaction. Using an excess of CO₂ (40 atm) had a beneficial effect on the carbonylation of primary aliphatic amines.

Development of a Manufacturing Route to 1-Hydroxy-4-(3-pyridyl)butan-2-one Using Heck Methodology

D. ANGE and L.-M. VAZ, *Org. Process Res. Dev.*, 2002, 6, (6), 811–813

The manufacturing route to a key synthetic intermediate, 1-hydroxy-4-(3-pyridyl)butan-2-one, was optimised and scaled-up. The Heck coupling of 3-bromopyridine with 3-butene-1,2-diol was utilised. The catalyst system Pd(OAc)₂ with NBu₃/P(*o*-tolyl)₃ required a reaction time of 3 h. The reaction was carried out in toluene under reflux conditions. For a 3 kg scale reaction, HPLC showed 80% consumption of 3-bromopyridine.

The Suzuki Coupling of Aryl Chlorides in TBAB–Water Mixtures

R. B. BEDFORD, M. E. BLAKE, C. P. BUTTS and D. HOLDER, *Chem. Commun.*, 2003, (4), 466–467

Pd catalysts formed *in situ* from Pd(OAc)₂ in the presence of tetrabutylammonium bromide (TBAB) and H₂O and in the absence of added ligands are found to be effective in the Suzuki coupling of deactivated aryl chlorides. For these reactions, the true active catalysts are Pd colloids supported by the TBAB. Further studies are being carried out to optimise the use of such catalysts in a range of aryl chloride coupling reactions.

An Efficient Synthesis of 4-Alkenyl/Alkynyl-6-methyl-2-pyrones via Pd-Catalysed Coupling on 4-Bromo-6-methyl-2-pyrone

L. R. MARRISON, J. M. DICKINSON, R. AHMED and I. J. S. FAIRLAMB, *Tetrahedron Lett.*, 2002, 43, (49), 8853–8857

The syntheses of biologically active 4-alkenyl- and 4-alkynyl-6-methyl-2-pyrones was achieved using Pd-catalysed coupling procedures. Pd/C with PPh₃ was the most effective catalyst combination for Sonogashira cross-coupling of terminal acetylenes with 4-bromo-6-methyl-2-pyrone in yields ≤ 95%. Only when the alkyne possessed strongly electron-withdrawing substituents were the Pd(0) catalysts, Pd(OAc)₂/PPh₃ and Pd(PPh₃)₄, more effective.

Extended Scope of Dirhodium(II)-Catalysed Enantioselective Intramolecular 1,3-Dipolar Cycloadditions of Carbonyl Ylides with Alkene and Alkyne Dipolarophiles

D. M. HODGSON, A. H. LABANDE and F. Y. T. M. PIERARD, *Synlett*, 2003, (1), 59–62

The effect on ee of altering the dipolarophile in intramolecular carbonyl ylide cycloadditions was examined. Various substrates with Rh₂[(*S*)-DOSP]₄ and Rh₂[(*R*)-DDBNP]₄ catalysts in hexane were used. The stereospecificity of the process, the creation of up to 4 stereocentres, and enantioselective intramolecular cycloadditions with alkynes (≤ 86% ee) were all demonstrated for the first time.

Hydroformylation of Alkenes in Supercritical Carbon Dioxide Catalysed by Rhodium Trialkylphosphine Complexes

M. F. SELLIN, I. BACH, J. M. WEBSTER, F. MONTILLA, V. ROSA, T. AVILÉS, M. POLIAKOFF and D. J. COLE-HAMILTON, *J. Chem. Soc., Dalton Trans.*, 2002, (24), 4569–4576

[Rh₂(OAc)₄] modified by simple trialkylphosphines gives catalysts which are soluble in sc-CO₂, and allows hydroformylation of alkenes to take place. The Rh catalyst derived from PEt₃ is more active and slightly more selective for the linear products in sc-CO₂ than in toluene. Under supercritical conditions of 200 bar total pressure, aldehydes are obtained with 97% selectivity.

FUEL CELLS

CO Tolerance of Pd-Rich Platinum Palladium Carbon-Supported Electrocatalysts

D. C. PAPAGEORGIOPOULOS, M. KEIJZER, J. B. J. VELDHUIS and F. A. DE BRUIJN, *J. Electrochem. Soc.*, 2002, 149, (11), A1400–A1404

The use of PtPd_y/C (*y* = 1–6) electrocatalysts as CO tolerant anodes for PEMFCs has been investigated. CV at 80°C revealed that upon CO saturation, a lower fraction of the PtPd_y surface sites are poisoned compared to Pt, resulting in higher amounts of adsorbed H. PtPd_y improved performance compared to Pt and PtRu, especially at CO ≥ 100 ppm in the fuel stream. PtPd₄ gave the best performance.

Array Membrane Electrode Assemblies for High Throughput Screening of Direct Methanol Fuel Cell Anode Electrocatalysts

R. LIU and E. S. SMOTKIN, *J. Electroanal. Chem.*, 2002, 535, (1–2), 49–55

A fuel cell with an array MEA was developed for the high throughput screening of electrocatalysts. Standard MEA and electrode assembly methods were employed. The use of modified fuel cell hardware enabled catalyst testing with realistic reactant exposure histories (conditioning) and steady state reaction conditions. The device accommodates an array of 25 spots permitting repetitive testing of catalysts.

Correlation of Electrochemical and Physical Properties of PtRu Alloy Electrocatalysts for PEM Fuel Cells

G. A. CAMARA, M. J. GIZ, V. A. PAGANIN and E. A. TICIANELLI, *J. Electroanal. Chem.*, 2002, 537, (1–2), 21–29

PtRu/C (1) electrocatalysts were prepared by a sulfide-complex method and modified in oxidising and reducing environments. For non-treated (1), the Ru atoms are segregated from the Pt f.c.c. structure, probably forming an amorphous Ru oxide phase, while for (1) heat treated at 700°C under H₂ a true alloy with a metal Pt:Ru composition of ~ 3:1 was formed. This alloy gave the best CO tolerance.

Influence of Preparation Process of MEA with Mesocarbon Microbeads Supported Pt–Ru Catalysts on Methanol Electrooxidation

Y.-C. LIU, X.-P. QIU, Y.-Q. HUANG, W.-T. ZHU and G.-S. WU, *J. Appl. Electrochem.*, 2002, 32, (11), 1279–1285

The effects of a mesocarbon microbead support material for Pt–Ru catalysts on the anode performance of a DMFC were studied. Polarisation characteristics of the anode were low due to the fast rate of mass transport in the electrode. The anode with appropriate Nafion content (10 wt.%) and hot press pressure (7.5 MPa) for the MEA exhibited the best performance at MeOH concentrations > 1.0 M at high cell temperature.

Electrochemical Oxidation of NADH Catalyzed by Diaphorase Conjugated with Poly-1-vinylimidazole Complexed with Os(2,2'-dipyridylamine)₂Cl

S. TSUJIMURA, K. KANO and T. IKEDA, *Chem. Lett.*, 2002, 31, (10), 1022–1023

A redox polymer containing poly-1-vinylimidazole (PVI) and Os ($E^{\circ} = -0.15$ V vs. Ag|AgCl), PVI-Os(dpa)₂Cl (1), was synthesised. (1) was an efficient mediator of the diaphorase-catalysed electrochemical oxidation of NADH and a support to immobilise enzyme(s) on electrode surfaces. NAD-enzyme/diaphorase-coimmobilised Os polymer electrodes can be used as biofuel cell anodes.

ELECTRICAL AND ELECTRONIC ENGINEERING

Admittance Study of a Pt/C₆₀/In/Al Schottky-Barrier Cell

I. HIROMITSU, R. SHINTO, M. KITANO, T. KITAUCHI and T. ITO, *Jpn. J. Appl. Phys., Part 1*, 2002, 41, (11A), 6517–6524

The electrical properties of a Pt/C₆₀/In/Al photo-voltaic cell, in which the Schottky barrier is formed at the Pt/C₆₀ interface, were studied by an admittance measurement, and also by a current density-voltage measurement. The latter shows that the rectification is caused by the asymmetry of the electron injection efficiencies from the electrodes. The conductance and capacitance are significantly affected by the localised charges produced by the injection or by illumination.

Low-Resistance and Thermally Stable Pd/Ru Ohmic Contacts to p-Type GaN

J.-S. JANG, C.-W. LEE, S.-J. PARK, T.-Y. SEONG and I. T. FERGUSON, *J. Electron. Mater.*, 2002, 31, (9), 903–906

The tile ohmic contacts to surface treated p-GaN (3×10^{17} cm⁻³) have been prepared. Annealing at 500°C for 2 min in N₂ improved ohmic contact properties (specific contact resistance of $2.4(\pm 0.2) \times 10^{-5}$ Ω cm²). AFM showed that the surface of the as-deposited and annealed Pd/Ru contacts were smooth with root mean square roughness of ~ 0.6 nm. For the as-deposited contact, thermionic field emission is dominant, while for the annealed contact, field emission dominates the current flow.

MEDICAL USES

Monofunctionally *trans*-Diammine Platinum(II)-Modified Peptide Nucleic Acid Oligomers: A New Generation of Potential Antisense Drugs

K. S. SCHMIDT, M. BOUDVILLAIN, A. SCHWARTZ, G. A. VAN DER MAREL, J. H. VAN BOOM, J. REEDIJK and B. LIPPERT, *Chem. Eur. J.*, 2002, 8, (24), 5566–5570

A solid-phase approach allows access to monofunctionally *trans*-Pt^{II}-modified PNA oligomers of arbitrary sequence for potential use in both antigene and antisense strategies. The synthesis of a platinated building block and its subsequent incorporation into 3 different PNA oligomers by solid-phase synthesis was achieved. In a model cross-linking reaction, one of the latter recognised sequence-specifically a target oligonucleotide and cross-linked to it. This gave a *trans*-Pt^{II} cross-linked PNA/DNA duplex.

Preparation, Spectral Characterization, *In Vitro* Antitumour and Thermal Studies of New Platinum(IV) and Palladium(II) Thiohydrazone Complexes

N. MANAV and N. K. KAUSHIK, *Transition Met. Chem.*, 2002, 27, (8), 849–855

[Pt(L)₂Cl₂] and [Pd(HL)Cl₂] (HL = thiohydrazone derivatives) were prepared by addition of the desired thiohydrazone dissolved in H₂O/EtOH (1:1) to an aqueous solution of K₂PtCl₆ and PdCl₂, respectively. The *in vitro* antitumour activity of some complexes was measured.

Thermally Inert Metal Amines as Light-Inducible DNA-Targeted Agents. Synthesis, Photochemistry, and Photobiology of a Prototypical Rhodium(III)-Intercalator Conjugate

C. G. BARRY, E. C. TURNEY, C. S. DAY, G. SALUTA, G. L. KUCERA and U. BIERBACH, *Inorg. Chem.*, 2002, 41, (26), 7159–7169

[Rh(NH₃)₅L]⁴⁺ (L = 1-[2-(acridin-9-ylamino)-ethyl]-1,3,3-trimethylthiourea; acridinium cation) was shown to be a true “light-only” cytotoxic agent in clonogenicity assays. In HL-60 leukemia, (1) showed a pronounced photocytotoxic effect with IC₅₀ = 44 nM. The photoreactivity and DNA interactions of (1) and its individual components were studied.