

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Mechanism of Platinum-Enhanced Oxidation of Silicon at Low Temperatures

H. KOBAYASHI, T. YUASA, K. YAMANAKA, K. YONEDA and Y. TODOKORO, *J. Chem. Phys.*, 1998, **109**, (12), 4997–5001

Pt-enhanced oxidation of Si below 300°C was studied using a Pt layer deposited on 1 nm thick Si oxide-covered Si. The Si oxide layer grew between the Pt layer and the Si substrate on low temperature heat treatment, but where Pt was directly deposited on the Si substrate Si oxide formed, mainly on the Pt layer. Oxidation is enhanced by applying a positive bias voltage to the Si substrate during heat treatment. O ions are the moving species in the oxide layer. The reaction at the interface is the rate-determining step.

Transformations in Undercooled Molten Pd_{40.5}Ni_{40.5}P₁₉

C. W. YUEN and H. W. KUI, *J. Mater. Res.*, 1998, **13**, (11), 3034–3042

Liquid phase separation by nucleation and growth (LNG) occurred in undercooled molten Pd_{40.5}Ni_{40.5}P₁₉ for undercooling $\Delta T \leq 60$ K ($\Delta T = T_i - T$, where T_i is the liquidus and T is the kinetic crystallisation temperature). Liquid state spinodal decomposition (LSD) occurred for $\Delta T \geq 100$. The transition regime from LNG to LSD occurs for $60 \leq \Delta T \leq 100$ K. LSD is an important factor in glass-forming in metallic alloys.

Surface Composition of Ru Containing Duplex Stainless Steel after Passivation in Non-Oxidizing Media

G. MYBURG, K. VARGA, W. O. BARNARD, P. BARADLAI, L. TOMCSÁNYI, J. H. POTGIETER, C. W. LOUW and M. J. VAN STADEN, *Appl. Surf. Sci.*, 1998, **136**, (1/2), 29–35

The passive layers which form spontaneously on duplex stainless steels (DSSs) and 0.3% Ru duplex stainless steel (DSS:Ru) in HCl and H₂SO₄ were studied. Cr concentrations were ~3% higher in the passive layers of both, but Ni concentrations were lower. Mo enrichment was only observed for DSS:Ru passivated in HCl. The passive layer on DSS:Ru contained more Cr₂O₃ than Cr(OH)₃, and more Fe²⁺ than Fe³⁺, compared to DSS.

The Shape Memory Effect in Equiatomic TaRu and NbRu Alloys

R. W. FONDA, H. N. JONES and R. A. VANDERMEER, *Scr. Mater.*, 1998, **39**, (8), 1031–1037

Shape memory (SM) alloys based on Nb₅₀Ru₅₀ (1) and Ta₅₀Ru₅₀ (2), have SM transition temperatures > 1000°C. The SM effect is due to the high temperature, tetragonal-to-cubic (β to β') phase transition at 885°C for (1) and 1120°C for (2), and occurs at Ru contents of ~ 40–55%.

Time-Reversal Symmetry-Breaking Superconductivity in Sr₂RuO₄

G. M. LUKE, Y. FUDAMOTO, K. M. KOJIMA, M. I. LARKIN, J. MERRIN, B. NACHUMI, Y. J. UEMURA, Y. MAENO, Z. Q. MAO, Y. MORI, H. NAKAMURA and M. SIGRIST, *Nature*, 1998, **394**, (6693), 558–561

Muon spin-relaxation measurements are reported on the superconductor Sr₂RuO₄. These show the spontaneous appearance of an internal magnetic field below the transition temperature. The superconducting state is characterised by the breaking of time-reversal symmetry which, with other symmetry considerations, suggests that superconductivity in Sr₂RuO₄ is of 'p-wave' (odd-parity) type, analogous to superfluid ³He.

CHEMICAL COMPOUNDS

Pt^{II}-Directed Self-Assembly of a Dinuclear Cyclophane Containing Two Fullerenes

T. HABICHER, J.-F. NIERENGARTEN, V. GRAMLICH and F. DIEDERICH, *Angew. Chem. Int. Ed.*, 1998, **37**, (13/14), 1916–1919

Self-assembly of two C₆₀ hexakis-adducts, each with a di(4-pyridyl)methano addend, and two Pt^{II} centres yielded the fullerene-containing rigid dinuclear cyclophane (1), a new class of supramolecular multifullerene arrays. X-ray crystallography of (1) showed a perfectly planar parallelogram formed by four vertex atoms of the cyclophane at the cost of substantial angle strain. Larger complex fullerene arrays should be possible.

Synthesis and Characterization of New Rh(III) Compounds with the K₂CdCl₆ Structure-Type: Sr₃MRhO₆ (M = Y, Sc, In)

R. C. LAYLAND, S. L. KIRKLAND, P. NUÑEZ and H.-C. ZUR LOYE, *J. Solid State Chem.*, 1998, **139**, (2), 416–421

Sr₃MRhO₆ (M = Y, Sc, In) compounds were synthesised and structurally characterised by Rietveld refinement of powder XRD data in the space group R $\bar{3}c$; Z = 6. The compounds, which are isostructural with K₂CdCl₆, have a structure of infinite one-dimensional chains of alternating face-shared RhO₆ octahedra and MO₆ trigonal prisms. The Sr cations are located in a distorted square antiprismatic position.

Ruthenium Carbonyl Clusters in Faujasite Cages: Synthesis and Characterization

G.-C. SHEN, A. M. LIU and M. ICHIKAWA, *Inorg. Chem.*, 1998, **37**, (21), 5497–5506

[Ru₃(CO)₁₂] clusters in faujasite, Na₅₆Y, cages are activated at 298–363 K in H₂ giving intrafaujasite anchoring of [H₄Ru₄(CO)₁₂]. Ru^{III}(NH₃)₆ in Na₅₆X in CO/H₂ activated slowly at 298–363 K, via conversion of intermediates [Ru(NH₃)₃(CO)]²⁺ and Ru^I(CO)₃ to [Ru₆(CO)₁₈]²⁺. The Na⁺ α -cage cations and faujasite topology are significant in the anchoring mechanism.

PHOTOCONVERSION

Relay of Positive Holes from Photoirradiated Pt-Loaded TiO₂ Particles in an Aqueous Phase to *t*-butylhydroquinone in an Oil Phase

T. OHNO, K. NAKABEYA, K. FUJIHARA and M. MATSUMURA, *J. Photochem. Photobiol., A: Chem.*, 1998, 117, (2), 143–147

Evolution of H₂ and oxidation of I⁻ ions proceeded concurrently on photoirradiated Pt-loaded TiO₂ particles suspended in aqueous KI-containing solution. The photochemical reaction is stopped by the back reaction, when I₃⁻ ions, which are preferentially reduced over H₂ evolution, reach a certain level. Addition of *t*-butylhydroquinone/*t*-butylquinone dissolved in an oil phase, produced a redox reaction where the I₃⁻ ions oxidise the *t*-butylhydroquinone. The product concentration in the aqueous phase can thus be kept low.

Chemiluminescence and Catalysis of the Decomposition of Dimethyldioxirane Adsorbed on the Gas Phase on Silipore Containing a tris(bipyridyl)ruthenium Complex Ru(bpy)₃Cl₂ and 9,10-diphenylanthracene

D. V. KAZAKOV, A. I. VOLOSHIN, N. N. KABAL'NOVA, S. L. KHURSAN, V. V. SHERESHOVETS and V. P. KAZAKOV, *Izv. RAN, Ser. Khim.*, 1998, (8), 1516–1521

The kinetics of the decomposition of dimethyldioxirane (DMD) adsorbed on the gas phase on a silipore surface was studied in the presence of chemiluminescent (CL) activators, such as Ru(bpy)₃Cl₂ (1) and 9,10-diphenylanthracene. The CL yield of the DMD decomposition was estimated at 4×10^{-9} Einstein mol⁻¹ and the chemiexcitation yield of methylacetate was estimated at 4×10^{-4} .

Intrazeolitic Photoreactions of Ru(bpy)₃³⁺ with Methyl Viologen

S. K. DAS and P. K. DUTTA, *Langmuir*, 1998, 14, (18), 5121–5126

The reaction of Ru(bpy)₃³⁺-zeolite Y with H₂O to give Ru(bpy)₃²⁺ was greatly accelerated (hours) by visible light, compared to the dark (days), even though intermediate species were similar. The promotion of reactivity by light is attributed to the nature of the visible charge-transfer bands. Reactivity is enhanced when ion-exchanged methyl viologen is in nearby supercages and there is spectral evidence of pyridone production.

Multistep Photocatalytic Reduction of Dioxygen by Immobilized [Ru(bpy)₃]²⁺ in Nafion and Cellulose Matrices and Macrocyclic Cobalt(III) Complexes

J. PREMKUMAR and R. RAMARAJ, *J. Chem. Soc., Dalton Trans.*, 1998, (21), 3667–3672

The multistep one-electron photocatalytic reduction of O₂ to H₂O₂ was performed using systems of [Ru(bpy)₃]²⁺ (1) incorporated into membranes of Nafion and cellulose, and macrocyclic Co(III) complexes, as the catalyst. The electron transfer process took place efficiently in the membrane rather than in homogeneous solution.

Efficient Light-to-Electrical Energy Conversion with Dithiocarbamate-Ruthenium Polypyridyl Sensitizers

R. ARGAZZI, C. A. BIGNOZZI, G. M. HASSELMANN and G. J. MEYER, *Inorg. Chem.*, 1998, 37, (18), 4533–4537

Ru(dcbH)(dcbH₂)(L) sensitizers, where L is diethyldithiocarbamate, dibenzylidithiocarbamate or pyrrolidinedithiocarbamate, dcbH is 4-(COOH)-4'-(COO)-2,2'-bipyridine, and dcbH₂ is 4,4'-(COOH)₂-2,2'-bipyridine, were anchored to nanocrystalline TiO₂ films for light to electrical energy conversion in regenerative photoelectrochemical cells. The sensitizers have intense MLCT bands centred at ~380 and 535 nm that sensitise TiO₂ over a broad spectral range. Interfacial electron transfer processes are quantified.

Effects of RuO₂ on Activity for Water Decomposition of a RuO₂/Na₂Ti₃O₇ Photocatalyst with a Zigzag Layer Structure

S. OGURA, M. KOHNO, K. SATO and Y. INOUE, *J. Mater. Chem.*, 1998, 8, (11), 2335–2337

Na₂Ti₃O₇ (1), having a zigzag layer structure containing highly dispersed RuO₂, decomposes H₂O to H₂ and O₂ upon UV irradiation. Photocatalyst (1) was impregnated with RuCl₃ aqueous solution or Ru₃(CO)₁₂ dissolved in tetrahydrofuran. The Ru loading was 0.7 wt.%. The ability to form O surface radicals upon UV irradiation may be correlated with the photocatalytic activity in this layered titanate.

New DNA-Binding Ruthenium(II) Complexes as Photoreagents for Mononucleotides and DNA

C. MOUCHERON and A. KIRSCH-DE MESMAEKER, *J. Phys. Org. Chem.*, 1998, 11, (8/9), 577–583

The spectroscopic properties of two photoprobes for DNA, Ru(phen)₂(PHEHAT)²⁺ (1) and Ru(TAP)₂(PHEHAT)²⁺ (2) (phen = 1,10-phenanthroline, TAP = 1,4,5,8-tetraazaphenanthrene, PHEHAT = 1,10-phenanthroline[5,6-*b*]-1,4,5,8,9,12-hexaazatriphenylene) were studied and compared with complexes containing either an extended planar ligand or π-acceptor ligands. Complex (1) luminesces upon intercalation between DNA and base pairs while the luminescence of (2) was quenched by binding to DNA.

ELECTRODEPOSITION AND SURFACE COATINGS

Preparation of Hydrophobic Platinum Electrodes by Composite-Plating

Y. ONO, T. KAMATA, S.-H. KIM, M. YASUDA, A. YOSHIYAMA, T. NONAKA and Y. NISHIKI, *Denki Kagaku*, 1998, 66, (7), 720–726

Hydrophobic Pt electrodes were prepared by composite-plating Pt with PTFE fine particles on Pt substrate in an amidosulfuric acid-dinitrodiammine Pt complex bath, containing a cationic surfactant under ultrasonic irradiation. Optimised electrodes had contact angles with water > 150°, and were stable in strongly acidic, neutral and alkaline solutions, after anodic and cathodic polarisation at 200 mA cm⁻², for 10 h.

Electrodeposited Platinum Microparticles in a Sulfonate-Polyaniline Film for the Electrosorption of Methanol and Sorbitol

C.-H. YANG and T.-C. WEN, *Electrochim. Acta*, 1998, 44, (2-3), 207-218

Studies of Pt microparticles electrodeposited into a 2,5-diaminobenzenesulfonic acid-modified polyaniline (SPANI) film on IrO₂ electrodes showed that under constant deposition potential the microparticles were dispersed in the SPANI in a three-dimensional array. This procedure yielded spherical catalyst particles. For catalyst loadings of ~ 7 mg cm⁻² deposited at -200 mV, the electrosorption coverages of sorbitol are greater than those of MeOH by ~ 15%.

Formation of Catalytic Pd on ZnO Thin Films for Electroless Metal Deposition

R. D. SUN, D. A. TRYK, K. HASHIMOTO and A. FUJISHIMA, *J. Electrochem. Soc.*, 1998, 145, (10), 3378-3382

The formation of highly dispersed Pd species on ZnO thin films as a catalyst for electroless metal deposition was studied. A yellow-brown Pd species, identified as hydrolytic Pd(OH)₂, was efficiently adsorbed onto the ZnO surface which had been made highly porous by partial dissolution in acidic PdCl₂. In the subsequent electroless metal deposition step, Pd(OH)₂ was first reduced to Pd(0) by a reductant, such as HCHO, contained in the deposition bath. Pd particles can thus act as highly active catalytic nuclei for several types of electroless metal depositions.

Pulsed Electrodeposition Synthesis and Hydrogen Absorption Properties of Nanostructured Palladium-Iron Alloy Films

K. J. BRYDEN and J. Y. YING, *J. Electrochem. Soc.*, 1998, 145, (10), 3339-3346

Nanostructural pure Pd and Pd-Fe alloy films for H₂ separation and membrane reactions were prepared by pulsed electrodeposition. Crack-free films were prepared using short pulse duration, long times between pulses and a plating temperature of 60°C. Films containing > 20 at.% Fe were stable against grain growth to 400°C without any $\alpha \rightarrow \beta$ phase transition. The Pd-Fe nanoalloys had very fast H₂ absorption kinetics at room temperature, without activation.

APPARATUS AND TECHNIQUE

Photoelectrochemical Fabrication of Submicrometer Platinum Pattern on Titanium Dioxide Single Crystal Surface

H. ISHII, S. JUODKAZIS, S. MATSUO and H. MISAWA, *Chem. Lett. Jpn.*, 1998, (7), 655-656

Submicrometer patterning of TiO₂-rutile single crystal surfaces by Pt was achieved using photocatalytic reduction of PtCl₄²⁻ to Pt in an aqueous solution of H₂PtCl₆. Pt patterns, ~ 700 nm wide, were fabricated along the focal point traces of a 380 nm wavelength laser beam (power 158 μ W) on the rutile substrates. The stage velocity was 0.43 μ m s⁻¹. Using this technique, fabrication of well defined Pt patterns, formed of Pt islands 50-200 nm in size, is possible.

A Novel Ni-Ru-P Amorphous Alloy Composite Membrane and Its Performance Study

G. WU, B. LIU and J.-F. DENG, *Chem. Lett. Jpn.*, 1998, (9), 889-890

A Ni-Ru-P amorphous alloy composite membrane supported on ceramic tube was prepared by electroless plating, first by high temperature activation of the outer surface with a paste containing PdCl₂, then by plating in a solution containing NiCl₂·6H₂O, NaH₂PO₄, RuCl₃, Na₃C₆H₅O₇·2H₂O, NH₄Cl and triethanolamine. The Ni_{88.8}Ru_{0.2}P_{11.2} amorphous membrane had better permselectivity for H₂ than porous and Ni-P membranes. The Ni-Ru-P membrane reactor itself had a promoting effect on EtOH dehydrogenation.

Determination of Sulfite in Sugar and Sulfur Dioxide in Air by Chemiluminescence Using the Ru(bipy)₃²⁺-KBrO₃ System

F. WU, Z. HE, H. MENG and Y. ZENG, *Analyst*, 1998, 123, (10), 2109-2112

Sulfite in sugar and SO₂ in air were determined by a chemiluminescence (CL) method using Ru(bipy)₃²⁺-SO₃²⁻-KBrO₃ (bipy = 2,2'-bipyridyl) and triethanolamine as SO₂ absorbent material. The sulfite concentration was proportional to the CL intensity in the range 2.5 × 10⁻⁸ - 9.5 × 10⁻⁵ mol l⁻¹. The limit of detection was 3.8 × 10⁻⁹ mol l⁻¹ and the relative standard deviation was 4.6% for 5 × 10⁻⁵ mol l⁻¹ sulfite solution.

Light Emitting Electrochemical Devices from Sequentially Adsorbed Multilayers of a Polymeric Ruthenium(II) Complex and Various Polyanions

A. WU, J. LEE and M. F. RUBNER, *Thin Solid Films*, 1998, 327-329, 663-667

Solid-state light-emitting electrochemical devices were made from sequentially adsorbed multilayers, 7-59 Å thick per bilayer, of a positively charged polyester containing Ru(bpy)₃²⁺ polyester and polyanions. Devices fabricated with polyanions containing weakly acidic carboxylic acid groups displayed symmetric behaviour but more diode-like behaviour was observed where the polyanions contained the strongly acidic sulfonic acid group. The best devices had an external quantum efficiency of 3.2% (photons/electron) and a maximum light output of ~ 1350 nW with poly(acrylic acid) as the polyanion.

HETEROGENEOUS CATALYSIS

Oxidative Conversion of Methane to CO and H₂ over Pt or Pd Containing Alkaline and Rare Earth Oxide Catalysts

V. R. CHOUDHARY, B. PRABHAKAR, A. M. RAJPUT and A. S. MAMMAN, *Fuel*, 1998, 77, (13), 1477-1481

The activity and selectivity of Pt and Pd (1.0 wt.%) catalysts containing MgO, CaO and rare earth oxides, were studied in the oxidative conversion of CH₄ to CO and H₂ at 700 and 800°C for low contact times. Pt/Gd₂O₃ and Pd/Sm₂O₃ performed best, with high selectivity for CO but low selectivity for H₂ due to the reverse H₂O gas shift reaction.

Ultrasonic Irradiation as Activity and Selectivity Improving Factor in the Hydrogenation of Cinnamaldehyde over Pt/SiO₂ Catalysts

G. SZÖLLÖSI, B. TÖRÖK, G. SZAKONYI, I. KUN and M. BARTÓK, *Appl. Catal. A: Gen.*, 1998, 172, (2), 225–232

The effect of ultrasound on the Pt catalysed hydrogenation of cinnamaldehyde was studied in the liquid phase over Pt/SiO₂, Pt/Al₂O₃, Pt/C and EuroPt-1 catalysts at 333 K and under 1 atm H₂. Over the Pt/SiO₂ catalyst, sonochemical pretreatment greatly improved the chemoselectivity of the formation of cinnamyl alcohol (80%), with the reaction rate increasing two-fold. The beneficial effect of the ultrasound is explained by assuming the formation of effective metal-support active centres, which provide stronger acceptor sites for C=O adsorption.

Water-Promoted Ammonia Oxidation by a Platinum Amine Complex in Zeolite HZSM-5 Catalyst

A. C. M. VAN DEN BROEK, J. VAN GRONDELLE and R. A. VAN SANTEN, *Catal. Lett.*, 1998, 55, (1–4), 79–82

[Pt(NH₃)₄]²⁺HZSM-5 was found to be an active catalyst for NH₃ oxidation at low temperature (473 K) and becomes even more active in the presence of H₂O. The reaction was carried out both with a reaction mixture containing H₂O and one which was dry. The selectivity to N₂ was increased in the presence of H₂O and it appears that H₂O enhances the reaction rate for N₂ production.

Two Reaction Paths at Different Temperatures in the Reduction of Nitrogen Monoxide with Hydrogen over Supported Palladium Catalysts

A. UEDA, T. NAKAO, M. AZUMA and T. KOBAYASHI, *Chem. Lett. Jpn.*, 1998, (7), 595–596

Two conversion maxima at 373 and 573 K, were discovered in NO reduction with H₂ over Pd catalysts supported on metal oxides, when O₂ is present in the stream of reactants. This is due to a switch in the reaction path, as the temperature is raised, between the direct reduction of NO by H₂ and the reduction by H₂ of *in situ* generated NO₂. Among the Pd catalysts studied, Pd/TiO₂ showed the highest conversion of NO.

Polymer-Supported Palladium-Nickel Bimetallic Catalyst for the Regioselective Hydroesterification of Styrene

B.-S. WAN, S.-J. LIAO, Y. XU and D.-R. YU, *J. Mol. Catal., A: Chem.*, 1998, 136, (3), 263–268

The polymer-supported PVP-PdCl₂-4NiCl₂-PPH₃ bimetallic system [PVP = poly(*N*-vinyl-2-pyrrolidone)] gave 100% conversion and 99% selectivity to the branched ester in styrene hydroesterification at 80°C and 2.1 MPa CO pressure in 10 h. The remarkable selectivity and activity were caused by a strong synergic effect of PdCl₂-NiCl₂ and a polymer protection effect. The catalytically active species are nm sized particles with Pd(0) species.

HOMOGENEOUS CATALYSIS

Orthopalladated Triaryl Phosphite Complexes as Highly Active Catalysts in Biaryl Coupling Reactions

D. A. ALBISSON, R. B. BEDFORD, S. E. LAWRENCE and P. N. SCULLY, *Chem. Commun.*, 1998, (19), 2095–2096

Orthopalladation of tris(2,4-di-*tert*-butylphenyl) phosphite produced a dimeric Pd complex which is a very active catalyst in biaryl coupling reactions. For the coupling of aryl halides (4-bromoacetophenone as substrate) with phenylboronic acid (Suzuki reaction) high turnover numbers (TONs) of 1,000,000 [mol product (mol Pd)⁻¹] and turnover frequencies of ~900,000 [mol product (mol Pd)⁻¹h⁻¹] were obtained in toluene at 110°C, while when aryl bromides (4-bromoacetophenone) reacted with aryltin reagents (Stille reaction) TONs of ≤ 830,000 were obtained.

A Highly Selective Water-Soluble Dicationic Palladium Catalyst for the Biphasic Hydroxycarbonylation of Alkenes

M. SCHREUDER GOEDHEIJT, J. N. H. REEK, P. C. J. KAMER and P. W. N. M. VAN LEEUWEN, *Chem. Commun.*, 1998, (22), 2431–2432

The biphasic Pd-catalysed formation of carboxylic acids from alkenes and CO in the presence of a water-soluble bidentate diphosphine catalyst with a xanthene-type backbone and a Brønsted acid cocatalyst is described. The dicationic Pd/Xantphos-s/TsOH system was very effective and 100% selective in the hydroxycarbonylation of alkenes. Under optimised conditions, metallic Pd formation was not observed and initial turnover frequencies dropped only slightly within hours, showing the high stability of the system.

A Water-Soluble Rhodium Complex as a Catalyst Precursor for the Hydroformylation of Olefins

S. U. SON, J. W. HAN and Y. K. CHUNG, *J. Mol. Catal., A: Chem.*, 1998, 135, (1), 35–39

A H₂O-soluble cationic (sugar-substituted arene) rhodium complex was prepared by the reaction of [Rh(COD)Cl]₂ with AgBF₄ and then with phenyl-β-D-glucopyranoside. The Rh complex displays exceptionally high regioselectivity and high conversion to branched-chain aldehydes in the hydroformylation of styrene derivatives.

Rhodium-Catalyzed Hydrocarbonylation of Acetic Acid into Higher Acids

P. SERP, L. CHATEAU, R. FEURER, A. KIENNEMANN and P. KALCK, *J. Mol. Catal., A: Chem.*, 1998, 136, (3), 269–278

The hydrocarbonylation of acetic acid into higher homologues catalysed by Rh/iodide systems was studied at 20 MPa and 220°C. The [RhI₂(CO)]₂ homogeneous precursor had mean turnover frequencies of 67 h⁻¹ and selectivity ≤ 80% in propionic acid; while for heterogeneous catalysis, Rh/activated C was efficient for the conversion of acetic acid into propionic acid (80% selectivity) in a fixed bed reactor.

Ruthenium Catalyzed Asymmetric Transfer Hydrogenation of β -Ketoesters

K. EVERAERE, J.-F. CARPENTIER, A. MORTREUX and M. BULLIARD, *Tetrahedron: Asymmetry*, 1998, 9, (17), 2971–2974

Chemiselective transfer hydrogenation of β -ketoesters to the corresponding alcohols is achieved in the presence of catalytic combinations of $[\text{RuCl}_2(\eta^6\text{-arene})_2]$ and ephedrine or diamino-type chiral ligands. Activities up to 190 h^{-1} were achieved at 20°C and moderate to good enantiomeric excesses of 36–94% were obtained. The results showed the dramatic effect of the arene ligand both on the enantioselectivity and the activity of the catalyst.

Calixarene-Core Multifunctional Initiators for the Ruthenium-Mediated Living Radical Polymerization of Methacrylates

J. UEDA, M. KAMIGAITO and M. SAWAMOTO, *Macromolecules*, 1998, 31, (20), 6762–6768

Calixarene-core initiators with four, six and eight dichloroacetate units initiate living radical polymerisation of methyl methacrylate (MMA) catalysed by $\text{RuCl}_2(\text{PPh}_3)_2$ in the presence of $\text{Al}(\text{O}i\text{Pr})_3$ in toluene at 80°C to give tetra-, hexa-, and octa-armed star polymers of controlled lengths, respectively. The polymers that were produced had controlled molecular weights and narrow molecular weight distributions. Octa-armed star polymers with block copolymers of MMA and *n*-butyl methacrylate as arm chains were also prepared by sequential block copolymerisation initiated by the calix[8]arene-core initiators.

FUEL CELLS

Pt Inclusion Compounds as Oxygen Reduction Catalysts in Polymer-Electrolyte Fuel Cells

G. FAUBERT, D. GUAY and J. P. DODELET, *J. Electrochem. Soc.*, 1998, 145, (9), 2985–2992

Pt-based catalysts for the cathodes of PEFCs were prepared from the intercalation of PtCl_2 in high specific area graphite or C black. When the intercalated Pt was reduced by K-naphthalene complex, metallic Pt inclusions were obtained in HS300 or Vulcan. The Pt-inclusion catalysts performed best after a conditioning period of 48 h at 0.5 V vs. RHE. In the high-current region, Pt inclusions in graphite or C black performed better than commercial catalyst with higher Pt loadings. Thus higher current densities can be achieved or the Pt loadings can be lowered.

Fabrication and Testing of a H_2 - O_2 Fuel Cell Using $\text{Mo}_x\text{Ru}_y\text{Se}_z$

T. ROMERO, R. RIVERA, O. SOLORZA and P. J. SEBASTIAN, *Int. J. Hydrogen Energy*, 1998, 23, (11), 1041–1044

$\text{Mo}_x\text{Ru}_y\text{Se}_z$ electrocatalyst (1) for O_2 reduction in a fuel cell was synthesised and characterised. A H_2 - O_2 fuel cell was constructed, using H_2SO_4 as the electrolyte, and (1) supported on C as cathode and Pt/C as anode. The cell was tested at room temperature and atmospheric pressure. The H_2 - O_2 cell was ~32% efficient with no degradation in the output with time.

ELECTRICAL AND ELECTRONIC ENGINEERING

Preparation of High Quality RuO_2 Electrodes for High Dielectric Thin Films by Low Pressure Metal Organic Chemical Vapor Deposition

J. M. LEE, J. C. SHIN, C. S. HWANG, H. J. KIM and C.-G. SUK, *J. Vac. Sci. Technol. A*, 1998, 16, (5), 2768–2771

Pure, conducting and crack-free RuO_2 thin films with electrical resistivity of 45–60 $\mu\Omega \text{ cm}$ were deposited on a Si substrate at 250–450 $^\circ\text{C}$ by low pressure MOCVD using $\text{Ru}(\text{C}_{11}\text{H}_{10}\text{O}_2)_2$ as a precursor. At the lower deposition temperature, with small O additions, smoother and denser RuO_2 thin films were deposited. These films had better step coverage needed for high dielectric electrodes in ULSI DRAM.

Role of Yttria-Stabilized Zirconia Produced by Ion-Beam-Assisted Deposition on the Properties of RuO_2 on SiO_2/Si

Q. X. JIA, P. ARENDT, J. R. GROVES, Y. FAN, J. M. ROPER and S. R. FOLTYN, *J. Mater. Res.*, 1998, 13, (9), 2461–2464

Highly conductive biaxially textured RuO_2 thin films were deposited on SiO_2/Si substrates by pulsed laser deposition, using yttria-stabilised ZrO_2 (YSZ) prepared by ion-beam-assisted-deposition (IBAD) as a template. The biaxially oriented RuO_2 had a room-temperature resistivity of 37 $\mu\Omega \text{ cm}$ and residual resistivity ratio > 2 . $\text{Ba}_{0.5}\text{Se}_{0.5}\text{TiO}_3$ thin films deposited on $\text{RuO}_2/\text{IBAD-YSZ}/\text{SiO}_2/\text{Si}$ had a pure (111) orientation normal to the substrate surface and a dielectric constant above 360 at 100 kHz.

Ferroelectric Properties of $\text{SrRuO}_3/(\text{Ba,Sr})\text{TiO}_3/\text{SrRuO}_3$ Epitaxial Capacitor

T. KAWAKUBO, S. KOMATSU, K. ABE, K. SANO, N. YANASE and N. FUKUSHIMA, *Jpn. J. Appl. Phys.*, 1998, 37, (9B), 5108–5111

The ferroelectric properties of $\text{SrRuO}_3/(\text{Ba}_x\text{Sr}_{1-x})\text{TiO}_3/\text{SrRuO}_3$ ($x = 0-1$) all-perovskite heteroepitaxial capacitors were studied on SrTiO_3 substrates. A peak relative dielectric constant of 870 and maximum remanent polarisation of 58 $\mu\text{C cm}^{-2}$ were obtained, dependent on the Ba content at a dielectric film thickness of 20 nm. These are the highest storage capacitors and the thinnest ferroelectric capacitors reported so far. Deep submicron ferroelectric and dielectric memory applications are discussed.

Preparation and Characterization of RuO_2 Thin Films

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RuO_2 thin films prepared by MOCVD and reactive sputtering under various conditions are reported. The films were specular, crack-free and adhered well to the substrate. Films deposited at substrate temperature $> 100^\circ\text{C}$ had metallic character. The grain-boundary scattering model fits well for films of grain size ~12–50 nm. With MOCVD a nearly strain-free, high-quality RuO_2 thin film can be deposited on Si substrate.