

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Cyclic Oxidation of Ru-Containing Single Crystal Superalloys at 1100°C

Q. FENG, B. TRYON, L. J. CARROLL and T. M. POLLOCK, *Mater. Sci. Eng.: A*, 2007, 458, (1–2), 184–194

The cyclic oxidation behaviour at 1100°C of Ru (3.5–9 at.%) containing Ni-base single crystal superalloys (1) with Cr additions (0–8 at.%) has been investigated. High levels of Cr additions (8 at.%) significantly improved oxidation resistance. A multilayered scale formed on (1); this generally consisted of an external layer of NiO, an intermediate layer of spinel and an α -Al₂O₃ inner layer (2). (2) improved oxidation performance. Ru-rich precipitates were observed in the spinel layer of (1) which displayed poor oxidation resistance.

Electronic Properties of the Semiconductor RuIn₃

D. BOGDANOV, K. WINZER, I. A. NEKRASOV and T. PRUSCHKE, *J. Phys.: Condens. Matter*, 2007, 19, (23), 232202

Single crystals of RuIn₃ (1) were grown using the flux method with In as reactant and flux medium. Temperature-dependent measurements of the resistivity of (1) show a semiconducting behaviour, in contrast to previously published results. In the high-temperature range the semiconducting gap is 0.4–0.5 eV. An anisotropy of the resistivity along [110] and [001] orientations of the tetragonal (1) was observed.

CHEMICAL COMPOUNDS

Organometallic Molecular Materials: Self-Assembly through Hydrogen Bonding of an Organoplatinum Network Structure with Zeolite-Like Topology

F. ZHANG, M. C. JENNINGS and R. J. PUDEPHATT, *Chem. Commun.*, 2007, (15), 1496–1498

[Pt(OH)₂Me₂(dpa)] (1) (dpa = di-2-pyridylamine) was formed by oxidation of [PtMe₂(dpa)] by H₂. [Pt₂(μ-OH)₂Me₂(dpa)₂][B(OH)(C₆F₅)₃]₂ (2) was obtained by abstraction of a hydroxo ligand from (1) by reaction with B(C₆F₅)₃. (1) and (2) contain both H-bonding PtOH groups and NH groups. Self-assembly of (1) to form a complex network structure gave the first “organometallic zeolite”.

Solvent-Free Synthesis of Metal Complexes

A. LAZUEN GARAY, A. PICHON and S. L. JAMES, *Chem. Soc. Rev.*, 2007, 36, (6), 846–855

Polymeric PtCl₂ will react with solid phosphines after grinding in a ball mill to give *cis*-[PtCl₂(PPh₃)₂], which can subsequently react with solid K₂CO₃ to give [Pt(CO)₃(PPh₃)₂]. Also, supramolecular host structures, such as a tetraplatinum square and a nano-scale bowl-shaped hexapalladium cage, self-assemble with remarkable efficiency in the solid state. (39 Refs.)

ELECTROCHEMISTRY

Electrochemical Performance of Nano-Pt-Supported Carbon Anode for Lithium Ion Batteries

W.-S. KIM, H. S. KIM, I.-S. PARK, Y. KIM, K.-I. CHUNG, J. K. LEE and Y.-E. SUNG, *Electrochim. Acta*, 2007, 52, (13), 4566–4571

The title anode (1) was prepared by supporting Pt nanoparticles onto C powder. The Pt nanoparticles on the C surface helped to suppress the solvent decomposition reaction: a protective film was formed as soon as (1) had contact with the electrolyte. In addition, the Pt nanoparticles act as catalyst reaction sites to improve the Li discharge reaction.

Compositional and Electrochemical Characterization of Noble Metal–Diamondlike Carbon Nanocomposite Thin Films

N. MENEGAZZO, C. JIN, R. J. NARAYAN and B. MIZAIKOFF, *Langmuir*, 2007, 23, (12), 6812–6818

Pt- and Au-diamondlike C (DLC) nanocomposite films (1) were deposited onto Si substrates by modified pulsed laser deposition. Cross-sectional TEM revealed that metal was present as arrays of noble metal islands embedded within the DLC matrix. (1) exhibited greater conductivity than their metal-free counterparts. The electrochemical properties of (1) were studied using quasi-reversible redox couples.

PHOTOCONVERSION

Photocatalytic Oxidation of NO_x by Pt-Modified TiO₂ Under Visible Light Irradiation

Y. ISHIBAL, J. SATO, S. AKITA, T. NISHIKAWA and S. MIYAGISHI, *J. Photochem. Photobiol. A: Chem.*, 2007, 188, (1), 106–111

Photooxidation of NO_x was carried out using TiO₂ (Ishihara ST-01) treated with H₂PtCl₆. Pt-modified TiO₂ was obtained with different ligand structures according to the Pt treatment method. TiO₂ photocatalysts with certain Pt complexes produced significant photocatalytic activity under visible light irradiation without decreasing photoactivity under UV light irradiation. The visible-light-induced photocatalytic activity depended on the amount of Pt.

An Investigation on Palladium Sulphide (PdS) Thin Films as a Photovoltaic Material

I. J. FERRER, P. DÍAZ-CHAO, A. PASCUAL and C. SÁNCHEZ, *Thin Solid Films*, 2007, 515, (15), 5783–5786

Polycrystalline PdS thin films (1) with tetragonal structure were grown by direct sulfuration of Pd layers. (1) exhibited a Seebeck coefficient, $S = -250 \pm 30 \mu\text{V K}^{-1}$. Electrical resistivity of (1), measured by a four contact probe, was $(6.0 \pm 0.6) \times 10^{-2} \Omega \text{ cm}$. Hall effect measurements confirmed n-type conductivity. Optical absorption coefficient in the range of photon energies $h\nu > 2.0 \text{ eV}$ was higher than 10^5 cm^{-1} .

Iridium(III) Complexes Bearing Quinoxaline Ligands with Efficient Red Luminescence Properties

K. TANI, H. FUJII, L. MAO, H. SAKURAI and T. HIRAO, *Bull. Chem. Soc. Jpn.*, 2007, 80, (4), 783–788

Excellent quantum efficiencies (50–79%) for photoluminescence were attained for cyclometallated Ir(III) complexes (1) bearing 2,3-diphenylquinoxalines in CH₂Cl₂. Luminescence peak wavelengths of (1) were within the preferred range of 653–671 nm in thin films. The most vivid red electrophosphorescence was achieved with an acetylacetonato Ir complex bearing 2,3-diphenylquinoxaline.

ELECTRODEPOSITION AND SURFACE COATINGS

In Situ Raman Spectroscopy of Annealed Diamondlike Carbon–Metal Composite Films

C. JIN, H. ZHOU, S. GRAHAM and R. J. NARAYAN, *Appl. Surf. Sci.*, 2007, 253, (15), 6487–6492

Films of diamondlike C, diamondlike C–Pt composite and diamondlike C–Au composite were annealed to 523°C. The Raman spectra for these films were fitted using a two-Gaussian function. The variations of the G-peak position, the D-peak position, and the I_D/I_G ratio were examined as a function of temperature. The diamondlike C film exhibited greater thermal stability than the diamondlike C–noble metal composite films.

Synthesis of PVP Stabilized Cu/Pd Nanoparticles with Citrate Complexing Agent and Its Application as an Activator for Electroless Copper Deposition

S. H. Y. LO, Y.-Y. WANG and C.-C. WAN, *J. Colloid Interface Sci.*, 2007, 310, (1), 190–195

Cu/Pd nanoparticles (1) were synthesised in aqueous solution using trisodium citrate as additive. The protecting agent PVP was added after the citrate. (1) exist in a stable suspension. XPS of (1) revealed small amounts of oxidised Pd on the surface and the existence of zerovalent Cu and oxidised Cu. (1) exhibited catalytic activity comparable to that of conventional Pd/Sn activator. (1) have potential as an activator for electroless Cu deposition in the PCB industry.

Electrodeposition of Magnetic CoPd Thin Films: Influence of Plating Condition

F. M. TAKATA and P. T. A. SUMODJO, *Electrochim. Acta*, 2007, 52, (20), 6089–6096

The title thin films (1) were electrodeposited from a chloride plating bath containing glycine as additive. The Co content in (1) could be varied from 6.4–94.0 at.% by controlling the pH and [Co²⁺]/[Pd²⁺] ratio in the bath. Current densities > 50 mA cm⁻² gave deposits with a typical ‘cauliflower’ morphology. For current densities < 25 mA cm⁻² cracks were observed. XRD showed that (1) were amorphous. The magnetic properties for (1) revealed that the coercivity (H_c) values ranged from 84–555 Oe and the magnetic saturation (M_s) from 0–1.73 T.

APPARATUS AND TECHNIQUE

Pd Encapsulated and Nanopore Hollow Fiber Membranes: Synthesis and Permeation Studies

B. K. R. NAIR and M. P. HAROLD, *J. Membrane Sci.*, 2007, 290, (1–2), 182–195

“Pd encapsulated” (1) and “Pd nanopore” (2) membranes on α-Al₂O₃ hollow fibres were synthesised by sol slip casting, film coating, and electroless plating steps. The unaged (1) exhibited good performance with ideal H₂/N₂ separation factors of 3000–8000 and H₂ flux ~ 0.4 mol m⁻² s⁻¹ at 370°C. The unaged (2) had a lower initial flux and permselectivity, but exhibited superior performance after 200 h.

HETEROGENEOUS CATALYSIS

HCN Synthesis from Methane and Ammonia over Platinum

S. DELAGRANGE and Y. SCHUURMAN, *Catal. Today*, 2007, 121, (3–4), 204–209

TAP (temporal analysis of products) experiments were conducted for the synthesis of HCN from NH₃ and CH₄ over Pt black. At 1173 K the HCN production rate depends on the order of introducing the reactants. HCN is formed rapidly on the CH₄ pulse just after introducing NH₃. A slow formation of HCN is observed on the NH₃ pulse that follows a CH₄ pulse. The rate-determining step for the formation of HCN is the NH₃ decomposition rate.

Synthesis and Characterization of Pt/Mg(Al)O Catalysts Obtained From Layered Double Hydroxides by Different Routes

O. LORRET, S. MORANDI, F. PRINETTO, G. GHIOTTI, D. TICHIT, R. DURAND and B. COQ, *Microporous Mesoporous Mater.*, 2007, 103, (1–3), 48–56

Pt-containing Mg/Al layered double hydroxides at different Pt loadings (0–3.2 wt.%) were prepared by coprecipitation, impregnation and sol-gel methods. After activation and reduction treatments, Pt nanoclusters interacting with Mg(Al)O supports were obtained. The behaviour of Pt/Mg(Al)O systems as multifunctional catalysts was investigated in the cascade reaction between benzaldehyde and propanal.

Pd-Based Sulfated Zirconia Prepared by a Single Step Sol-Gel Procedure for Lean NO_x Reduction

E. M. HOLMGREEN, M. M. YUNG and U. S. OZKAN, *J. Mol. Catal. A: Chem.*, 2007, 270, (1–2), 101–111

The title catalysts (1) were obtained *via* a single-step sol-gel procedure. Tetragonal zirconia was formed at lower temperatures; larger zirconia crystallites were obtained when Pd was added to the gel. Raman spectra of (1) calcined at 700°C showed both the tetragonal and the monoclinic phases, indicating a surface phase transition. (1) were active for the reduction of NO₂ with CH₄ under lean conditions. (1) calcined at 700°C were much more active than (1) calcined at 600°C, despite the observed transition to the monoclinic phase.

XPS and ^1H NMR Study of Thermally Stabilized Rh/CeO₂ Catalysts Submitted to Reduction/Oxidation Treatments

C. FORCE, E. ROMÁN, J. M. GUIL and J. SANZ, *Langmuir*, 2007, 23, (8), 4569–4574

Rh/CeO₂ (1) was prepared by incipient wetness impregnation of CeO₂ with a solution of Rh(NO₃)₃. (1) was submitted to different H₂ reduction, Ar⁺ sputtering, and oxidation treatments. Below 473 K, reduction increased the amount of OH and Ce³⁺ species; above this temperature, reduction produced O vacancies at the surface of the support. From ^1H NMR, the metal dispersion was deduced and the mean size of the metal particles (38 Å) estimated.

HOMOGENEOUS CATALYSIS

Screening of a Modular Sugar-Based Phosphite-Oxazoline Ligand Library in Asymmetric Pd-Catalyzed Heck Reactions

Y. MATA, O. PÀMIES and M. DIÉGUEZ, *Chem. Eur. J.*, 2007, 13, (12), 3296–3304

A library of phosphite-oxazoline ligands (1) derived from D-glucosamine was synthesised. (1) were successfully screened in the Pd-catalysed Heck reaction of several substrates with high regio- ($\leq 99\%$) and enantioselectivities (ee 's $\leq 99\%$) as well as with improved activities. The catalytic activity was highly affected by the oxazoline and biarylphosphite substituents and the axial chirality of the biaryl moiety of (1).

Development of a Concise Scaleable Synthesis of 2-Chloro-5-(pyridin-2-yl) Pyrimidine via a Negishi Cross-Coupling

C. PÉREZ-BALADO, A. WILLEMSSENS, D. ORMEROD, W. AELTERMAN and N. MERTENS, *Org. Process Res. Dev.*, 2007, 11, (2), 237–240

A Negishi cross-coupling between an *in situ* prepared 2-pyridylzinc chloride and 5-iodo-2-chloropyrimidine catalysed by Pd(PPh₃)₄ afforded 2-chloro-5-(pyridin-2-yl) pyrimidine (1) in one step. Chromatography can be omitted as a convenient purification was developed. The method has been used on a mini-plant scale to produce 16 kg of (1). The Pd and Zn content of (1) was acceptable for the production of its derived API, a selective PDE-V inhibitor.

FUEL CELLS

Nanoscale Current Imaging of the Conducting Channels in Proton Exchange Membrane Fuel Cells

D. A. BUSSIAN, J. R. O'DEA, H. METIU and S. K. BURATTO, *Nano Lett.*, 2007, 7, (2), 227–232

A Pt-coated AFM tip was used as a nanoscale cathode in a PEMFC. Inhomogeneous distributions of conductive surface domains at several length scales were found. Phase current correlation microscopy showed that a large number ($\sim 60\%$) of the aqueous domains present at the surface of the operating Nafion membrane were inactive.

Surface-Modified Carbons as Platinum Catalyst Support for PEM Fuel Cells

A. GUHA, W. LU, T. A. ZAWODZINSKI and D. A. SCHIRALDI, *Carbon*, 2007, 45, (7), 1506–1517

The ability of functionalised high surface area graphitic (C nanofibres) and amorphous (activated C) C to homogeneously support Pt particles was investigated. Functionalisation by conc. acid treatment created various O carrying functionalities on the C surfaces. Chemical reduction of the Pt precursor complex, using milder reducing agents at 75–85°C, and using ethylene glycol at 140°C, gave the smallest Pt particle sizes. XPS confirmed the existence of Pt in (primarily) its metallic state on the functionalised C.

Characterization and PEMFC Testing of Pt_{1-x}M_x (M = Ru, Mo, Co, Ta, Au, Sn) Anode Electrocatalyst Composition Spreads

D. A. STEVENS, J. M. ROULEAU, R. E. MAR, A. BONAKDARPOUR, R. T. ATANASOSKI, A. K. SCHMOECKEL, M. K. DEBE and J. R. DAHN, *J. Electrochem. Soc.*, 2007, 154, (6), B566–B576

Pt_{1-x}M_x random alloy samples were deposited *via* magnetron sputtering through shadow masks onto a nanostructured thin-film support for testing in a 64-electrode PEMFC. CO stripping voltammograms and H₂ oxidation polarisation curves with pure H₂ and reformat (≤ 50 ppm CO) were measured. Ru, Mo, and Sn were confirmed to improve the CO tolerance of Pt, although the intrinsic H₂ oxidation activity of Pt decreased significantly as the Sn content increased.

Autothermal Reforming of Gasoline on Rh-Based Monolithic Catalysts

A. QI, S. WANG, C. NI and D. WU, *Int. J. Hydrogen Energy*, 2007, 32, (8), 981–991

0.3 wt.% Rh/3 wt.% MgO/20 wt.% CeO₂-ZrO₂ supported on cordierite monolith was used for ATR. At 650–800°C, O₂/C molar ratio of 0.38–0.45 and H₂O/C ratio of 2.0, octane was fully converted into reformat (+ small amount of CH₄), whereas toluene converted into CH₄-free reformat at a relatively higher temperature. A 1 kW gasoline fuel processor for fuel cell application was successfully operated at a (H₂ + CO) throughput of 0.9–1.0 m³ h⁻¹ for 60 h.

MEDICAL USES

Corrosion Behaviour of FePt-Based Bulk Magnets in Artificial Saliva Solution

A. GEBERT, S. ROTH, R. GOPALAN, A. A. KÜNDIG and L. SCHULTZ, *J. Alloys Compd.*, 2007, 436, (1–2), 309–312

The corrosion behaviour of Fe₅₀Pt₅₀, Fe₃₅Pt₃₅P₃₀ and Fe₃₃Pt₄₄C₃ magnets was investigated in artificial saliva solution at 37°C. Electrochemical polarisation measurements and SEM showed that the alloys exhibit a Pt-like behaviour (highly stable). Enhanced corrosion activity did not occur when these alloys were coupled with commercial Fe- and CoCr-based dental alloys. A low-corroding state was attained in combination with the dental spring steel Fe-18Cr-18Mn-2Mo-1N.