

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Optimization of Composition and Heat Treatment of Age-Hardened Pt-Al-Cr-Ni Alloys

M. HÜLLER, M. WENDEROTH, S. VORBERG, B. FISCHER, U. GRATZEL and R. VÖLKL, *Metall. Mater. Trans.*, 2005, **36A**, 681–689

Pt-base alloys (1) with various contents of Al, Cr and Ni were arc melted. Solution heat treatments at 1450°C followed by water quenching gave single phase alloys. Ageing at 1000°C caused the precipitation of L1₂ ordered particles. (1), comprising (in at.%): 11 Al; 3 Cr; 6 Ni and balance Pt, had cuboidal precipitates with edge lengths of 200 to 500 nm along with a volume fraction of 23% and a lattice misfit of -0.1%. Ageing at 1100°C coarsened the precipitates.

Enthalpies of Mixing of Metallic Systems Relevant for Lead-Free Soldering: Ag-Pd and Ag-Pd-Sn

C. LUEF, A. PAUL, H. FLANDORFER, A. KODENTSOV and H. IPSER, *J. Alloys Compd.*, 2005, **391**, (1–2), 67–76

Two different Calvet type microcalorimeters were used to determine the enthalpies of mixing for liquid Ag-Pd (≤ 55 at.% Pd) and Ag-Pd-Sn alloys at 1400 and 900°C, respectively. The ternary interaction parameters were fitted using the Redlich-Kister-Muggiano polynomial model for substitutional solutions. The isoenthalpy curves of the integral molar enthalpy of mixing in the liquid state were constructed.

Limited Penetration Depths of Hydrides in Cylindrical Pd-Ni Alloy Samples

B. BARANOWSKI and L. DEBOWSKA, *Polish J. Chem.*, 2005, **79**, (4), 783–787

The penetration depths of hydrides, formed in 6.8 kbar of gaseous H₂, were studied at 25°C in cylindrical samples of Pd-Ni alloys with diameters 80, 120, 150, 200 and 250 μm. The exposure time was ~ 4 months. The penetration depth was limited, showing a linear increase with radii of the wires, with a slope of ~ 0.6 μm per 1 μm of the wire radius.

Oxidation Behavior of Ru(Al)-RuAl Intermetallic Eutectics Produced by Ingot and Powder Metallurgy

N. ILIC, F. SOLDERA and F. MÜCKLICH, *Intermetallics*, 2005, **13**, (5), 444–453

Oxidation of RuAl was examined in air at 1100 and 1300°C for ≤ 100 h. At 1100°C, oxidation of the lamellar eutectic produced by ingot metallurgy formed an external porous Al₂O₃ scale and an internal oxidation zone (1) mostly with periodic structure. (1) consisted of discontinuous bands of Al₂O₃ and Ru-rich phase. At 1300°C, the oxidation resistance and stability of the lamellar microstructure greatly decreased. The eutectic alloy was less affected by oxidation at 1100°C than ingot metallurgy alloy.

Synthesis of Well-Dispersed Ruthenium Nanoparticles Inside Mesostructured Porous Silica under Mild Conditions

V. HULEA, D. BRUNEL, A. GALARNEAU, K. PHILIPPOT, B. CHAUDRET, P. J. KOOYMAN and F. FAJULA, *Microporous Mesoporous Mater.*, 2005, **79**, (1–3), 185–194

Well-dispersed Ru nanoparticles (1) of controlled size were loaded into micelle-templated silica (MTS), via the mild decomposition of Ru(COD)(COT) (COD = η⁴-cycloocta-1,5-diene; COT = η⁶-cycloocta-1,3,5-triene), embedded inside the SiO₂. The regular channels of MTS hosted and stabilised (1).

CHEMICAL COMPOUNDS

Compounds of Triphenylstibine and Platinum:

Synthesis, Properties and Reactivity

R. S. BARBIÉRI, C. R. BELLATO and A. C. MASSABNI, *Transition Met. Chem.*, 2005, **30**, (2), 217–220

The reactivity of zerovalent compound [Pt(SbPh₃)₃] is described. [{Pt(SbPh₃)₃}₂N₂] containing bridging N₂, [{Pt(SbPh₃)₃}₂C₂], with an ethynediyl group also bridging, and [Pt(CO)₂(SbPh₃)₂] were synthesised under N₂, acetylene, or CO, respectively, at ordinary pressures. Reaction products included the dimer [PtBr₃(SbPh₃)₂]₂ and mixed complexes [PtL₂(SbPh₃)₂]₂ (L = PPh₃, AsPh₃).

Improved Synthetic Routes to Rhodium Bipyridine Complexes: Comparison of Microwave vs. Conventional Synthesis

D. AMARANTE, C. CHERIAN, C. EMMEL, H.-Y. CHEN, S. DAYAL, M. KOSHY and E. G. MEGHEE, *Inorg. Chim. Acta*, 2005, **358**, (7), 2231–2238

cis-[Rh(bpy)₂X₂][PF₆] (1) (X = Cl, Br, I) were produced in a one-step synthesis from RhX₃·nH₂O using the title methods. Pure (1) were achieved by maintaining a 2:1 ratio of bpy to Rh in solution. (1) are pure enough for emission spectroscopy after minimal work-up. The first CV data on *cis*-[Rh(bpy)₂I₂][PF₆] are reported. The irreversible Rh(III)–Rh(I) redox potential becomes more positive from Cl to I.

ELECTROCHEMISTRY

Electrochromism in Spray Deposited Iridium Oxide Thin Films

P. S. PATIL, R. K. KAWAR and S. B. SADALE, *Electrochim. Acta*, 2005, **50**, (12), 2527–2532

The title films (1) were deposited onto F doped Sn oxide coated glass from IrCl₃ solution by pneumatic spray pyrolysis. (1) exhibited anodic electrochromism due to the Ir⁺⁴ ↔ Ir⁺³ intervalence charge transfer transition. The *in situ* transmittance measurement depicts the colouration-bleaching process of (1).

Remarkably High Activity of Electrodeposited IrO₂ Film for Electrocatalytic Water Oxidation

M. YAGI, E. TOMITA and T. KUWABARA, *J. Electroanal. Chem.*, 2005, 579, (1), 83–88

An aqueous solution containing K₂IrCl₆ and oxalic acid that had been aged to give an IrO₂ colloid was used for anodic electrodeposition of an IrO₂ film (1) on an ITO electrode (2). CV of (1)-coated (2) in 0.1 M KNO₃ aqueous solution showed the steep rise of an anodic current at 1.0 V vs. SCE for catalytic H₂O oxidation. The anodic current at 1.3 V on the CV was 660 times higher than that for a blank bare (2).

PHOTOCONVERSION

Substituent Effects of Iridium Complexes for Highly Efficient Red OLEDs

S. OKADA, K. OKINAKA, H. IWAWAKI, M. FURUGORI, M. HASHIMOTO, T. MUKAIDE, J. KAMATANI, S. IGAWA, A. TSUBOYAMA, T. TAKIGUCHI and K. UENO, *Dalton Trans.*, 2005, (9), 1583–1590

The emission spectra and phosphorescence quantum yields of Ir complexes with substituted 1-phenylisoquinoline ligands differ from those of tris(1-phenylisoquinolinato-C²,N)Ir(III). The substituents attached to the phenyl ring affect the stability of the HOMO and contribute to mixing between ³π-π* and ³MLCT for the lowest excited states. An OLED based on tris[1-(4-fluoro-5-methylphenyl)isoquinolinato-C²,N]Ir(III) gave an external quantum efficiency of 15.5% and power efficiency of 12.4 lm W⁻¹ at a luminance of 218 cd m⁻².

Conduction and Photoelectrochemical Properties of Monomeric and Electropolymerized Tetraruthenated Porphyrin Films

H. WINNISCHOFER, A. L. B. FORMIGA, M. NAKAMURA, H. E. TOMA, K. ARAKI and A. F. NOGUEIRA, *Photochem. Photobiol. Sci.*, 2005, 4, (4), 359–366

Tetraruthenated porphyrin films (1) were deposited directly on transparent ITO electrodes. (1) showed typical *p*-type semiconductor behaviour, under an applied bias potential and in the presence of O₂ as electron acceptor. However, (1) deposited on nanocrystalline TiO₂ in a Grätzel-type cell behaved as a sensitizer of an *n*-type semiconductor.

APPARATUS AND TECHNIQUE

Gas Sensing with Films of Nanocrystalline WO₃ and Pd Made by Advanced Reactive Gas Deposition

A. HOEL, L. F. REYES, S. SAUKKO, P. HESZLER, V. LANTTO and C. G. GRANQVIST, *Sens. Actuators B: Chem.*, 2005, 105, (2), 283–289

The title films with Pd:W atomic ratios of 0, 0.5 and 13% were sintered at ≤ 873 K. Their gas sensing properties, shown by relative changes in conductivity, were studied at temperatures ≤ 773 K. Pd decreased the recovery time and increased the low concentration sensitivity to H₂S (0.5 ppm). The sensors were also able to detect formaldehyde (45 ppm).

Electrocatalytic Properties of [Ru(bpy)(tpy)Cl]PF₆ at Carbon Ceramic Electrode Modified with Nafion Sol-Gel Composite: Application to Amperometric Detection of L-Cysteine

A. SALIMI, R. HALLAJ and M. K. AMINI, *Anal. Chim. Acta*, 2005, 534, (2), 335–342

The title electrode (1) was prepared by forming a bulk-modified C ceramic electrode with Nafion, and then immersing the electrode into a Ru-complex solution for 5–25 s. CV of (1) showed a stable and well-defined redox couple due to the Ru(II)/Ru(III) system, with surface-confined characteristic. (1) exhibited excellent catalytic activity toward the electrooxidation of L-cysteine at pH 3–9. The antifouling effect of the Nafion film increases the reproducibility of results. (1) could be used in a flow system.

HETEROGENEOUS CATALYSIS

Hydrodesulfurization of Model Diesel Using Pt/Al₂O₃ Catalysts Prepared by Supercritical Deposition

S. HAJI, Y. ZHANG, D. KANG, M. AINDOW and C. ERKEY, *Catal. Today*, 2005, 99, (3–4), 365–373

Pt nanoparticles (0.5–11 wt%)/Al₂O₃ (1) were obtained by a sc-CO₂ deposition method. (1) were found to be active for the hydrodesulfurisation of dibenzothiophene dissolved in *n*-hexadecane without sulfiding the metal phase. The hydrodesulfurisation proceeded only *via* the direct hydrogenolysis route at 310–400°C and atmospheric pressure. Increasing the metal loading of (1) increased the activity.

Effect of Lanthanum Oxide on Catalytic Performance of Pd/Al₂O₃ Catalyst for Anthraquinone Hydrogenation to H₂O₂

R. WANG, C. LIN, S. MAO, T. CHEN and J. LIN, *Chin. J. Catal.*, 2005, 26, (4), 296–300

Pd/Al₂O₃ (1) promoted with La₂O₃ was prepared by successively impregnating Al₂O₃ with aqueous solutions of La nitrate and Na₂PdCl₄. La₂O₃ was shown to be a good promoter of (1) in the anthraquinone hydrogenation to H₂O₂. La₂O₃ inhibited the growth of Al₂O₃ crystals at high temperature, increased the surface area, enhanced the surface alkalinity of Al₂O₃, improved the Pd dispersion on the support, increased the Pd concentration and/or decreased the Pd layer thickness on (1).

Direct Synthesis of Palladium-Containing Mesoporous Carbon

Q. HU, J. PANG, N. JIANG, J. E. HAMPSEY and Y. LU, *Microporous Mesoporous Mater.*, 2005, 81, (1–3), 149–154

Pd-containing mesoporous C materials (1) were synthesised using a sol-gel process on Si(OEt)₄ in the presence of C and Pd nitrate followed by carbonisation and SiO₂ template removal processes. (1) contain uniformed pores with 2.2 nm average pore diameter and surface areas > 1500 m² g⁻¹. (1) exhibited high catalytic activities for the Heck reaction of iodobenzene and styrene.

Microwave Plasma Assisted Preparation of Pd-Nanoparticles with Controlled Dispersion on Woven Activated Carbon Fibres

P. KOROVCHENKO, A. RENKEN and L. KIWI-MINSKER, *Catal. Today*, 2005, 102–103, 133–141

Low-pressure air-microwave-plasma can be used to increase the acidity of activated C fibres (1). Selective removal of surface carboxylic acid groups occurs, but phenolic groups (2) remain intact. Pd was deposited on (1) from $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ solution *via* ion-exchange with protons from surface groups of (2). Reductive activation in H_2 at 573 K gave Pd(0) nanoparticles (< 3 nm). This reduction can also be carried out using a H_2 microwave-plasma treatment for < 1 min.

Growth of Polystyrene Films via Gas-Phase Polymerization with $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ Thin Film Catalyst

K. S. WAIN, A. SEN and S. H. KIM, *J. Polym. Sci. A: Polym. Chem.*, 2005, 43, (9), 1930–1934

$[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ was deposited as a thin film (1) by nebulisation of dilute solutions onto a quartz crystal microbalance. Styrene vapour was then passed over (1) in a controlled environment. The polymerisation occurred rapidly after a short induction time and appeared to involve the entire catalyst film.

Asymmetric Hydrogenation Using Chiral Rh Complexes Immobilised with a New Ion-Exchange Strategy

W. P. HEMS, P. McMORN, S. RIDDEL, S. WATSON, F. E. HANCOCK and G. J. HUTCHINGS, *Org. Biomol. Chem.*, 2005, 3, (8), 1547–1550

Rh diphosphine complexes using DuPhos and JosiPhos as chiral ligands were immobilised by ion exchange into MCM-41. When these catalysts (1) are used for enantioselective hydrogenation, their catalytic performance is comparable to the corresponding homogeneous catalysts. (1) can be readily recovered and reused. $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ was also initially immobilised by ion exchange and subsequently modified by the chiral diphosphine.

HOMOGENEOUS CATALYSIS

Enantioselective Pd-Catalyzed C^*-C , C^*-N , and C^*-S Bond Formation Reactions Using First P,P,N,N -Tetradentate Chiral Phosphites

V. N. TSAREV, S. I. KONKIN, A. A. SHYRYAEV, V. A. DAVANKOV and K. N. GAVRILOV, *Tetrahedron: Asymmetry*, 2005, 16, (10), 1737–1741

Chiral P,P,N,N -tetradentate ferrocene-derived iminophosphite and iminodiamidophosphite ligands (1) were synthesised for the first time. (1) have high efficiency in Pd-catalysed allylic substitution. The iminodiamidophosphite was the best stereoselector for the substitution of 1,3-diphenylallyl acetate with dimethyl malonate ($\leq 90\%$ ee), pyrrolidine ($\leq 85\%$ ee) and Na *p*-toluene sulfinate ($\leq 81\%$ ee).

Highly Active and Selective Catalysts of Hydrogenation Based on Palladium Bis-acetylacetonate and Phenylphosphine

L. B. BELYKH, T. V. GOREMYKA, L. N. BELONOVA and F. K. SCHMIDT, *J. Mol. Catal. A: Chem.*, 2005, 231, (1–2), 53–59

$\text{Pd}(\text{acac})_2/\text{PH}_2\text{Ph}$ was highly active for the hydrogenation of unsaturated bonds, carbonyl and nitro groups. Interaction of PH_2Ph with $\text{Pd}(\text{acac})_2$ in DMF at 80°C in H_2 gave nanoparticles containing Pd(0), Pd phosphine (1) and Pd phosphinidene complexes (2). The associates of (2) and (1) act as a carrier for the Pd(0) clusters.

First Example of 'Palladium-Nanoparticle'-Catalyzed Selective Alcoholysis of Polyhydrosiloxane: A New Approach to Macromolecular Grafting

B. P. S. CHAUHAN, J. S. RATHORE and N. GLOXHANI, *Appl. Organomet. Chem.*, 2005, 19, (4), 542–550

Nanocomposites of 'Pd-polysiloxane' (1) were obtained as stable and isolable powder by reduction of $\text{Pd}(\text{OAc})_2$ with polymethylhydrosiloxane. The latter functions as a reducing agent and a capping agent for the generation and stabilisation of 'Pd'-nanoclusters (2). Redispersion of (1) in organic solvents, in the presence of polymethylhydrosiloxane, gave catalytically active polysiloxane-wrapped (2). (2) were used as recyclable catalyst for macromolecular grafting via alcoholysis of polyhydrosiloxane.

Oxidation of Ketones by Ceric Perchlorate Catalysed by Iridium(III)

P. K. TANDON, S. SAHGAL, A. K. SINGH, GAYATRI and M. PURWAR, *J. Mol. Catal. A: Chem.*, 2005, 232, (1–2), 83–88

IrCl_3 was found to be a more efficient catalyst in aqueous perchloric acid for the oxidation of aliphatic ketones by $\text{Ce}(\text{ClO}_4)_4$ than Os and Ru. The rate decreases in low acid concentrations at the start, reaches a minimum and then becomes proportional to $[\text{HClO}_4]$. Reduction of oxidant by H_2O is dependent on the concentrations of acid and $[\text{Ce}(\text{IV})]$ initially used. Orders are one with catalyst, one initially with respect to oxidant and ketones tending to zeroth order at higher concentrations.

FUEL CELLS

High Dispersion and Electrocatalytic Properties of Platinum on Functional Multi-Walled Carbon Nanotubes

D.-J. GUO and H.-L. LI, *Electroanalysis*, 2005, 17, (10), 869–872

Pt nanoparticles were electrochemically dispersed on 4-aminobenzene monolayer-grafted C MWNTs by a potential-step method. The resulting Pt-C MWNT composites (1) were shown by CV to have high electrocatalytic activity for MeOH oxidation. This was attributed to the small particle size, high dispersion of Pt particles and the properties of the C MWNTs. The long-term cycling stability of (1) was investigated. (1) have potential for use in DMFCs.

Deposition of Platinum Nanoparticles on Organic Functionalized Carbon Nanotubes Grown *In Situ* on Carbon Paper for Fuel Cells

M. M. WAJE, X. WANG, W. LI and Y. YAN, *Nanotechnology*, 2005, 16, (7), S395–S400

Pt nanoparticles (1) (2–2.5 nm) have been deposited on C nanotubes (CNTs) grown directly on C paper. Sulfonic acid functionalisation of the CNTs facilitates the uniform deposition of Pt ions on the CNT surface. After removal of the organic groups during high temperature reduction, (1) are in electrical contact with the C paper backing. A typical Pt loading of ~ 0.09 mg cm⁻² was obtainable. The electroactive specific surface area of the Pt/CNT electrode from the H desorption peak was 50 m² g⁻¹.

A Method for Optimizing Distributions of Nafion and Pt in Cathode Catalyst Layers of PEM Fuel Cells

D. SONG, Q. WANG, Z. LIU, M. EIKERLING, Z. XIE, T. NAVESSIN and S. HOLDCROFT, *Electrochim. Acta*, 2005, 50, (16–17), 3347–3358

When optimisation of the Nafion content and Pt loading on the cathode catalyst layers in a PEMFC was carried out with either of them as the single variable, the optimal distribution was a linearly increasing function from the gas diffusion layer side to the membrane side. For a two-variable optimisation, the Nafion content distribution was still a linearly increasing function, but the Pt loading was a convex increasing function. The optimisation of the Nafion content was more important.

Rate Expression for Electrochemical Oxidation of Methanol on a Direct Methanol Fuel Cell Anode

T. VIDAKOVIC, M. CHRISTOV and K. SUNDMACHER, *J. Electroanal. Chem.*, 2005, 580, (1), 105–121

A cyclone flow cell was used to study the kinetics of MeOH oxidation at a PtRu catalyst on a MEA. The reaction order with respect to MeOH varied from 0 (low potential, high concentrations) to close to unity (high potentials), when limiting currents are recorded. A model for the anodic oxidation of MeOH is suggested, based on a bifunctional mechanism which includes MeOH adsorption on the Pt sites, formation of OH_{ads} on the Ru sites, and surface reaction between these adsorbed species.

PtRu–LiCoO₂—An Efficient Catalyst for Hydrogen Generation from Sodium Borohydride Solutions

P. KRISHNAN, T.-H. YANG, W.-Y. LEE and C.-S. KIM, *J. Power Sources*, 2005, 143, (1–2), 17–23

H₂ generation by the hydrolysis of aqueous NaBH₄ solutions was carried out using Pt, Ru catalysts dispersed in IRA-400 anion-exchange resin (1) and LiCoO₂ supported Pt, Ru and PtRu catalysts (2). (2) were better than (1). The efficiency of PtRu–LiCoO₂ was \sim double that of either Ru- or Pt–LiCoO₂ for NaBH₄ concentration ≤ 10 wt.%. This hydrolysis may have potential for H₂ production for PEMFCs.

ELECTRICAL AND ELECTRONIC ENGINEERING

Novel Superconductivity Coexisting with Incipient Electric-Multipolar Order in CePt₃Si

M. ISHIKAWA, S. YAMASHITA, Y. NAKAZAWA, N. WADA and N. TAKEDA, *J. Phys.: Condens. Matter*, 2005, 17, (23), L231–L234

Measurements of the specific heat C_p of annealed CePt₃Si (1) in magnetic fields $B \leq 10$ T confirmed two anomalies. The lower-temperature anomaly at 2.2 K was depressed with increasing B and was absorbed at ~ 4 T into the other anomaly at ~ 2.8 K. The latter anomaly continues to grow into a solid peak with increasing B . The superconductivity of (1) may be mediated by magnetic or electronic excitation, influenced by quadrupolar-like order induced at ~ 2.8 K.

Characterization of Pd/Ni/Au Ohmic Contacts on p-GaN

H. K. CHO, T. HOSSAIN, J. W. BAE and I. ADESIDA, *Solid-State Electron.*, 2005, 49, (5), 774–778

A low-resistance ohmic contact (1) to Mg-doped p -type GaN grown by MOCVD with a carrier concentration of 2×10^{17} cm⁻³, using a Pd/Ni/Au metallisation was formed. An anneal at 500°C for 1 min in flowing N₂ produced (1) with a specific contact resistivity as low as 2.4×10^{-3} Ω cm². Ni and Pd interdiffusion toward the GaN surfaces reduces specific contact resistance. The reduction of the native oxide by Ni diffusion together with the formation of Pd and Ni related-gallide phases at the p -GaN surface causes the low contact resistance.

Novel Ir-Ti Alloy Electrodes for High-Density Ferroelectric Memory Applications

J.-M. KOO, S. SHIN, S. KIM, J. K. LEE and Y. PARK, *Jap. J. Appl. Phys., Part 1*, 2005, 44, (6A), 4052–4056

Alloy Ir-Ti, in high-density ferroelectric memory applications, was improved by controlling the interface layer between Pb(Zr, Ti)O₃ (PZT) and an electrode. The Ir-Ti electrode was resistant to O₂ annealing and the surface did not roughen much. The Ti in Ir-Ti assisted the growth of (111) grains of PZT, with Ir-Ti acting as a seed layer. In ultrathin films of PZT and a bottom electrode, IrTiO_x (20 nm)/IrTi (10 nm) could protect the reliability of the thin PZT.

A New Method to Prepare RuO₂·xH₂O/Carbon Nanotube Composite for Electrochemical Capacitors

G. H. DENG, X. XIAO, J. H. CHEN, X. B. ZENG, D. L. HE and Y. F. KUANG, *Carbon*, 2005, 43, (7), 1566–1569

Carbon nanotubes (CNT)s-Ru composites were grown directly on graphite substrate by CVD using electrodeposited Ni-Ru catalysts. RuO₂·xH₂O/CNT electrode (1) was obtained by electrooxidation of Ru/CNT composite. (1) shows excellent capacitive properties and long-term cycle stability. At 6% w/w RuO₂, the specific capacitance of (1) composite is six times larger than that of CNT electrode (25 F g⁻¹).