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Introduction

Polymer electrolyte fuel cells (PEFCs) are promising electrochemical power generators, especially for transport and portable applications. Pure hydrogen or a hydrogen-rich gas is often used as the fuel in order to obtain high electrical efficiency at ambient temperature. However, storage, transport and refuelling are more problematic for a gaseous fuel than for a liquid. If fuel reforming is used, this renders the system even more complex.

Therefore, research has recently been focused on the use of hydrogen carriers such as aqueous solutions of small organic solvents, which offer easier storage, improved safety and high energy densities (between 1750 and 7080 Wh l\(^{-1}\) depending on the component) compared to hydrogen gas (180 Wh l\(^{-1}\) at 1000 psi and 25ºC) (1).

At present, of the liquid systems, only the direct methanol fuel cell (DMFC) has been widely studied (2–7). Disadvantages of methanol include its toxicity, high flammability and tendency to permeate through the widely-used Nafion® membrane — a phenomenon known as ‘crossover’. However, several other organic fuels that possess higher boiling points and lower crossover rates than methanol have shown promising preliminary results (8–13).

At low temperatures, Pt nanoparticles are widely used as catalyst materials for organic fuels in the fuel cell anode. However, pure Pt catalysts only extract the hydrogen atoms from the carbon chain. They cannot cleave the carbon–carbon bond or oxidise the carbon–oxygen bond at the range of potentials normally encountered in a liquid-fuelled fuel cell. Therefore, Ru is added to offer a possible catalyst site for water to decompose to hydrogen and hydroxyl (OH) groups at lower potentials (6, 14), enabling the organic fuel to be oxidised completely to carbon dioxide.
The aim of the present study is to compare the behaviour of different liquid fuels for a PtRu (60:40) catalysed PEFC. The chosen fuels are all short-chained carbon compounds. The crossover rates of the fuels through the commonly used Nafion® 115 (N-115) membrane were explored, followed by their performance in a PEFC with a Nafion® 115 membrane as the electrolyte.

Measurement Conditions and MEA Preparation

The solutions used were prepared from methanol (Fluka, p.a.), formaldehyde (Merck, p.a.), formic acid (Riedel-de Haën, p.a.), ethanol (Altia, Grade A), acetaldehyde (Merck, p.a.), 1-propanol (Merck, extra pure), 2-propanol (Merck, p.a.), ethylene glycol (Aldrich, 99.89%), glycerol (Fluka, p.a.) and ultrapure water (Milli-Q® (MQ), Millipore, 18.2 MΩ cm).

To observe the crossover phenomenon with as few variables as possible, the crossover experiments were performed in a two-compartment diffusion cell. The Nafion® 115 membrane was pressed between the two compartments, then one side of the cell was filled with a 1 M solution of the fuel and the other with deionised water. 30 μl samples were taken every 10 min for 60 min and were analysed with a gas chromatograph (HP 6890 GC) using an HP Innowax column at a heating rate of 5ºC min⁻¹. An internal standard of 10 μl of 1,4-dioxane was added to each sample.

The membrane electrode assembly (MEA) was made by spraying a mixture of 2 mg cm⁻² catalyst powder (anode: Pt:Ru (60:40) on Vulcan XC-72 carbon (40%); cathode: Pt on Vulcan (40%)), Nafion® liquid ionomer (5 wt.%, Aldrich) and 2-propanol on the surface of the Nafion® 115 membrane. After spraying both sides, the MEA was hot pressed at a temperature of 130ºC and a pressure of 50 kN for 2 min.

All measurements were performed in a fuel cell with an active area of 7.26 cm². The 1 M liquid fuels were fed to the anode compartment at room temperature at a rate of 1.5 ml min⁻¹, and the gas (Instrument Oxygen 5.0, AGA) to the cathode at 270 ml min⁻¹. The cell was allowed to stabilise overnight (liquid fuel 0.2 ml min⁻¹ and oxygen 30 ml min⁻¹ at 30ºC) before the measurements were taken. Prior to each fuel change, the cell was rinsed with MQ-water for 2 h. All measurements were made at temperatures of 30ºC, 50ºC and 70ºC.

Fuel Cell Efficiency and Crossover Rates

The results obtained show that fuel cell efficiency, defined as current density at a particular cell voltage, is temperature-related. Fuel cell efficiency increases with increasing temperature for all the fuels tested, as shown in Figure 1 for a DMFC. However, the crossover rate also increases with temperature, as shown in Figure 2. Figures 1 and 2 present the behaviour of methanol; the results for the other fuels are similar.

Increasing the temperature of the DMFC from 30ºC to 50ºC increases the fuel cell efficiency by

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**Fig. 1 Effect of temperature on the efficiency of the direct methanol fuel cell (DMFC)**

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**Platinum Metals Rev., 2009, 53, (2)**
96%, and from 50°C to 70°C by 43% (Table I). This is due to the faster electrode kinetics at the anode and the cathode when the temperature is increased. For other fuels, a temperature change from 30°C to 50°C leads to an increase in efficiency of between 36% and 109%, while an increase from 50°C to 70°C increases efficiency by 31% to 77% (Table I). The open circuit potential (OCP) of the fuel cell represents the difference in potential between the anode and the cathode when there is no external current flow. This also shows a slight increase when the temperature is raised, but this phenomenon is related to the catalyst material of the electrodes and the fuel used. Therefore, only the OCP for each fuel at 50°C is presented in Table I.

Raising the temperature also increases the fuel crossover from the anode to the cathode (Figure 2). Changing the temperature from 30°C to 70°C more than doubles the amount of methanol being transported to the cathode, causing a decrease in fuel cell performance. The crossover rate of the fuel depends not only on the temperature but also on the fuel and membrane used (15). Crossover through the Nafion® 115 membrane during the

![Fig. 2 Effect of temperature on the crossover of 1 M methanol through the Nafion® 115 membrane](image)

Table I

Open Circuit Potentials (OCPs) in a Fuel Cell and Increase in Fuel Cell Efficiency when the Temperature is Raised*

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Number of carbons in chain</th>
<th>OCP at 50°C, V</th>
<th>Increase in fuel cell efficiency with temperature, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mehtanol</td>
<td>C₁</td>
<td>0.58</td>
<td>96 43</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>C₁</td>
<td>0.57</td>
<td>79 43</td>
</tr>
<tr>
<td>Formic acid</td>
<td>C₁</td>
<td>0.64</td>
<td>36 32</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂</td>
<td>0.53</td>
<td>73 49</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>C₂</td>
<td>0.54</td>
<td>54 77</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>C₂</td>
<td>0.46</td>
<td>109 76</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>C₃</td>
<td>0.44</td>
<td>63 50</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>C₃</td>
<td>0.81</td>
<td>55 48</td>
</tr>
<tr>
<td>Glycerol</td>
<td>C₃</td>
<td>0.44</td>
<td>107 31</td>
</tr>
</tbody>
</table>

* All measurements were carried out at a potential of 0.05 V
first 60 minutes in the diffusion cell at 25ºC is presented for all the studied fuels in Figure 3. The crossover information for formic acid and glycerol was not included because of very low crossover for these fuels and the difficulty of analysing very small volumes of dilute formic acid samples.

Figure 3 demonstrates that methanol, being a small and neutral molecule which behaves similarly to water, permeates easily through the membrane. This results in losses in fuel cell efficiency. In contrast, formaldehyde, an even smaller molecule, has a lower crossover rate, due to the formation of methylene glycol with water (16) which due to its larger size permeates less easily through the Nafion® 115 membrane.

Permeability of alcohols through the membrane decreases with increasing size and complexity of the molecule, which justifies the interest in higher alcohols. Even though the crossover of ethanol and 2-propanol is not as severe as that of methanol, these fuels have shown a tendency to swell the membrane, influencing the MEA structure (17, 18). This results from the fact that the alcohols replace water molecules in the proton conducting membrane, decreasing the mobility of the protons, which increases electrolyte resistance. As shown in Figure 3, for most fuels the crossover through the Nafion® 115 membrane at 25ºC over 60 minutes is linear, but for 1-propanol and ethylene glycol the crossover increases sharply after 30 minutes. This fact strongly supports the idea that these larger organic molecules might interact with the membrane, causing changes to the membrane morphology.

Open Circuit Potentials with Different Fuels

For all the fuels, the theoretical OCP can be calculated from thermodynamic values. For the fuels studied, the calculated OCP values lie between 1.00 V and 1.25 V under standard conditions. However, in real processes, the OCP is substantially lower due to mixed potentials caused by fuel crossover lowering the total potential of the cathode, and activation overpotentials caused by surface phenomena at both electrodes.

Figure 4 shows that the observed OCP of a PtRu-catalysed fuel cell lies between 0.4 V and 0.6 V at 50ºC for all the fuels tested except 2-propanol, which produces a higher OCP of 0.8 V (Table I), in accordance with previous results (13, 18). The high OCP of 2-propanol is presumably the result of two different phenomena. Firstly, 2-propanol has a low crossover rate through the Nafion® 115 membrane (Figure 3), resulting in lower cathode overpotentials. Secondly, when the OH-group is situated on the central carbon atom of the molecule, the electronegative oxygen draws electrons from the carbon, which then attracts electrons from the C–C bonds. This changes the adsorption of the molecule to the catalyst surface, which leads to a different oxidation path to that seen for primary alcohols. This causes lower overpotentials at the anode, again resulting in a higher OCP.
Another fuel also reaches slightly higher over-potentials than other alcohols and aldehydes. Formic acid produces an OCP of 0.64 V (Table I). Formic acid has previously been shown to have a very small crossover through cation exchange membranes, due to the anionic nature of the dissolved molecule (19). Formic acid has also shown higher electrochemical activity compared to methanol (20). These phenomena would be expected to result in a higher OCP than that seen for light alcohols with high crossover rates.

The lowest OCP values (under 0.5 V) are attained with 1-propanol, ethylene glycol and glycerol (Table I). The low OCP of 1-propanol is probably caused by the dramatic increase in 1-propanol crossover after the fuel has been in contact with the Nafion® 115 membrane for 40 minutes (Figure 3). The OCP values of ethylene glycol and glycerol are around 0.1 V lower than those of methanol and ethanol. It is reasonable to assume that this is due to the OH-groups connected to every carbon atom in the diol and triol, changing the adsorption mechanisms on the PtRu surface.

Performance of One-Carbon Fuels

Figure 4 shows that organic molecules containing only one carbon atom are superior fuels for the PtRu-catalysed fuel cell, producing current densities at least three times higher than larger molecules. The difference between methanol and formaldehyde performance is surprisingly minor. Methanol has a higher energy density and a higher OCP, therefore it might have been expected to offer better performance. The observed result indicates that the performance loss when using methanol as a fuel is significant, likely due to severe methanol crossover. Investigation of new membrane materials to decrease methanol crossover may eventually lead to increased OCP and improved efficiency of the DMFC.

Formaldehyde exhibits a much lower crossover than methanol and performs better at lower current densities, but when higher current densities are reached, its performance declines gradually. As mentioned earlier, formaldehyde forms methylene glycol in water, and this greatly increases the size of the reactant. At the high current densities as the reaction rate increases, neither the products nor the reactant are able to diffuse from or to the surface fast enough, causing a rapid decrease in performance starting from 90 mA cm$^{-2}$ (Figure 4). Therefore, the rate determining step for formaldehyde seems not to be the electrode kinetics as is the case for methanol.

The smallest one-carbon molecule, formic acid, produces roughly half the current density of the other C$_1$ fuels, even though the crossover of formic acid is nearly negligible. However, when using a more concentrated solution, formic acid performs better because the current density rises with more concentrated solutions, which is not the case for alcohols (19).

Fig. 4 The efficiency of the investigated one-, two- and three-carbon liquid fuels in a single cell at 50°C.
To explore more carefully the effect of the length of the carbon chain in the fuel, the performances of the studied primary alcohols are presented in Figure 5. This figure illustrates that current density with methanol is more than three times higher than has been obtained with ethanol, and up to seven times higher than with 1-propanol. The longer the carbon chain, the lower the performance. This is due to partial oxidation of molecules with several carbon atoms, which is not seen in one-carbon molecules. These results are in accordance with a previous study (21), suggesting that the PtRu catalyst cannot effectively dissociate the C–C bond. However, it is clear that PtRu is an excellent catalyst for C₁ fuels at low temperatures.

Performance of Two- and Three-Carbon Fuels

In contrast to the case of C₁ molecules, ethanol shows more than double the current densities measured for its corresponding aldehyde, acetaldehyde, even though the OCP values of the two fuels remain nearly identical (Figure 6). This indicates that at low temperatures on the PtRu electrode, oxidation of ethanol and acetaldehyde stops at acetic acid, which is not oxidised further. Therefore, acetaldehyde displays inferior performance to ethanol. Experiments with acetic acid as a fuel gave such poor performance that the data have been excluded from this study. The other C₂ alcohol, ethylene glycol, performed in an almost identical way to ethanol, despite the fact that the
OCP of the former molecule was nearly 0.1 V lower. This indicates that the electrode processes of ethylene glycol differ from those of ethanol. Further studies need to be carried out to determine specific reaction mechanisms.

Figure 7 shows the performance of C$_3$ alcohols in terms of fuel cell efficiency. Similarly to the C$_2$ alcohols, the primary alcohol (1-propanol) and glycerol perform equally. However, in this case the primary alcohol also has a low OCP. These C$_3$ alcohols produce roughly half the current density of C$_2$ alcohols. Furthermore, the polarisation curve of the secondary alcohol 2-propanol behaves differently to that of the other compounds. Firstly, the OCP of 2-propanol is very high at 0.81 V, which is almost 0.3 V higher than that measured for methanol. Secondly, even at low current densities, 2-propanol reacts to form an intermediate, most likely acetone (22), which does not undergo further oxidation but remains at the surface, impeding the adsorption of 2-propanol. Therefore, when a current density of 20 mA cm$^{-2}$ is reached, the surface of the catalyst is completely blocked by this intermediate, resulting in a rapid drop in current. At lower potentials, around 0.5 V, the intermediate either desorbs into the solution, allowing 2-propanol to adsorb on to the catalyst sites, or is oxidised further.

In contrast to our results, two separate research groups have reported fuel cell performances for 2-propanol involving no rapid current drop (13, 18). However, Qi et al. (13) also conclude that...
the electrode surface of the PtRu catalyst is being poisoned with intermediates of 2-propanol oxidation and suggest a periodic cleaning of the surface by an electrical pulse.

Power densities of the fuels can be calculated from the cell voltage and current density (Figure 8). The highest power densities were reached with C1 fuels, providing almost five times more power than fuels with a carbon chain. Almost all the fuels studied have their power density maximum between 0.15 V and 0.3 V. However, 2-propanol produces an additional power density peak at a potential of 0.66 V. Even though 2-propanol cannot produce higher power density than C1 fuels (due to the catalyst used), it can still provide the highest power density of the fuels containing a carbon chain at 0.22 V.

**Fuel Choice for a PtRu-Catalysed Fuel Cell**

The results found during this study are in agreement with previous work by several groups (6, 23, 24) showing that a PtRu catalyst performs best for methanol and other C1 fuels. The crossover of methanol is the most severe of all the organic components studied. Methanol also produces the highest current density when used with a PtRu catalyst, therefore much research on DMFCs has concentrated on the development of impermeable electrolyte materials. However, the highest power density is produced by formaldehyde, which also seems to oxidise completely on the PtRu surface. Formaldehyde exhibits a lower crossover than methanol through the Nafion® 115 membrane, therefore it may be another possible candidate fuel for use in a PEFC.

Formic acid produces only half the current density of other C1 fuels, even though it has the lowest crossover rate through the Nafion® 115 membrane and therefore, the highest OCP of the C1 fuels. Formic acid has shown promising results when used in a fuel cell at high concentrations, even as high as 12 M (19). On the other hand, the PtRu catalyst appears not to be the optimum catalyst material for formic acid oxidation. Palladium-based and platinum-bismuth catalysts have both shown higher performances than the PtRu catalyst (25, 26).

Unfortunately, the PtRu catalyst shows no activity towards breaking the C–C bond, resulting in only partial oxidation of fuels with carbon chains. To improve the performance of the oxidation reaction for organic molecules with higher molecular weight, a second or third metal must be introduced with the Pt catalyst. For instance, tin alloyed with Pt has shown promising results towards ethanol oxidation (27, 28). Electrooxidation kinetics for organic molecules with higher molecular weight are extremely complicated and difficult to control. However, their crossover through the Nafion® 115 membrane is low and therefore they are interesting candidates and worthy of further study.

Of all the investigated organic molecules with a carbon chain, 2-propanol exhibits the most interesting results, producing the highest OCP and power density. However, there remains a problem with the formation of an intermediate which blocks the catalyst surface at higher current densities, causing a rapid drop in current. Further work is needed to characterise this intermediate and prevent its formation. Nevertheless, of the fuels tested in this study, 2-propanol appears to be the only light organic compound containing more than one carbon atom that has an appropriately high OCP. Therefore it would be an interesting focus for further research.

**Conclusions**

This paper presents the main features of temperature dependence, crossover and fuel cell efficiency for different fuels oxidised using a PtRu catalyst in a fuel cell. When the temperature of a fuel cell is increased, the performance increases. However, at the same time more fuel is transferred from the anode to the cathode compartment through the membrane. This crossover depends on the size and the charge of the fuel molecule, as well as the concentration of the fuel solution. Therefore, organic compounds with high molecular weight might offer a solution to the crossover problem.

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References

“Palladacycles: Synthesis, Characterization and Applications”

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Palladium compounds containing chelating ligands with at least one palladium–carbon bond are commonly known as palladacycles. Related compounds exist for other late transition metals. There are two distinct types of palladacycle where the ligand is either an anionic four-electron donor (Structure 1) or a six-electron donor (Structure 2).

These types of compound were first characterised in the 1960s (1, 2), but came to prominence in the 1990s when their potential as catalysts for cross-coupling reactions was highlighted by Herrmann (3); Herrmann’s palladacycle is shown in Structure 3. The compounds have high thermal stability, permitting them to be used with low cost, but poorly reactive, aryl chloride substrates. There are many variations on the basic structural types shown in Structures 1 and 2, differing both in the nature of the supporting donor atom Y (commonly Y = nitrogen, phosphorus or sulfur) and the size of the chelate ring, ranging from three to ten atoms. Compounds containing five- and six-membered rings are the most easily prepared. The compounds may be neutral or charged, and dimeric compounds related to Structure 1 with bridging ligands X (such as chloride, or acetate as in Structure 3) are common.

There have been increasing numbers of papers related to palladacycles in recent years and this book provides a timely review of this literature. There are fifteen chapters contributed by authors interested in the field, which describe the formation, characterisation, properties and applications of palladacycles. They are most commonly formed by activation of an aryl carbon–hydrogen bond (less commonly, reaction can also occur at an aliphatic C–H bond). This transformation has attracted much interest, since C–H activation is key to the efficient utilisation of hydrocarbon natural resources, and has been the focus of both practical and theoretical studies (4). Although palladacycles show excellent thermal stability with respect to decomposition to Pd metal, they are far from inert. This has led to their exploitation as catalysts for cross-coupling reactions. Initially it was thought that these compounds might be stable to reduction to Pd(0) and so a catalytic cycle involving Pd(II) and Pd(IV) was proposed, but to date clear experimental evidence to support this idea has not been obtained, and it is believed that in many cases palladacycles act as steady-state sources of colloidal Pd nanoparticles as the catalytically active species. This application of
palladacycles is rightly placed at the heart of the book and is divided into two chapters, one on Heck and Sonogashira coupling and the other dealing with Suzuki coupling and Buchwald-Hartwig amination. There is also a further chapter describing a range of other synthetic applications of palladacycles.

The book is completed by a number of chapters describing alternative applications of palladacycles. The thermal stability of these compounds arising from the chelating ligand structure allows them to be melted without the decomposition that is typical of many organometallic compounds. This has encouraged their study as liquid crystals. Their stability also makes palladacycles an interesting topic for study in thermomorphic systems, where highly temperature-dependent solubility allows effective recovery and recycling of these materials, and makes them useful for functionalising dendrimer structures. The incorporation of chiral centres into palladacycles allows them to be used as resolving agents for racemic mixtures of ligands.

Other chapters deal with the photophysical properties of palladacycles and their similarities to and interactions with biological systems and possible anticancer action.

Overall, the editors of this book are to be congratulated on delivering a well-organised, interesting and readable overview of this topic. Certainly, palladacycles will continue to provide many opportunities for further study and new applications for years to come and this book will provide an excellent introduction to the subject for those deciding to contribute to this work.

References

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Chris Barnard is a Scientific Consultant in the Catalysts and Materials Group at the Johnson Matthey Technology Centre, Sonning Common, U.K., with interests in homogeneous catalysis employing the platinum group metals. He is also interested in the application of platinum compounds as cancer therapy.
The Platinum Development Initiative: Platinum-Based Alloys for High Temperature and Special Applications: Part II

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Under the Platinum Development Initiative, platinum-based alloys were being developed for high-temperature and special applications requiring good corrosion and oxidation resistance. Work on ternary alloys had previously identified that the best of these alloys for both mechanical properties and oxidation resistance were Pt-Al-Cr and Pt-Al-Ru, as reported in Part I of the present series (1). This paper (Part II) describes transmission electron microscopy work undertaken on a range of ternary alloys to understand the strengthening mechanisms of the alloys, ascertain the nature of the ~ Pt$_3$Al precipitates and deduce the misfits between the precipitates and the matrix. A binary Pt-Al alloy was also studied in an attempt to resolve the two different versions of the phase diagram. A modified D0$_{21}$ tetragonal version of one of the lower temperature forms of ~ Pt$_3$Al was discovered. The transformation producing the D0$_{21}$ structure was confirmed as displacive, since there were distinct bands in the precipitates, which were identified as twins at higher magnifications. The dislocation interactions were also studied, and found to be more complex than nickel-based superalloys, mostly due to the different precipitate types.

Introduction

This is the second paper of a series of four on the work undertaken under the auspices of the Platinum Development Initiative (PDI), which was in operation from April 1997 until October 2007, comprising Anglo Platinum, Impala Platinum, Lonmin (previously Lonrho) and Mintek. The aim was to encourage new research into Pt-based alloys which would eventually lead to an increased use of Pt (1). Earlier reviews have already been published on the development of the thermodynamic database used to calculate phase diagrams, phases and
phase proportions (2–4). It had been found that the addition of ternary alloying elements, and in particular chromium and ruthenium, was beneficial. More extensive work was carried out on the phase relations, and Cr was found to stabilise the cubic form of the ~ Pt₃Al phase, whereas Ru acted as a solid solution strengthen (5–7).

An extensive transmission electron microscopy (TEM) investigation was undertaken in order to try to understand the differences between the precipitates in the different alloys. Since the Pt-based alloys had been conceived as analogues of the nickel-based superalloys (NBSAs), the same terminology can be used here as for the NBSAs. Thus, the Pt-rich solid solution, \( \gamma \), is \( \gamma' \) and the ~ Pt₃Al precipitates are \( \gamma'' \).

The reason why Pt₃Al was not chosen at the outset as the basis of the strengthening precipitate for the development of Pt-based alloys for high-temperature applications in aggressive environments is that it has at least two forms: a high-temperature cubic form which is identical to Ni₃Al, and at least one (8), if not two (9), lower temperature non-cubic forms. To be useful in service over a range of temperatures, the more desirable high-temperature L1₂ form needs to be stabilised, and transformations to the lower temperature form(s) stopped. The third and lowest temperature form (9) has yet to be fully confirmed, although work at Mintek has found a transformation at the identified temperature (10). Thus, there are two conflicting phase diagrams regarding the transformation temperatures of \( \gamma' \), Pt₃Al. According to McAlister and Kahan (8), there is a transformation of the high-temperature Pt₃Al phase from L1₂ to a tetragonal low-temperature variant (designated D0₁̅₂) at ~1280°C. However, Oya et al. (9) report an additional transformation at a lower temperature. The transformation temperatures given by Oya et al. are \( \gamma' \to \gamma'_1 \) at ~340°C and \( \gamma'_1 \to \gamma'_2 \) at 127°C (9).

**Structure of Low-Temperature Pt₃Al in the Binary Alloys**

It was necessary to ascertain the lower temperature structures of the Pt₃Al phases in a representative binary alloy before deriving the strengthening effects in the ternary alloys. As for all the alloys described here (11–19), the samples were made originally by arc-melting, then annealed for 96 h at 1350°C, before deformation to 0.2% proof stress, and then 3 mm diameter cylinders were cut by spark erosion. The TEM samples were sectioned as discs of 1 mm thickness, mechanically lapped to 100 μm and dimpled to 30 μm. Low angle (4°) argon ion milling was carried out at room temperature, using an acceleration voltage of 4 kV before perforation on a Gatan Inc 691 Precision Ion Polishing System (PIPS™) ion mill.

The atomic structure of the tetragonal (D0₁̅₂) phase of Pt₃Al was constructed by using the atomic positions determined by Bronger et al. (20) for the space group P4/mmm. The unit cells were constructed using the JEMS software package from P. A. Stadelmann, CIME-EPFL, Lausanne, Switzerland, which was also used to simulate the diffraction patterns. The unit cell construction was repeated using the MacTempas software package from Total Resolution LLC, Berkeley, U.S.A., which gave the same results, and high resolution images were also simulated.

Figure 1 is a bright-field TEM image of a typical Pt₃Al precipitate in the Pt₈₆:Al₁₄ (at.%.) alloy, containing a number of stacked plates or laths (P)

![Figure 1](bright-field-TEM-image-of-a-Pt₃Al-precipitate-in-a-Pt₈₆:Al₁₄-(at.%)-alloy-(19).-P-stacked-plates-or-laths-M-(Pt)-solid-solution-matrix.-The-arrows-indicate-individual-platelets-inside-the-plate-of-stacked-platelets-in-the-region-below)
characteristic of alloys in which a martensitic transformation has occurred, in a (Pt) solid solution matrix (M). Electron diffraction analysis of the stacked plates revealed that they were in twin orientation to each other. The [001] directions (or c-axes) of the tetragonal D0\textsuperscript{\textprime}c unit cells are perpendicular to one another in adjacent plates, and the twin plane is {112}. These [001] directions were parallel to the <100> type directions in the cubic matrix, consistent with Khachaturyan and Shatalov (21). Comparison of the experimental primary spots in the [110] selected area diffraction (SAD) with the simulated D0\textsuperscript{\textprime}c diffraction pattern revealed some differences. There were no experimental <001> and <003> reflections, and there were extra experimental spots with reciprocal lattice vectors ±1/3[002] and ±2/3[002]. The reflections at ±1/3[002] indicated that the precipitate phase had a tetragonal unit cell with a c-axis 1½ times that of the D0\textsuperscript{\textprime}c unit cell.

Various modelling attempts were tried for the D0\textsuperscript{\textprime}c structure, and only one modification was successful. The atomic configuration of the D0\textsuperscript{\textprime}c structure is shown in Figure 2(a), and a modified tetragonal Pt₃Al unit cell, with the c-axis equal to 1½ times that of the D0\textsuperscript{\textprime}c structure, is shown in Figure 2(b). The modified unit cell was constructed by repeating half of the D0\textsuperscript{\textprime}c structure, as shown in the dashed rectangles in Figure 2. The modified unit cell produced excellent agreement with both experimental and calculated electron diffraction patterns, and also with simulated high resolution (HR) TEM lattice images of the Pt₃Al precipitates.

**Ternary Alloys**

After studying the high-temperature compressive strengths of Pt-Al-Z alloys (where Z = chromium, iridium, ruthenium, tantalum or titanium) (1, 11, 22, 23), reasons for the different strengths were sought, and TEM was used to study the precipitate structures of the various alloys at the different testing temperatures. The samples had only a small amount of deformation (11). The precipitates showed at least a bimodal distribution, which could even be interpreted as a trimodal distribution (Figure 3(a)) (24). The elements Cr, Ta and Ti partitioned to ~Pt₃Al and stabilised the cubic L1\textsubscript{2} structure, giving precipitates of cuboid appearance with no discernable inner structure (Figure 3(a)). Conversely, Ir and Ru partitioned to the matrix, and the precipitates transformed to the D0\textsuperscript{\textprime}c structure (Figure 3(b)), with alternating contrast bands. These are acknowledged as being due to the twinning of the stacked plates and the modified D0\textsuperscript{\textprime}c structure (19), although the transformation had already been recognised as displacive (8, 9).

The lattice misfits between the matrix and precipitate phases were also measured at room temperature and at 800ºC by X-ray diffraction (XRD) on a JEOL JDX-3500 diffractometer, with a copper source (11). The (220) peak was used to derive the (Pt) lattice parameters, (112) was used for tetragonal D0\textsuperscript{\textprime}c ~Pt₃Al, and (211) was used for cubic L1\textsubscript{2} ~Pt₃Al. Lattice misfits, $\delta$, were then calculated from these measurements, using Equation (i) (25):

$$\delta = 2 \frac{(a_{\text{ptt}} - a_{\text{matrix}})}{(a_{\text{ptt}} + a_{\text{matrix}})} \quad (i)$$

![Fig. 2](a) Unit cell of the D0\textsuperscript{\textprime}c structure of a typical Pt₃Al precipitate in a Pt₈₆-Al₁₄ (at.%) alloy, B = [110]; (b) Unit cell of the modified tetragonal D0\textsuperscript{\textprime}c structure of a Pt₃Al precipitate, B = [110] (19)
where $a_{ppt}$ denotes the lattice parameter for the $\sim Pt_3Al$ precipitate phase and $a_{\text{matrix}}$ denotes the lattice parameter for the (Pt) matrix phase. The results are presented in Table I. There was little difference between the misfits at different temperatures, and they were all negative. With the exception of the Ru alloy, all the other alloys showed an increased misfit at the higher temperature. The misfits were lower for the $L1_2$ phases (Cr, Ta and Ti alloys) than for the lower temperature $D0'_c$ structure (Ir and Ru alloys).

### Precipitates and Dislocation Interactions

Since the interaction of dislocations with the precipitates determines the mechanical properties, it was decided to study these interactions using TEM, and to compare the different effects of the ternary addition on the $\sim Pt_3Al$ precipitates. Different alloying additions are known to stabilise the high-temperature form: Cr, Ta, Ti (11, 26) and cobalt, hafnium, iron, manganese and zirconium (26, 27). Compression samples had been used before (11, 22, 23), and new samples were made from these to study the dislocation content and precipitation characteristics. The samples had been compressed at different temperatures ($21^\circ C, 800^\circ C, 1000^\circ C$ and $1300^\circ C$) for Pt$_{86}:Al_{10}:Z_4$ (at.%) alloys where $Z = Cr, Ir, Ru, Ta$ and Ti (18). Lattice parameters of the (Pt) matrix phase in Pt-Al-Z ($Z = Cr, Ru$ and Ti) alloys were derived from selected area electron diffraction (SAED), and all the patterns were $<112>$-zone type. The results were slightly different from those of Hill et al. (11); this was attributed to calibration differences in the microscope’s camera. Unlike NBSAs which have

**Table I**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Pt$_3$Al type</th>
<th>Room temperature</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_{\text{matrix}}$, nm</td>
<td>$a_{ppt}$, nm</td>
<td>$\delta$</td>
</tr>
<tr>
<td>Pt$<em>{86}:Al</em>{10}:Cr_4$</td>
<td>L$_1_2$</td>
<td>3.9022</td>
<td>3.8741</td>
</tr>
<tr>
<td>Pt$<em>{86}:Al</em>{10}:Ir_4$</td>
<td>D$_0'_c$</td>
<td>3.8983</td>
<td>3.8507</td>
</tr>
<tr>
<td>Pt$<em>{86}:Al</em>{10}:Ru_4$</td>
<td>D$_0'_c$</td>
<td>3.9001</td>
<td>3.8530</td>
</tr>
<tr>
<td>Pt$<em>{86}:Al</em>{10}:Ta_4$</td>
<td>L$_1_2$</td>
<td>3.8941</td>
<td>3.8682</td>
</tr>
<tr>
<td>Pt$<em>{86}:Al</em>{10}:Ti_4$</td>
<td>L$_1_2$</td>
<td>3.8921</td>
<td>3.8642</td>
</tr>
</tbody>
</table>
precipitates with \{100\} interfaces, the interfaces of the Pt-based alloys were not necessarily \{100\}, and this made the dislocations more complex, as did the different lower temperature structure. However, the dislocations were analysed to have a Burgers vector of \(\pm \frac{1}{2}\langle110\rangle\), similar to those found for NBSAs.

**Platinum-Aluminium-Chromium**

The precipitates in the Pt-Al-Cr system were not cuboidal, but octahedral in shape. The density of small precipitates decreased with increasing compression temperature, while the dislocation density in the matrix increased, but the changes were not large in either. There were paired dislocations in all the large precipitates, and these were interpreted to be misfit dislocations because there were different types of dislocations at different parts of the precipitate, and networks around the edges. With increasing temperature, the structure of the dislocation system remained the same, and no other slip systems were activated.

**Platinum-Aluminium-Iridium**

The morphology of the precipitates in the Pt-Al-Ir alloys was different from those of the samples with Cr, Ta or Ti, as shown in Figure 4 (24). They were ‘ogdoadically-diced’ (28) (often described as cruciform or Maltese Cross-shaped), consisting of eight interconnected lobes (four in cross-section). At room temperature, there were no dislocations associated with the precipitates, although some matrix dislocations appeared to extend to the precipitate/matrix interface. After compression at 800°C, the precipitate edges straightened (although the corners were still rounded) and the first dislocations appeared in the precipitate. Isolated dislocations traversed the matrix. At 1100°C, the precipitates had become more spherical, with twin bands and multiple twinning. The dislocations associated with the large precipitates were in pairs. At 1300°C, the precipitates were more irregular, with a high dislocation density associated with all twin bands.

**Platinum-Aluminium-Ruthenium**

The precipitates in the Pt-Al-Ru alloys appeared similar to those in the Pt-Al-Ir sample, and showed twinned regions, confirming that there was a displacive transformation and a tetragonal structure. Their edges were curved, showing low surface energy for their boundaries, but were more regular at higher compression temperatures. The twin bands were better developed at higher temperatures, with dislocations observed in alternating twin bands. Once again, the dislocations occurred in pairs, indicative of dissociated dislocations.

**Platinum-Aluminium-Tantalum**

The precipitates in the Pt-Al-Ta system had straight interfaces with a high density of interfacial dislocations, and a low density within the precipitates. Isolated tangles of mixed screw and edge dislocations were observed in the matrix. After compression at 800°C, irregular precipitates with no dislocations were observed, while the matrix had a high dislocation density and small cubic precipitates. At 1100°C, the matrix dislocations disappeared, while the precipitates (which were now more regular) showed dislocations. At 1300°C, the interfaces of the precipitates were much better defined. Considering the dislocations, the Ta alloy was the strongest, but earlier work (29, 30) had showed that its oxidation resistance was insufficient for high-temperature and special applications.
**Platinum-Aluminium-Titanium**

After compression at 20ºC, the precipitates had well-defined and straight edges, with no dislocations, although the matrix had a high density of dislocation tangles. After compression at 800ºC, there were still no dislocations within the precipitates, although the matrix dislocation density was lower. There was also a high density of smaller precipitates in the matrix, which could add to strengthening of the matrix. Only after compression was carried out at 1100ºC were dislocations observed in the precipitates (Figure 5) (24). It is not certain whether these were misfit dislocations at the interfaces between the precipitates and the matrix, or dislocations which penetrated through the precipitates, but they shared the same Burgers vector as the dislocations in the other alloys. The low matrix dislocation density indicated significant recovery at elevated temperatures. At 1300ºC, the precipitates were again void of dislocations, also due to recovery.

**In Situ High-Temperature TEM**

TEM studies of samples compressed at 0.2% proof stress at different temperatures (11, 22, 23) showed the differences between the conditions, and an opportunity arose to study samples *in situ* (31). This allowed the stability of the different Pt-Al phases to be studied, and the Al-Pt phase diagram to be verified, at least for the alloys used. McAlister and Kahan (8) give the L1₂ ⇔ D0₀' transformation at ~ 1280ºC, whereas Oya *et al.* (9) have two transformations: γ' ⇔ γ₁ at ~ 340ºC and γ₁ ⇔ γ₂ at 127ºC. Previous attempts to resolve this question by scanning electron microscopy (SEM), XRD and differential thermal analysis (DTA) have been unsuccessful. Therefore, *in situ* heating of the alloy in a transmission electron microscope was used in an attempt to find an answer. The alloys investigated were Pt₆₅:Al₁₅ (at.%) and Pt₆₅:Al₁₅:Ir₄, and the *in situ* study was undertaken using a heating stage up to 1100ºC in a JEOL 4000EX transmission electron microscope. The heating rate used was 10ºC min⁻¹, with 5ºC min⁻¹ being used when more detailed changes were to be observed.

Bright-field TEM imaging as shown in Figure 6 (31) for the Pt₆₅:Al₁₅ (at.%) was used, with increasing temperature. At low temperature, the Pt₆₅Al precipitate was characterised by alternating twin bands, one with apparently no dislocations (black arrow) and the other with a high density of dislocations (white arrow). The number of dislocations decreased with increasing temperature (and time), which indicates that a transformation was occurring. The twin bands disappeared as atoms moved between the bands and as the crystal structure changed during the phase transformation, confirming that the transformation was displacive, and associated with dislocations. The transformation was also observed in diffraction mode as confirmation, since any changes in the crystal structure would also manifest in the γ₁ diffraction patterns. The diffraction patterns were selected at temperatures close to the transformation temperatures of Oya *et al.* (9). In a diffraction pattern close to the <211> zone, there were extra spots in the fine structure, which is an indication of additional ordering in the crystal. Above 340ºC, which is above the γ₁ ⇔ γ₂ transformation temperature of Oya *et al.* (9), the extra spots had almost completely disappeared, indicating a phase transformation. Thus, for the alloys used, this confirmed that the phase diagram of Oya *et al.* (9) for the Pt-Al system is more accurate than that of McAlister and Kahan (8). However, other workers using Pt from a different source achieved results...
which were in better agreement with a higher transformation temperature (32, 33). Thus, the transformation temperatures could be affected by minor impurities.

Since the strength of an alloy is partly dependent on the presence of small precipitates to act as a barrier to dislocation motion, the precipitates should persist at high temperatures to provide high-temperature strengthening. However, this did not occur in the Pt86:Al14 alloy. Figure 7 shows the same ~ Pt3Al precipitate in bright-field TEM images (31). There is a high density of small precipitates (with the exception of one precipitate-free zone) in the matrix surrounding the large precipitate at 580°C (Figure 7(a)). At 810°C, the precipitates started to dissolve. Between 810°C and 870°C, precipitate dissolution became rapid, and most of the small precipitates had disappeared by 870°C (Figure 7(b)). All small precipitates had dissolved at 960°C. The loss of the small precipitates would be deleterious for strengthening at high temperatures, although the contributions of the different sized precipitates have not yet been ascertained. The large precipitate was noticeably smaller at 1170°C than at 1030°C, and the interfacial dislocation network had completely disappeared. However, the precipitates in the ternary alloy Pt86:Al10:Ir4 had better stability.

Conclusions

An in-depth TEM study was undertaken on selected binary and ternary (Pt) and ~ Pt3Al alloys (roughly equivalent to the γ / γ′ nickel-based superalloys (NBSAs)) to ascertain how the ternary elements were substituting so that a greater understanding of the cubic L12 form of ~ Pt3Al could be...
A modified form of the D0$_2$$_1$ lower temperature Pt$_3$Al phase was identified by simulation and comparison with experimental data. The dislocations were studied and compared to those in NBSAs. The dislocations were more complex than those in NBSAs, mainly because of the presence of the lower temperature form of $\gamma$ Pt$_3$Al ($\gamma'$) and the different misfits. In situ heating showed that for the binary alloy, the small precipitates disappeared at high temperatures, and the larger precipitates reduced in size. The ternary alloy Pt$_{65}$Al$_{10}$Ir$_{4}$ had more stable precipitates than the binary alloys.

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**References**


28 J. H. Westbrook, Z. Kristallogr., 1958, 110, 21-9


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Hydrogen and Fuel Cells: For a Low Carbon Future

HIGHLIGHTS FROM THE FOURTH HYDROGEN AND FUEL CELL CONFERENCE

Reviewed by Bruno G. Pollet
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The Hydrogen and Fuel Cells: For a Low Carbon Future conference and exhibition was again held at the Gallery Suite, the National Exhibition Centre (NEC), Birmingham, U.K., on the 2nd April 2008 (1) and was sponsored by Advantage West Midlands (AWM), East Midlands Development Agency (emda) and the Hydrogen Technology Transfer Project (HYTETRA). This conference, the fourth in the series, attracted over 250 delegates from eleven countries and the attendance was higher than in 2007 (up by 30%). While the Grove Fuel Cell Symposium remains the largest fuel cell gathering in Europe (2), the Hydrogen and Fuel Cells conference at the NEC is now gaining interest among hydrogen and fuel cell stakeholders in the U.K., Europe and worldwide.

The conference, officially launched by Birmingham City Council and Professor Stuart Palmer (The University of Warwick, U.K.), was split into four main sessions: Session 1 on ‘European Progress on Hydrogen and Fuel Cells’; Session 2 on ‘Regional European Activities on Hydrogen and Fuel Cells’; Session 3 on ‘Hydrogen Generation and Storage’; and Session 4 on ‘Fuel Cells for Transport and Buildings’. During lunchtime, consortium building was organised by Alex Mauser (Coventry University, U.K.) and an exhibition and poster session was organised by Dr Bruno G. Pollet and Professor Kevin Kendall (Fuel Cells Group, The University of Birmingham, U.K.).

Highlights of the Conference

There has been a surge of interest in clean and efficient energy generated locally through fuel cells and hydrogen. The Joint Technology Initiative (JTI) is part of a €1 billion European Union (EU) programme to roll out this technology, and the Energy Technologies Institute (ETI) is a £1 billion U.K. project aimed at accelerating the development of low carbon energy technologies. The conference explained the reasons behind these investments, outlined progress made to date within the U.K. Midlands region and at international level, and sought to bring together interested parties across Europe for the development of future collaborative projects. More information on the participants and background to the conference can be found in the Conference Programme (1), and links to the individual presentations can be found through The University of Birmingham Fuel Cells Group website (3).

European Progress on Hydrogen and Fuel Cells

Session 1 was chaired by Professor Kevin Kendall (The University of Birmingham, U.K.). In the first presentation, Professor Jim Skea (U.K. Energy Research Centre, London) explained ‘Hydrogen and Fuel Cells for a Low Carbon Future’ and focused on the current importance of climate change and energy security, which are two of the most pressing issues of the early 21st century. He emphasised that the urgent need to reduce carbon emissions and secure diverse, reliable energy supplies does not sit easily alongside current business-as-usual trends and models. The Stern Review (4) identified the nature of the failures in current U.K. energy markets and the steps required to remedy these. In his talk, Skea explained why action is urgently required, outlined the options available for moving forward and described the rapidly changing policy environment at the U.K., EU and wider international levels.
Dr André Martin (European Joint Technology Initiative for Fuel Cells and Hydrogen, Brussels, Belgium) explained in detail the JTI, which is the result of many years of campaigning for industry to undertake and take control of hydrogen and fuel cell development programmes in the European Framework. He explained that over a hundred stakeholders have invested more than €100 million in preparation for the JTI, starting with the original vision in 2003, moving on to the strategy in 2005 and ending up with the implementation plan in March 2007. Those documents are available on the HFP website (5). Martin highlighted that the council gave its approval in February 2008 and the EU Parliament’s agreement was anticipated by the end of April 2008, with final adoption in May 2008. The interim structure was funded by the industry partners. The work programmes were expected to start later in 2008, and handover to the JTI was scheduled to occur at the end of 2008. The outcome will be an industry-led development project with a large number of European collaborators participating in projects worth €1 billion, up to 2013. Martin’s talk highlighted the direction of the projects and the expected budget breakdown.

Professor Richard Green (The University of Birmingham, U.K.), on behalf of Dr David Clarke (ETI, U.K.), outlined ‘The Energy Technology Institute: Prospects’ and its main role in the U.K. The ETI was established in late 2007 as a £1.1 billion public-private partnership with its headquarters at Holywell Park, Loughborough University, U.K. Green explained that the ETI has a vision to secure sustainable and affordable energy for present and future generations, with a mission to accelerate development, demonstration and eventual commercial deployment of a focused portfolio of energy technologies and services, which will increase energy efficiency, reduce greenhouse gas emissions and help achieve energy and climate change goals. Both ‘supply-side’ and ‘demand-side’ will be addressed in projects delivered through multi-partner consortia, which will be both national and international. The outputs are to be made available as widely as possible following delivery, in line with partner needs and agreed ETI outcomes.

Jeremy Harrison (E.ON UK) explained the role of the utility company in the race for a low carbon future. Climate change has created some significant challenges for the energy industry, in combination with aspects of the U.K. Government’s energy policy. Harrison emphasised that achieving a goal of 80% reduction in CO2 by 2050, while cost-effectively ensuring security of energy supplies, all within a very competitive market, means that the company is working hard to find new ways of delivering energy to its customers. Harrison pointed out that recent experience has shown that gas cannot be relied upon at a secure low price. He added that the utility company is looking to play an important part in replacing the U.K.’s ageing electricity generating infrastructure through the construction of a variety of plants: renewable, nuclear and even new coal plants with carbon capture and storage. He explained that the company needs to do this if generating assets are not to become ‘stranded’ and too expensive to run in a market which demands low carbon solutions. Within this context, fuel cells offer the potential to deliver heat and power at very high conversion efficiencies from a range of primary fuels, even at the relatively low power levels appropriate for distributed generation. The use of fuel cells in distributed generation further enhances their performance by minimising distribution losses for both the heat and electricity generated. E.ON UK is currently engaging in a range of fuel cell development and evaluation activities, aimed at gaining a deeper understanding of the technical and commercial challenges of bringing this technology to a promising market.

Regional European Activities on Hydrogen and Fuel Cells

Session 2, formally opened by Ralph Hepworth (AWM, U.K.), focused on hydrogen and fuel cell activities at the European regional level. The first talk in this session was delivered by Dr Frank Koch (The Fuel Cell and Hydrogen Network, Germany), who outlined the ‘Fuel Cell and Hydrogen Network North Rhine-Westphalia’. The network, a non-profit organisation, is supported by the Ministry of Economic Affairs and Energy, and
the Ministry of Innovation, Science, Research and Technology of the State of North Rhine-Westphalia and is co-funded by the EU Regional Development Fund. Currently, the network consists of more than 300 members including companies (70%), research institutes (20%) and other stakeholders such as industrial chambers of commerce and government institutions (10%).

The main role of the network is to initiate projects, for example, the North Rhine-Westphalia (NRW) region of Germany is following an ‘early market strategy’ for fuel cell technology and hydrogen infrastructure. The network is pushing early markets for the deployment of fuel cells, for instance in the logistics, leisure, military and power supply markets. To date, eighty-one fuel cell and hydrogen projects have been funded by the state’s government (partially co-funded by the EU), with a total budget of €210 million. Within the main industrial area of the Rhine-Ruhr valley, a 230 km hydrogen pipeline exists, connecting many chemical plants and producers as well as hydrogen users. Koch emphasised that this hydrogen pipeline could be the ‘nucleus’ for a German or even a European wide hydrogen infrastructure. Finally, he added that the City of Essen, located in North Rhine-Westphalia, will be hosting the 18th World Hydrogen Energy Conference (WHEC) in 2010 and he is hoping that the region will become an international platform and showcase for hydrogen and fuel cell technology.

Professor Kevin Kendall (Fuel Cells Group, The University of Birmingham, U.K.) gave an overview of hydrogen and fuel cell activities at the University (under the Supply Chain Research Applied To Clean Hydrogen (SCRATCH) project) and in the English West Midlands region. The SCRATCH project is aimed at the future hydrogen economy, which many analysts believe will be dominating the energy structure of the U.K. by 2050 as a result of the high efficiencies, zero emissions and easy conversions that can be attained with hydrogen technologies. He pointed out that the chemical industry already operates ‘mini-hydrogen economies’ on its sites; for example, the Teesside plant in the North East of England produced up to 100,000 tonnes of hydrogen in 2005, operated a twenty-one mile hydrogen pipeline, used salt caverns to store hydrogen, and set up several demonstrations of fuel cell power including road signs and a lighthouse. The main aim of SCRATCH is to make such hydrogen economies available to consumers to drive vehicles, power homes and run portable appliances. At present, hydrogen vehicles are not generally used in the U.K., as the supply chain is not yet implemented. There is an urgent need for hydrogen filling stations and for hydrogen vehicles (see for example Figure 1). However, at The University of Birmingham, a fleet of five hybrid hydrogen fuel cell vehicles (Figure 2) has been introduced on campus, and the various component supply chain companies have been signed up to a £2 million development project. These are zero emission vehicles (ZEVs), which are currently being tested for efficiency compared to the standard diesel and ‘purely’ electric fleets on campus. Preliminary results show that the hydrogen fuel cells can achieve an energy efficiency of 1 km MJ⁻¹.

Kendall emphasised that homes in the U.K. do not have hydrogen supplies in place to run combined heat and power (CHP) systems. At Birmingham, hydrogen infrastructure has been installed in a building to test the use of proton exchange membrane fuel cell (PEMFC) CHP. In addition, Baxi Innotech has installed two of their PEMFC CHP units running on pipeline natural gas through a reformer. One of these is operating in a family home (in Lye, West Midlands, U.K.,
with the help of the Black Country Housing Association), and the other at The University of Birmingham Fuel Cells Laboratories. Other types of fuel cell CHP systems based on solid oxide fuel cells (SOFCs) are also being installed at present to compare the technological options.

However, a key question is the supply of ‘green’ hydrogen. The SCRATCH project has brought together a consortium which is working to build and extend the supply chain, from the sources of green hydrogen, through its production, storage and supply, to utilisation and products in the market. Kendall added that the main weaknesses in the hydrogen economy need to be considered, including the lack of current renewable sources, storage issues, market demand and economic barriers. The University of Birmingham is focusing on innovative systems and on the ways in which these can be spread from chemical industry sites. A particular objective is to design a zero-emission campus based on a hydrogen economy. £1.5 million of funding from EPSRC and £0.5 million from AWM are currently supporting five research associates over a three-year period, from 2007 to 2010, to carry out research in the technical areas prioritised by the industries. This revenue project fits in with the £6.5 million capital project on hydrogen funded by AWM as part of the AWM Birmingham Science City. This provides test equipment, CHP systems, fuel cell vehicles and a hydrogen refuelling station on the university campus.

‘Review of U.K. Regional Activities on Hydrogen and Fuel Cells’ was presented by Dr Jon Helliwell (Centre for Process Innovation (CPI), Wilton, U.K.). He highlighted a variety of hydrogen and fuel cell related projects that have been established in the U.K., covering a number of regions. His presentation reviewed these projects in a regional context and commented on the regional and national strategies supporting them. A great emphasis of the projects was the context of the hydrogen supply chain itself, including hydrogen production, storage, distribution and use. Having reviewed the current picture of hydrogen activity in the U.K., Helliwell raised the important question of whether or not these projects offered a coherent demonstration and development strategy.

Ian Williamson (Air Products PLC, U.K.) gave a talk on ‘Hydrogen Development’, giving a vision of hydrogen and fuel cells in Europe. His presentation covered the role of Air Products in this growing market and gave some examples of urban scenarios and short-term demonstrations. Air Products is the world’s largest producer of commercial hydrogen (~ 50% market share). Their capacity amounts to around 1.75 million tonnes per annum, which could eventually support seven to eight million hydrogen-powered vehicles. Air Products has been active in this market since 1993, having built over eighty hydrogen station projects and supplied over 50,000 fuellings in fourteen countries. Future hydrogen infrastructure will include pipelines delivering hydrogen, similar to those in existence for natural gas, plus a multitude of hydrogen feed sources, from biomass to geothermal, wind, solar, nuclear and coal and methane reforming. Williamson also listed the main hydrogen fuelling station requirements, such as:

(a) Safety;
(b) Capacity, as per the U.S. Department of Energy’s (DoE) H2A Model (1,500 kg per day, utilisation of 70% and flexibility to meet daily, weekly, seasonal or growing demand);
(c) Dispensing capability (350 bar and 700 bar with a fill time of three to seven minutes);
(d) Reliability (> 99.9%);
(e) Location, for example urban.
Small footprint, i.e. a transparent operation to the consumer. Some examples of successful projects were shown, for example, the seventeen mile Los Angeles basin hydrogen pipeline through an urban area and Air Products’ operation of over 500 miles of hydrogen pipeline worldwide.

Tommaso Giunti (Fiat Powertrain Technologies (FPT), Centro Ricerche Fiat SepA (CRF), Italy) gave an overview on the ‘State of Art for Automotive Fuel Cell in Northern Italy’. Many Italian regions located along the Po Valley suffer from pollution and environmental damage. These are caused by the presence of heavy or ‘dirty’ industries, as well as an increasing population density which leads to a growing number of vehicles on the road. Together with poor weather conditions, these factors combine to cause problems that require immediate action through an integrated sustainable mobility and energy strategy.

In 2007, the regions of Piemonte and Lombardia (13 million residents and 9.3 million vehicles) signed a strategic agreement for the deployment of hydrogen and fuel cell technologies, in line with European Seventh Framework Programme (FP7) hydrogen and fuel cells JTI programmes on sustainable energy and mobility (the REGIO-ISEM programme). The agreement is open to other Italian regions, and to countries located along the fifth corridor in the Mediterranean area which are willing to share research and technological development (RTD) programmes and infrastructures. It aims to achieve a common energy and mobility strategy, with an effective critical mass in the European Research Area (ERA) context.

Currently, the Fiat Group are operating and testing three Panda Hydrogen fleet vehicles under real conditions. The main objectives of this project are to improve on the vehicles’ performance, power (aiming to improve from 7 kW to 75 kW) and load (from two to four seats including a full luggage compartment).

**Hydrogen Generation and Storage**

Dr Rupert Gammon (British Midlands Hydrogen Forum (BMHF), U.K.) opened Session 3 by announcing the British Midlands Hydrogen Ring (MHR). The MHR is an initiative launched by the BMHF to establish a cluster of hydrogen refuelling facilities across the West and East Midlands regions of the U.K. The MHR will include trials of a variety of hydrogen vehicles in controlled environments, such as university campuses, vehicle testing centres, airports and visitor attractions. As confidence in the hydrogen and fuel cell technologies grows, the vehicles will be trialled on the open road, allowing them to travel between refuelling stations. Each hydrogen refuelling station will be strategically situated and will incorporate other examples of sustainable energy systems (solar, wind etc.). All these facilities will build upon the Midlands’ knowledge base in the relevant technology areas. Gammon concluded that the Midlands could become the centre of a U.K.-wide network of hydrogen highways, with a significant part of this initiative being the fostering of links with neighbouring regions and those active in the development of hydrogen technologies. A number of locations for the refuelling stations have been proposed.

Professor Pieternal Claassen (Agrotechnology and Food Sciences Group (AFSG), Wageningen University and Research Centre, The Netherlands) presented on ‘Non Thermal Hydrogen Production from Biomass’. In order to support the sustainability of the future hydrogen economy, hydrogen should be produced from renewable primary energy. The main methods for the production of ‘green’ hydrogen are either by electrolysis using electricity from renewable resources (such as sunlight, wind and hydropower), or from biomass. Currently, there are two methods for hydrogen production from biomass: the thermochemical method (for example gasification) and the biochemical method using microorganisms. For the latter method, the composition of the biomass is paramount – for example, its water content governs the suitability of the technology. One of the many advantages of the biochemical route is the production of ‘green’ hydrogen with no carbon footprint.

Professor Claassen showed that many microorganisms are able to produce hydrogen from
mono- and disaccharides, starch and cellulose or hemicellulose under full anaerobic conditions. Claassen went on to say that, by uncoupling hydrogen production from methane production, hydrogen becomes available for recovery and exploitation. For example, during fermentation organic acids are produced together with hydrogen. In subsequent photofermentation, these organic acids can also be converted to hydrogen using light. Combining these fermentation methods leads to complete conversion of carbohydrates to hydrogen and CO₂.

Professor Martin Wills (The University of Warwick, U.K.) gave a presentation on ‘Chemical Catalysts for Hydrogen Generation’, in which he featured examples of the use of organometallic catalysts for the generation of hydrogen from organic compounds, including formic acid and alcohols. He gave examples of developed catalysts based on rhodium and ruthenium (Figure 3). Professor Wills showed that the catalysts are believed to work through a mechanism in which hydrogen atoms are removed ‘in pairs’ from the organic compounds, through a transition state. Loss of H₂ then regenerates the catalytic complex for another cycle. There is a precedent for this mechanism in asymmetric transfer hydrogenation chemistry.

![Rhodium catalyst and Ruthenium catalyst](image)

Professor Duncan Gregory (University of Glasgow, U.K.) presented his current work on ‘Solid State Storage Solutions: Hydrogen Storage in Nitrogen-Containing Materials’. He explained that inorganic nitrogen-containing compounds (nitrides, imides and amides) are becoming increasingly important as potential materials for sustainable energy applications. For example, lithium compounds with nitrogen could be extremely useful, both in power generation and conversion (for example in rechargeable batteries) and also as hydrogen storage devices. He conclusively showed that materials containing lithium and nitrogen can offer high capacity reversible storage with potentially fast sorption (ad-/desorption) kinetics and good cycleability. Nitrides, imides and amides present a multitude of opportunities for doping, catalysis and control of morphology and size. Professor Gregory concluded that nitrogen-containing materials could potentially solve solid-state hydrogen storage problems and reach targets set by the U.S. DoE.

Dr Torgeir Nakken (Norsk Hydro ASA, Norway) presented on ‘Experiences from the Wind-Hydrogen Plant at Utsira’. He explained that the use of hydrogen fuel cell systems employed as stand-alone energy devices in remote locations (where traditional power supply is mainly based on diesel) is thought to be one of the most promising early markets for stationary applications. In order to demonstrate the feasibility of such autonomous energy systems, from 2003 to 2004 the Norwegian energy company StatoilHydro, together with German wind turbine manufacturer Enercon, built a wind-hydrogen plant on the island of Utsira, Norway. The system produces hydrogen through an electrolyser when an excess of wind energy is available. It provides electricity to local domestic customers via a fuel cell and a hydrogen internal combustion engine (ICE) when the wind turbine slows or stops. Nakken emphasised that Utsira is the only operational full-scale autonomous wind-hydrogen system in the world. During the first three years of operation, the project has shown that it is possible to supply local customers with reliable power using this type of system. However, Nakken added that one of the many challenges of the technology has been the high number of interfaces in the system, necessary to control a grid with a large wind turbine supplying a relatively small load, together with the operation of the fuel cell, electrolyser and hydrogen engine.
**Fuel Cells for Transport and Buildings**

The final session of the conference was opened by Professor Martin Wills (The University of Warwick, U.K.) and focused on fuel cells for transport and buildings. Professor Andreas Züttel (EMPA, Swiss Federal Laboratories for Materials Testing and Research, Zurich, Switzerland) described ‘Hydrogen for a Low Carbon Future’. He outlined that much emphasis is currently being placed on the use of hydrogen and fuel cells for vehicular applications. This presents problems with regard to the use of solid-state hydrogen stores, particularly in the case of compact motor vehicles, due to their size and weight. However, in marine transport applications, these factors are less important as the weight of the solid-state hydrogen stores can be a positive advantage in terms of the ballast required in the vessel.

Professor Züttel described the hybrid canal boat project being carried out at The University of Birmingham (under Professor Rex Harris).

Following the presentation from Professor Züttel, Professor Rex Harris (The University of Birmingham, U.K.) presented on ‘Hydrogen, Magnets and the Protium Project’, focusing on the Hydrogen Hybrid Canal Boat project. The zero-emission hydrogen hybrid canal boat was developed by Professor Rex Harris and engineers at the University of Birmingham. The canal boat, called The Ross Barlow (Figure 4), is fully operational and demonstrates how a combination of magnet and fuel cell technologies could be used to power inland waterways craft.

The Ross Barlow has been created by converting a standard maintenance boat which was donated to the university by British Waterways. The diesel engine was removed and replaced by a zero-emission propulsion system and the central part of the boat was converted into a covered demonstration area. The hydrogen is stored on board in a large-scale metal hydride storage system which was developed by The University of Birmingham Hydrogen Materials Group (headed by Dr David Book) with Swiss collaborators at the EMPA laboratories in Zurich. This provides an effective means of storing large amounts of hydrogen at room temperature and moderate pressure (around 10 bar). The hydrogen is released from the hydride by decreasing the pressure, providing the platinum group metal (pgm)-catalysed PEMFC with ultra-pure hydrogen. The metal hydride system weighs 130 kg and is thought to be the only store of its kind in the U.K. Rare earth permanent magnets are used in the highly efficient motor and rudder system. There is a synergy between the magnets and hydrogen as they are manufactured by a hydrogen-based process invented by the Birmingham research group.

Harris recognises that the world has no more than twenty years to meet the urgent challenges of climate change and oil depletion. Much can be gained from the operation of hydrogen-based demonstrations, and the canal boat project
represents one step in the journey towards a hydrogen society.

Renewable electricity can be stored as hydrogen by splitting water using electrolysis. Hydrogen can subsequently be converted back to electricity and water by using a gas turbine or fuel cell. ‘Green’ hydrogen is considered a clean fuel as it has minimal impact on the environment and could reduce emissions of CO₂ and other greenhouse gases.


Conclusions

Hydrogen and fuel cells are likely to be one answer to the consumer’s demand for energy replacement and increased power, along with current environmental issues. Furthermore, it is evident that fuel cells are currently playing an important role in moving towards a low carbon future and are gradually being accepted for other applications. This is an exciting time for the hydrogen and fuel cell community, as on a U.K. and EU level, funding towards programmes and projects is being channelled through research institutions, universities and directly or indirectly to industry and local companies to ‘catalyse’ hydrogen fuel cell R&D and demonstrations. Furthermore, the use of pgms for fuel cell applications has a promising future for both transport and domestic applications as demand is likely to increase.

The Fifth Annual Hydrogen and Fuel Cells Conference: Building the Hydrogen & Fuel Cells Future was scheduled for 25th March 2009 at the Gallery Suite, NEC, Birmingham, U.K. The conference was to focus on the application of low carbon built environment EU and U.K. programmes. Further information can be found on the Climate Change Solutions website (6).

Acknowledgements

The author would like to thank all invited speakers at the conference, Climate Change Solutions Ltd, the conference organising committee, The University of Birmingham Media and Communications team and Fuel Cells Group, AWM Science City team, The University of Warwick, Loughborough University, The University of Nottingham, AWM, emda and HYTETRA for their kind help and support.

References


The Reviewer

Dr Bruno G. Pollet, Lecturer in Hydrogen Energy and Fuel Cell Technologies, and Head of the Proton Exchange Membrane Fuel Cell (PEMFC) Group, Fuel Cells Group (FCG), The University of Birmingham, is an expert in the areas of PEMFCs, electrochemical engineering and sonochemistry. He is currently responsible for the £1.3 million U.K. government DECC HFCCAT Hydrogen Fuel Cell Vehicle project and PEMFC and MEA activities within the FCG. He is also the coordinator of the recently awarded £5.5 million EPSRC Doctoral Training Centre in Hydrogen. Fuel Cells and Their Applications, the first of its kind in the U.K. He has successfully implemented a Hydrogen and Fuel Cell Supply Chain (EPSRC and AWM projects) within the West Midlands with currently fifty small and medium enterprises (SMEs) involved in the development and manufacturing of hydrogen and fuel cell components (SCRATCH: http://www.hydrogen-wm-scratch.info/). For further information, please visit: http://www.fuelcells.bham.ac.uk/Pollet.shtml
Metals in Synthesis 2008 (MIS-08)

PGM-CATALYSED PROCESSES FOR ORGANIC SYNTHESIS

Reviewed by Wenbo Chen* and John S. Fossey**
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On the 15th October 2008, the University of Bath, U.K., hosted a half-day symposium entitled “Metals in Synthesis 2008 (MIS-08)”. The symposium was held in honour of Professor Masakatsu Shibasaki (Graduate School of Pharmaceutical Sciences, The University of Tokyo, Japan) (1), the winner of a prestigious Royal Society of Chemistry (RSC) Centenary Lectureship. Professor Shibasaki won the Lectureship for his numerous seminal contributions to the discovery and development of asymmetric catalysts for organic synthesis. As part of the lectureship tour, Professor Shibasaki visited six U.K. universities: the Universities of Sussex, Bath, Warwick, York, Strathclyde and Southampton, and was presented with the RSC Centenary Lectureship medal at MIS-08 at the University of Bath (2).

The MIS-08 symposium was organised by John S. Fossey (then at the University of Bath, now at the University of Birmingham, U.K., and co-author of this review) and aimed to showcase some of the U.K.’s leading talents in metal-mediated synthesis. As such, three other speakers, Professor Jonathan M. J. Williams (University of Bath, U.K.) (3), Michael Willis (University of Oxford, U.K.) (4) and Paul Davies (University of Birmingham, U.K.) (5), were invited to present their most recent and exciting results. This was followed by a well-attended poster session where researchers from all over the U.K. presented highlights of their work.

Conference Highlights

The MIS-08 symposium began in the University of Bath’s main University Hall lecture theatre in front of a packed audience of delegates from all over the U.K. Gareth Price, the head of the University of Bath’s chemistry department (6), welcomed delegates and handed over to the chair of the first session, Christopher Frost (University of Bath, U.K.) (7). Frost has developed his own metal-mediated tandem catalysis strategies for organic synthesis (8, 9). He gave an especially warm welcome to the first speaker, his former Ph.D. supervisor, Professor Jonathan Williams.

Professor Williams’ presentation detailed his methodology of ‘hydrogen borrowing’ for the formation of carbon–carbon and carbon–nitrogen bonds. In this chemistry, ruthenium or iridium catalysts temporarily remove hydrogen (H₂) from an alcohol to give an aldehyde. This aldehyde may then react to give an alkene (in a Wittig-like reaction) or with an amine to give an imine. The earlier ‘borrowed’ hydrogen is returned to the substrate, furnishing products in which the oxygen of the alcohol starting material is replaced with a –CH₂R carbon or an –NHR nitrogen, Figure 1 (10–14). These procedures allow alcohols to be used as alkylating agents in place of more conventional, but often toxic or mutagenic, alkyl halides. The usefulness of this methodology has been demonstrated by application to drug molecule synthesis.

Next, Michael Willis discussed developments surrounding intermolecular hydroacylation

![Fig. 1 Mechanism for the formation of C–C and C–N bonds via a ruthenium- or iridium-mediated removal of H₂ from an alcohol](image-url)
reactions with respect to reactivity and enantioselectivity. He detailed atom-economical reactions that involved rhodium(I)-catalysed addition of aldehydes across C–C multiple bonds, in conjunction with catalytic C–H activation and C–C bond formation. He elaborated on the impressive scope of intermolecular chelation (β-S- or β-O-substituted aldehyde) controlled alkene and alkyne hydroacylation, Figure 2 (15–17). Willis then showed that this process could be applied to some rather elegant asymmetric examples.

Paul Davies followed up with an impressive story of how his metal-activated reactions encompass activation of alkynes towards nucleophilic attack and the use of alkynes as masked ylides. When activated by gold or platinum catalysts, the alkynes can potentially react as an alkylidene carbenoid by the pull-push nature of the catalytic activation, Figure 3 (18, 19).

Davies went on to describe a one-pot cascade reaction catalysed by gold, which exploited his masked ylide protocol. The reaction proceeds via rearrangement of propargylic carboxylates in the presence of sulfides, to give 2-substituted 4-allyl-2,3-dihydrothiophenes, Figure 4 (20).

After a short break, John Fossey opened the second session and introduced Professor Masakatsu Shibasaki. At this point Mike Willis took to the floor once again for his second official role of the day: as a member of the Executive Committee of the Organic Division of the RSC, the privilege of presenting Professor Shibasaki with the Centenary Lectureship medal fell to him, Figure 5.

Professor Shibasaki proceeded to deliver his lecture entitled ‘Recent Progress in Asymmetric Two Centre Catalysis’. He began by revealing the requirement for enhanced activation modes in catalysis, and proposed that dual activation or ‘two centre’ catalysis has the potential to afford new reactivities and higher selectivities, particularly in asymmetric transformations. He provided details of asymmetric two centre catalysis promoted simultaneously by Lewis acid complexes (with metals such as aluminium, titanium, lanthanum, gallium or zinc) and Brønsted bases or by Lewis acids in conjunction with Lewis bases (for example S=O, P=O), Figure 6 (21).

Excellent results were achieved in a wide range of bond-forming transformations, with high enantiomeric excess and high yields possible under dual activation conditions (22–28). Furthermore, the methods have been used in the practical synthesis of a key intermediate for ranirestat, AS-3201, a highly potent aldose reductase inhibitor, Figure 7 (29, 30).
Poster Session and Prizes

Following an invigorating question and answer session, Fossey brought the seminar to a close and invited delegates to the poster session and wine reception held in the University’s Department of Chemistry. The poster session was an opportunity for more than thirty young scientists to present their work and discuss ideas with the other delegates. The Japan Society for the Promotion of Science (JSPS) was the main sponsor of the poster session and wine reception, which allowed it to distribute details of its exchange programmes connecting U.K. and Japanese researchers and facilitating bilateral research projects. Professor Yuko Furukawa, Director of the JSPS’s London Office attended the event. Full details of JSPS programmes for pre- and postdoctoral fellows may be obtained from the JSPS London Office’s website (31).

Professor Furukawa drew the event to a close by awarding prizes for the most innovative and exciting posters. The first prize of a signed copy of a book edited by Professor Shibasaki “Multimetallic Catalysts in Organic Synthesis” (32) (donated by Wiley: Chemistry – An Asian Journal) and a presentation lacquer-ware clock (from the JSPS) went to Michael Shaw, a Ph.D. student in Professor Varinder K. Aggarwal’s group at the University of Bristol, U.K., for his poster presentation on studies towards the synthesis of natural

![Fig. 5 Dr Michael Willis (left) presents Professor Masakatsu Shibasaki (right) with the RSC Centenary Lectureship medal](image)

![Fig. 6 Asymmetric two-centre catalysis promoted by Lewis acid complexes with Brönsted bases or Lewis bases](image)

![Fig. 7 Synthesis of an intermediate for the aldose reductase inhibitor ranirestat, AS-3201, catalysed by a lanthanum complex](image)
products (33), Figure 8. JSPS runner-up prizes were awarded to five Ph.D. students: Paul Fordred (in Steven Bull’s group, University of Bath), Marta P. Pereira Morais (co-supervised by John Fossey, University of Bath) Simon Pridmore (Professor Williams’ group, University of Bath), Tomoki Nishimura (Royal Society visiting scholar from the University of Kitakyushu, Sakurai Laboratory, Japan) and Hannah Edwards (Christopher Frost’s group, University of Bath).

Conclusions

Platinum group metals (pgms) are playing an increasingly important role in organic synthesis, especially in the asymmetric synthesis field. Synthetic methodologies based on pgm-catalysed reactions that form new chemical bonds under progressively milder conditions, with greater ease and increasing power, will continue to be at the heart of intriguing and useful discoveries.

Acknowledgements

As well as generous support from the RSC and the RSC Organic Division, the event was sponsored by the University of Bath’s ‘Bridging the Gaps’ initiative, TCI Europe, Wiley (Chemistry – An Asian Journal) and the JSPS. This support allowed the event to be free to attend for all.

References

1 Shibasaki Group, The University of Tokyo: http://www.f.u-tokyo.ac.jp/~kanai/e_index.html (Accessed on 30th March 2009)
2 RSC Centenary Lecture, Professor Masakatsu Shibasaki, ‘Recent Progress in Asymmetric Two Centre Catalysis’, RSC Conferences and Events: http://www.rsc.org/ConferencesAndEvents/conference/alldetails.cfm?evid=102683 (Accessed on 30th March 2009)
3 Professor Jonathan M. J. Williams, University of Bath: http://www.bath.ac.uk/chemistry/people/jmjwilliams/ (Accessed on 30th March 2009)
4 Willis Group, University of Oxford: http://mcwillis.chem.ox.ac.uk/ (Accessed on 30th March 2009)
7 Christopher G. Frost, University of Bath: http://people.bath.ac.uk/chpcjc/cgfrost/Home.html (Accessed on 30th March 2009)
The Reviewers

Dr Wenbo Chen is a Leverhulme Trust-funded postdoctoral research fellow working with John S. Fossey at the University of Birmingham, U.K. His work is focused on new asymmetric motifs for C–C bond forming catalysis. Prior to this, Wenbo was a Ph.D. student at the Shanghai Institute of Organic Chemistry, China, where he worked on organosulfur chemistry with Professor Long Lu.

Dr John S. Fossey is a recently appointed lecturer in chemistry at the University of Birmingham, U.K. Prior to this, he spent three years at the University of Bath where he established his research group and published on a range of topics, including nickel- and cobalt-mediated chemistry. Before that, John was JSPS postdoctoral research fellow in the laboratories of Professor Shu Kobayashi (The University of Tokyo, Japan), where he worked on nickel-catalysed reactions of enecarbamates. He obtained his Ph.D. from Queen Mary, University of London, U.K., under Dr Chris J. Richards, working on Group 10 pincer complexes as C–C bond forming catalysts. For more information please visit: http://www.chem.bham.ac.uk/staff/Fossey.shtml
Osmium (Os) and ruthenium (Ru) belong to the platinum group metals (pgms). Both Os and Ru are hard, brittle and have poor oxidation resistance. Both metals are mostly produced from mines in the Bushveld Complex, South Africa. Trace amounts of Os are also found in nickel-bearing ores in the Sudbury, Ontario region of Canada, and in Russia, along with other pgms. Os oxidises easily in air, producing poisonous fumes, and is the rarest of the pgms. Ru is also found in ores with other pgms in Russia, and in North and South America. Ru is isolated through a complex chemical process in which calcination and hydrogen reduction are used to convert ammonium ruthenium chloride, yielding a sponge. The sponge is then consolidated by powder metallurgy techniques or by argon arc welding. Ru is mostly used in hard disks and in alloys with platinum for jewellery and electrical contacts. It also has increasing use in catalysis (1). Os and Ru were discovered in 1804 (2) and 1844 (3), respectively.

Magnetic measurements of Ru and Os have been made by Hulm and Goodman (4). Savitskii et al. (5) investigated the microstructural, physical and chemical properties of these metals, and their mechanical properties have been explored by Buckley (6). Os and Ru both possess a hexagonal closed packed (h.c.p.) structure (6). Barnard and Bennett (7) studied their oxidation states.

The investigation of ultrasonic properties can be used as a non-destructive technique for the detection and characterisation of a material’s properties, not only after production but also during processing (8–10). However, none of the work reported in the literature so far is centred on the ultrasonic study of Os and Ru. Thus, in the present work, we have studied the ultrasonic properties of these metals. Ultrasonic attenuation, velocity and related parameters have been calculated for use in non-destructive testing (NDT) characterisation.

Higher-Order Elastic Constants

The higher-order elastic constants of h.c.p. structured materials can be formulated using the Lennard-Jones potential, \( \phi(r) \), Equation (i):

\[
\phi(r) = \left\{ -\frac{a_0}{r^m} + \frac{b_0}{r^n} \right\}
\]

where \( a_0, b_0 \) are constants; \( m, n \) are integers and \( r \) is the distance between atoms (11). The expressions of second- and third-order elastic constants are given in the set of Equations (ii):

Ultrasonic Study of Osmium and Ruthenium

DETERMINATION OF HIGHER-ORDER ELASTIC CONSTANTS, ULTRASONIC VELOCITIES, ULTRASONIC ATTENUATION AND ALLIED PARAMETERS

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Ultrasonic properties of two platinum group metals, osmium and ruthenium, are presented for use in characterisation of their materials. The angle-dependent ultrasonic velocity has been computed for the determination of anisotropic behaviour of these metals. For the evaluation of ultrasonic velocity, attenuation and acoustic coupling constants, the higher-order elastic constants of Os and Ru have been calculated using the Lennard-Jones potential. The nature of the angle-dependent ultrasonic velocity is found to be similar to those of molybdenum-ruthenium-rhodium-palladium alloys, Group III nitrides and lave-phase compounds such as TiCr2, ZrCr2, and HfCr2. The results of this investigation are discussed in correlation with other known thermophysical properties.
where \( p = c/a \) (the axial ratio); \( C' = \chi a/p^5 \); \( B = \Psi a^3/p^3 \); \( \chi = (1/8)\{n b_0 (n - m)\}/\{a^8 + 4\} \); \( \Psi = -\chi/\{6 a^2 (m + n + 6)\} \); and \( c \) is the height of the unit cell.

The basal plane distance \( 'a' \) and axial ratio \( 'p' \) of Os and Ru are given in Table I (6). The calculation of higher-order elastic constants was carried out using the set of Equations (ii), taking appropriate values of \( m \), \( n \), and \( b_0 \). The values of the second- and third-order elastic constants are shown in Table II.

The Young’s modulus \( 'Y' \) and bulk modulus \( 'B' \) were evaluated using the second-order elastic constants presented here. It is obvious from Table II that there is good agreement between the calculated values from this study and the previously reported values for the Young’s modulus and the bulk modulus (6, 12, 13). It is observed that the higher-order elastic constants of Os and Ru are analogous to those of gallium nitride and indium nitride, respectively (14). All the second-

| Table I | Basal Plane Distance, a, and Axial Ratio, \( p \), for Osmium and Ruthenium* |
|----------------------|----------------------|----------------------|
| Parameter | Units | Value | Value |
| a | Å | 2.729 | 2.700 |
| p | – | 1.577 | 1.582 |
| *All values obtained from Reference (6) |

| Table II | Second- and Third-order Elastic Constants for Osmium and Ruthenium |
|----------------------|----------------------|----------------------|----------------------|----------------------|
| Second-order elastic constant | Value, \( 10^{11} \) Nm\(^{-2} \) | Third-order elastic constant | Value, \( 10^{11} \) Nm\(^{-2} \) |
| Os | Ru | Os | Ru | Os | Ru |
| \( C_{11} \) | 8.929 | 6.279 | \( C_{111} \) | -145.620 | -102.400 |
| \( C_{12} \) | 2.193 | 1.542 | \( C_{112} \) | -23.088 | -16.236 |
| \( C_{13} \) | 1.774 | 1.255 | \( C_{113} \) | -4.550 | -3.220 |
| \( C_{13} \) | 7.938 | 5.654 | \( C_{123} \) | -5.783 | -4.093 |
| \( C_{33} \) | 2.128 | 1.506 | \( C_{133} \) | -26.815 | -19.098 |
| \( C_{44} \) | 3.166 | 2.463 | \( C_{222} \) | -25.139 | -17.904 |
| \( B^* \) | 4.119 | 2.911 | \( C_{344} \) | -6.738 | -4.768 |
| \( B^* \) | 3.800 | 2.920 | \( C_{144} \) | -4.491 | -3.178 |
| \( B^\star \) | 4.110 | – | \( C_{155} \) | -115.219 | -8.026 |
| \( Y \) | 5.525 | 3.971 | \( C_{333} \) | -93.777 | -67.211 |
| \( Y' \) | 5.600 | 4.300 | – | – | – |
| \( Y'' \) | 5.620 | 4.220 | – | – | – |
| *Reference (12); **Reference (13); ***Reference (6) |
and third-order elastic constants for Ru are found to be higher than those of Mo-Ru-Rh-Pd alloys (11). Thus we conclude that our calculated higher-order elastic constants and theory are correct and justified. The bulk modulus of Os is found to be higher than that of its nitride and carbide (15). The values of $C_{11}$ for the face centred cubic (f.c.c.) structured pgms, Pd and Pt, are $1.8 \times 10^{11}$ Nm$^{-2}$ and $2.2 \times 10^{11}$ Nm$^{-2}$, respectively (16). The high elastic modulus reveals that Os and Ru have low adhesion power and high hardness. Thus these metals are suitable for applications such as sliding electrical contacts, switches, slip rings, etc.

**Ultrasonic Velocities**

The anisotropic properties of a material are related to its ultrasonic velocities as they are related to higher-order elastic constants. There are three types of ultrasonic velocities in h.c.p. crystals. These include one longitudinal and two shear wave velocities, which are given by Equations (iii)–(v) (14), where $V_1$ is the longitudinal wave velocity, $V_2$ is the quasi-shear wave velocity and $V_3$ is the shear wave velocity; $\rho$ is the density of the material and $\theta$ is the angle with unique axis of the crystal. The densities of Os and Ru are taken from the literature (6). The angle-dependent ultrasonic velocities in the chosen metals were computed using Equations (iii)–(v) and are shown in Figure 1.

The longitudinal ultrasonic velocities of Os and Ru (see Figure 1) for wave propagation along unique axis are given in Table III, together with their sound velocities (17, 18). The nature of the ultrasonic velocity curves in these h.c.p. metals is similar to other h.c.p. structured materials (11, 14, 19). Comparison with these sources verifies our velocity results. The anomalous maxima and minima in the velocity curves are due to the combined effects of the second-order elastic constants. The angle-dependent velocities of Ru are greater than those of Mo-Ru-Rh-Pd alloys (11) due to the higher values of the elastic constants for Ru. Thus

$$V_1^2 = \left\{ C_{33} \cos^2 \theta + C_{11} \sin^2 \theta + C_{44} + \left[ (C_{11} \sin^2 \theta - C_{33} \cos^2 \theta + C_{44} (\cos^2 \theta - \sin^2 \theta))^2 + 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^2 \right]^{1/2} \right\} / 2 \rho \quad \text{(iii)}$$

$$V_2^2 = \left\{ C_{33} \cos^2 \theta + C_{11} \sin^2 \theta + C_{44} - \left[ (C_{11} \sin^2 \theta - C_{33} \cos^2 \theta + C_{44} (\cos^2 \theta - \sin^2 \theta))^2 + 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^2 \right]^{1/2} \right\} / 2 \rho \quad \text{(iv)}$$

$$V_3^2 = \left\{ C_{44} \cos^2 \theta + C_{66} \sin^2 \theta \right\} / \rho \quad \text{(v)}$$

**Fig. 1** Plot of ultrasonic velocity $V$, against angle with unique axis $\theta$ of osmium and ruthenium.
calculated results of ultrasonic velocities can be used for anisotropic characterisation of Os and Ru metals.

### Ultrasonic Attenuation and Allied Parameters

The predominant causes of ultrasonic attenuation in a solid at room temperature are phonon-phonon interaction (Akhieser type loss) and thermoelastic relaxation mechanisms. The ultrasonic attenuation coefficient $\alpha_{\text{Akh}}$ due to the phonon-phonon interaction mechanism is given by Equation (vi) (11, 14):

$$\left(\frac{\alpha}{f^2}\right)_{\text{Akh}} = 4\pi^2 (3E_0 <\gamma_{ij}^2> - <\gamma_{ij}^2>^2)C_V VT/\rho V^3$$  (vi)

where $f$ is the frequency of the ultrasonic wave; $V$ is the ultrasonic velocity for longitudinal and shear waves as defined in Equations (iii)–(v); $E_0$ is the thermal energy density; $T$ is the temperature and $\gamma$ is the Grüneisen number; $i$ and $j$ are the mode and direction of propagation. The Grüneisen number for a hexagonal structured crystal along the $<001>$ orientation or $\theta = 0^\circ$ is a direct consequence of the second- and third-order elastic constants. $C_V$ is the specific heat per unit volume of the material. The acoustic coupling constant $D$ is the measure of acoustic energy converted to thermal energy and is given by Equation (vii):

$$D = 3(3E_0 <\gamma_{ij}^2> - <\gamma_{ij}^2>^2)C_V T/E_0$$  (vii)

When an ultrasonic wave propagates through a crystalline material, the equilibrium of phonon distribution is disturbed. The time taken for re-establishment of equilibrium of the thermal phonon distribution is called the thermal relaxation time ‘$\tau$’ and is given by Equation (viii):

$$\tau = \tau_S = \tau_L/2 = 3K/C_V V_D^3$$  (viii)

where $\tau_L$ is the thermal relaxation time for the longitudinal wave; $\tau_S$ is the thermal relaxation time for the shear wave; and $K$ is the thermal conductivity. $V_D$ is the Debye average velocity and is calculated from the initial slopes of the three acoustic branches, Equation (ix):

$$V_D = \left[\frac{1}{3} \sum_{i=1}^{3} \frac{1}{V_i^3} \frac{d\Omega}{4\pi}\right]^{-1/3}$$  (ix)

The thermoelastic loss for the shear wave has no physical significance because the average of the Grüneisen number for each mode and direction of propagation is equal to zero for the shear wave. Only the longitudinal wave is responsible for thermoelastic loss because it causes variation in entropy along the direction of propagation.

The thermal conductivities of the selected metals are taken from the literature (6). The values of the specific heat per unit volume ‘$C_V$’ and energy density ‘$E_0$’ are obtained from the American Institute of Physics Handbook (20). The thermal relaxation time ‘$\tau$’ and Debye average velocity ‘$V_D$’ are evaluated from Equations (viii) and (ix) and are shown in Figure 2. The ultrasonic attenuation coefficients are calculated from Equations (vi) and (x). Calculated acoustic coupling constants ‘$D$’ and ultrasonic attenuation coefficients ‘$\alpha (f^2)$’ are presented in Table IV.

The angle-dependent thermal relaxation time varies between 6.5 ps and 9.55 ps. This indicates that after the propagation of a wave,
the distribution of phonons returns to the equilibrium position within 6.5–9.5 ps. The values of the thermal relaxation time in Pd and Pt are 8.8 ps and 13.4 ps, respectively (16). The thermal relaxation time of the chosen metals is directly affected by their Debye average velocity and the thermal conductivity of these metals.

The total attenuation is given by Equation (xi):

\[
\frac{\alpha}{f^2}\text{Total} = \frac{\alpha}{f^2}\text{Th} + \frac{\alpha}{f^2}\text{L} + \frac{\alpha}{f^2}\text{S}
\]

where \(\frac{\alpha}{f^2}\text{L}\) is the ultrasonic attenuation coefficient for the longitudinal wave and \(\frac{\alpha}{f^2}\text{S}\) is the ultrasonic attenuation coefficient for the shear wave. The value of \(\frac{\alpha}{f^2}\text{Total}\) is greater for Os than for Ru. The dominant mechanism for total attenuation is phonon-phonon interaction. The attenuation due to phonon-phonon interaction is directly related to the acoustic coupling constant and thermal relaxation time. Os has a lower thermal relaxation time than Ru, while the acoustic coupling constant of Os is greater than that of Ru due to its low value of \(C_T/E_0\). Thus total attenuation is mainly affected by the acoustic coupling constant. Total attenuation at the nanoscale in Pd and Pt has been reported as \(2.98 \times 10^{-15} \text{ Np s}^2 \text{ m}^{-1}\) and \(7.38 \times 10^{-15} \text{ Np s}^2 \text{ m}^{-1}\), respectively (16). These reported values are larger than those of Os and Ru. The total attenuation in the Ru alloy Mo_{30}Ru_{50}Rh_{15}Pd_{11} has been found to be \(1.044 \times 10^{-15} \text{ Np s}^2 \text{ m}^{-1}\) (11). A comparison of total attenuation indicates that these metals are more durable and ductile in alloy form than in

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value Os</th>
<th>Value Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_L)</td>
<td>–</td>
<td>56.002</td>
<td>55.825</td>
</tr>
<tr>
<td>(D_S)</td>
<td>–</td>
<td>1.532</td>
<td>1.473</td>
</tr>
<tr>
<td>(\frac{\alpha}{f^2}\text{Th})</td>
<td>(10^{-15} \text{ Np s}^2 \text{ m}^{-1})</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>(\frac{\alpha}{f^2}\text{L})</td>
<td>(10^{-15} \text{ Np s}^2 \text{ m}^{-1})</td>
<td>1.598</td>
<td>1.509</td>
</tr>
<tr>
<td>(\frac{\alpha}{f^2}\text{S})</td>
<td>(10^{-15} \text{ Np s}^2 \text{ m}^{-1})</td>
<td>0.158</td>
<td>0.144</td>
</tr>
<tr>
<td>(\frac{\alpha}{f^2}\text{Total})</td>
<td>(10^{-15} \text{ Np s}^2 \text{ m}^{-1})</td>
<td>1.758</td>
<td>1.655</td>
</tr>
</tbody>
</table>
their pure form. The performance of Ru as an alloy component for durability and ductility might be better than that of Os due to its lower ultrasonic attenuation.

The pulse echo technique (PET) can be used for the measurement of ultrasonic velocity and attenuation of materials, because it avoids heat loss and scattering loss. This method provides results with good accuracy and would provide useful information when combined with the theory presented here. For Ru, PET can be used directly for measurement. The high precision indirect approaches such as resonant ultrasound spectroscopy (RUS) and novel digital pulse echo overlap techniques can be used for the measurement of ultrasonic velocity in Os (21). By ultrasonic velocity measurements, the anisotropic mechanical properties of a material can be understood as they are related to velocity. This enables quality assurance of products made with these materials in combination with other materials to be carried out by measurements of ultrasonic attenuation, not only after production but also during processing.

Conclusions

The adopted method for theoretical study of higher-order elastic constants is justified for the pgms. The high values of the elastic constants of the h.c.p. metals Os and Ru provide evidence of their low adhesive power and high hardness. The results of the elastic constants substantiate the superiority of h.c.p. metals over f.c.c. metals in this regard. The anisotropic characterisation of the chosen metals can be carried out on the basis of directional ultrasonic velocity and thermal relaxation time. The phonon-viscosity mechanism is the dominant cause of total attenuation in these metals. The acoustic coupling constant is a governing factor for total attenuation. The mechanical behaviour of Ru is expected to be better in terms of durability and ductility than that of other pgms due to its low attenuation.

The results obtained in this investigation can be used for further study of these metals. Our whole theoretical approach can be applied to the evaluation of ultrasonic attenuation and related parameters to study the microstructural properties of h.c.p. structured metals.

References

8 S. K. Kor, Nature, 1958, 181, (4621), 1462
12 A. S. Darling, Platinum Metals Rev., 1966, 10, (1), 14
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Between 2000 and 2008, the Russian automotive market saw year on year double-digit growth. By 2008 it showed the potential to become one of the world’s leading markets. This trend was driven by the country’s economic growth, with factors such as increasing average income and the development of the credit system contributing to the growth in the market.

Total Russian car sales doubled between 2004 and 2008 – from 1.5 million units sold in 2004 to over 3 million in 2008 (see for example, (1)). Over the same period the value of the market grew even faster – from a total of U.S.$18 billion in 2004 to U.S.$36 billion for the first six months of 2008. Russian car sales reached second place in Europe in 2008, and at the end of 2008 Russia appeared likely to overtake Germany as Europe’s number one for car sales in the near future.

The growth of the Russian market has not been ignored by the global automotive industry. The Russian Government has also promoted the market to investors by establishing attractive conditions for companies investing in local production, and over the past few years all the major global automotive manufacturers have announced decisions to build new facilities in Russia.

Car production lags behind sales in Russia, but it is also on the increase, with many Western original equipment manufacturers (OEMs) investing or planning to invest in manufacturing plants to support Russia’s appetite for foreign-brand cars. Together with local players, which could retain reasonably good positions in the market, at the time of writing this article the total output of vehicles in Russia was expected to be in excess of 1.5 million units by 2012, with the potential to exceed 2 million units after 2015.

In turn, these developments have pushed Tier 1 and Tier 2 automotive suppliers to consider establishing production in Russia. The Russian Federation Government has been consistent in setting up similar promotional incentives, allowing foreign suppliers with local production capacity to operate under favourable conditions.

During the same period, new emissions legislation was introduced in Russia, with the adoption of Euro 2 for all types of on-road...
vehicles throughout the country in July 2006. Emissions legislation tightening followed promptly, and Euro 3 was implemented in January 2008. Further tightening is expected: Euro 4 should follow in 2010 and Euro 5 in 2014 (2).

Johnson Matthey made the strategic decision to invest in Russia and build a new facility, the 12th ECT plant, to support local market requirements. Krasnoyarsk in western Siberia was chosen as the location, having the advantages of a highly-skilled local workforce and the ability to source raw materials such as platinum group metal salts from the local precious metals refinery giant, JSC Krastsvetmet.

The new Johnson Matthey ECT plant was opened in August 2008. The opening ceremony was well attended by regional and state officials, as well as customers and potential business partners in Russia. The latest advanced technologies for emissions control, produced to the highest standards of quality, are now available locally. The plant is designed to supply the market with up to 1 million catalysts annually, with the potential to increase this capacity in the future.

Johnson Matthey ECT is looking forward to developing successful and effective partnerships with new customers in Russia, as well as meeting the requirements of its global customers who decide to set up in Russia.

ANDREY KOSSOV

References

1 Global Insight, March 2009: http://www.globalinsight.com/
2 Russian Federation Governmental Decree No. 609, 12th October, 2005, Special technical regulations “On Requirements for Pollutant Emissions by Motor Vehicles, Currently Produced and Imported in the Territory of the Russian Federation”

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Following the successful 2005 conference in Beijing (Solvent Extraction for Sustainable Development (1)), the 18th International Solvent Extraction Conference (ISEC 2008), Solvent Extraction: Fundamentals to Industrial Applications, was held in Tucson, Arizona, U.S.A., between 15th and 19th September 2008 (2). The programme emphasised the development from fundamentals to industrial applications of solvent extraction. Session topics were:

- Hydrometallurgy and Metals Extraction
- Process Chemistry and Engineering
- Nuclear Applications
- Analytical and Preparative Chemistry
- Biotechnology, Pharmaceuticals, Life-Science Products and Organic Products
- Fundamentals
- Novel Reagents, Materials and Techniques

The conference followed a traditional format with five excellent plenary lectures from experts in the various fields, five parallel oral programmes, two poster sessions and two panel discussion sessions specifically considering ‘Uranium Processing’ and ‘New Reagents and Their Design’. Full conference proceedings have been published (3).

The interesting and potentially exploitable aspects of the chemistry of the platinum group metals (pgms) in solvent extraction-based refining circuits continue to be of significant interest (4–10). Comments on selected oral and poster presentations most relevant to the furthering of fundamental chemistry, refining and processing of both the pgms and gold are given here under the titles of the sessions in which they appeared (with the relevant page numbers of the aforementioned proceedings given in brackets).

**Hydrometallurgy and Metals Extraction**

Several systems have been proposed for the replacement of cyanide as a lixiviant for gold and silver, and a thermodynamic model has been developed by G. T. Lapidus et al. (Universidad Autónoma Metropolitana-Iztapalapa, Mexico) (pp. 299–304) for the precious metal complexes extracted from an ammonium copper thiosulfate solution. Similarly, the use of thiourea as an alternative to cyanide for the recovery of gold and silver has several advantages, including improved kinetics and lower toxicity of the reagents. Z. Gamino-Arroyo et al. (École Centrale Paris, France) (pp. 293–298) presented a mechanistic study of the extraction of precious metals from a di(2-ethylhexyl)dithiophosphoric acid solution system. A study of the influence of residual gold on the solvent extraction-based recovery of cyanide from more traditional industrial cyanidation liquors was presented by M. B. Mansur et al. (Universidade Federal de Minas Gerais, Brazil) (pp. 311–316).

As part of the capacity expansion project within the Anglo Platinum Precious Metals Refinery in South Africa, S. F. Woollam (Anglo Research, South Africa) and R. A. Grant (Johnson Matthey Technology Centre (JMT), U.K.) (pp. 281–286) observed a significant increase in the rate of acid-catalysed degradation of the hydroxyoxime LIX 84I in the palladium solvent extraction circuit when the reagent concentration was increased. However, a reduction in strip acid concentration was found to alleviate this problem sufficiently, while leaving phase disengagement and overall strip circuit efficiency at acceptable levels. A number of reagents have been reported previously as
useful extractants for gold(III) from hydrochloric acid solutions, and more recently the use of liquid membranes for such a process has been described. An interesting poster by C. Vargas et al. (Instituto Politécnico Nacional, Mexico) (pp. 287–292), considering gold(III) extraction with 2-ethylhexanol, introduced ‘emulsion petraction’ in a hollow-fibre contactor, an arrangement which enjoys the benefits of the liquid membrane approach without the often-associated problems.

**Process Chemistry and Engineering**

Improved recovery of the entrained organic phase from the raffinate at the Morenci Mine operations of Freeport-McMoRan Copper and Gold, Inc (FMCG), U.S.A., was achieved using a Krebs hydrocyclone unit. The results were reported by M. A. Thumberg and E. P. Kramer (FMCG, U.S.A.) (pp. 491–496). R. A. Grant et al. (JMTC, U.K.) (pp. 415–420) presented the development of a computer simulation of the solvent extraction of platinum from a chloride matrix using an Amberlite LA-2 (a secondary amine) based system. This approach enabled several flow sheet options to be simulated and the results of the selected configuration were validated in a subsequent mini-pilot plant trial.

**Nuclear Applications**

A range of polycyclic molecules has been developed and tested for the separation of actinides from lanthanides. The method is potentially useful in a spent nuclear fuel treatment flow sheet, where the resistance of reagents to ionising radiation is clearly an issue. A presentation by A. Fermvik et al. (Chalmers University of Technology, Sweden) (pp. 551–556) reported the accelerated degradation after irradiation of C5-BTBP in cyclohexanone and the detrimental effect this has on such a separation. The presentation also addressed the associated deportment of fission products, including palladium and silver.

The less than ideal deportment of ruthenium in otherwise very promising simulated and ‘hot’ trials of the diglycolamide derivative TODGA/TBP process for the recovery of trivalent actinides from a PUREX (11) raffinate was reported by G. Modolo et al. (Institute for Energy Research, Germany) (pp. 521–526). Another PUREX raffinate treatment strategy involves the DIAMEX process developed by the French Atomic Energy Commission (Commissariat à l’énergie atomique, CEA), which employs a malondiamide as the extractant. Results from the successful recent tests on the DMDOHEMA malonamide based step of this process, including palladium deportment, were presented by C. Sorel et al. (pp. 715–720) from the CEA, France.

**Fundamentals**

Recovery and separation of the chloro complexes of the pgms continue to attract considerable research due to their fundamental interest and relevance to the pgm refining industry. For example, the rapid and highly selective recovery of palladium(II) from hydrochloric acid solutions in the presence of platinum(IV) using sulfur-containing monoamide and diamide compounds was presented by H. Narita et al. (National Institute of Advanced Industrial Science and Technology, Japan) (pp. 1445–1450). The results compared well to the slower separation achieved using more
conventional dialkylsulfide extractants. The effect of hydrochloric acid concentration on the kinetics and equilibrium data for the extraction of palladium(II) with novel pyridine carboxamide and phosphonium ionic liquid systems was reported by M. Wisniewski et al. (Institute of Chemical Technology and Engineering, Poznan, Poland (pp. 1295–1300), although reported issues with phase separation and solids formation will be the next hurdles to overcome with these systems.

M. G. Sánchez-Loredo et al. (Universidad Autónoma de San Luis Potosí, Mexico) (pp. 1049–1055) presented a series of polyamines based on the tris(2-aminoethyl)amine (tren) platform, together with results from testing these as extractants for the chloro complexes of palladium(II), platinum(II), rhodium(III) and ruthenium(III). The isolation and crystal structure characterisation of the complex \([2(trenH_4)^{1+} \cdot 2(PdCl_4)^{2-} \cdot 4Cl^- \cdot H_2O]\) during this study helped to confirm the importance of water in some of these structures. Similarly, P. A. Tasker et al. (University of Edinburgh, U.K.) (pp. 1457–1462) presented a series of new tripodal amido and urea group-based anion-binding ligands as potential extractants for \([PtCl_6]^{2-}\) from acidic chloride solutions, Figure 1. Much greater selectivity for the complex anion over chloride was reported compared to model reagents such as trioctylamine.

The radiation-induced interconversion of isomers of BDPDA from their trans to cis configurations was demonstrated by observing an increase in the resulting distribution ratio for gold(III), although K. Takeshita et al. (Tokyo Institute of Technology, Japan) (pp. 1505–1511) currently consider the process impractical for use. The introduction of a synergist, octanoic acid, into this system was effective for improving the extraction performance significantly and may offer further development opportunities.

The efficient extraction of soft metal ions, including silver(I) and palladium(II), onto various copolymers of N-isopropylacrylamide and thioethers was reported by K. Chayama et al. (Konan University, Japan) (pp. 1585–1590). Some potential for enhanced selectivity may encourage further development of these systems.

### Conclusions

The International Solvent Extraction Conference series (1, 2, 12), with its traditionally associated short course and technical tours (see Figure 2), continues to be the preeminent forum for sharing both incremental changes and breakthrough developments in operational practice and fundamental science and engineering in this area of technology. As long as solvent extraction technology continues to be an attractive option to pgm producers, this conference should remain on the calendars of anyone with an interest in this area. The organisers are to be congratulated on a fine conference and we look forward to the nineteenth such conference, ISEC 2011, which will be held in Santiago, Chile, between 16th and 20th October 2011 (12).

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**Fig. 1** Possible binding modes for the amide and urea arms of the tripodal reagents used as potential extractants for \([PtCl_6]^{2-}\) from acidic chloride solutions, as presented by P. A. Tasker et al., University of Edinburgh, U.K. (pp. 1457–1462) (3)
References


The Reviewer

David John Robinson was active in both fundamental and applied pgm chemistry research, and in particular, the development of improved separation technologies, over a fifteen-year career with Anglo Platinum. He was involved directly in their production process at the modern precious metals refinery near Rustenburg, South Africa. He is now Research Programme Leader for Base Metals Hydrometallurgy within CSIRO Minerals and Market Leader for Base Metals within the Parker Cooperative Research Centre for Integrated Hydrometallurgy Solutions, Karawara, Western Australia. His interests include developing improved industry-academia research collaborations and applying improved fundamental knowledge to the solution of real metal refining problems. He is active in the areas of fundamental and applied base metal hydrometallurgy and developing advantages for industry through better scientific research, optimising hydrometallurgical processing and efficient technology transfer.
Fuel cell shipments will exceed 5 million units per year by 2013, according to Fuel Cell Today’s latest Industry Review, titled “Fuel Cells: Emerging Markets”. The Review, published on 28th January 2009, reports that 2008 saw shipments of 18,000 units mainly in the portable and stationary sectors, an increase of 50% over the number shipped in 2007. In a series of five year forecasts, the Fuel Cell Today analysts anticipate that fuel cell shipments will substantially increase in key market areas such as uninterruptible power supplies (UPS); combined cooling, heating and power; and fuel cells for portable devices.

Drivers for change in the Middle East include Emirates such as Abu Dhabi and Dubai looking to diversify their economies into areas other than petroleum, including construction, tourism and potentially cleantech. A second key driver is the need to reduce fresh water consumption and to produce potable water. Buildings are one of the major resource users and design changes are being implemented to address this.

**State of the Fuel Cell Industry**

Shipments of both stationary and portable fuel cells continued to show steady growth in 2008, according to Fuel Cell Today. Over 80% of new units shipped were fuel cells with platinum-based catalysts, which represents some 10 MW of new installed capacity during 2008.

Drawing on recent developments in the portable fuel cell sector and in fuel cells for back-up power, Fuel Cell Today expects that there will increasingly be a move from a supply-driven to a demand-driven model, particularly in the areas of large stationary combined heat and power (CHP); small to medium UPS and backup power systems for data centres and telecommunications sites; fuel cell toys; auxiliary power units (APU); and, in Japan, micro-CHP (mCHP).

The final section of the 2009 Industry Review publishes a forecast for the five-year period 2009 to 2013 for transport, stationary and portable applications and breaks this information down by electrolyte and region of adoption. There is also a special forecast for each of the three emerging market regions of India, Latin America and the Middle East, and one-page overviews of ten other emerging market regions which could see substantial uptake in the next five years.

**Availability of the Review**

Copies of the Review are available for purchase, priced £500 / U.S.$1,000 / €750 / ¥120,000, from the Fuel Cell Today website at: http://www.fuelcelltoday.com/events/industry-review or by E-mail: review@fuelcelltoday.com.
ABSTRACTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS
Hydrogenation of Natural Rubber Latex in the Presence of [Ir(cod)(PCy3)(py)]PF6
[Ir(COD)(PCy3)(py)]PF6 (1) was an effective catalyst for the hydrogenation of natural rubber latex (NRL) in monochlorobenzene. The hydrogenation was first-order with respect to both H2 pressure and concentration of (1), which suggests that the active complex is mononuclear. Addition of a sulfonic acid helped suppress the poisoning of (1) by impurities in the NRL.

CATALYSIS – REACTIONS
Pd Nanoparticles Immobilized on Sepiolite by Ionic Liquids: Efficient Catalysts for Hydrogenation of Alkenes and Heck Reactions
Pd/sepiolite catalysts (1) were prepared by immobilising Pd2+ on sepiolite using an ionic liquid containing a guanidine cation, followed by reduction with H2 at 150ºC. XPS established that the loaded Pd is mainly Pd(0), with a small amount of its oxides, and distributed uniformly with particle size ~ 5 nm, as confirmed by TEM. (1) exhibited very high efficiency for the hydrogenation of alkenes and Heck reactions.

Catalyst Leaching as an Efficient Tool for Constructing New Catalytic Reactions: Application to the Synthesis of Cyclic Vinyl Sulfides and Vinyl Selenides
Catalyst leaching from Pd and Ni particles stabilised by organic S and Se ligands was found to occur in solution in the presence of phosphines. This process was monitored in real time by 1D and 2D NMR. The mechanism of the EtOH oxidation reaction (EOR) on a Pd electrode (1) in alkaline media was studied using CV. The dissociative adsorption of EtOH proceeded quickly and the rate-determining step was the removal of the adsorbed ethoxide ion by the adsorbed hydroxyl ion on (1). At potentials below –0.4 V, the Tafel slope was 130 mV dec–1. At potentials above –0.4 V, the Tafel slope increased to 250 mV dec–1, as the mechanism of the EOR was complicated by oxide layer formation on the Pd surface at higher potentials.

EMISSIONS CONTROL
The Effect of Sulphur on the Activity of Pd/Al2O3, Pd/CeO2 and Pd/ZrO2 Diesel Exhaust Gas Catalysts
Pd/Al2O3, Pd/CeO2 and Pd/ZrO2 diesel oxidation catalysts and their washcoat materials were studied after S treatment. The catalytic activities were analysed in a simplified diesel exhaust gas mixture by FTIR spectroscopy. S treatment was shown to deactivate these Pd-based diesel oxidation catalysts.

Cleaner Water Using Bimetallic Nanoparticle Catalysts
Pd-based catalysts are effective in hydrodechlorination of chlorinated ethenes and related compounds. However Pd-on-Au bimetallic nanoparticles (1) were recently found to exhibit superior catalytic activity and improved deactivation resistance for groundwater remediation. (1) are significant in the development of a viable hydrodechlorination catalysis technology.

FUEL CELLS
Mechanism Study of the Ethanol Oxidation Reaction on Palladium in Alkaline Media
The mechanism of the EtOH oxidation reaction (EOR) on a Pd electrode (1) in alkaline media was studied using CV. The dissociative adsorption of EtOH proceeded quickly and the rate-determining step was the removal of the adsorbed ethoxide ion by the adsorbed hydroxyl ion on (1). At potentials below –0.4 V, the Tafel slope was 130 mV dec–1. At potentials above –0.4 V, the Tafel slope increased to 250 mV dec–1, as the mechanism of the EOR was complicated by oxide layer formation on the Pd surface at higher potentials.

METALLURGY AND MATERIALS
Growth and Field Emission of Reactive Sputtered Pd–PdO Core–Shell Nanoflakes on Platinum
PdO was reactive sputter deposited on Pt. The PdO thin film grown had a flakelike morphology. The nanosized flake had a core–shell structure with a single Pd grain encapsulated by a crystalline PdO surface layer. The formation of the nanoflakes is attributed to a large interfacial stress due to a lattice mismatch between PdO and Pt.

High Temperature Interface Reactions of TiC, TiN, and SiC with Palladium and Rhodium
Reactions of TiC, TiN and SiC with Pd and Rh at ≤ 1600ºC were studied using bulk diffusion couple experiments. Intermetallic phases at the ceramic-metal interfaces were observed. The reactivity order of the ceramics was: SiC > TiC > TiN, and reactivity order of the pgms was: Pd > Rh. The TiN–Pd interfaces gave no intermetallic phase formation under the annealing conditions. The formation of distinct intermetallic phases at the SiC–Rh and TiC–Rh interfaces followed a non-parabolic behaviour.
Synthesis and Structure-Specific Functions of Patchy Nanoparticles
The close coupling of different components on the nanoscale in anisotropically phase-segregated nanoparticles, ‘patchy nanoparticles’, may improve performance for various applications or even create new properties. A seed-mediated growth method was used to synthesize patchy nanoparticles consisting of a combination of metals, metal sulfides and metal oxides, such as PdSx/CoSx and CdS/PdCd2S/CdS.

CHEMISTRY

Kinetics of Complex Formation between Palladium(II) Acetate and Bis(diphenylphosphino)ferrocene

31P NMR spectroscopy was used to study the kinetics of complex formation between Pd(OAc)2 and dppf. The mole ratio and the 31P-chemical shifts in DMSO-d6 revealed the formation of an intermediate, which gradually converts into the more stable [Pd(dppf)(OAc)]2 with dppf acting as a chelate ligand. The rate constant for the complexation was evaluated.

Photophysical Properties, X-Ray Structures, Electrochemistry, and DFT Computational Chemistry of Osmium Complexes

Phosphorescent [Os(N–N)L–L] or Os(L–L)(N–N)2+ (PF6)2 [N–N = derivative of 1,10-phenanthroline; L–L = 1,2-bis(dimethylphosphino)ethane, 1,2-bis(dicyclohexylphosphino)ethane or 1,2-bis(dimethylarseno)benzene] were synthesised. The luminescence emission lifetimes of Os(II)(N–N)2(L–L) were longer than those of Os(II)(L–L)2(N–N). DFT calculations show that there is significant mixing of the π→π* charge-transfer state for Os(II)(L–L)(N–N) giving a longer lived excited state.

ELECTRICAL AND ELECTRONICS

Direct-Write Patterning Palladium Colloids as a Catalyst for Electroless Metallization for Microwave Composites
Inkjet printing was used to pattern a Pd-Sn electroless catalyst (Cataposit 44, Rohm & Haas) for electroless Cu metallisation on paper. Low-resistance Cu traces can be produced. Large-area microscale patterning was demonstrated. Sample patterns of frequency-selective surface designs were manufactured and shown to conform to computationally modelled expectations in the microwave regime.

Effect of pH in Ru Slurry with Sodium Periodate on Ru CMP
NaIO4 acted as both oxidant and etchant on a Ru chemical mechanical planarisation slurry for the formation of Ru bottom electrodes in DRAM capacitors. Below pH 7.5, a high static etch rate was measured due to dissolution of RuO4. Above pH 7.5, the static etch rate decreased due to formation of insoluble RuO2·2H2O and depletion of periodate ions. A Ru to oxide selectivity of ~ 23:1 was achieved at pH 8–9. In a slurry of pH 9, Ru overetching was prevented.

ELECTROCHEMISTRY

Electrochemical Preparation of Pd Nanorods with High-Index Facets
Fivefold twinned Pd nanorods (I) with \{h{k}k\} or \{h{k}h\} high-index facets were obtained using an electrochemical square-wave potential method with well-controlled potential limits. This is attributed to the different degrees of surface reconstruction induced by O2 adsorption/desorption. (I) with \{h{k}k\} high-index facets exhibited 2–3 times higher catalytic activity per unit surface area than a commercial Pd black catalyst towards the electrooxygenation of EtOH in alkaline solution (0.1 M NaOH + 0.1 M EtOH).

PHOTOCONVERSION

New NIR-Emitting Complexes of Platinum(II) and Palladium(II) with Fluorinated Benzoporphyrrins
Pt(II) and Pd(II) complexes with fluorinated benzoporphyrrins were synthesised. The complexes possess highly efficient room temperature Near IR phosphorescence and are excitable with blue and red light. The fluorinated derivatives exhibited improved photophysical properties and photostability. The new dyes can be used as indicators in optical O2 sensors.

Luminescence Color Change of a Platinum(II) Complex Solid Upon Mechanical Grinding
The yellow luminescence of crystalline Pt(5dpb)Cl (5dpbH = 1,3-di(5-methyl-2-pyridyl)benzene) changed to orange when grinding into fine powder on a glass substrate. A broad emission band was observed at ~ 670 nm for the powder. This disappeared below 120 K. Pt(dpdp)Cl (dpdpH = 1,3-di(2-pyridyl)benzene) also exhibited luminescent mechanochromism. However, the broad emission that appeared upon grinding still remained at 77 K; the ground sample of Pt(dpdp)Cl was amorphous.
NEW PATENTS

CATALYSIS – APPLIED AND PHYSICAL ASPECTS

Improved Heterogeneous Palladium Catalyst
ALMQUEST AB European Appl. 1,994,983

A stable Pd catalyst formulation is claimed. The porous carrier consists of a core and covalently-bonded ion exchange groups in which > 90% (preferably > 95%) of the ions are HCOO-. These reduce Pd in a Pd(II) salt and facilitate Pd(0) deposition on the surface of the carrier at reaction temperature 30–70ºC (preferably 45–55ºC). The catalyst is suitable for Heck, Suzuki-Miyaura and Buchwald-Hartwig reactions.

Catalysts for Decomposition of Organic Acids
NIPPON SHOKUBAI CO LTD Japanese Appl. 2008-178,766

Collection of ultrafine PM in vehicle exhaust by a DPF is enhanced though use of a Pt or Rh catalyst layer containing micropores of 0.1–0.2 μm diameter. The catalyst layer is deposited on an undercoat which has the dual function of suppressing exfoliation of the catalyst layer and promoting combustion (the co-catalyst is a Ce-, Zr- or perovskite-type composite oxide).

Catalysts for Decomposition of Organic Acids
NIPPON SHOKUBAI CO LTD Japanese Appl. 2008-238,063

A novel metal selected from Pt, Pd, Rh, Ru, Ir and Au (preferably Pt or Pd) is deposited on a Ce-Zr or a Ce-Zr-X compound oxide, where X = La, Y or Pt. Al and/or W can also be added. Efficient decomposition of organic acids with C1–C6 in industrial flue gas is achieved. High activity and durability are claimed.

FUEL CELLS

Platinum Alloy for Membrane Electrode Assembly
JOHNSTON MATTHEY PLC World Appl. 2009/013,540

A new Pt alloy catalyst PtX is described which contains ~10–80 at.% Pt at the surface, which is at least 25% greater than the content of Pt in the bulk (~ 5–50 at.%). X may be Ru, Rh, Pd, Ir, Os, Au, Ag, Sn or Ru-Sn (preferably Ru and/or Sn). The catalyst can be unsupported or supported on a dispersed material such as conductive C. Further, it can be incorporated into an electrode, a catalysed membrane or a transfer substrate, and may constitute various parts of a MEA in a polymer electrolyte membrane fuel cell.

CATALYSIS – INDUSTRIAL PROCESS

Novel Fluoropolyether Compositions
SHIN-ETSU CHEM. CO LTD European Appl. 1,995,278

A composition containing a polyfluorodialkenyl compound, a fluorinated organohydrogenpolysiloxane and a pgm complex, usually Pt (0.1–500 ppm w/w), to catalyse the curing process is combined with hydrophobic SiO2 powder, a Si-based tackifier and a dispersant. These allow the fluoropolyether to adhere to organic resins but not to metal moulds so that composite resin-rubber moulded parts can be produced.

Production of Alcohols Using Carbon Dioxide
HITACHI CHEM. CO LTD European Appl. 2,000,453

Alcohols are produced by hydroformylation of an organic compound using CO2 rather than CO as a raw material. The reaction is catalysed by a Ru compound (preferably a clustered Ru compound such as Ru12(CO)3Cl4 or Ru3(CO)12) combined with an acid compound (preferably a clustered Ru compound such as Ru12(CO)3Cl4 or Ru3(CO)12) combined with an acid and optionally a halide salt. The reaction proceeds at 100–180ºC and 1–50 MPa. High yields are claimed.

Stable Catalyst for Metathesis of Nitrile Rubber
LANXESS DEUTSCHLAND GmbH U.S. Patent 7,470,750

Degradation of nitrile rubbers is achieved through olefin metathesis catalysed by a Ru or Os complex bearing an imidazolidine ligand and a carbene ligand having a phosphine radical. The complex is described as forming a stable solution in the solvents which would typically be used for the process, even at high temperatures, and no gelling of the rubber is observed.

EMISSIONS CONTROL

Barium-Free Catalyst for Lean NOx Trap
FORD GLOBAL TECHNOLOG LLC European Appl. 1,990,081

A novel formulation and production process are claimed for a LNT catalyst which gives efficient NOx conversion at low temperatures. High-temperature calcination of the base metal oxide takes place prior to the addition of the pgms, preferably Pt-Rh, Pt-Pd or Pt-Pd-Rh. The base metal is Pt or Pr-La which is claimed to confer advantages to the formulation over commercially available Ba-based mixtures.

Enhanced Diesel Particulate Filter
MAZDA MOTOR CORP Japanese Appl. 2008-178,766

Collection of ultrafine PM in vehicle exhaust by a DPF is enhanced though use of a Pt or Rh catalyst layer containing micropores of 0.1–0.2 μm diameter. The catalyst layer is deposited on an undercoat which has the dual function of suppressing exfoliation of the catalyst layer and promoting combustion (the co-catalyst is a Ce-, Zr- or perovskite-type composite oxide).

METALLURGY AND MATERIALS

Iridium Alloys for High-Temperature Applications
JOHNSTON MATTHEY PLC U.S. Patent 7,481,971

Ir alloys are presented that include Rh (0.1–2.5 wt.%) and at least one of W (0.01–5 wt.%) and Zr (0.01–0.5 wt.%). They may also contain Pt (0.1–5 wt.%) and/or one or more of Ta, Nb, Mo, Cr, Ce, Sc, Lu, Co, Ni, Hf, Y, Ti, Ru and Pd (each 0.01–10 wt.%). The alloys are claimed to show significantly improved performance in high-temperature oxidising environments compared to pure Ir. Potential applications include electrode materials in spark plugs, crucibles and fabricated components for the glass and chemical industries.
IrOx neural interface.

the retina can be electrically stimulated through the

tates a high resolution sensor as very precise areas of

imaging applications. The nanowire technology facili-

parent conducting electrode, making it suitable for

ment of blindness caused by retinitis pigmentosa etc.

RESULTS

small amounts of Pd, Ir, Ru or alternatively In and Ga may also be added to the 70–79.5 wt.% Pt alloy. The colour of the alloy is claimed to corres-

pond to a white PtCu950 alloy and it can be cast to

form a variety of jewellery items such as rings, neck-

laces, watch bands or watch bodies.

PHOTOCONVERSION

White OLEDs

Y. CHI et al. U.S. Appl. 2009/0,001,875

A design for stable organic white light-emitting
devices is presented, based on a combination of Os

and Ir complexes. The Os complexes emit in the

range 580–630 nm (orange-red light) and the Ir com-

plexes emit in the range 450–500 nm (blue-green

light). An OLED emitting virtually white light is

obtained. External quantum efficiency and luminous

efficiency are stated as 28.8% and 47.5 lm W−1 (17% and

28 lm W−1 in the forward-viewing direction).

Novel Organometallic Complex for DSSC

S. M. ZAKKEERUDDIN et al. U.S. Appl. 2009/0,000,658

Heteroleptic polypyridyl complexes of Ru, Os or Fe

(preferably Ru) containing 4,4′-disubstituted

bipyridines as anchoring ligands are described. The

complexes are formulated to have improved light-har-

vesting capacity compared to known polypyridyl Ru

complexes. A dye sensitised solar cell containing the

complex as a photosensitising dye in combination

with a compacting compound is claimed. This mixture

is theorised as forming a closely-packed hydrophobic

monolayer on the anode semiconductor, insulating

against back electron transfer and thereby increasing

the cell open circuit voltage. The molten salt may offer

improved thermal stability over electrolyte solutions.

REFINING AND RECOVERY

Separating Apparatus and Method for Fire Assay

ANGLO AMERICAN PLATINUM CORP LTD

World Appl. 2009/007,911

A novel apparatus for fire assay determination of Au

and pgms in ore is described which permits controlled

venting of trapped air during casting and is construct-

ed such that the collector material is not exposed to

oxidation between the separation vessel and the

collector mould. A method for quantitatively separat-

ing molten salt and collection material is presented.

SURFACE COATINGS

Pt-Al Coatings on Gas Turbine Components

MTU AERO ENGINES GMBH

World Appl. 2008/145,093

A monophasic Pt-Al coating is obtained after diffusion

heat treatment (0.2–4 h) and aluminising of the

Pt-layer (3–11 h), specified as < 4 μm thick. A biph-

asic coating requires an aluminising period of 8–15 h

and a Pt-layer of 5–6 μm. A single-phase PtAl layer

based on a Pt coating of 1–2 μm is also claimed.

High-Speed Plating of Palladium

ROHM & HAAS ELECTRON. MATER. LLC

European Appl. 2009/0,017,373

Methods for NH3-based bath deposition of Pd and

Pd-based alloys at current densities of 10–100 A dm−2

are claimed. Low levels (< 50 g l−1) of free NH3 in the

electroplating baths are maintained by adding urea.

The method is suitable for producing Pd or Pd-alloy

coatings on electronic components and jewellery.
Surface Characterisation of Heterogeneous Catalysts by XPS: Part II

In Part I of this Final Analysis series (1), the identification and quantification of elements by X-ray (excited) photoelectron spectroscopy (XPS) was discussed. A statement was made that the core energy levels do not vary a great deal — but there is usually some variation for a given element in different chemical forms. This can be thought of as being caused by variations in the oxidation state and the local chemical or structural environment resulting in a variation in the net electrical charge on a given atom. The change in the electrical charge affects the energy of the photoelectron and so manifests as a slight shift in the measured core level binding energy. Such chemical shifts can be resolved in XPS spectra and this is a key aspect of the technique for catalyst characterisation.

Qualification of Elements

In our earlier example, a platinum-gold fuel cell catalyst material was studied in an “as-received” form (1). Basic chemistry teaches us that only gold is likely to have no surface oxide at all, and that even platinum is not as inert (see for example, (2)). So an interesting exercise might be to compare signals from the surface of the catalyst material before and after reduction using hydrogen gas. This can be achieved in a suitably-equipped spectrometer. Although the system is evacuated, a reaction cell isolated from the vacuum system can be used to create a reactive surface for study without the oxidation that would be expected on exposure to air. In the case of our catalyst material, a flow of hydrogen over the material while heating to 100°C was performed before re-evacuation and re-analysis.

Figure 1 shows the region of the platinum and gold 4f signals, their most useful photoemission lines, in much more detail than the survey spectrum shown in the previous Final Analysis article (1). The signals before and after the reduction of the material are shown. The platinum 4f signal is from 70 eV to 76 eV and that of gold is from 84 eV to 88 eV.
82 eV to 90 eV. In both cases the level is split into two peaks due to electron spin and angular momentum considerations in the core level (this is termed spin-orbit coupling or $jj$-coupling), but in general the stronger line is considered.

The principal gold line at 84 eV is typical of the metal as a bulk material in both spectra. The lack of a significant change in the line shape after reduction implies that the element was not changed by this process.

The same is not true of the platinum line, at about 71 eV. There is a distinct tail on the high-binding-energy side of the doublet peaks before reduction. This is characteristic of an oxidised surface layer, perhaps a platinum(II) hydroxide or similar species. There are few other ways of determining this type of chemical information from the near-surface region selectively. Therefore XPS is a valuable analytical tool for heterogeneous catalysts, since the surface chemistry determines catalytic activity. Detailed quantification is possible: the application of numerical methods can afford an estimate of the relative contribution from the oxidised material compared with the metal. In this case, it is perhaps one-third as intense as the signal from the metal. The intensity of the signals, when averaged over the whole system, is directly related to the relative amount of the form considered. The results are usually best considered in conjunction with other analytical techniques, such as electron microscopy, which can give a good idea of structure. This information can then help in interpreting the XPS data.

Still more spectral interpretation is possible. The post-reduction platinum signal is asymmetric and very similar to that of the bulk metal, but the maximum of the signal is at 70.7 eV, compared with reference data for bulk platinum at 71.1 eV. As a result, we can also say that the surface layers might be something like an alloy rather than discrete particles of pure elements, as a change in binding energy from the pure element is the result of a degree of electron transfer between the elements in an alloy. In this case, X-ray diffraction (XRD) measurements determined that the material is indeed an alloy of Pt and Au.

**Summary**

The results presented in this two-part series show several aspects of the use of XPS for the surface characterisation of heterogeneous catalyst materials. The major point of note is that a material's surface is not necessarily the same as the bulk in terms of its chemical composition. Analysis of the bulk catalyst material here revealed pure metals, while the surface has a very large amount of carbon present, together with impurities deposited during or after synthesis. Furthermore, the surface has some degree of oxidation.

In any field where the surface is important, in particular catalysis, understanding its chemical nature is vital. XPS is best seen as a (semi)-quantitative tool for comparative studies to obtain chemical information from the outer few atomic layers of a surface. Indeed, Nobel Laureate Kai Siegbahn (3), who developed the technique, originally termed it “electron spectroscopy for chemical analysis” (ESCA) (4).

**References**


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