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222  Johnson Matthey Highlights
Shale gas has received much attention in recent years particularly in the USA and in Europe. It is a useful fuel source but also comes with the attendant risks and challenges associated with maximising the useful extraction of fuel, minimising costs and also protecting the environment. Its constituent component is essentially methane, the same as any other source of natural gas and it is this which makes itself useful in a variety of ways as a fuel and feedstock.

The extraction of unconventional gas as well as unconventional oil requires new technologies, with one of the challenges being to develop the most economical extraction process, given the large investments required. Tracerco, a Johnson Matthey company, provides solutions to this problem with its tracer technologies and an article outlining a case study of their application is included in this issue (1).

Methane, the major component of both shale gas and conventionally derived natural gas, also occurs in a number of other applications and it is not always welcome.

Extracting Methane

One such example is methane found during coal mining activities. While some forms of methane are able to be extracted in useful form (coal bed methane and to some extent coal mine methane also) there is a third type, ventilation air methane, present at concentrations of less than 1% and which is not currently economical to extract for use. At the same time this low level methane constitutes the largest amount, in tonnage terms, of the methane emissions from coal mining. To mitigate this Johnson Matthey Davy Technologies Ltd (JM Davy) has developed the technology known as COMET™ which is discussed in another of the articles in the present issue, by Ian Mitchell et al. (2).

A UK-based development and process engineering company, JM Davy licenses its proprietary process technologies worldwide for the oil, gas and chemicals industries. It also has a research and development (R&D) centre located in the Tees Valley, UK, where it undertakes development, demonstration and process engineering to support its portfolio of processes, technologies and catalysts. It licenses processes and their individual core technologies to clients who wish to build a new plant or make a new product.

Emissions Abatement

Natural gas can be used as a fuel in various sorts of engines both mobile (typically vehicle combustion engines in the form of compressed natural gas (CNG) fuel) and stationary engines. Although today’s engines are increasingly efficient there is a small amount of escape into the vehicle exhaust and this must be mitigated with an emissions control solution. A forthcoming article in this journal will look at ways in which these emissions can be eliminated when used in various engine types.

Collaborative Programmes

Methane is well known as an unreactive hydrocarbon meaning that it is challenging to process. A number of European funded projects have been set up looking at ways to more efficiently process methane as well as other hydrocarbons, whether sourced from fossil reserves or from biomass. The improvement of such processing will be crucial to the sustainable future of many industries and an article in this issue, derived from one of the European projects ‘Catalytic Membrane Reactors Based on New Materials for C1-C4 Valorization’ (known as CARENA) details some of the work undertaken within Johnson Matthey in the context of this programme (3).
Overall Johnson Matthey is well placed to offer a number of solutions to areas of industry which deal with the difficult challenges posed by methane and other hydrocarbons, whether as a fuel, feedstock, or unwanted emissions. As part of its commitment to sustainable industry and the sustainable use of resources, it drives innovation through its R&D activities towards this goal.

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References
Selected Electrical Resistivity Values for the Platinum Group of Metals Part III: Ruthenium and Osmium

Improved values obtained for ruthenium and osmium

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Anisotropic and average intrinsic electrical resistivity measurements of ruthenium were evaluated from 10 K to 1600 K and average values above this temperature up to the melting point. For osmium average values were evaluated from 30 K to 273.15 K and anisotropic and average values above this temperature and up to 1600 K.

Introduction

Previous reviews on electrical resistivity were given in Part I for palladium and platinum (1) and in Part II for rhodium and iridium (2).

The elements ruthenium and osmium are both superconducting with transition temperatures of 0.49 ± 0.015 K for ruthenium and 0.66 ± 0.03 K for osmium (3). Both have hexagonal close-packed structures and resistivity values are therefore selected along directions both perpendicular to the c axis (ρ⊥) and parallel to the c axis (ρ∥). The average resistivity is then given by ρavr = (2ρ⊥ + ρ∥)/3. The melting point of ruthenium is a secondary fixed point on the International Temperature Scale of 1990 (ITS-90) at 2606 ± 10 K (4) whilst the melting point of osmium is estimated as being 3400 ± 50 K (5).

Ruthenium

Selected resistivity values at 273.15 K are given in Table I. Because of the possibility of preferred orientation in polycrystalline samples only results for single crystals are considered in the selection. On this basis the selected values are an average of the measurements of Powell et al. (11), Azhazha et al. (12) and Volkenshteyn et al. (13).

At 30 K and below selected intrinsic anisotropic and average values are given by the equations of Volkenshteyn et al. (10) as Equations (i) to (iii).

Anisotropic measurements of Azhazha et al. (12) to 25 K lead to identical values at 20 K whilst the average value at 20 K of 0.0019 μΩ cm is in excellent agreement with the value of 0.0017 μΩ cm calculated from the equation of Schriempf and Macinnes (15) (4–20 K).

Between 30 K and 273.15 K for Volkenshteyn et al. (10) and below 273.15 K for Azhazha et al. (12) and Volkenshteyn et al. (13) the anisotropic resistivity measurements were only shown graphically with actual values estimated from these graphs. Average resistivity values of White and Woods (6, 7) (25–295 K) when normalised to the selected value at 273.15 K using the ratio 6.16/6.69 show excellent agreement with average values of Volkenshteyn et al.
(13) estimated at 80 K and above with the average bias being only 0.01 μΩ cm low at 120 K and above. The measurements of Volkenshteyn et al. (13) were therefore selected to 260 K, combined with the selected values at 273.15 K and fitted to Equations (iv) to (vi) to represent the range from 100 K to 273.15 K. The overall accuracies as standard deviations of ±0.03 μΩ cm and ±0.02 μΩ cm respectively indicate a satisfactory degree of correlation considering that the values were only estimated.

Below 100 K the measurements of White and Woods (6, 7) over the range 40 to 60 K were converted from average to anisotropic values using ratios of ρ ||/ρ ⊥ determined from the measurements of Volkenshteyn et al. (10) after correction for ρ0 whilst values of ρ ⊥ and ρ || at 70 K and 90 K were estimated by interpolation.

In comparison with Equations (iii) and (iv) the estimated measurements of Azhazha et al. (12) show a maximum deviation of 0.19 μΩ cm low at 180 K along both axes whilst after correction for residual resistivity the measurements of Volkenshteyn et al. (10) trend to values at 273.15 K of 0.48 μΩ cm high perpendicular to the c axis but only 0.12 μΩ cm high parallel to the c axis.

In the high temperature region anisotropic resistivity measurements of Savitskil et al. (16) (300–1600 K) were only shown graphically with actual data points given by Savitskil et al. (17). These can be made to show satisfactory agreement with the selected values at 273.15 K only when considered over the range 600 K to 1600 K while the values at 300 K and 400 K showed marked deviations and were therefore rejected. After correction for thermal expansion using length values selected by the present author (18) the electrical resistivity values over the range 273.15 K to 1600 K were represented by Equations (vii) to (ix) with derived values given in Table II. Along the axes overall accuracies as standard deviations are ±0.27 μΩ cm and ±0.10 μΩ cm respectively.

Average electrical resistivity measurements of Binkele and Brunen (19) (273–1421 K) trend from initially 4.9% high to 0.5% high at 1100 K and then increases to 1.4% high at 1421 K whilst average measurements of Milošević and Nikolić (20) (250–2500 K) trend from initially 7.3% high to 0.7% low at 1600 K. These two sets of measurements differ sharply above 1100 K with the difference reaching 1.7% at 1421 K, the experimental limit of Binkele and Brunen. Since the measurements of Milošević and Nikolić were fitted to a quadratic equation it was found that the values at 2300 K and above showed a reasonable degree of correlation with an extrapolation of Equation (ix) and therefore the selected average value at 1600 K was combined with the high temperature measurements of Milošević and Nikolić at 2300 K, 2400 K and 2500 K and fitted to Equation (x) to give a fairly satisfactory representation of the average electrical resistivity in the range from 1600 K up to the melting point. Values derived from Equation (x) are given in Table III.

Percentage deviations from the selected values of the average measurements of Savitskil et al., Binkele

<table>
<thead>
<tr>
<th>Authors</th>
<th>Ref.</th>
<th>ρ⊥, μΩ cm</th>
<th>ρ∥, μΩ cm</th>
<th>ρavr, μΩ cm</th>
<th>Temperature of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>White and Woods</td>
<td>6, 7</td>
<td>–</td>
<td>–</td>
<td>6.69</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>8</td>
<td>–</td>
<td>–</td>
<td>6.54</td>
<td>At 273.15 K. Corrected ρ0 0.57 μΩ cm</td>
</tr>
<tr>
<td>Tainsh and White</td>
<td>9</td>
<td>–</td>
<td>–</td>
<td>6.72</td>
<td>At 273.15 K. Corrected ρ0 0.02 μΩ cm</td>
</tr>
<tr>
<td>Volkenshteyn et al.</td>
<td>10</td>
<td>7.15</td>
<td>5.26</td>
<td>6.52</td>
<td>At 273.15 K. Corrected ρ0 ⊥ 0.10 μΩ cm; ρ0</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>11</td>
<td>6.75</td>
<td>5.12</td>
<td>6.21</td>
<td>Interpolated 200–400 K. Corrected for both axes by ρ0 0.07 μΩ cm</td>
</tr>
<tr>
<td>Azhazha et al.</td>
<td>12</td>
<td>6.61</td>
<td>5.14</td>
<td>6.12</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>Volkenshtein et al.</td>
<td>13</td>
<td>6.65</td>
<td>5.15</td>
<td>6.15</td>
<td>At 273.15 K. Estimated by Bass (14) from a graphical representation</td>
</tr>
</tbody>
</table>

**Selected** | 6.67±0.08 | 5.14±0.02 | 6.16±0.05 | At 273.15 K
and Brunen and Milošević up to 2500 K are shown in Figure 1.

**Osmium**

Selected resistivity values at 273.15 K are given in Table IV. As with ruthenium, because of the possibility of preferred orientation in polycrystalline samples only results for single crystals are considered in this selection. Values given by Powell et al. (11) were corrected for residual resistivity based on the ratio $\rho_{273 K} / \rho_{4.2 K} = 33.3$ given as a private communication to Ho et al. (21). The selected values in Table IV are based on the values of Volkenshtein (22) since they were precision determinations on high purity material at 273.15 K.

Schriempf (23) (2–20 K) determined the anisotropic resistivities at 60º and 16º to the c axis but did not give values of $\rho_{\perp}$ and $\rho_{||}$. The average values of White and Woods (6, 7) (25–295 K) were corrected to conform to the selected value at 273.15 K using the ratio 8.07/8.35 and at 80 K and above fitted to Equation (xi)

### Table II Intrinsic Electrical Resistivity of Ruthenium (10 K to 1600 K)

| Temperature, K | $\rho_{\perp}$, $\mu\Omega$ cm | $\rho_{||}$, $\mu\Omega$ cm | $\rho_{\text{avr}}$, $\mu\Omega$ cm | Temperature, K | $\rho_{\perp}$, $\mu\Omega$ cm | $\rho_{||}$, $\mu\Omega$ cm | $\rho_{\text{avr}}$, $\mu\Omega$ cm |
|----------------|-------------------------------|-------------------------------|-----------------------------------|----------------|-------------------------------|-------------------------------|-----------------------------------|
| 10             | 0.0003                        | 0.0003                        | 0.0003                            | 230            | 5.30                          | 4.12                          | 4.91                              |
| 20             | 0.0020                        | 0.0017                        | 0.0019                            | 240            | 5.62                          | 4.36                          | 5.20                              |
| 30             | 0.0093                        | 0.0079                        | 0.0088                            | 250            | 5.94                          | 4.60                          | 5.49                              |
| 40             | 0.038                         | 0.030                         | 0.035                             | 260            | 6.25                          | 4.83                          | 5.78                              |
| 50             | 0.11                          | 0.08                          | 0.10                              | 270            | 6.57                          | 5.07                          | 6.07                              |
| 60             | 0.25                          | 0.17                          | 0.22                              | 273.15         | 6.67                          | 5.14                          | 6.16                              |
| 70             | 0.42                          | 0.33                          | 0.39                              | 280            | 6.91                          | 5.28                          | 6.37                              |
| 80             | 0.63                          | 0.52                          | 0.59                              | 290            | 7.26                          | 5.48                          | 6.67                              |
| 90             | 0.89                          | 0.73                          | 0.84                              | 300            | 7.61                          | 5.68                          | 6.96                              |
| 100            | 1.20                          | 0.96                          | 1.12                              | 400            | 11.1                          | 7.74                          | 9.97                              |
| 110            | 1.51                          | 1.21                          | 1.41                              | 500            | 14.6                          | 9.89                          | 13.0                              |
| 120            | 1.83                          | 1.46                          | 1.71                              | 600            | 18.0                          | 12.1                          | 16.1                              |
| 130            | 2.14                          | 1.71                          | 2.00                              | 700            | 21.5                          | 14.4                          | 19.2                              |
| 140            | 2.46                          | 1.95                          | 2.29                              | 800            | 25.0                          | 16.8                          | 22.3                              |
| 150            | 2.77                          | 2.20                          | 2.58                              | 900            | 28.5                          | 19.3                          | 25.4                              |
| 160            | 3.09                          | 2.44                          | 2.87                              | 1000           | 32.0                          | 21.9                          | 28.6                              |
| 170            | 3.40                          | 2.88                          | 3.16                              | 1100           | 35.4                          | 24.5                          | 31.8                              |
| 180            | 3.72                          | 2.93                          | 3.46                              | 1200           | 38.9                          | 27.3                          | 35.0                              |
| 190            | 4.04                          | 3.17                          | 3.75                              | 1300           | 42.4                          | 30.1                          | 38.3                              |
| 200            | 4.35                          | 3.41                          | 4.04                              | 1400           | 45.9                          | 33.0                          | 41.6                              |
| 210            | 4.67                          | 3.65                          | 4.33                              | 1500           | 49.3                          | 36.0                          | 44.9                              |
| 220            | 4.99                          | 3.89                          | 4.62                              | 1600           | 52.8                          | 39.1                          | 48.2                              |

### Table III Average Intrinsic Electrical Resistivity of Ruthenium (1600 K to 2606 K)

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$\rho_{\text{avr}}$, $\mu\Omega$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>48.2</td>
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<tr>
<td>1700</td>
<td>51.4</td>
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<td>1800</td>
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<td>1900</td>
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<td>2300</td>
<td>50.8</td>
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<td>2400</td>
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<td>2500</td>
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<tr>
<td>2600</td>
<td>61.0</td>
</tr>
<tr>
<td>2606</td>
<td>64.2</td>
</tr>
</tbody>
</table>
with an overall accuracy as a standard deviation of ±0.02 μΩ cm. Values were only given at 30 K and above because of the possibility of unaccounted for residual resistivity.

In the high temperature region anisotropic resistivity measurements of Savitskii et al. (24) (300–1600 K) were only shown graphically with actual data points given by Savitskii et al. (17). These only show satisfactory agreement with the selected values at 600 K and above for the axis perpendicular to the c axis and 1000 K and above for the axis parallel to the c axis and therefore lower temperature measurements were rejected in each case. The values were corrected for thermal expansion using the length values selected by the present author (25). However these extended only to 1300 K and values above this temperature were obtained by extrapolation. The corrected values were then fitted to Equations (xii) to (xiv) which were used to represent the thermal expansion from 273.15 K to 1600 K with overall accuracies as standard deviations of ±0.40 μΩ cm and ±0.51 μΩ cm respectively. Percentage deviations of the measurements of Savitskii et al. from the selected values are shown in Figure 2 whilst selected values of intrinsic electrical resistivity for osmium are given in Table V.

![Graph showing electrical resistivity of osmium](image)

**Table IV Electrical Resistivity of Osmium at 273.15 K**

| Authors          | Ref. | \(\rho_{||}\), \(\mu\Omega\) cm | \(\rho_{\perp}\), \(\mu\Omega\) cm | \(\rho_{\text{avr}}\), \(\mu\Omega\) cm | Temperature of data               |
|------------------|------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| White and Woods  | 6, 7 | –                               | –                               | 8.35                            | At 273.15 K                      |
| Powell et al.    | 8    | –                               | –                               | 8.26                            | At 273.15 K. As received sample corrected for \(\rho_0\) 0.27 μΩ cm |
| Powell et al.    | 11   | –                               | –                               | 7.88                            | At 273.15 K. Sample annealed at 1813 K corrected for \(\rho_0\) 0.24 μΩ cm |
| Volkenshteyn     | 22   | 9.346                           | 5.532                           | 8.075                           | Interpolated 200–400 K. Corrected for \(\rho_0\) 0.24 μΩ cm |
| **Selected**     |      | **9.35**                        | **5.53**                        | **8.07**                        | At 273.15 K                      |
Anisotropic measurements of Schriempf (23) at 297 K differs significantly from the selected value perpendicular to the c axis being 0.98 μΩ cm low whilst the value along the c axis is 0.15 μΩ cm high. The corrected average value of Powell et al. (11) at 500 K is 15% low whilst average values of L’vov et al. (26) (100–1700 K) over the mutual high temperature range 500 K to 1300 K average 22% low. Average measurements of Gugnin et al. (27) (373–1973 K) were only shown in the form of small graphs.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>ρ₁ avr, μΩ cm</th>
<th>Temperature, K</th>
<th>ρ₁⊥, μΩ cm</th>
<th>ρ₁∥, μΩ cm</th>
<th>ρ₁ avr, μΩ cm</th>
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<tr>
<td>30</td>
<td>0.027</td>
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<td>1600</td>
<td>66.5</td>
<td>44.2</td>
<td>59.1</td>
</tr>
</tbody>
</table>
Low Temperature Intrinsic Resistivity of Ruthenium Below 30 K
\[
\rho_i \parallel (\mu\Omega \text{ cm}) = 2.8 \times 10^{-6} T^2 + 2.8 \times 10^{-10} T^5 \mu\Omega \text{ cm} \quad (i)
\]
\[
\rho_i \perp (\mu\Omega \text{ cm}) = 2.3 \times 10^{-6} T^2 + 2.4 \times 10^{-10} T^5 \mu\Omega \text{ cm} \quad (ii)
\]
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 2.6 \times 10^{-6} T^2 + 2.7 \times 10^{-10} T^5 \mu\Omega \text{ cm} \quad (iii)
\]

Low Temperature Intrinsic Resistivity of Ruthenium (100 to 273.15 K)
\[
\rho_i \parallel (\mu\Omega \text{ cm}) = 3.13425 \times 10^{-2} T + 7.13667 \times 10^{-7} T^2 - 1.94445 \quad (iv)
\]
\[
\rho_i \perp (\mu\Omega \text{ cm}) = 2.57537 \times 10^{-2} T - 4.37527 \times 10^{-6} T^2 - 1.56817 \quad (v)
\]
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 2.94796 \times 10^{-2} T - 9.82645 \times 10^{-7} T^2 - 1.81902 \quad (vi)
\]

High Temperature Intrinsic Resistivity of Ruthenium (273.15 to 1600 K)
\[
\rho_i \parallel (\mu\Omega \text{ cm}) = 3.48448 \times 10^{-2} T - 3.42085 \times 10^{-6} T^2 - 2.84530 \quad (vii)
\]
\[
\rho_i \perp (\mu\Omega \text{ cm}) = 1.77020 \times 10^{-2} T + 4.20211 \times 10^{-6} T^2 - 8.82460 \times 10^{-3} \quad (viii)
\]
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 2.91305 \times 10^{-2} T + 1.37790 \times 10^{-6} T^2 - 1.89981 \quad (ix)
\]

High Temperature Intrinsic Resistivity of Ruthenium (1600 to 2606 K)
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 2.68820 \times 10^{-2} T + 1.37576 \times 10^{-6} T^2 + 1.70317 \quad (x)
\]

Low Temperature Intrinsic Resistivity of Osmium (80 to 273.15 K)
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 4.68970 \times 10^{-2} T - 4.94870 \times 10^{-5} T^2 + 6.71192 \times 10^{-5} T^3 - 2.41554 \quad (xi)
\]

High Temperature Intrinsic Resistivity of Osmium (273.15 to 1600 K)
\[
\rho_i \parallel (\mu\Omega \text{ cm}) = 5.41521 \times 10^{-2} T - 5.90401 \times 10^{-6} T^2 - 5.00114 \quad (xii)
\]
\[
\rho_i \perp (\mu\Omega \text{ cm}) = 2.96326 \times 10^{-2} T - 2.67298 \times 10^{-7} T^2 - 2.54420 \quad (xiii)
\]
\[
\rho_{i\text{ avr}} (\mu\Omega \text{ cm}) = 4.59789 \times 10^{-2} T - 4.02511 \times 10^{-6} T^2 - 4.18216 \quad (xiv)
\]

References
22. N. V. Volkenshtein, Private communication, quoted in ref. 17

The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
By Jon Spencer
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Email: Jon.Spencer@tracerco.com

The expansion of unconventional oil and gas development has placed a new emphasis on better understanding well performance. The cost of horizontal and stimulated wells is higher than of conventional wells and requires reservoir professionals to look to new technologies to ensure optimal return on drilling, completion and stimulation. Using tracers allows the user to pinpoint stages of the well that are successfully producing, thereby saving costs by eliminating unproductive areas. Tracerco provides unique technologies for this purpose; this article explains how the tracers are applied and presents a case study illustrating their use.

Introduction

Historically the analysis of hydraulic stimulation (1) effectiveness has been based on modelling to evaluate the outcomes of completion along with petrophysical analysis to assess reservoir characteristics such as porosity, permeability, mineralogy and total organic carbon (TOC). Radioactive-based proppant and water tracers have been used in many wells, evolving more recently into water-based chemical tracers to determine spent fluid (water) relative flowback (clean out) and radioactive or neutron absorbing proppant tags to verify the position of its placement. It is imperative to address criteria such as:

• the nature of the geology
• whether the well spacing is appropriate
• the productivity of each stage
• correct interval spacing.

In 2014 Tracerco patented a new technology which provides information on stimulation water, native oil and gas that is produced from distinct sections or ‘stages’ of the wellbore (2). This technology utilises a range of specialist chemicals to the wellbore. The hydrocarbon phase tracer chemistry includes a variety of light aromatics dissolved in solvent. 17 tracers are available to tag the gas phase, 37 to tag the oil phase and 42 to tag the water phase. The tracers are added to the hydraulic fracturing fluid at the point of injection into the well.

Tracer Production Log™ (TPL)

Specialised tracers are orientated for the aqueous or hydrocarbon phases. At the onset of well production, water, gas and oil migration to the surface will transport the specific tracer placed in each stage of the wellbore. Samples of the produced water, gas and oil are collected from the wellhead and analysed for the presence and concentration of each tracer over time. A comparative analysis of the amount of tracer from each stage in a particular sample can then be related to the amount of
water and hydrocarbon produced, with more water and hydrocarbon production resulting in increased tracer displacement.

As the concentration of each tracer is directly proportional to the volume of gas and fluids flowing from the stage, each sample collected acts like a ‘production log’ finding the production of each stage at the time of the sample. Reviewing the analysis of sequential samples provides a continuous measure of each stage production.

The Tracer Production Log™ (TPL) (Figure 1) is used to study the production of each stage over the sampling period and to compare between stages, for example whether production from one stage began sooner or lasted longer than another stage. This provides an indication of how the operation of the well affects the production from certain stages and identifies how the well comes on stream, with diverse and changing individual stage productions as reservoir pressures stabilise.

Value from Output

Value from using chemical tracer tagging comes from its ability to gauge the success of drilling and completion activities to optimise future well design. Analysis of reservoir characteristics such as stress, TOC, Poisson’s ratio, Young’s modulus or permeability can show areas along the lateral with similar properties, and thereby locate potential areas where lateral coverage and completion efficiency can be maximised. Once such areas have been found, Tracerco’s chemical tracer diagnostics measure the success of these efforts.

The TPL of the well in Figure 2 is compared to the wellbore location and petro-data collected during completion. This data, combined with knowledge of natural faults present within the strata, allows a boost in effective production according to the known rock properties and flow dynamics of the petroleum in the area.

Case Study: Eagle Ford Shale

An Eagle Ford Shale, USA, customer had two wells with the same geophysical formation properties. The customer wanted to compare two stimulation strategies to determine their effectiveness for future well development and ensure that results were not skewed by an anomaly giving isolated dominant flow in one or more stages. In challenging market conditions, decreasing lift costs is paramount. Stimulation optimisation was identified as the key to reducing costs and yielding maximum production.
With tracer the customer would be able to spot the exact stages that were affected by the stimulation. Tracers provided a detailed profile of what was happening day by day in each stage of the well so it was possible to see where each of the strategies was performing best. Unique tracers were used to tag the native oil reached in each stage in the two wells, obtaining accurate stage flow data to decide the most effective stimulation conditions.

The results were as follows:
- stimulation strategy 1 yielded 18,000 barrels per month
- stimulation strategy 2 yielded 30% more products at 26,000 barrels per month
- no anomaly showed majority flow from one stage due to unforeseen geological properties.

Further analysis showed that in both strategies the stimulation was ineffective in Stages 8 and 9 of each well (see Figure 3). Diminishing the stimulation of these two stages in either strategy would yield a 20% cut in costs with only a 4% depletion in production, which is effectively offset by the saving.

**Design Strategy**

These tracer results have been used to assist in the future design of landing zone strategy, number of perforations, cluster or stage spacing and number of clusters or

---

**Fig. 2.** Evaluation incorporating TPL, bore location and petro-data

<table>
<thead>
<tr>
<th>Stage</th>
<th>Oil produced, bbl/month⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7000</td>
</tr>
<tr>
<td>2</td>
<td>6000</td>
</tr>
<tr>
<td>3</td>
<td>5000</td>
</tr>
<tr>
<td>4</td>
<td>4000</td>
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<td>5</td>
<td>3000</td>
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<tr>
<td>6</td>
<td>2000</td>
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<tr>
<td>7</td>
<td>1000</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

**Fig. 3.** Comparison of two stimulation strategies in side by side wells over one month
stages in future wells. All these parameters can have huge impact on creating the transverse fractures along the lateral and resulting hydrocarbon productivity.

Looking forward at informational requirements of the oil and gas community, ongoing research and development in hydrocarbon tracer tagging will see an ever increasing number of unique tracers developed to service increased multi stage stimulations beyond those currently available. Industry should also anticipate improvement in the TPL expectancy, with data contribution moving from several months to several years after well start up.

Acknowledgements

Helena Barras, Dave Bucior and Paul Hewitt are acknowledged for their contribution.

References


Glossary Terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Completion</td>
<td>Making the well ready to begin production of oil or gas</td>
</tr>
<tr>
<td>Flowback water</td>
<td>Water that flows back to the surface during hydraulic fracturing operations</td>
</tr>
<tr>
<td>Hydraulic stimulation or hydraulic fracturing</td>
<td>The process of injecting water-based fracturing fluid into a reservoir to stimulate production of oil or gas</td>
</tr>
<tr>
<td>Proppant</td>
<td>Particles, such as sand or ceramic which prop open the fractures</td>
</tr>
<tr>
<td>Stages</td>
<td>Sections of a well</td>
</tr>
<tr>
<td>Tracers</td>
<td>Chemicals added to the fracturing fluid to follow the flow of hydrocarbons from the reservoir</td>
</tr>
<tr>
<td>Well or wellbore</td>
<td>The hole or shaft drilled to obtain oil or gas from underground</td>
</tr>
</tbody>
</table>

The Author

Jon Spencer is currently working as the Technical Advisor for Reservoir and Completion Tracer Technologies for Tracerco, a division of Johnson Matthey. Tracerco is a world leading industrial technology company, providing unique and specialised detection, diagnostic and measurement solutions to the oil and gas industry. Mr Spencer has been with Tracerco since 1993, collaborated on three papers for the Society of Petroleum Engineers and is co-sponsor of the patent on oil tracer technology for hydraulic stimulation production measurements, a member of the Society of Petroleum Engineers, and an officer of the Society of Petroleum Engineers – Gulf Coast Section Northside Study Group. He has been in the oil industry since 1976. After obtaining an engineering degree he spent 15 years with Halliburton Logging Services performing open hole, cased hole and production logging services in Texas, South America, the Middle East and Far East before joining Tracerco where he worked in various technical and managerial roles in Texas, Alberta and Brazil leading the reservoir tracer technology group.
1. Introduction

The European Union (EU) has invested heavily in palladium membrane technology, as reflected by numerous multi-million Euro research projects funded over the last decades. As a result, many research groups in Europe, both from academia and research institutes, have been leading the development of Pd membrane technology targeting hydrogen production, carbon capture and other important industrial applications. However, much of this research has yet to make a major impact commercially, mainly due to the slowdown in global economic growth in recent years which, in turn, has slowed the adoption of the hydrogen economy. This book complements another recent book (1), with this one covering in greater detail the challenges in manufacturing Pd membranes and focuses on using Pd membranes in different H₂ manufacturing processes. In contrast, the earlier book concentrated on a wider range of potential applications for Pd membranes but the discussion on membrane manufacturing was more limited. The earlier book (1) has also been reviewed in this journal (2).

The chapters from the present book feature contributions from the participants in several multi-million Euro collaborative research projects and also from Tokyo Gas, Japan. This book collects many of the advancements in Pd membrane technology made within the EU, covering both fundamental and applied aspects. The book is divided into two parts, namely: (a) Pd membrane fabrication and reactor design (Chapters 2 to 9) and (b) potential application of Pd membranes in industrial processes (Chapters 10 to 16).

Chapter 1, by K. Atsonios (National Technical University of Athens and Centre for Research and Technology Hellas, Greece) et al., gives a very good overview on the current status of Pd membrane technology. It begins with a comparison between Pd membranes and other H₂ permselective membranes in terms of their operating characteristics and separation...
mechanisms. The authors then explain the different benefits brought about by alloying Pd membranes and also the past and current research trends in alloying. The manufacturing of Pd membranes is briefly covered by examining the different methods of depositing the dense Pd layer, the support characteristics required and the advantages and disadvantages of using different supports. The chapter then concludes by introducing the potential benefits of using Pd membranes in electricity production and carbon capture, in the H2 economy for pure H2 production and the chemical industry for chemical upgrading.

2. Palladium Membrane Fabrication

2.1 Fabricating the Dense Palladium Layer

The various methods of fabricating the dense Pd layers, such as magnetron sputtering, electroplating and self-supporting Pd membranes, are covered more in-depth in Chapters 2, 3, 5 and 6. Chapter 2 by T. A. Peters, M. Strange and R. Bredesen (SINTEF Materials and Chemistry, Norway) discusses the two-stage physical vapour deposition (PVD) Pd membrane fabrication method developed at SINTEF. Essentially this method involves: (a) depositing a thin layer of Pd or Pd alloy onto a polished silicon crystal substrate and (b) manually removing the dense Pd or Pd alloy layer from the substrate, with the dense layer subsequently integrated onto a support or module.

Numerous examples in this chapter illustrate the flexibility of the two-stage PVD fabrication method where various binary and ternary Pd alloy compositions were investigated. Examples in Chapter 2 also show the integration of Pd membranes into micro-channel systems which is only possible when the membrane is fabricated by PVD.

Another important and very popular method to fabricate Pd membranes is electroless plating and this is reviewed in Chapter 3 by M. J. den Exter (Energy Research Centre of the Netherlands (ECN), The Netherlands). The Hysep® pre-commercial Pd membranes were developed and are offered by ECN. These membranes are synthesised by electroless plating. The chapter begins with the chemistry behind this process followed by an overview of electroless plating of various metals for other applications. The authors then present various thin film deposition technologies and consider whether each method will be suitable for fabricating Pd membranes. The chapter then concludes with ECN’s experience in upscaling electroless plating to manufacture Pd membranes and the possible pitfalls are deliberated.

Pore-fill Pd membrane fabrication, which was developed by, among others, Tecnalia Research and Innovation, Spain, is a variation of electroless plating and is scrutinised in Chapter 5 by D. A. Pacheco Tanaka (Tecnalia Research and Innovation), J. Okazaki (JGC Corporation, Japan), M. A. Llosa Tanco (University of Porto, Portugal) and T. M. Suzuki (National Institute of Advanced Industrial Science and Technology (AIST), Japan). Pore-fill Pd membrane fabrication is a four step process which involves: (a) coating the support with a nanoporous ceramic layer; (b) seeding where Pd particles are deposited on the porous ceramic; (c) coating the protective layer and (d) electroless plating where a dense Pd layer is deposited on the porous ceramic layer. The authors suggest that this membrane exhibits better mechanical stability as the dense Pd layer is not exposed on the surface. They illustrate an example of the pore-fill Pd membranes exhibiting higher H2 permeance compared to other Pd membranes, thereby illustrating the need for a thinner Pd layer with improved mechanical durability. This chapter concludes by showing that the choice of support is an important factor in determining the stability of Pd membranes.

The manufacturing of self-supported palladium-silver membranes is comprehensively described in Chapter 6 by S. Tosti (Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Italy). The physical properties of Pd-Ag alloy are discussed and the author takes a theoretical approach to show the compromise in durability and selectivity when using a supported Pd membrane. The kinetic and thermodynamic expressions for H2 transport through Pd membranes are presented, and the ways in which these follow and deviate from Sieverts’ law are analysed. The use of cold-rolling and diffusion welding to produce thin walled Pd-Ag membranes is then discussed. The module designs for the dense Pd-Ag membranes are investigated and ENEA’s dense Pd-Ag membranes for producing ultra-pure H2 via dehydrogenation, water gas shift and reforming reactions are demonstrated in a laboratory-scale unit. The dense membranes are also shown to be useful for recovery of H2 isotopes in the fusion reactor fuel cycle.

Although Chapters 2, 3, 5 and 6 give a very good background on the fundamentals and applications of different methods to fabricate Pd membranes, there
is very little synergy and links between these chapters where the different methods are evaluated against each other. The explanation of the potential difficulties of each method is rather limited.

### 2.2 Support Fabrication for Composite Palladium Membranes

Composite or supported Pd membranes are by far the most widely investigated type, especially for industrial applications, due to the need to decrease the thickness of the Pd layer, for both performance and economic reasons, and also to increase the mechanical strength of the membrane in order to withstand the applied differential pressures. Chapter 4 by H. Richter (Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Germany), features the fabrication of ceramic substrates to use as supports in Pd membranes. One of the advantages of using a ceramic substrate is the ability to tailor its pore size to suit the method by which the dense Pd layer is fabricated. The method to tailor the pore size of the ceramic substrate builds upon the vast experience of preparing ceramic membranes for microfiltration (MF) and ultrafiltration (UF). The author gives a general introduction to the fabrication of tubular and flat ceramic substrates for MF. However, ceramic MF membranes are not directly suitable as supports for the deposition of the dense Pd layer due to their large surface pore sizes. Ceramic MF membranes will require post-synthesis modification via coating or sol-gel to make UF membranes. The details for these post-synthesis modifications are reported in this chapter. Although similar, the ceramic UF membranes used for liquid filtration may also not be satisfactory as direct supports for Pd membranes. The additional requirements to use UF ceramic membranes as supports for Pd membranes are examined. Finally, the chapter concludes by considering the opportunities of decreasing the cost of ceramic membranes.

This chapter gives a very good overview on the technology behind making ceramic supports used for manufacturing Pd membranes. However, due to the brittle nature of ceramic supports, many large scale industrial applications would prefer more robust stainless steel supports for Pd membranes. The reader would gain a better appreciation of the supports if a chapter on stainless steel supports were also included.

### 2.3 Pilot Scale Membrane Testing

Chapter 7 by G. Iaquaniello, E. Palo (Kinetics Technology (KT) SpA, Italy), A. Salladini and B. Cucchiella (Processi Innovativi Srl, Italy), shares the authors’ experience of testing Pd membrane modules in their membrane-assisted steam methane reforming pilot plant, some details of which were presented in the earlier book (2). This pilot plant is based on an open architecture, where a reformer and a membrane unit are connected in series to form a reformer and membrane module (RMM). The number of modules can be increased to achieve the desired performance. The purpose of this pilot plant is to investigate the feasibility of implementing such a system at industrial scale and to study the membrane performance and stability. KT provided the details on the specification of their RMM pilot plant and the different modes of operation tested. After briefly summarising the differences of the pre-commercial Pd membranes from three different suppliers, namely ECN (The Netherlands), NGK (Japan) and MRT (Canada), the performances and relative merits of these membranes were compared against one another.

### 2.4 Modelling Palladium Membrane Reactors

Chapters 8 and 9 explain the use of modelling to design an integrated Pd membrane reactor. The modelling of steam methane reforming and of propane dehydrogenation for both a packed bed membrane reactor (PBMR) and a RMM were analysed in Chapter 8 by M. Sheintuch (Technion – Israel Institute of Technology). There is a general discussion on the parameters which are essential in a membrane reactor design. Equations were derived to relate the $\text{H}_2$ removal rate ($\text{H}_2$ permeance through a membrane) to the rate of reaction assuming that only a single reaction is taking place. The equation was then used to estimate the required membrane area from the required conversion. Similar equations were derived for RMM, where the required membrane area and number of stages can be predicted. Building on these basic models, further parameters were included taking into account side reactions and the supply of heat from both adiabatic systems and heated systems. The modelling results for propane dehydrogenation are reviewed.

Chapter 9 by J. C. Morud (SINTEF Materials and Chemistry) examines in detail the building of the model to describe a single-tube reactor design (a membrane is placed within an outer tube). The model is then programmed in FORmula TRANslation (FORTRAN) and made callable using Excel. Based on user input data, the simulator can be used for sizing the reactors or separators while simultaneously assessing the mass transfer, pressure drop and membrane area. The
model consists of mass and energy balance, reactions and discretisation to account for the radial direction. Sub-models are then included to account for the fluid flow field, membrane fluxes, reaction kinetics and pressure drop calculations. This chapter concludes by discussing the use of this single-tube model as an approximation for a multi-tube design.

Both chapters gave a very good overview on the approach and assumptions to derive models to simulate Pd membrane reactors or separators. The models derived in Chapter 9 are more rigorous than the approach used in Chapter 8. Chapter 8 gives clear examples on the information which can be attained from the models; however, the reviewers would have liked to have seen a short example included from the more rigorous modelling in Chapter 9.

3. Palladium Membranes in Reactors: Designs and Applications

3.1 Palladium Membranes in Steam Reforming

Pd membranes have been proposed to be combined with steam reforming to remove H₂ from the reactor, thereby driving the reaction forward at lower temperature with a reasonable conversion. Chapters 10, 13, 14 and 15 describe the use of Pd membranes in steam reforming.

A novel concept of using solar energy as a heat source for steam reforming is presented in Chapter 10 by A. Giaconia (ENEA Research Centre). By using molten salts as the heat carrier in a concentrating solar power (CSP) plant, energy is supplied to drive the reaction. However, these molten salts can only be heated to 600°C, so the Pd membrane must be used to recover the H₂ to increase the conversion at lower temperatures. A comparison between an integrated and non-integrated reactor-membrane system in a solar powered steam reforming unit is included.

The experience KT gained in studying a 20 Nm³ h⁻¹ H₂ capacity RMM pilot plant is outlined in Chapter 13 by G. Iaquaniello, E. Palo, A. Salladini and B. Cucchiella. The chapter, which again builds on the material in the earlier book (2), begins with a brief description of the pilot plant and its different operating modes. The pilot plant was used to gather relevant data and issues related to the operation of the RMM on an industrial scale. The influence of the reformer temperature and membrane area on the methane conversion was discussed. Based on the data collected, the number of RMM required to achieve different conversion was also estimated. The results indicated the reliability of a semi-industrial scale RMM and the flexibility of operating a non-integrated reactor-membrane system.

The development route which enabled Tokyo Gas to study a 40 Nm³ h⁻¹ H₂ capacity integrated membrane reformer is described in Chapter 14. A brief synopsis of the membrane-reformer system is given with details on the thickness of the Pd membrane, number of membranes in each module and the arrangement of the modules into the reactor system. Tokyo Gas first evaluated the membrane reformer with and without carbon dioxide capture before proceeding to demonstrate the long-term durability of a single membrane reformer module. The failure of their first test after 3000 hours due to serious leaks has led to the progression of an improved membrane module which was shown to be stable for over 13,000 hours of continuous operation, forming the basis for the development of the 40 Nm³ h⁻¹ reformer-membrane system. In order to reduce cost of the system, Tokyo Gas and NGK are currently developing a membrane-on-catalyst (MOC) module which is claimed to exhibit higher performance at a lower cost.

Chapter 15 by F. Gallucci, M. van Sint Annaland (Eindhoven University of Technology, The Netherlands), L. Roses (HyGear BV, The Netherlands) and G. Manzolini (Politecnico di Milano, Italy) looks at the possible use of Pd membrane reactors in micro-combined heat and power (m-CHP) applications. This chapter briefly outlines the development of m-CHP followed by a general comparison between packed bed and fluidised bed membrane reactors, and the differences between these membrane reactors used in m-CHP in terms of efficiency and energy losses are studied.

3.2 Palladium Membranes in Combined Cycle Power Plant

The use of Pd membranes in integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) power plants is discussed respectively in Chapter 11 by M. Gazzani (Eidgenössische Technische Hochschule (ETH) Zurich, Switzerland) and G. Manzolini and in Chapter 12 by K. Atsonios et al. In both chapters, which are quite thorough in their overviews, Pd membranes were used as separate units instead of an integrated Pd membrane reactor. This decision was based on techno-economic evaluations and on operability studies. Both chapters are presented in a very similar way; an overview is given on the IGCC or
NGCC power plant, followed by a discussion of the operating parameters of the power plant performance and finally the techno-economic evaluation is examined. However, the focus of the explanation in both chapters is very different.

Chapter 11 is dedicated to the requirements of the Pd membrane in an IGCC power plant and contains an in-depth analysis of its design and concepts. A very good introduction is given to existing sulfur removal technologies and how they can be accommodated with Pd membrane systems, which are notoriously susceptible to surface poisoning, and future sulfur removal technologies which are in development.

Chapter 12 explores the NGCC plant in depth and contains a detailed techno-economic analysis with case studies. However, the different options of using Pd membrane in a NGCC plant and its implications are, perhaps, not as well covered, although the conclusion that the application will be driven only by proven membrane stability and robustness is common with all other areas.

3.3 Palladium Membranes in Speculative Applications

Over the years Pd membranes have been investigated in numerous applications where H\(_2\) is involved and a selection of these are reported in Chapter 16 by K. Atsonios et al. The key advantages of using Pd membranes in areas such as separation, H\(_2\) production, chemicals production, fuel upgrading and waste water treatment are briefly summarised. This chapter would have been beneficial to the reader if the potential drawbacks or problems of using Pd membranes in the above mentioned areas were more clearly highlighted. Some of the applications discussed were only investigated in modelling but not demonstrated experimentally. It would have been clearer if the authors distinguished between these.

4. Conclusion

Overall this book provides a very good overview on the recent development of Pd membranes mainly in the EU. It covers both the fabrication of Pd membranes and their potential utilisation in numerous applications. Each chapter gives a brief introduction to the fundamental aspects of Pd membranes before a further in-depth discussion commences. Most chapters assess the potential benefits of using Pd membranes in different applications. It would have been helpful to the reader if the potential pitfalls and technology gaps in applying Pd membranes were addressed in greater detail.

Researchers in Pd membranes will be familiar with various sections of the book, since portions have appeared in other texts and publications. Nevertheless, the breadth and depth of the Pd membrane technology advances are well covered in this book, which makes it a suitable reference for people who are looking for a good introduction to Pd membranes and also for experts in this field who are looking for a good ‘all-in-one-place’ overview.

5. References

The Reviewers

Xavier (Xian-Yang) Quek graduated with a BEng in Chemical Engineering from Nanyang Technological University, Singapore, and a PhD in heterogeneous catalysis from Eindhoven University of Technology, the Netherlands. In 2013, he joined the Low Carbon Technology group at Johnson Matthey Technology Centre, Sonning Common, UK. His research focused on the use of palladium and palladium alloy membranes for pre-combustion carbon capture. He also has a wider interest in membranes and the use of membranes in various processes. He left Johnson Matthey in April 2016.

Hugh Hamilton has worked at the Johnson Matthey Technology Centre, Sonning Common, UK, for nearly 28 years, during which time he has researched in a range of areas including autocatalysts, palladium membranes, fuel cell membrane electrode assembly manufacture, hydrogen storage, titanium powder metallurgy, sorbent development for removing mercury from syngas and modified atmosphere packaging. His current role includes reviewing technologies in areas of interest to Johnson Matthey and various external collaborations around materials development.
Thermally Induced Deactivation and the Corresponding Strategies for Improving Durability in Automotive Three-Way Catalysts

A review of latest developments and fundamentals

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Increasingly demanding exhaust emissions regulations require that automotive three-way catalysts (TWC) must exhibit excellent catalytic activity and durability. Thus, developing TWC based on an accurate understanding of deactivation mechanisms is critical. This work briefly reviews thermally induced deactivation mechanisms, which are the major contributor to deactivation, and provides an overview of the common strategies for improving durability and preventing deactivation. It highlights the interaction of metals with supports and the diffusion inhibition of atoms and crystallites in both washcoats and metal nanoparticles and concludes with some recommendations for future research directions towards ever more challenging catalyst manufacture to meet increasing durability requirements both now and in the future.

1. Introduction

Concerns about the environment mean that new, increasingly demanding emissions standards have been gradually introduced around the world to improve urban air quality. California has the most demanding emissions legislation in the world. Its super ultra low emission vehicle (SULEV2) standard mandates durability over 120,000 miles and the zero emission vehicle (ZEV2) limits require up to 150,000 miles durability (1, 2). The typical exhaust gas temperatures of gasoline engines (≤800–850°C) are higher than those of diesel engines, but with very low start-up temperatures (≤250°C) that severely hinder hydrocarbon emissions control (3). In stoichiometric engines, close-coupled catalysts are exposed to bed-temperatures reaching 1050°C, resulting in difficulties in terms of the durability.
Therefore, both the catalytic activity and stability of the TWC must be carefully designed to meet both the stringent emissions norms and durability requirements.

There are many factors, for instance phase changes, poison adsorption, coking, mechanical and thermal lash, that can seriously affect the catalyst's structural and textural properties, metal dispersion, oxygen storage capacity (OSC) and redox activity (4, 5). The key deactivation mechanisms of catalysts are basically three-fold: chemical, mechanical and thermal. Thermal deactivation remains a fundamental problem to be resolved in TWC deactivation (6).

Compared with the base metals, precious metals are more commonly employed in automotive catalysts because of their intrinsic reactivity, preferable poisoning resistance and higher thermal stability that are required for automotive applications (7). However, precious metals also have intrinsic defects, for example particle growth and coalescence will occur under the complex reaction environment, resulting in rapid reduction of catalytic activity. This review is especially focused on providing an overview of the deactivation mechanisms in rare earth-based TWC and the corresponding strategies for improving durability.

2. Oxide Washcoat Materials

Alumina is employed as the most common washcoat material in TWC owing to its excellent chemical and thermal stability. Ceria-based additives play a critical role in providing oxygen mobility and oxygen storage in TWC due to their recognised ability to undergo rapid reduction/oxidation cycles, according to Equation (i) (8):

\[
4\text{CeO}_2 \rightleftharpoons 2\text{Ce}_2\text{O}_3 + \text{O}_2 \tag{i}
\]

However, \(\text{Al}_2\text{O}_3\) and \(\text{CeO}_2\)-based materials, as the main components of washcoats, are subjected to significant sintering as presented in Figure 1. Sintering is seen as one of the major deactivation mechanisms (4, 9). Washcoat sintering typically occurs at very high temperatures with coalescence and growth of particles as well as collapse and elimination of pores leading to a decrease of the specific surface area and encapsulation of active metal nanoparticles by washcoat, as well as a sharp loss of active surface area.

In the case of \(\text{Al}_2\text{O}_3\), sintering is accompanied by thermally induced phase transformation. According to Arai and coworkers, \(\gamma\)-\(\text{Al}_2\text{O}_3\) (100–200 m\(^2\) g\(^{-1}\) surface area) undergoes consecutive and irreversible phase transformation at high temperatures (10). The porous \(\gamma\)-\(\text{Al}_2\text{O}_3\) starts to turn gradually to \(\delta\)-\(\text{Al}_2\text{O}_3\) at an approximate temperature of 900°C, which successively changes to \(\theta\)-\(\text{Al}_2\text{O}_3\) at approximately 1000°C and finally to non-porous \(\alpha\)-\(\text{Al}_2\text{O}_3\) (only ~5 m\(^2\) g\(^{-1}\) surface area) above 1200°C (7, 11), which results from the coalescence of particles and the elimination of pore structures.

Compared to other washcoat materials for TWC, \(\text{Al}_2\text{O}_3\) has a higher specific surface area and better thermal and chemical stability that is particularly significant for metal dispersion. Hence, improving skeleton stability and suppressing phase transformation of \(\gamma\)-\(\text{Al}_2\text{O}_3\) are necessary. These can be achieved through skeletal doping with specific dopants (i.e. lanthanum oxide (\(\text{La}_2\text{O}_3\)), zirconia (\(\text{ZrO}_2\)) and yttrium(III) oxide (\(\text{Y}_2\text{O}_3\)). Inserting metal ions (especially La\(^{3+}\) with a large ionic radius) into the skeleton of transitional \(\text{Al}_2\text{O}_3\) to prevent the diffusion of \(\text{O}^2-\) and \(\text{Al}^{3+}\) ions should be the most effective strategy for improving thermal stability. However, atomic scale insertion is still a technical challenge and remains an interesting research field.

\(\text{CeO}_2\) readily crystallises and sinters with growth of particles and loss of surface area, leading to rapid reduction of the oxygen storage and release properties that are the most critical feature of TWC. Similarly, the formation of \(\text{CeO}_2\)-\(\text{ZrO}_2\) solid solution achieved through introduction of \(\text{Zr}^{4+}\) ions into the \(\text{CeO}_2\) skeleton not only stabilises the host lattice of crystalline \(\text{CeO}_2\) at high temperatures, but also enhances the catalytic activities of water-gas shift reactions and hydrocarbon steam-reforming reactions in catalytic converters (12, 13).
CeO₂-ZrO₂ mixed oxides have a surface area below 2 m² g⁻¹ and the particles undergo significant coalescence and growth. One study found a crystallite size of 19.6 nm after thermal treatment at 1000°C for 5 hours under static air (14). Although total oxygen storage capacity (OSC-cl) and the amount of O₂ adsorption/desorption per mol of CeO₂ (OSC-clI) showed no obvious changes, the oxygen release rate (OSC-r) suffered a sharp decrease as shown in Table I.

For the further improvement of stability of the CeO₂-ZrO₂ composite, ternary CeO₂-based composite materials were introduced. As Lee’s group reported, La³⁺ and Sm³⁺ can effectively stabilise the cubic Ce₀.₄₀Zr₀.₆₀O₂ phase that plays a critical role in oxygen mobility and OSC, while other rare earth elements have the opposite effect (15). The ternary component content also affects the OSC stability according to Chen et al. (16): a high neodymium content will gradually convert the CeO₂-ZrO₂ cubic phase into a Nd₀.₅₀Zr₀.₅₀O₁.₇₅ cubic phase which leads to a decline in the OSC.

Another strategy for improving the stability of CeO₂-ZrO₂ materials is the use of Al₂O₃ particles as diffusion barriers, introduced to form Al₂O₃-CeO₂-ZrO₂ hybrid oxides as shown in Figure 2. Compared to CeO₂-ZrO₂ mixed oxides, the Al₂O₃-CeO₂-ZrO₂ hybrid oxides still have a high surface area and OSC after durability ageing under the same conditions (14). There is however difficulty in controlling the metal-support interfaces which may have a negative effect on particular reactions occurring in the catalytic converter (17). The most negative influence for automotive exhaust catalysts is the formation of rhodium aluminate compounds at the Rh-Al₂O₃ interface (18).

As mentioned above, strategies that simultaneously take into account catalyst stability and control of the metal-support interface should be developed, to ensure high activity and sufficient durability, which are then able to meet upcoming emission standards. This is a promising research field but with some great technological challenges.

### 3. Active Precious Metals

Besides a sufficient washcoat surface area, two other key contributors to high catalytic activity are the surface area and dispersion of the precious metal nanoparticles. Over time in operation, the active precious metal nanoparticles will be subjected to crystallite growth due to sintering, resulting in reduced activity, even to the point of total deactivation.

Atomic and crystallite migration are two hypotheses for sintering of supported catalysts (19) as shown in Figure 2.
in Figure 3. In these cases, particle migration and coalescence (PMC) and Ostwald ripening (OR) are the two main sintering mechanisms according to Bowker (20). Both PMC and OR are dynamic processes which involve atomic exchange. The PMC sintering mechanism occurs when two or more particles touch or collide and then merge to form a larger particle. In contrast, the OR sintering mechanism occurs when material evaporates from the surface of a smaller particle with higher surface energy, and transfers onto the surface of a larger particle.

Sintering of active precious metal nanoparticles is closely related to reaction temperature and the size and composition of the nanoparticles (17). When quasi-liquid layers form on the crystal surface, migration of surface atoms and crystallites will occur at the Hüttig or Tamman temperatures of the bulk phase that are often used to semi-empirically describe the temperatures at which atomic migration and crystallite migration can occur. The ratio of the melting point \( T_{\text{melting}} \) of unique particles with radius, \( r \), and heat of fusion, \( L \), to that of the bulk phase \( T_0 \) can be given by Equation (ii) (21):

\[
\frac{T_{\text{melting}}}{T_0} = 1 - \frac{2}{\rho_s L r} \left( \gamma_s - \gamma_l \left( \frac{\rho_s}{\rho_l} \right)^{2/3} \right)
\]

where \( \gamma \) and \( \rho \) represent the surface free energy and density of the solid and liquid, respectively. Table II exhibits \( T_0 \), \( T_{\text{Tamman}} \) and \( T_{\text{Hüttig}} \) of platinum, palladium, Rh and their compounds. Metallic Pt, Pd and Rh have higher Hüttig and Tamman temperatures than the corresponding compounds, demonstrating that higher valency metals may have poorer thermal stability. Equation (ii) highlights that the melting point of unique particles depends on their composition, size and also surface free energy.

The experimental observations show that temperature is a dominant factor for sintering (22). The sintering behaviours of active precious metals can also be affected by any other conditions that lead to changes in the surface energy of the particles, such as reaction atmosphere (23), shape and composition of metal nanoparticles (24), metal dispersion (25), the loading of the metal on supports (26) and the interactions between the supports and metals (27).

Higher durability requires a lower sintering rate to maintain enough metal surface for long-term use and this is often accomplished through stabilising the active metal nanoparticles. Figure 4 shows the three typical strategies for precious metal sintering suppression (28–30): (a) support anchoring for metal nanoparticles, (b) alloying of active metals and (c) inhibition of atomic and crystallite migration via support encapsulation technology, for instance the construction of core-shell nanostructures and atomic layer deposition. In TWC,
precious metal sintering is difficult to suppress by support anchoring due to the fluctuations of exhaust gas compositions and temperatures under operating conditions. In addition, support anchoring effects only occur at given temperature windows (31). Alloying by the introduction of a second metal with a higher melting point is a simpler and more controllable way to control metal sintering and improve thermal durability. Hence, additional composition and content optimisation of bimetallic catalysts for better self-stabilisation effect may be of great importance. However, according to our years of experience, allying is both difficult to control and to avoid the negative metal-support interactions for industrial applications remains a challenge.

For the third strategy, support encapsulation technology can form additional metal-support interfaces, but both the stability of shells in core-shell nanostructure catalysts and the cost of atomic layer deposition technology still require further technical breakthroughs.

4. Redispersion and Regeneration

The metal dispersion and sintering rates of supported metal catalysts strongly depend on ageing atmosphere, as shown in Table III (32), indicating that the atmosphere found in exhaust gases can accelerate the deactivation rate over that seen in inert atmosphere. It is noted that redispersion is the opposite process to sintering. The reactant-induced disintegration of the active phase is of great importance in redispersion of active precious metals for long-term use. The disintegration strongly depends on the formation rate of adatom complexes such as PtO\textsubscript{x}, Pd(CO)\textsubscript{x} and Rh(NO)\textsubscript{x}. These adatoms will form when metal-metal or metal-support interactions are replaced by metal-reactant bonds (33). Newton et al. found that Pd nanoparticle redispersion occurs during CO/NO cycling, which points to the formation of Pd(CO)\textsubscript{x} and Pd(NO)\textsubscript{x} adatom complexes (34).

Sintering and redispersion occur under reducing and oxidising atmospheres, respectively (35). Similar phenomena can be observed in Rh-based catalysts as well as Pt-based catalysts (36, 37). Thus, redispersion of the active phase in TWC might be interpreted as shown in Figure 5. The redispersion of precious metal particles in TWC can be achieved in two ways: disintegration or oxidation. The changes of chemical states that affect oxidation reactions largely depend on air-to-fuel ratio fluctuations and operating temperatures (38).

Grunwaldt’s group found that regeneration of deactivated bimetallic catalysts could be achieved by hydrogen reduction due to the formation of alloyed particles leading to enhanced oxidation activity under lean combustion conditions (39). This regeneration mechanism entirely differs from reduction-induced sintering because oxidation improves the precious metal dispersion for monometallic catalysts while the opposite is seen during the reduction process.

As reported by Birgersson’s group, regeneration of TWC can also be achieved through a thermal treatment under an atmosphere containing chlorine.

<table>
<thead>
<tr>
<th>Ageing atmosphere</th>
<th>Pt</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}, 1100°C</td>
<td>21 nm</td>
<td>97 nm</td>
<td>14 nm</td>
</tr>
<tr>
<td>Simulated exhaust gas, 1100°C</td>
<td>78 nm</td>
<td>68 nm</td>
<td>88 nm</td>
</tr>
<tr>
<td>Air, 1100°C</td>
<td>97 nm</td>
<td>not determined</td>
<td>not determined</td>
</tr>
</tbody>
</table>

**Fig. 5.** A schematic representation of redispersion for active precious metals
However, it should be noted that oxy-chlorination may cause a narrow temperature window for oxidation of metallic species and the loss of precious metals due to the formation of volatile MO_xCl_y compounds. In the case of Pt, Pt(OH)Cl_x and α-PtO_2 will transform into PtOCl_y above 500°C, resulting in Pt loss, as reported by Lieske et al. (41). Christou and coworkers reported a new ‘oxalic acid’ regeneration methodology for aged commercial TWC without any negative effects, which may be a promising method for further investigation to improve durability (42). In our experience, however, artificial regeneration of TWC is difficult to achieve for industrial applications. Thus, these regeneration methods are considered undesirable for improvement of durability of TWC and more attention should be given to other strategies.

The composition of gasoline engine tail-pipe emissions fluctuates quickly and dramatically between oxidation and reduction environments during operation. This makes ‘on-board’ redispersion and regeneration of TWC highly unsuitable and hardly controllable. CeO_2, used as the most common additive in TWC, provides oxygen mobility capability from the surface of CeO_2 to precious metal particles and promotes the dispersion of active metals (43). Nagai et al. reported that the stability of oxidation states depends on the precious metal oxide-support interaction (44). In our opinion, improving the oxygen activation properties of CeO_2 and optimising the interaction between precious metals and CeO_2 should be investigated to enhance the redispersion and regeneration capability of the active phase.

5. Conclusions

Thermally induced deactivation mechanisms are attributed to metal surface loss and the sharp decline of washcoat specific surface area as well as the collapse of pore structures caused by sintering. Redispersion and regeneration phenomena of TWC are only experimental observations and there is still a long development path towards industrial application due to real-world challenges and exhaust gas composition that can actually accelerate deactivation. To improve the durability of TWC, further attention should be given to understanding the metal-support interactions and the diffusion inhibition of atoms and crystallites in order to reduce the sintering rate of the precious metal and stabilise the structure of washcoats. Inserting specific ions into the skeleton of Al_2O_3 and CeO_2-ZrO_2 mixed oxides is an effective method for improving structure stability, but atomic scale insertion still presents a challenge in manufacture. In our opinion, the use of alloying effects to stabilise precious metal nanoparticles is very helpful for the improvement of thermal durability. Nevertheless, further optimising the composition and content of the alloys and reducing undesirable metal-support interactions still pose great challenges in TWC application and manufacture.

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References


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Lithium Battery Discussions – Electrode Materials

Recent advancements in negative electrode materials

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1. Introduction

2015 may prove to be a pivotal point in managing the world’s climate following the United Nations Conference of Parties (COP21) in Paris (1). The gathering of nearly 200 countries to tackle climate change and their determination to limit global temperature rises to below 2°C by the end of the century was highly significant. However, to meet these ambitious aims requires corresponding energy strategies.

In this context, secondary or rechargeable batteries represent a tool or an alternative to existing and more polluting technologies. Capable of being repeatedly charged and discharged, they hold interest for their energy storage capabilities (coupled to renewable technologies, for example solar power or wind) and supplementing the internal combustion engine. Although gaining momentum since the 1990s, metal-ion battery technologies have yet to meet all of the prerequisites of the automotive industry in terms of cost and range (2, 3). Extensive research is taking place globally at all levels: electrode and electrolyte materials, cell and battery design, pack management and optimisation. The ultimate target is to deliver the battery of tomorrow, that is long-lasting, affordable, safe and with greater energy and power performance.

Every two years, the Lithium Battery Discussion (LiBD) hosts leading scientists in Arcachon, France. In 2015 LiBD was held between 21st and 26th June, and approximately 200 scientists attended the conference, with 9 invited lectures, 61 oral communications and over 130 poster presentations. This was divided into 11 plenary sessions, centred on positive and negative electrode materials beyond lithium-ion technologies (Li-air and Li-sulfur) and transverse discussions on interfaces and characterisation (4).

In this short review, the focus will be on negative electrode (anode) materials, covered both during plenary talks and within the poster presentations. Both industrial and academic contributors reported the latest results related to negative materials for Li or sodium secondary batteries, with a substantial number devoted to high capacity silicon-containing electrodes.

2. A Brief Overview of the Type of Anodes

Negative electrodes can typically be split into three main categories, depending on the way the material stores Li or Na cations (Figure 1) (5). Intercalation materials, the simplest, take advantage of interstitial insertion, without much strain on the lattice. In the case of an alloying reaction, the crystallographic structure of the host, such as Si or tin, changes upon lithiation. This is generally accompanied with an increase in the volume of the particles, leading to stress. However, since this is not solely reliant on the availability of interstitial sites, it is usually possible to store more Li and therefore, obtain...
higher gravimetric or volumetric capacities using this class of material. The final family of materials involves the storage of Li via conversion or a combination of alloying and conversion reactions. These materials (for example CaFe₂O₄ → CaO + Fe + Li₂O) present intermediate values in terms of energy storage but usually have low stability and coulombic efficiency.

3. Graphite and Carbons

3.1 Graphite

The first commercial use of graphite in a Li-ion battery dates back 20 years and since then the system has been extensively characterised and has been the subject of many reviews (6–8). The Li cation can be intercalated between the graphene sheets, with a ratio of one Li per carbon atom. Graphite, made of an abundant element, carbon, is relatively low cost with an acceptably low volume expansion upon lithiation. Coupled with a low potential versus Li, a high electrical conductivity and good Li diffusivity, it is unsurprising that graphite has conquered the market since the beginning of the century. Interestingly, there were no scientific talks on graphite at the conference, which may be due to the maturity of the technology.

Despite all of the qualities of graphite, considerable research is ongoing to find a substitute. This is mostly due to the relatively low theoretical capacity of the material, 372 mAh g⁻¹. Negative electrodes with higher capacities will need to be developed to take full advantage of the latest positive electrode improvements (9). It is also worth noting that graphite mines and factories are not environmentally benign and can have an adverse impact on clean air (10). Some examples of alternative technologies being investigated are highlighted below.

3.2 Hard and Soft Carbons

Unlike graphite, hard and soft carbons have limited crystallinity and can be described as glassy carbons. Because of inter and intra-layer disorders, Li is stored in the structure differently to that of graphite, with published gravimetric capacities of 200 to 330 mAh g⁻¹. There was significant academic interest in these materials during the conference especially as negative electrodes in Na-ion batteries where pure Na electrodes cannot be used due to safety issues and graphite presents limited Na insertion (11). However, these carbons suffer from a low tap density and high irreversible capacities.

Virginie Simone (Université Grenoble Alpes, France) discussed the control of porosity and microstructures via different post treatment temperatures to promote interstitial storage of Na. A poster presentation by Damien Saurel (CIC Energigune, Spain) examines
disordered carbons as negative electrode materials in Na-ion batteries. Some studies have also emerged combining hard carbons and graphite. Alexandre Ponrouch (Institut de Ciência de Materials de Barcelona, Spain) explained that hard carbons are less susceptible to exfoliation and complex core-shell systems, such as graphite@hard carbon, could be interesting despite the high irreversible losses of hard carbons.

4. Beyond Lithium-ion Materials: Short, Medium and Long Term

4.1 Titanium-based Materials for Lithium-ion: Titania and Lithium Titanate

Spinel-based Li$_4$Ti$_5$O$_{12}$ (LTO) has been extensively researched since it was first reported as an anode material. LTO crystallises in the $Fd\bar{3}m$ space group and can store up to three Li cations in the structure via intercalation. It is often referred to as a ‘zero-strain’ material due to the negligible volume change upon Li insertion. Based on the stability and three-dimensional (3D) intercalation process, LTO is a very good candidate especially for long life and higher power density applications. It has a relatively high operating voltage, 1.55 V vs. Li, which is a significant benefit; no electrolyte decomposition can occur at the surface, with no solid electrolyte interphase (SEI) formation (12). This enables greater cell lifetimes as the capacity decay is limited. However, the higher voltage means that LTO needs to be coupled with a high voltage cathode material to maintain a good electromotive force overall. Other disadvantages of LTO are its low gravimetric capacity, 175 mAh g$^{-1}$ and the additional costs associated with titanium.

At LiBD, LTO was the object of two poster presentations and one talk. A poster presentation by Marlena Uitz (Graz University of Technology, Austria) described the different syntheses to induce porosity in the materials and control their morphologies, in particular nanorods. Katia Guérin (Institut de Chimie de Clermont-Ferrand, France) examined the plans to substitute oxygen by fluorine leading to titanium oxyfluoride (TiOF$_2$) which provides higher gravimetric capacities in a collaborative project with the Centre National d’Etudes Spatiales (CNES), France. Incorporation of fluorine in any materials, however, is associated with often costly, potentially hazardous processes and further research on size, porosity and morphologies will be needed before a possible penetration of LTO into the market.

4.2 Silicon

There is currently considerable industrial and academic interest in using Si as an anode material in Li-ion batteries. Of all the ‘post-graphite’ technologies, Si-containing electrodes seem the closest to commercialisation. Through alloying reactions, Si is able to store up to 4.4 Li per Si, leading to the highest known gravimetric capacity (apart from Li) of all negative materials, at 4200 mAh g$^{-1}$. However, the lithiation (delithiation) process is linked with dramatic volume changes causing the pulverisation of the electrodes, loss of contact between active material and collector, and a subsequent increase in cell resistance (9). The working voltage of Si is low, around 400 mV vs. Li and is therefore vulnerable to SEI formation through electrolyte degradation. Coupled with the volume expansion upon lithiation, this SEI is likely to crack at each cycle and be unstable. High irreversible losses and fast cycle decays are currently holding back the technology. Different strategies (going nanometric helps alleviate the stress, it is also common in the literature to use morphology-controlled particles such as nanorods (volume changed in just one direction) and/or to add additives to the electrolyte to form a better SEI) are used to atone for the impact of the volume expansion and SEI. Panasonic uses, among others, graphite-silicon composites. Indeed, the latest Tesla pack (made by Panasonic) contains Si and the business plan is to incrementally increase the amount of Si (13). “This is just sort of a baby step in the direction of using Si in the anode”, Elon Musk (CEO – Tesla Motors, USA).

At LiBD, Si electrodes were the object of a plenary session of five talks and fourteen posters:

- Arnaud Bordes (Chimie ParisTech, France), Tahar Azib (Institut de Chimie et de Matériaux Paris Est, France), Dragoljub Vrankovic (Technische Universität Darmstadt, Germany) and Kristof Van Havenbergh (University of Antwerp, Belgium) explored new morphologies and structures (thin films, core shells) in order to minimise the impact of the volume change by promoting growth in one or two controlled direction(s)
- Mark Obrovac (Dalhousie University, Canada) and David Duveau (Institut Charles Gerhardt, France) presented the use of SiNiSn/Al/C, GeSi, Ni as anchors and inactive phase
- Lauren Maceachern (Dalhousie University) presented a poster on FeSiZn negative electrodes,
Andreas Gonser (Technische Universität Chemnitz, Germany) presented a poster on electrolyte additives, to promote the durable formation of a SEI. This study shows that fluorethylene carbonate (FEC) is one of the best candidates in terms of stability. However, with constant consumption at the surface, electrolyte depletion is likely to happen. Most of these strategies are well known in the literature (14, 15) and provide a good fundamental understanding of the chemistry of the alloy, electrodes and electrochemistry. This is helpful considering the increasing commercial interest in Si-based anode technology.

4.3 Polyanions Involving Conversion Reactions

Polyanions involve conversion reactions following redox reaction between Li⁺ and the host, most often lithium oxide (Li₂O) which is formed along with metallic particles. More than one Li cation can be stored per formula unit depending on the materials and the valence states of its elements leading to a higher capacity than graphite. Conversion materials involve breaking and forming chemical bonds. This feature coupled with the presence of (possibly inert) Li₂O is associated with large hysteresis during cycling and high irreversible losses (5). Conversion materials were the subject of four posters. Geethu Balachandran (Karlsruhe Institute of Technology (KIT), Germany) presented a poster on ferrites MFe₂O₄ (with M = Zn, Fe, Co, Ni) which are relatively low cost materials with capacities between 750 and 1000 mAh g⁻¹, more than double the capacity of graphite. Samantha Bourrioux (Commissariat à l'énergie atomique et aux énergies alternatives (CEA), France; and National Center for Scientific Research (CNRS), France) presented a poster on the synthesis of ZnFe₂O₄ nanoparticles by laser pyrolysis. Most of the presentations aimed at understanding the complex intermediate phases and crystallographic rearrangements during charge and discharge.

5. Conclusions

Mainly focused on materials and characterisation techniques, LiBD was an interesting conference related to European secondary battery research within both industry and academia. Researchers from a number of major automotive companies attended, confirming the interest in developing new battery technologies for transport applications. It is also worth noting that Li metallic electrodes were absent in the talks and poster presentations. Despite better understanding of dendrite formation (16), current technologies have not yet managed to solve this 50 year challenge. Research on negative materials has long been less intensive than on their positive counterparts but the emergence of novel positive electrodes has recently intensified the search for a graphite substitute. The recent inclusion of Si in commercial cells may well catalyse the more widespread industrial adoption of these, up-to-now, next generation materials.

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References


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Johnson Matthey’s industry standard publication analysing supply and demand trends in the platinum group metal (pgm) markets, the “PGM Market Report” was published on 16th May 2016 by the company’s Precious Metals Management team. Its May release each year marks the start of Platinum Week in London, UK, celebrating the anniversary of the inauguration of the London Platinum Quotation (the forerunner of the present London Metal Exchange (LME) auction) in 1973 (1). The “PGM Market Report May 2016” provides detailed data, analysis and commentary on the pgm markets, and includes estimates of supply by country and demand by application for platinum, palladium and rhodium, and demand figures for ruthenium and iridium, detailed by application.

Platinum

Primary supplies of platinum rose by 19% to 6.08 million oz in 2015, the highest level in four years. This was led by sales from South African producers, but partly offset by lower supplies from other countries and a steep fall in recoveries from scrapped cars and old jewellery. Demand trends were broadly positive with expectations of weakness in the Chinese jewellery market proving overstated and net selling of platinum by exchange traded fund (ETF) investors in Europe, the USA and South Africa outweighed by a surge of physical investment demand in Japan. Consumption of platinum in autocatalysts was strong, while industrial offtake was stable, leaving total demand for platinum up 4%, and the 2015 market as a whole in a significant deficit of 659,000 oz. Fundamental deficits since 2012 in the supply-demand balance have as yet failed to have any noticeable impact on market liquidity, confirming the existence of substantial market stocks prior to 2012. The forecast for platinum supply and demand in 2016 expects a slight decline in shipments of newly mined metal, although when combined with recycled metal, total supply could rise marginally. On the demand side, 2016 should be the peak year for platinum use on Euro 6 diesel cars, lifting global consumption of platinum in autocatalysts by nearly 2% to 3.50 million oz. Industrial consumption is expected to be unusually strong, rising by nearly 10% driven by capacity expansions in the chemicals and glass sectors. When combined with continued Japanese investment buying, a fourth year of significant market deficit of 861,000 oz is expected in 2016.

Palladium

The palladium market moved closer to balance in 2015, due to a strong recovery in South African supplies helping global primary supplies of palladium rise by 6%. Gross demand plunged by 13% during the year with investment demand moving abruptly into negative territory, almost entirely due to a dramatic reversal in
ETF purchasing: investors, who had acquired over 940,000 oz of palladium the previous year, sold around 660,000 oz of their holdings in 2015. This greatly offset overall improvements in automotive and industrial demand, and a steep fall in the recovery of palladium from scrapped catalytic converters. The total market deficit shrank from nearly 2 million oz in 2014 to under 500,000 oz in 2015.

This trend is expected to reverse in 2016, led by a reduction in profit-taking by ETF investors and growth in other demand sectors, widening the deficit in the palladium market to 843,000 oz. Combined primary and secondary supplies are forecast to rise marginally to 9.02 million oz, with a decrease in South African shipments being offset by a modest recovery in autocatalyst recycling. Excluding investment, demand for palladium in ‘consuming applications’ (autocatalyst, industrial and jewellery) will exceed 10 million oz for the first time: significant growth in sales to automakers in China is anticipated, while demand from the Chinese chemical industry is also set to reach record levels.

Rhodium

The rhodium market moved back into surplus in 2015, totalling 33,000 oz, after two years of deficit. Gross demand fell slightly: small gains in autocatalyst consumption were offset by a fall in purchasing by glass makers and investors. Meanwhile, supplies rose strongly, as South African production returned to near-normal levels following the Association of Mineworkers and Construction Union (AMCU) strike in 2014. This outweighed a decline in the recycling of rhodium from scrapped vehicles, leaving combined primary and secondary shipments up 11%.

Gross demand for rhodium is predicted to rise by 6% in 2016, as auto demand is lifted by strong car sales and tighter legislation in China, and greater use of nitrogen oxides (NOx) traps in Europe. It should also be a good year for industrial demand: purchasing by glass makers is set to rise significantly, while consumption in the chemicals industry remains unusually firm. With mine supplies expected to fall, and any recovery in autocatalyst recycling volumes likely to be modest, combined primary and secondary shipments will rise by less than 1%, pushing the market back into an expected deficit of 16,000 oz.

About the PGM Market Report

The “PGM Market Report” includes data tables showing the five-year history of supply and demand for each metal, and a forecast for the current year. The report is published twice yearly in May and November and the latest edition can be downloaded free of charge from: www.platinum.matthey.com/services/market-research/pgm-market-reports

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COMET™ – A New Ventilation Air Methane (VAM) Abatement Technology

Reducing greenhouse gas potential from the mining industry

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Ventilation air methane (VAM) found in coal mines is a huge and global problem because it acts as a greenhouse gas (GHG) contributing to climate change. Methods for removing this methane and reducing its impact have to date been limited due to a lack of legislative drivers and a technological focus on reducing the emissions of higher hydrocarbons. Now a new technology, known as COMET™, has been developed at Johnson Matthey in collaboration with Anglo Coal for abating this methane emission source. This article describes the development of the catalytic system and its engineering aspects to the point where the technology is ready for commercial launch.

What is VAM?

To understand VAM one has to understand the effect methane has as a GHG. A GHG is a gas in or released to the atmosphere that absorbs and emits radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect which is identified as a contributory factor to global warming (1). Methane is a potent GHG and has been shown to have a global warming potential (GWP) of at least 21 times higher than carbon dioxide (1). Methane is often found around and within coal. In open cast mining the methane is lost to the atmosphere as the coal is removed from the ground. With deep shaft mining the methane is contained within the mine system. This methane is classified according to its concentration, location and method of extraction. Figure 1 shows the different types of methane associated with coal mines along with the source, methane concentrations, relative flow rates and GHG impact. In 2012 VAM accounted for 61% of all methane emissions from coal mines in the US with 91.2 billion cubic feet (BCF) of emissions, whilst coal bed methane only accounted for 5% (7.0 BCF) of emissions (2).

Looking at each type of methane associated with coal mining in turn:

![Coal bed methane](fig:coalbedmethane)

- **Chemical formula**: CH₄
- **Concentration**: 60–94%
- **Flow rate**: Few m³ sec⁻¹
- **Impact**: Easiest to capture or use

![Coal mine methane](fig:coalminemethane)

- **Chemical formula**: CH₄
- **Concentration**: 30–96%
- **Flow rate**: Few m³ sec⁻¹
- **Impact**: Highest GHG impact

![Ventilation air methane](fig:ventilationairmethane)

- **Chemical formula**: CH₄
- **Concentration**: 0.1–0.8%
- **Flow rate**: 100s m³ sec⁻¹
- **Impact**: Extracted from mine to allow safe working

Fig. 1. The different types of methane emissions associated with coal mines
**Coal Bed Methane** is present in very small quantities (<10% of methane associated with coal mining) and is typically used as a fuel as the methane concentration is sufficiently high that it can be used, after appropriate treatment, in natural gas pipelines.

**Coal Mine Methane** has sufficient methane that it can be combusted, therefore depending on location and nearby requirements for heat, it is either combusted to provide heat for nearby users or flared to reduce environmental impact. Due to the varying and reduced concentration of coal mine methane, especially when compared to coal bed methane, it is not suitable for use as a pipeline gas.

**Ventilation Air Methane** is present in huge quantities (>60% of methane associated with coal mining) and has insufficient methane to support combustion without supplementation with additional fuel and is seen as difficult and uneconomic to combust.

One should also consider the safety aspects associated with methane. Methane has an explosive range between 5 and 15% by volume in air (3). Coal bed methane and coal mine methane have concentrations of methane above the upper explosive limit although through further dilution, from air ingress, explosive compositions can be formed as the methane concentration is lowered. The concentration of VAM is below the explosive limit and therefore is less of a risk.

When looking at the GHG potential of methane there are varying measures to compare to that of CO₂. The chemistry shows that oxidising methane to CO₂ produces 2.7 tonnes of CO₂ for every tonne of methane. The US Environmental Protection Agency (EPA) states that methane is more than twenty-one times more potent than CO₂ as a GHG (2). Therefore by oxidising methane the benefit in greenhouse reduction is at least 17.3 tonnes of CO₂ equivalent compared to letting methane escape to the environment.

**Drivers for Abatement**

There is a clear environmental benefit to abating methane as it will reduce the amount of GHG emitted to the atmosphere. This has been recently underlined at the United Nations Conference of Parties (COP21) in Paris held in December 2015 (4), as for the first time ever, there is now a single global agreement in place to tackle climate change as summarised by the authors in the key points below:

- global temperature rises should be capped at 2.0°C with ambitions to achieve 1.5°C
- within a century there should be net zero CO₂ emissions (i.e. human sources = natural sinks)
- every five years there will be a stocktake of each country’s contribution to cutting emissions
- the richer countries will provide at least £67 billion per year of ‘climate finance’ to help poorer countries adapt to climate change and switch to renewable energy.

Prior to the global Paris agreement, some progressive thinking mining companies (5, 6) had already embraced environmental control technologies in principle. Fiscal incentives and other benefits will help motivate others to adopt the technologies required to reduce these emissions. At time of writing there are two legislative schemes in place that have clear guidelines for abatement of methane as a GHG; the European Union Emissions Trading Scheme (EU ETS) (7) and California’s Cap-and-Trade Program (8). Due to current pricing and the inclusion of a price floor the Californian scheme is of most interest to companies wanting to abate methane emissions with an economic return.

There are other schemes either in place, rescinded or under consideration in other parts of the world that could harness and benefit from methane abatement, although this may not be currently viable either economically or legislatively. The impact of last December’s Paris conference is yet to be fully understood although one can say with reasonable certainty that control of GHG emissions is important and that GHG abatement technologies, such as COMET™, are a method of achieving this aim.

The EPA estimated that the worldwide mine methane emissions for 2010 contributed more than 584 million tonnes of CO₂ equivalent to the atmosphere each year which is around 8% of total man-made methane emissions (9).

The EPA also estimated that 236 million tonnes of CO₂ equivalent was released to atmosphere from coal mine VAM during the calendar year 2000 (10). Global coal production and consumption since 2000 has increased considerably from 4.72 billion tonnes per annum to 8.16 billion tonnes per annum (11). This increased coal production has increased VAM emissions to an estimated 410 million tonnes of CO₂ equivalent, split globally as shown in Figure 2.

This article will focus on efforts to abate emissions of VAM since this is currently the most difficult to address and the most damaging source of methane emissions from deep coal mines.
Current Technologies for Methane Abatement

The simplest way to reduce methane emissions is to oxidise the methane to produce CO₂ and water (Equation (i)):

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  

(i)

This can be done by flame combustion, such as flaring or as a fuel, for higher concentrations of methane, but for the lower concentrations present in VAM streams, it is oxidised thermally at high temperatures (1000°C) or at lower temperature (<600°C) catalytically.

Due to the relative lack of toxicity of methane and hence lack of historical legislative requirement for methane control, most commercially available hydrocarbon oxidation catalysts have been developed to oxidise longer chain hydrocarbons in volatile organic compounds (VOC) abatement, for example propene and automotive emission applications have little ability to oxidise methane effectively at low temperature.

Regenerative thermal oxidiser (RTO) technology (Figure 3) was developed to reduce VOC emissions from ventilation streams. VOC are chemicals which typically have a significantly larger global warming potential with hundreds or thousands of times that of CO₂ (12). Typically VOC abatement is carried out on exhaust streams from chemical production sites with flowrates considerably lower than that encountered on a coal mine ventilation stream. The technology has subsequently been adapted to deal with methane abatement.

Only a handful of VAM abatement installations exist worldwide as the application of the technology is novel. The problem is that these systems operate at temperatures in the region of 1000°C and cannot

Fig. 2. The global split of VAM emissions by country from calculations based on the change in coal production since 2000 and data from the EPA (10)

Fig. 3. A typical RTO system
effectively convert the methane at an economic cost. The high temperature of operation has also been a barrier to adoption on safety grounds, as it is above the auto-ignition temperature of methane (617°C) (13) which could increase the likelihood of explosion in the mine or mine ventilation system.

Recuperative catalytic oxidation (RCO) systems have also been developed (14). However for VAM and general methane abatement these offerings still operate above the auto-ignition temperature of methane and therefore safety concerns limit their usefulness in this application.

Recently, Johnson Matthey chemical engineers and scientists and Anglo Coal mining engineers, have developed COMET™: a new, lower temperature abatement solution for VAM from active or abandoned coal mines which overcomes many of these challenges.

**Catalytic Materials for Methane Oxidation**

Many academic groups have studied catalytic materials for methane oxidation over the last 50 years; of the metal oxides studied, tin oxide (15) and chromium(III) oxide (16) are considered among the most active. Of the aluminium oxide (Al₂O₃) supported metals studied, the following ranking under their chosen conditions, in order of decreasing activity per gram of metal, has been given in the literature (16): platinum, palladium, chromium, manganese, copper, cerium, cobalt, iron, nickel and silver. It is not just the metal that has an influence on the catalytic activity with high surface area support materials such as Al₂O₃ also playing an important role, contributing to the performance of the catalyst through interaction with the supported metal particles for example by maintaining a high dispersion of the metal particles.

One of the products of the methane oxidation reaction, water, strongly inhibits the reaction (17). It has been suggested that the inhibition is due to the formation of water which covers the active sites for CH₄ oxidation (18). The presence of 4–5% water in the ventilation air exhaust (from 80–100% humidity at 25–30°C) further inhibits the reaction, over and above the effect of water as a product of the reaction and this effect is only reduced at elevated temperatures (>500°C).

Sulfur is widely known to be a poison for oxidation catalysts and may be present as low levels of hydrogen sulfide (H₂S) within the mine. It is also possible for a gaseous region to be exposed during mining operations that can lead to a rapid increase in the amount of H₂S present in the ventilation air exhaust.

Pt is widely considered to be a sulfur tolerant metal that is active for hydrocarbon oxidation reactions, while Pd is often selected for methane oxidation duties due to its higher activity and lower cost. For these reasons, a bimetallic catalyst based on Pt and Pd was selected for development. Pd catalysts can be readily poisoned by exposure to high levels of sulfur and while this can be improved by adding Pt, even with Pt present sulfur can still be a significant poison to a bimetallic PtPd catalyst.

**COMET™ Catalyst Development**

Criteria for a viable commercial process technology for the abatement of VAM are a catalyst that can:

- achieve high conversion of methane throughout its lifetime at temperatures below 600°C
- enable lower grade materials of construction to be used
- be manufactured at sufficiently low catalyst cost for economic viability
- withstand the arduous and variable feed conditions experienced in a mine environment
- be suitably robust for coating onto a low pressure drop support.

To tackle this challenge Johnson Matthey utilised its research and development facilities and its experience in the development of platinum group metals (pgm) catalysts to carry out an extensive experimental programme to develop the selected catalyst formulation and physical form. This work programme was undertaken using purpose built experimental testing rigs (see Figures 4 and 5) to study pgm catalysts.

Following initial formulation development work using powdered catalysts in a screening rig (Figure 4), catalysts in a range of physical forms were tested with experiments being extended to other variables including long term poison resistance, coating technique and particulate loading.

Further experimental work on the most promising catalysts in their final form suitable for commercial application was then carried out using innovative purpose built equipment (Figure 5) under actual feed conditions. An understanding of likely contaminants in the feed gas was obtained from development partner Anglo Coal. **Table 1** shows conditions that were tested.
The following characteristics of the catalyst formulation were investigated and optimised for the conditions present in a typical coal mine:

- ratio of active materials, Pt:Pd (Figure 6)
- active metal loading
- metal-metal physical state
- support material.

For each of the above variables the effect of changing the reaction conditions was also studied. These changes included:

- methane concentration, see Figure 7
- water concentration
- sulfur concentration
- temperature (of pre-treatment and operation) see Figure 8
- space velocity – ratio of catalyst volume to gas flow
- start-up and shutdown regimes.

Multiple studies (21) have reported different methane oxidation kinetics (between first and half order). It is important to derive a representative model appropriate to our system for control purposes. During these studies an understanding of the reaction kinetics was gained which proved to be of a higher complexity than first expected. This is due to the complex nature of the catalyst and the methane oxidation mechanism taking place via a Mars-van Krevelen redox reaction (22) that included the active metals. This complexity was further compounded by the impact of the support material and oxygen supply mechanism on the dynamic performance of the catalyst. Multiple approaches to understand the behaviour of the catalyst were employed including, for example, the use of isotopic labelled gas to determine...
Fig. 5. The long term ager rig used to simulate realistic gas composition and flow rates for extended time periods (thousands of hours) over coated components made to production standard.

Notes
1. Reactors are coated monoliths and are therefore scalable.
the temperatures at which oxygen transport became apparent by different mechanisms.

It was also important to consider the catalyst presentation. As well as the catalyst formulation, the way the catalyst is presented to the incoming gas, for example in terms of size, shape, substrate material and coating thickness can have a significant impact on the performance of the system. These variables can affect the pressure drop, heat and mass transfer and attrition resistance of the system and need to be selected in parallel to the design of the reactor to ensure optimum performance. The method of catalyst presentation used in this instance is a development of a standard Johnson Matthey technique mixing novel support variants and coating techniques with established industrial processes.

Johnson Matthey has successfully demonstrated the lifetime of the catalyst by testing the catalyst over a period of two years in an experimental pilot rig (Figure 9). Extensive experimental testing was also carried out to develop a kinetic model sufficiently robust to accurately predict the performance of the technology when applied to mines with varying VAM composition and conditions. Technical success has been achieved by developing a long lived catalyst that can maintain approaching 100% methane conversion, at low temperatures.

**COMET™ Engineering Development Process**

The development objectives were to engineer a complete solution for the catalytic oxidation of VAM whilst providing distinct advantages over existing RTO and RCO abatement technologies. Once the
catalyst was selected, the remaining challenges were engineering based. Desired characteristics of the COMET™ system included:

- operating at low temperatures
- keeping the process simple with a simple control scheme to match
- enabling easy relocation of the unit, low maintenance requirements and operational flexibility
- maintaining a high level of safety with a fail-safe design
- minimising operating and capital expenditure.

The process safety of the COMET™ technology was considered paramount in the engineering development phase due to the working coal mine environment. Anglo Coal’s participation in the project has enabled Johnson Matthey to gain an understanding of the associated safety requirements. Johnson Matthey process engineers worked to address the concerns of the potential for sudden methane releases by using quantitative methods to carry out a hazard and risk analysis. This was carried out in accordance with the well-established functional safety standards of International Electrotechnical Commission (IEC) 61508 (23) and IEC 61511 (24), as used in the petrochemical industry. The use of these safety standards is recommended in guidelines issued by the US Mine Safety and Health Administration (MSHA) (25).

Operating at temperatures significantly below the auto-ignition temperature of methane will provide an invaluable benefit as the level of safety is increased by removing a permanent source of ignition. In a once-through process such as COMET™, it is the performance of the catalyst which determines the operating temperature range. As the catalyst had been already developed with this in mind, the unit was then designed around the catalyst.

The low temperature operation, when compared to an RTO system, allows the system to be constructed from lower grade materials reducing capital expenditure (CAPEX) investment, as well as avoiding operation above the auto-ignition temperature of methane as already described.

The developed unit has been designed using pre-existing equipment items, all of which are well proven and commonly used in similar petrochemical applications. There are few moving parts, all in low temperature service, increasing operational reliability and reducing the level of maintenance required. The control scheme has been developed to give optimal control whilst enabling the unit to be almost completely automated, limiting the required attention by operators. These aspects were incorporated within the design by doing so capital investment, operating costs, operator resources required and level of technology risk were all reduced.

Normal mining operations require the ventilation shafts which expel the VAM to the atmosphere to change location (26), as the focus of mining activities move with time. The location of underground coal mines are quite often at remote, difficult to access sites which could make the transport of large process equipment items expensive. The COMET™ unit addresses these potential issues having been developed to comprise of modules which are ‘bolted together’ on site. All selected equipment items are scalable for high flows of VAM, eliminating the need for several smaller process trains and reducing the footprint required.

The COMET™ technology provides a method for removing methane from feed gas by passing the feed gas through a heat exchanger to raise the temperature of the gas to the desired inlet temperature; passing the resulting heated stream to the oxidation reactor containing the oxidation catalyst, where the methane is adiabatically oxidised; removing a gas stream including the products of the oxidation reaction from the reactor at an outlet temperature and passing the oxidised gas stream through the heat exchanger against the feed gas to allow the heat to be recovered, wherein the inlet temperature is controlled by means of a bypass around the heat exchanger in which the amount of bypass is controlled by measuring the outlet temperature.

The engineering design has yielded a comprehensive, safe, controlled system that meets the requirements of the coal mining industry at a cost that could prove attractive under current conditions. The COMET™ technology is very different from the currently available solution to VAM abatement (Figure 10) and its economic advantages are summarised below.

Economic Benefits

Utilising a once through catalytic system has some features which are advantageous when applied to VAM abatement. The design can utilise economy of scale from using a single stream system. It is suitable for use on a wide range of flowrates and a high methane conversion can be maintained at all times whilst operating with a high thermal efficiency. The system performance envelope allows the technology to be adapted to varying VAM concentrations.
Running below the auto-ignition temperature of methane gives a safe and robust VAM abatement solution.

The viability of the technology is largely dependent upon carbon credit prices (28) therefore it has been vital to reduce the capital and operating expenditures. The operating expenditure of the technology has been successfully reduced by developing the catalyst and the process together. This has resulted in a system with minimal pressure drop to minimise power consumption. At sufficient VAM concentrations the Johnson Matthey technology will be power neutral or even able to export power to the grid.

Given sufficient methane concentration there is an option to generate power and export power. With lower concentrations there may not be sufficient energy to export electrical power although there may be an option for power neutral operation.

**Conclusions**

The COMET™ VAM abatement technology provides a novel solution to the problem of VAM and is ready for deployment.

By using novel approaches to a problem that was identified by Anglo Coal, Johnson Matthey has successfully developed a catalyst and process which provides a safe, easy to operate, scalable, GHG reducing and economically viable technology for the abatement of large quantities of VAM which, if not treated, would be released into the atmosphere as a potent GHG. Both the catalyst and the process have undergone significant development to ensure all the required objectives to make this technology commercially attractive on a global scale have been met. This has resulted in a technology which excels in all the key areas when compared to existing technologies.

Johnson Matthey is currently further developing the COMET™ VAM abatement technology to broaden the range of methane containing vent streams to which the catalyst and process can be applied. This will maximise both the commercial and environmental benefits of the technology.

COMET™ is a registered trademark of the Johnson Matthey group of companies.

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References


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Martin Riddell is a Process Engineer at Johnson Matthey Plc, where he is the lead process engineer for the COMET™ technology. Martin graduated from the University of Sheffield, UK, in 2011 before starting his current role at Johnson Matthey.
Johnson Matthey Highlights

A selection of recent publications by Johnson Matthey R&D staff and collaborators

FINE CHEMICALS

Stereoselective Synthesis of the Halaven C14-C26 Fragment from D-Quinic Acid: Crystallization-Induced Diastereoselective Transformation of an α-Methyl Nitrile


Total synthesis of the synthetic breast cancer drug Halaven involves stereocontrol of four centres and these were successfully derived from the D-quinic acid source. This allowed a crystallographic purification route in place of the chromatographic technique. It illustrates the first example of a crystallisation induced diastereoselective transformation of an α-methyl nitrile, as well as benefiting from the rigid bridged polycyclic system. The tangible benefits are an 80% reduction in cost and waste compared to the conventional route, largely due to the elimination of chromatography solvents, in accordance with green chemistry principles.

Chemists Introduce a User’s Guide for Palladium Acetate


Pure palladium acetate (Pd₃(CO₂CH₃)₆) and its two main impurities : the nitro analogue Pd₃(CO₂CH₃)₅(NO₂) and polymeric [Pd(CO₂CH₃)₂]ₙ was investigated by Process Development Engineer William A. Carole and Global R&D Manager Thomas J. Colacot (Johnson Matthey Catalysis and Chiral Technologies, USA). Various Pd₃(CO₂CH₃)₆ preparation processes were explored and depending on the reaction conditions, different amounts of the nitro and polymeric impurities appear. Next the team studied procedures for creating Pd₃(CO₂CH₃)₆ which terminate the development of impurities. The structures of Pd₃(CO₂CH₃)₆ and its impurities are very closely related so the purity of Pd₃(CO₂CH₃)₆ can be difficult to determine. The researchers used the results to create a Pd₃(CO₂CH₃)₆ user guide for the chemistry community. Details of the optimum synthesis of the material, how to confirm its purity and show the effect of Pd₃(CO₂CH₃)₆ and its impurities on catalyst performance were included in this guide.

Preparation of Pincer 4-Functionalized 2-Aminomethylbenzo[h]quinoline Ruthenium Catalysts for Ketone Reduction


Hydrogenation of carbonyl compounds using Ru, Rh and Ir catalysts is an increasingly attractive industrial process to produce alcohols without the use of hydrogen gas and can also eliminate other requirements for workup and removal of side products. Ru pincer complexes A and B were found to have TOF up to 6.7 × 10³ min⁻¹ and S/C < 20,000. A one-pot synthesis of the catalytic complexes using no hazardous oxidants was demonstrated. Deactivation is reduced in these complexes because of the stable orthometallated pincer structure. Further studies will extend their use into other organic transformations of interest to industry.

NEW BUSINESSES: BATTERY TECHNOLOGIES

Porous and Hollow NiO Microspheres for High Capacity and Long-Life Anode Materials of Li-ion Batteries

Anode materials for Li ion batteries were developed based on hollow NiO structures. Improved reversible capacity and improved cycling stability were found compared to a previously reported ZnO-NiO composite. Capacities >700 mAh g\(^{-1}\) at a current rate of 1 C were found and this was maintained after 400 cycles. The preparation route was straightforward and used chemical etching following ion exchange of Zn citrate template. The impressive performance is thought to be due to the unique nanostructure which allows for faster mass transport and accommodates the volume change during the cycling process.

PRECIOUS METAL PRODUCTS: NOBLE METALS

Effects of Single- and Simultaneous Triple-ion-beam Irradiation on an Oxide Dispersion-strengthened Fe12Cr Steel

The stability of an ODS Fe12Cr after single-(Fe\(^{4+}\)) and concurrent triple-ion-beam irradiation (Fe\(^{3+}\), He\(^{+}\) and H\(^{+}\)) at room temperature to doses of 4.4 and 10 dpa was studied by TEM at the Joint Accelerators for Nanosciences and NUclear Simulation (JANNUS) Saclay facility. The authors compared the results after single-ion-beam irradiation with those from a reference Fe12Cr steel produced using the same procedure. The irradiation-induced loop size and density in the ODS and reference materials were determined, and the grain boundary microchemistry and evolution of the secondary phases present were assessed. The Y-rich nanoparticles in the ODS steel are somewhat stable under these irradiation conditions despite the potential evolution of substantial Cr-rich carbides.

PROCESS TECHNOLOGIES

An Experimental Investigation of Biodiesel Steam Reforming

Biodiesel steam reforming was investigated at different operating conditions using a precious metal based catalyst to find optimum conditions for coke-free performance, therefore circumventing catalyst deactivation. These conditions include a range of temperatures from 600ºC to 800ºC, pressures from 1 bar to 5 bar and the molar steam-to-carbon ratio from 3 to 5. Coke formation and sintering were found to be the main deactivation mechanisms. The start of catalyst deactivation is determined by catalyst inlet temperature and feed mass flow per open area of catalyst. Coking can be reduced by using a precious metal catalyst at low feed flow rates (31 g h\(^{-1}\) cm\(^{-2}\)) and a high catalyst inlet temperature (>750ºC). A stable product gas composition near equilibrium attained a biodiesel conversion rate of 99% for over 100 h.

Carbon Uptake and Distribution in Spark Plasma Sintering (SPS) Processed Sm(Fe, Cu, Zr)\(_2\)

The C uptake in permanent magnet Sm alloys processed using SPS as an alternative to other powder processing techniques was analysed by EPMA. Higher levels of C were found in the surface down to 10 \(\mu\text{m}\) with some C also found within the body of the sample. This C originates from the graphite dies and was used to process the powders. It is not thought to affect the magnetic properties of the Sm based alloys as the levels are very low. However the C content may affect other materials processed using the same technique, such as spinels and glass ceramics which can have reduced transparency. C removal from the surface is recommended before heat treatment at high temperatures to prevent potential C migration into the body of the material.

The Effect of Mg Location on Co-Mg-Ru/\(\gamma\)-Al\(_2\)O\(_3\) Fischer-Tropsch Catalysts

Fischer-Tropsch catalysts for the conversion of coal, gas or biomass to clean liquid fuels are based on Co with metal oxides, pgms and a Mg promoter. In this study, the catalyst was Co-Ru/Al\(_2\)O\(_3\) with Mg as a structural promoter and the effect of order of addition of this metal to the support was found to have an effect on the activity, particle size and stability of the Co based catalyst. Incorporation of Mg into the Al\(_2\)O\(_3\) phase increases the stability and activity at high temperature. However the inclusion of Mg with the Co phase significantly reduces its performance. High resolution TEM studies were used to confirm the location of the Mg after various impregnation strategies.

Importance of Surface Carbide Formation on the Activity and Selectivity of Pd Surfaces in the Selective Hydrogenation of Acetylene
B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, Surf. Sci., 2016, 646, 45

Density functional calculations on Pd nanoparticle catalysts for the selective hydrogenation of acetylene demonstrate that Pd(100) carbide should give higher
activity and selectivity than Pd(111) carbide. In contrast, pure Pd(111) would be expected to give higher activity and ethylene selectivity than pure Pd(100). Therefore, to explain recent experimental results reported elsewhere, the authors conclude that the catalyst surface is most likely in the carbide form under the experimental reaction conditions. The Pd(100) hydride surface was also found to be less stable than the Pd(111) hydride surface, also in accordance with published experimental results.
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