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Guest Editorial

Making the Most of Our Materials

Recent advances in energy technology are driven by the need to mitigate climate change and find sustainable, non-polluting ways to power our communities. However, a large proportion of the impact arises from the materials used to make energy devices (1) and it is therefore important to generate and use materials effectively, while finding ways to minimise waste, energy use and harmful chemicals during device fabrication. This editorial describes the materials science toolbox for making the most of our resources.

The True Value of Materials

Materials have value beyond their price. Raw materials extraction, processing and distribution embody energy and costs which are not reflected in their market value, such as irreversible ecosystem damage, use and contamination of clean drinking water and pollutants produced at every stage. Some materials require scarce or extractively costly minerals (2, 3), for instance cobalt mining involves severe toxins.

Worldwide population growth and rising demand makes sustainability a key consideration. Recycling is one way to achieve this, but it requires considerable resources and often results in low quality products. Therefore, techniques encouraging the best use of virgin materials are needed, for example advanced processing techniques producing highly functional micro- and nanostructures from smaller quantities. Multifunctionality – coupling related functions into a composite material – may increase resource efficiency across the whole supply chain.

A whole systems perspective can ensure that we are focussing on the right aspects and account for costs and impacts over a product’s lifecycle. Lightweighting and extending the lifespan of energy products are effective ways to achieve efficiencies across the entire supply chain (3).

Multiscale, Multifunctional Design

Materials should primarily be functional at device level, fulfilling an application’s key performance indicators. However, material choice should also consider processing costs, device lifetime, environmental impacts and safety. Device performance is an inherently multiscale challenge, since material properties are strongly linked to atomistic, nanoscale and microscale structures (4), well-structured materials often performing better than their unstructured equivalents (5).

The choice of material for a particular device arises from its constituent elements and atomic structure, defining its electrical, mechanical, chemical and magnetic properties. Databases of structure-property relationships of energy materials are emerging from experimental and theoretical studies, enabling data mining for materials suited to a particular application, termed rational design. Abundant elements forming benign chemistries are indicated, for example sodium-ion batteries replacing lithium (see Titirici’s work in Edge et al. (6)).

Quantum effects and large surface area to volume ratios at the nanoscale (1–100 nm) enhance or endow new properties. Integration of one-dimensional and two-dimensional nanostructures into composites has led to significant advances, for example carbon-based nanomaterials conferring outstanding electrochemical properties and strong mechanical stability (7). Other important properties, such as porosity and mechanical strength, often rely on microstructures (100 nm to a few cm).

One route to fabricating high precision micro- and nanostructures is additive manufacturing: a range of processes building complex, three-dimensional structures from the bottom up, with minimal waste of both materials and energy and few toxic chemicals. Other advanced, resource-efficient techniques producing complex...
microstructures include electrospinning and graphitising nanostructures from waste biological matter (see Cooper and Titirici’s work (6)). Combining single function devices into systems creates unnecessary complexity in manufacturing and packaging, adding to weight and cost. Functional diversity, where coupled functions are integrated into hybrid materials, creates efficiency opportunities across the supply chain. For example, George's work in Edge et al. (6) embeds solar cell structures into battery electrodes.

**Modelling Real Materials: The Importance of Defects and Heterogeneity**

Advanced simulation capabilities speed up research into new materials and systems and allow technologies to be deployed safely and efficiently (3). Rational design’s structure databases consist largely of X-ray diffraction performed on pure crystals, while real materials are heterogeneous, for example through interfaces between components, where critical reactions occur (8) and contain a wide range of defects, such as impurities, vacancies and dislocations. The heterogeneity of materials can define their properties, for example Lucid et al. (9) looks at how to simulate grain boundaries: nanoscale interfaces in polycrystalline materials. Defects can diminish performance, but there are many materials, such as semiconductors, whose critical qualities exist because of their impurities. Understanding defects is key to enhancing material properties, for example in battery electrode materials (10). Incorporating both defects and heterogeneity into models will enable more accurate tuning of properties and performance.

**Finishing Touches**

Given that it is expensive to extract, process and distribute raw materials (1), particularly if they are scarce and particularly for energy devices (1), it is important that energy materials are used as effectively as possible. However, materials are subject to a range of processes throughout the supply chain, including the application of additives or coatings and packaging, all of which may exert mechanical stress, exposure and ageing. The effects of these processes are not well understood and may not have immediately detectable effects, only influencing the long-term performance. Some studies are emerging, examining the effects of processes such as calendering on battery electrodes (11). There is a need for holistic studies and the application of green chemistry principles (12) throughout the supply chain, as well as studies on degradation and its mitigation, to stretch resource usage.

**References**

Platinum-rhodium gauzes are frequently used to catalyse the high temperature ammonia oxidation step for production of synthetic nitrogen-based fertilisers. The gauzes suffer from Pt loss in the form of platinum dioxide ($\text{PtO}_2$), due to the highly exothermic nature of the oxidation reaction. Industrially this is mitigated by installing one or more palladium-nickel catchment gauzes directly downstream of the combustion gauzes, to capture the lost Pt. The Pd-Ni catchment gauzes undergo severe structural modification during operation. In this study, we undertake a systematic study in a laboratory-scale furnace system to determine the role of each of the constituent gases $\text{O}_2$, $\text{H}_2\text{O}$ and $\text{PtO}_2$ on the structural changes of the Pd-Ni gauzes. In addition, some samples are exposed to real industrial conditions in an ammonia combustion pilot plant reactor. Fresh and spent catchment gauzes are analysed by means of scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA) and inductively coupled plasma mass spectroscopy/optical emission spectroscopy (ICP-MS/OES). By combining analysis of samples from furnace and pilot scale experiments, the main findings are that Pd-Ni gauzes undergo internal oxidation to nickel(II) oxide (NiO); which in the presence of steam results in Ni depletion and that $\text{PtO}_2$ vapour causes severe grain reconstruction. Furthermore, in laboratory-scale experiments no significant Pd loss is observed, which is in contrast to observations from the pilot plant where the samples are exposed to real post-ammonia oxidation conditions. Pd loss is likely attributed to some gas species contained in the real post-ammonia oxidation gas stream.

Introduction

Ammonia oxidation is one of the key reaction steps in the production of synthetic nitrogen-based fertilisers. Industrially, the reaction is typically carried out at 900°C and a pressure of 1–13 bar over metallic Pt-Rh catalytic gauzes (1). During operation, the Pt-Rh catalyst undergoes several structural changes, such as grain growth of the wire core, surface formation of so-called cauliflowers and enrichment of Rh on the wire surface, due to a significant loss of Pt (2, 3). The Pt is mainly lost as gaseous $\text{PtO}_2$ and it is anticipated to be caused by hot spots on the Pt-Rh gauze due to the extreme
exothermic nature of the oxidation of ammonia to NO (2) (selectivity ~96% (1)), Equation (i) (4):

\[4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)\]

\[\Delta H_{r,298}^0 = -908 \text{ kJ mol}^{-1}\]  

Depending on plant conditions, the Pt loss is in the range of 0.05–0.4 g per tonne nitric acid (HNO\(_3\)) produced i.e., noble metal loss in a modern plant producing on average 1000 tonnes HNO\(_3\) per day, represents a huge financial cost for the fertiliser industry (1). State of the art technology to reduce this cost proceeds via catchment of the formed PtO\(_2\) vapour by Pd-Ni alloy gauzes, located just downstream of the Pt-Rh ammonia oxidation catalyst. The predecessor of this catchment technology, a palladium-gold (80:20 wt%) alloy gauze, was developed by Degussa in the late 1960s (5). The Pd-Au gauzes quickly outperformed other catchment systems, such as glass wool filters, Raschig rings and marble chips (6). Later, cheaper metals such as Ni and cobalt replaced Au in the Pd-Au alloy, as they gave an enhanced catchment efficiency in addition to lower costs (7). Still, the Pd-Ni catchment unit has several drawbacks. During operation, the Pd-Ni gauze wires reconstruct completely and swell in size. This results in a significant loss of mechanical strength and additionally, it is the dominant cause of a large pressure drop increase over the gauze pack during the campaign, see Figure 1. Furthermore, during operation, the gauze is depleted in Ni and depending on plant conditions, 0.2–0.4 g Pd is lost per gram Pt captured (6).

Despite the fact that the aforementioned drawbacks of the Pd-Ni catchment system have been known for several decades, only a handful of studies related to this topic have been published in the last 50 years (5–18). Ning et al. (8) report on the surface reconstruction of the catchment gauze and both Fierro et al. (9) and Ning et al. (10) discuss the catchment mechanisms. Recently, Pura et al. (11) suggested that the alloying element Ni is not participating in the catchment process, but that grain boundary attack may be a mechanism responsible for grain reconstruction. This was further investigated by Pura et al. (18) suggesting that a rapid loss of Ni from grain boundaries causes the initial porosity in the wire. Still, sufficient understanding of the occurring reactions is not achieved and knowledge on how to improve or modify the Pd-Ni based catchment systems is still lacking. The common denominator between all the mentioned investigations is that they are based on gauzes used in industrial operation, where several different parameters such as temperature and gas composition are in play simultaneously. To the best of our knowledge, no or only minor focus has been put on systematic, single-parameter studies to unravel the underlying reasons for the grain reconstruction phenomena.

Here we report the results of systematic studies to understand the role of the individual constituents of the reaction gas mixture (O\(_2\), H\(_2\)O and PtO\(_2\) diluted in N\(_2\)) in the reconstruction of Pd-Ni gauzes, at conditions relevant for high-temperature ammonia oxidation. By exposing pure Pd and Pd-Ni wires and woven gauzes in a laboratory-scale furnace to the individual gas components in a systematic manner, we investigate which gas species cause reconstruction. We will also discuss the role of Ni with respect to Pt catchment, Ni loss and the existing Ni species during operation (metal, oxide and hydroxide). Finally, we compare the laboratory-scale results with two samples treated in a pilot plant at the Yara Technology Center facility (Herøya, Norway), where the samples experience the real conditions of high temperature ammonia oxidation in terms of gas mixture, linear gas velocity, temperature and pressure.

**Experimental**

Wires and woven gauzes of the industrial alloys Pd-Ni (95:5 wt%) and pure Pd were supplied by K. A. Rasmussen (wire diameters of 76 μm and 120 μm) which were used for the laboratory-scale experiments. In addition, pure Pd catchment gauzes
(76 µm) were used in pilot plant experiments with a pure Pt net and a lanthanum cobaltite (LaCoO$_3$)-based ammonia oxidation catalyst, the latter in the form of 3 mm cylindrical pellets. For the laboratory-scale furnace experiments, samples were heat treated in a six-zone furnace at 900–1050°C (ambient pressure) in a quartz tube (inner diameter = 6 mm) in various gas atmospheres containing synthetic air (5.0, Praxair, USA), steam and PtO$_2$ vapour. The composition of the water vapour mixture was 33 vol% H$_2$O, 14 vol% O$_2$ and 53 vol% N$_2$. PtO$_2$ vapour was generated from a rolled up Pt gauze (~0.4–0.8 g) located upstream of the sample at 1050°C, producing a p(PtO$_2$) of approximately 1 × 10$^{-8}$ bar (2.5 mg Pt loss over 20 days in a flow of 1 l air per min). During heat treatment, samples were positioned perpendicular to the length direction of the quartz tube to enhance gas exposure to the gauze and wire in the gas flow. Samples from the Yara pilot plant were treated at 900°C and 5 bar in a gas mixture containing 10 vol% NH$_3$ in compressed air, before the ammonia oxidation combustion catalyst. This implies that the gas mixture contained approximately 9 vol% NO, 15 vol% H$_2$O and 6 vol% O$_2$, 2000 ppm or 100 ppm N$_2$O (pure Pt or oxide catalyst) and the rest N$_2$ when exposed to the catchment alloy. The pilot plant samples were exposed to exactly the same conditions as industrial catchment gauzes and are compared with laboratory-scale samples (as described above) and industrial samples treated at 900°C at 5 bar for 47 days below an industrial Pt-Rh (95:5 wt%) catalyst in the industrial gas mixture (10 vol% NH$_3$ in compressed air).

Various sample surfaces and cross-sections were examined with a high-resolution Hitachi Regulus 8230 field-emission scanning electron microscope (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Images were obtained by collecting the secondary electrons produced by the electron beam (FE-SEM). Samples were heat treated in a six-zone furnace at 900°C for 24 h, a mass gain of 1.47 wt% is

Results and Discussion

As-Received Palladium-Nickel and Palladium Catchment Gauzes

Prior to exposing the as-received Pd-Ni and Pd wires to any gases, SEM and EDX analysis was performed on both wire surfaces and their cross-sections. In Figure 2, representative overview images of the wire surface (Figure 2(a)) and the cross-section (Figure 2(b)) of the 120 µm Pd-Ni alloy are shown. Overall, EDX analysis confirms the cross-sections of the alloys to contain minute quantities of oxygen, with slightly enhanced amounts at the surface, see Table I. In addition, EDX analysis of three randomly selected points on the Pd-Ni cross-section reveal the Ni content to be in the range from 4.4–5.0 wt%, close to the value provided by the supplier. EDX mapping did not reveal any obvious heterogeneities or impurities, neither within the grains nor along the grain boundaries. Based on this we conclude the Pd-Ni alloy to be a homogeneous solid-solution, of ~95:5 wt% Pd-Ni, within the uncertainty of the EDX analysis. Finally, it should be noted that light microscopy of chemically etched cross-sections reveal sharp grain boundaries and a grain size of 5–20 µm for 76 µm wires, of both Pd and the Pd-Ni alloy, see Figure 2(c) for the Pd-Ni alloy.

Effect of Oxygen

When the metallic Pd-Ni gauze (wire diameter 76 µm) is exposed to air in the TGA instrument at 900°C for 24 h, a mass gain of 1.47 wt% is
recorded, see Figure 3(a). The observed mass gain is slightly larger than the theoretical value (1.36 wt%) for complete oxidation of Ni to NiO for a 95:5 wt% Pd-Ni alloy. When exposing the metallic Pd gauze to similar conditions, only a minor mass gain is observed (not shown). With reference to Ning et al. (10) and Gegner et al. (19), we assign the observed mass gain of the Pd gauze to a small oxygen solubility and formation of PdO on the Pd surface. The minor mass gain observed for pure Pd may indeed contribute in the slightly larger observed mass gain relative to theory for the Pd-Ni sample. The internal oxidation of the Pd-Ni alloy is shown visually in Figure 3(b)–(d). Here, cross-sections of the Pd-Ni wire heated for 1 h and 4 h, analysed by SEM and EDX, show small precipitated particles approaching the wire centre with time. By EDX point analysis, the precipitated particles are found to consist of oxygen and nickel in an approximately 1:1 molar ratio, indicating NiO formation (Figure 3(c)).

As shown in Figure 3(e) and Figure 3(f), chemical etching prior to SEM and EDX analysis reveals that the largest NiO precipitates are located at the grain boundaries and that the grain size has increased to 10–30 µm. Additionally, the NiO precipitates are found at equal depth within the grains as in the grain boundaries, indicating that oxygen diffusion is approximately equally fast in grains and grain boundaries (Figure 3(b)–(d)). Notably, at the same time as oxygen diffuses towards the wire centre, EDX mapping show a distinct reduction in Ni concentration in the wire core (Figure 3(b)–(d)). EDX point analysis of the wire core indicate the Ni content to be 4.2 wt% and 2.7 wt% after 1 h and 4 h, respectively. This implies that during the oxidation process the Ni mobility is enhanced, causing a heterogeneous distribution of Ni with more NiO at the outer part of the wire. These observations coincide well with reports by Gegner et al. (19) on internal oxidation of alloys with a non-noble element in a solid solution with a more noble element. Finally, it should be noted that the initial grain growth is seen during the first 24 h, but no significant grain growth is observed after another 20–30 days of heat treatment (see Figure S1 in the Supplementary Information).
Palladium-Nickel Gauzes Exposed to Wet Air

When water vapour is included in the feed gas (wet air: 33 vol% H$_2$O, 14 vol% O$_2$, 53 vol% N$_2$), the internal oxidation of Ni to NiO occurs in a similar manner as in dry air, see Figure 4(a). However, based on gravimetry, the Pd-Ni gauze has lost 2.4 wt% of its initial mass after heat treatment for two weeks in wet air at 1050°C. ICP-MS analysis of the exposed gauze give a total Ni concentration of only 2.7 wt% relative to Pd, compared to 4.8 wt% on a comparable sample treated in dry air. In addition, SEM analysis reveal that the outer parts of the Pd-Ni wire is depleted in Ni (Figure 4(b)) and that some surface roughness has appeared (Figure 4(c)). The data also shows that only 0.1 wt% Pd is lost during two weeks’ treatment in wet air; far below the industrial Pd loss observed during ammonia oxidation (see below). There is also no observed Pd loss in dry air. This correlates well with the work of Opila (20), which shows no Pd loss in wet or dry oxygen and Ar and other literature on Pd loss in dry air (21). Notably, these findings are in contradiction to the calculations of Factsage (22, 23), which estimate a significant Pd loss as PdOH (22, 23) in wet gas and a smaller loss as PdO$_2$ and Pd(OH)$_2$ (22, 23) (see Figure S2 in the Supplementary Information). This leads to the conclusion that the observed mass loss of Pd-Ni in wet air is due to NiO being hydrolysed by the wet air and forming volatile Ni(OH)$_2$, which in turn causes Ni depletion. This observation is in line with Chen et al. (24).

Finally, after the two weeks’ treatment in wet air the NiO precipitates are no longer seen at the grain boundaries. Unfortunately, chemical etching prior to SEM analysis has not revealed the exact position of the grain boundaries and thus the occurrence of grain growth is uncertain. In many ways the situation is similar to the grain growth observed during the initial oxidation process of Ni to NiO. During the initial oxidation, inwards/outwards diffusion of O-Ni increased the mobility of O-Ni, just as treatment in wet air may have increased Ni mobility by Ni diffusion towards the surface. The increased mobility may again contribute to grain growth. However, we are currently not in position to elaborate in detail on how grain growth is interwoven and connected to diffusion and the
oxidation process. We suggest this as a topic for future investigations.

Effect of Platinum Dioxide Vapour in Dry and Wet Air

The effect of exposing Pd and Pd-Ni wires to PtO₂ vapour in both dry and wet air is evaluated. First, we investigated if the presence of Ni in the catchment alloy would influence reactivity of PtO₂ toward Pd. Based on this, both materials were heat treated in dry air at 1050°C with Pt gauzes installed upstream. The results of exposing the two catchment materials to PtO₂ in dry air at 1 h, 4 h and 10 h are presented in Figure 5. Both materials undergo an immediate surface reaction and small Pd-Pt particles or crystals (size ~2–3 µm) are already formed on the wire surfaces after 1 h exposure, as shown in Figure 5(a) and Figure 5(d). The crystals show roughness and have several small ladders on their sides, which increase in size from 4 h to 10 h (Figure 5(b)–(c) and Figure 5(e)–(f)). Notably, for Pd-Ni (Figure 5(a)–(c)), some smaller (1–2 µm) and more faceted crystals appear with a darker contrast in the SEM images. EDX mapping and point analysis of these crystals indicate NiO formation, in line with previous observations of Ni-oxidation in air. From the SEM images reported in Figure 5, it appears as if Pd-Pt based crystals develop at a similar rate in both Pd-Ni and Pd (Figure 5). We
therefore conclude that the NiO particles are not participating in the reconstruction and growth process of the Pd-Pt crystals. With further heat treatment (≥1 day), the interior of the Pd and Pd-Ni wires become subject to the earliest stage of grain reconstruction and ladder-like growth, as if PtO$_2$ is penetrating sub surface from the formed Pt-Pd crystal layer reacting with more fresh metal on the wire, see Figure 6(a) and Figure 6(b). At longer exposure time (≥3 days), the surface crystals show beautiful single crystal shapes. The ladders causing further crystal growth (from ~10–30 µm) are large, slowly growing over a face of an already existing crystal (Figure 6(c)). Prolonged exposure times (20 days) result in complete grain reconstruction to large surface crystals (~20–30 µm) (Figure 6(d)–(f)). The grain reconstruction and crystal formation also causes significant wire swelling; the wire diameter increases by up to 60% after 20 days, see Figure 6(e) and Figure 6(f) and Table II. Additionally, the grain reconstruction of the wire or gauze causes a significant reduction of mechanical strength.

Selected crystals on both the Pd-Ni and the Pd wires are analysed with respect to Pt content by means of EDX analysis and the results are summarised in Table II. Pt concentration in the average top-layered crystals increases rapidly the first day (~10–12 at%), followed by a slower accumulation. This observation goes hand in hand with the fact that the reconstruction starts to occur below the top layer of crystals, after one day on stream (Figure 6(a) and Figure 6(b)), indicating that Pt catchment is preferred on the Pd rich areas below the outermost Pd-Pt crystals. After 20 days on stream (Figure 6(a) and Figure 6(b)), indicating that Pt catchment is preferred on the Pd rich areas below the outermost Pd-Pt crystals. After 20 days on stream, the average surface crystals reach a Pt content of ~22 at% Pt, while the outermost exposed crystals reach a Pt content up to ~40 at% (65 wt%). This is similar to an industrial sample treated for 47 days, where the average Pd-Pt crystal on the wire surface has a Pt concentration of ~30 at%.

At this point it is worth commenting that the Pd-Pt crystal growth rate depends on how a specific part of the gauze or wire is directed toward the high velocity gas stream. The PtO$_2$ molecules have better access to such areas, which is reflected in a

### Table II: Relative Increase in Wire Diameter and Qualitative EDX Results of Pt Concentrations in Pd-Pt Surface Crystals on Pd-Ni (120 µm) and Pure Pd (76 µm) Wires, After Heat Treatments at the Indicated Conditions

<table>
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<th>Gas conditions</th>
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<th>Pt content, at %</th>
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<td>Pd</td>
<td>Pd-Ni</td>
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<tr>
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<td>–</td>
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<tr>
<td>1050</td>
<td>4 h</td>
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<tr>
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<td>Dry air</td>
<td>–</td>
<td>–</td>
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*All EDX measurements have an estimated uncertainty of ~10% of the measured value, while the values of swelling have an uncertainty of ~20% of the indicated value due to local variations in sample diameter.

\(^b\)Crystal located on wire edge, making it subject to a large gas flow and PtO$_2$-concentration during laboratory scale experiments.
higher Pt content; more reconstruction and larger crystal facets (Table II). This is more prominent in laboratory-scale experiments, where the gas is not passing equally uniformly through the gauze as in the industrial or pilot plant. Correspondingly, on laboratory-scale samples, reconstruction is slower and Pt catchment lesser at the wire crossings and at the side(s) of the wire not directly exposed to the gas stream. These observations are applicable to both the Pd-Ni and the Pd catchment gauzes.

We can now combine the two previous experiments and perform a heat treatment with both wet air and PtO$_2$. If a Pd-Ni gauze is heated for two weeks at 1050°C in wet air with PtO$_2$, a mass increase of 6.5 wt% is observed. From ICP-MS/OES, the resulting Pd-Ni wire contains only 2.8 wt% Ni relative to Pd, at the same time as the gauze has reached a Pt content of 9.3 wt%. This indicates simultaneous Ni loss and Pt catchment. Furthermore, if the Pd-Ni gauze is heated for 30 days in total, the exterior of the wire becomes completely reconstructed, at the same time as the wire is almost fully depleted of Ni, see Figure 7(a) and Figure 7(b). Only the wire core shows the presence of NiO particles. We therefore state that Ni-loss and grain reconstruction are individual effects, caused by the presence of water vapour and PtO$_2$, respectively.

Comparing with investigations by Pura et al. (18), we have also observed diffusion and segregation of NiO in the grain boundaries. However, this seems not to cause grain reconstruction or porosity in dry or wet air. Our findings coincide well with the statement by Pura et al. (11), i.e. grain reconstruction is not caused by the presence of Ni or loss of Ni from the Pd-Ni alloy, but rather by catchment of Pt.

**Pilot Scale Experiments – Testing at Industrial Conditions**

Finally, two samples have been exposed in the ammonia oxidation pilot plant at the Yara Technology Center industrial facility. Here, NH$_3$ is included in the gas stream (10 vol% in air) and combusted over an ammonia oxidation catalyst just upstream of the catchment unit. Two scenarios were explored: (i) six pure Pt ammonia combustion gauzes and (ii) a bed of LaCoO$_3$-based ammonia oxidation catalyst pellets, positioned just upstream of a 76 µm pure Pd catchment gauze. As Ni does not significantly affect Pt catchment it was chosen to use pure Pd and not Pd-Ni gauzes in the pilot plant. The experiments were run for nineteen days at 900°C at total pressure of 5 bar, during which each combustion catalyst produced ca. 28 tonnes of nitric acid.

In the first case, when the ammonia oxidation catalyst was a pure Pt gauze, similar features occurred compared to samples heat-treated in the laboratory scale furnace in wet air with Pt upstream. This includes Pt catchment, grain...
reconstruction and swelling, see Figure 7(c) and Figure 7(d). The Pd-Pt crystals on the wire surface are in the range of 10–30 µm in size, with an average Pt concentration of ~30 at% (44 wt%), while the gauze in total had a Pt concentration of ~14 at% (23 wt%). The Pt concentration of the surface crystals obtained by EDX is similar to those found in samples treated in the laboratory scale furnace, confirming the validity of the laboratory scale experiments on Pt catchment. In contrast to our laboratory scale experiments, we now observe a significant Pd loss (0.036 g tonne$^{-1}$ HNO$_3$ produced), very similar to the loss observed with a Pt combustion catalyst (see above). Since the Pd loss in the pilot plant occurs both with a Pt and LaCoO$_3$ combustion catalyst, it is unlikely to be connected to the Pt catchment or grain reconstruction caused by PtO$_2$. In addition, there is no known thermal loss mechanism for Pd in wet or dry air that can explain such a large thermal Pd loss in the process gas (20). This leads to the conclusion that Pd loss is most probably caused by interaction with the demanding gas stream conditions of ammonia oxidation and thus by the gas constituents that were not present in the laboratory-scale experiments. Identifying the species or combination of species, present in the combusted process gas that lead to Pd loss is a very relevant topic for future investigations.

Fig. 7. SEM images of: (a) and (b) a Pd-Ni gauze (76 µm) heated for 30 days at 1050°C in wet air with PtO$_2$; (c) and (d) a Pd catchment gauze (76 µm) used in the pilot plant for 19 days with a pure Pt combustion catalyst at 900°C; (e) and (f) a Pd catchment gauze used in the pilot plant for 19 days with an LaCoO$_3$-based combustion catalyst at 900°C.

**Conclusion**

In this work we have observed that the Pd-Ni catchment system in a dry oxygen containing atmosphere is subject to internal oxidation of Ni to NiO. Further, in a wet oxygen enriched environment, Ni is also oxidised to NiO, but subsequently lost, most probably as Ni(OH)$_2$. Furthermore, the presence of
PtO$_2$ vapour in wet or dry air causes severe grain reconstruction of both Pd and Pd-Ni wires, which in turn causes wire swelling and pore formation similar to industrial Pd-based catchment systems used during ammonia oxidation. In laboratory furnace experiments, no distinct Pd loss accompanies the Pt catchment. However, pilot-scale testing in an ammonia oxidation atmosphere shows significant Pd loss, both with a Pt and LaCoO$_3$-based (non-Pt containing) combustion catalyst. In addition, a second type of pore formation is observed when using the LaCoO$_3$ catalyst in the pilot plant. Therefore, we suspect the Pd loss and the second type of pore formation to be related to gas species present only in the industrial gas mixture, not in our laboratory scale gas mixtures. We suggest this as a topic for further investigation.

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Interfaces are a type of extended defect which govern the properties of materials. As the nanostructuring of materials becomes more prevalent, the impact of interfaces such as grain boundaries (GBs) becomes more important. Computational modelling of GBs is vital to the improvement of our understanding of these defects as it allows us to isolate specific structures and understand resulting properties. The first step to accurately modelling GBs is to generate accurate descriptions of the structures. In this paper, we present low angle mirror tilt GB structures for fluorite structured materials (calcium fluoride and ceria). We compare specific GB structures which are generated computationally to experimentally known structures, wherein we see excellent agreement. The high accuracy of the method which we present for predicting these structures can be used in the future to predict interfaces which have not already been experimentally identified and can also be applied to heterointerfaces.

1. Introduction

When considering the properties of crystalline materials, the impact of defects is essential. Point defects such as vacancies and dopants are the defects most commonly considered in both computational and experimental studies of material properties. Furthermore, the modelling of materials at an atomic level is often confined to bulk systems which contain these point defects (1–4). Considerably less is known about extended defects which appear in polycrystalline systems such as surfaces, dislocations and GBs. As nanostructuring of materials is becoming more prevalent, the behaviour of these extended defects is becoming significantly more important (5–8). GBs give rise to structural discontinuities within materials which result in specific structures and potential non-stoichiometry and can lead to the segregation of point defects to varying degrees, depending on the specific structure (9–13). This can significantly affect the macroscopic properties, for example: ionic conductivity, electronic conductivity, thermal conductivity, thermal expansion, elasticity and strength – all of which are crucial for many applications. Therefore, the understanding of interfaces in these materials is key to optimising their performance. Despite this, relatively little is known about the structure and even less of the effects of these interfaces on material properties due to the inherent complexity of the issues.

An example of the importance of interfaces and polycrystallinity is in the fluorite structured fast oxide ion conductors (14), such as yttria stabilised zirconia (YSZ or ZrO$_2$-Y$_2$O$_3$) or trivalent doped ceria (CeO$_2$), used in solid oxide cells, oxygen membranes and oxygen sensors (6, 15, 16). It is reported that the ionic conductivity within the GBs of these materials is several orders of magnitude lower than the bulk (17–20) with the effect attributed to a wide range of causes including impurities, dopant segregation, defect cluster formations and space charge layers (7, 8, 20–25). In contradiction it has been observed that other materials, such as Bi$_2$O$_3$ (26) and nanostructured YSZ, that the ionic conductivity is enhanced (27, 28). Much of the experimental data...
is based on average effects observed in impedence spectroscopy, where all GBs are treated equally as an average effect (29, 30). In fact, GBs can take on specific structures, an example of this is shown in Figure 1. That is, the atomistic description of what is happening at the GB is incomplete when obtained from macroscopic observations. Another issue which may arise when only considering average effects is that it is likely that different specifically defined interfaces will behave in different ways. As it is difficult to isolate and study the effects of GBs experimentally, computational studies are invaluable to further our knowledge of these defects and their impact on material properties.

The failure to understand the basis of material properties in polycrystalline samples is a significant impediment to the development of new materials and the application of inexpensive processing methods to existing materials. An enhanced understanding of the impact of GBs and polycrystallinity on the properties of materials would allow us to explore alternative routes to optimise their properties and ultimately enhance devices. In order to model the properties of these interfaces we first require a method for accurate prediction of interfacial structures. In this paper we present a computational method for accurately predicting the structure of low angle mirror tilt GBs which can be applied to other interfaces and even heterointerfaces. This method utilises both atomistic simulation and classical molecular dynamic simulation with sophisticated, polarisable force fields derived from ab initio data. Previous theoretical studies of GB structures generally utilise static lattice simulations with empirical force fields and structures based on experimental structures (31, 32). These results often have to be validated using first principles due to the quality and limitations of the force field. In this work the structures are predicted and validated using high-quality force fields derived from ab initio data, this is discussed further in the methodology.

Two fluorite-structured materials are investigated in this study: calcium fluoride (CaF$_2$) and CeO$_2$. CaF$_2$ is the prototypical fluorite material which is a super-ionic conductor at high temperatures (>1100 K) (33). CeO$_2$ (usually doped) is a highly technologically significant material which is both an ionic and electronic conductor with a wide range of applications including catalysis, solid oxide fuel and electrolysis cells and oxygen sensing (6, 15, 16). We compare their predicted GB structures to experimental structures from the literature obtained via transmission electron microscopy (TEM).

### 2. Grain Boundary Structures: Generation and Definition

All GBs simulated here were generated using the minimum energy techniques applied to dislocation, interface and surface energies code (METADISE) (34). The most stable GB structures were found by carrying out optimisation scans of the GB. Surfaces with specific Miller indices were first cut and then reflected to form an interface. A potential energy surface (PES) was then calculated using a forcefield by scanning one surface relative to the other. From this scan, a two-dimensional (2D) PES for the boundary was calculated which allowed the minimum energy structure to be identified. The minimum energy GBs were then optimised and the most stable boundary was selected to investigate using molecular dynamics. The 2D potential energy scan along with the GB structure (before and after optimisation) for the Σ9(221) GB in CeO$_2$ is shown in Figure 2.

GBs are defined by a number of parameters: the crystallographic directions of the axes of the two grains which come together to form the interface ($h_j$, $k_j$, $l_j$), the rotation axis $o = (h_o$, $k_o$, $l_o$), the misorientation angle $\theta$ around the axis $o$ and the normal axis to the GB plane $n$. When $n$ is parallel to $o$ the boundary is defined as a twist GB and when $n$ is perpendicular to $o$ the boundary is defined as a tilt boundary. The GBs which are studied in this work are high-angle mirror tilt GBs ($n \perp o$) and the rotation axis is (001).

The geometric definition of the GBs used in this work is the coincidence site lattice model (35). A coincidence lattice site can be defined when there exists a finite fraction of coinciding lattice sites between the two lattices (grains). This model is based on the assumption that when the energy...
of the GB is low, the coincidence of the atomic sites between the two grains is high, i.e. there are few bonds which are broken across the boundary. The reciprocal density of coincidence lattice sites is known as $\Sigma$ and is used to characterise the geometry of the GB, as given in Equation (i):

$$\Sigma = \frac{\text{no. lattice sites in unit cell of coincidence site lattice}}{\text{total no. lattice points in unit cell of generating lattice}}$$

For cubic lattices, the $\Sigma$ value can be given by the sum of the squares of the Miller indices of the symmetrical tilt boundary, given by Equation (ii):

$$\Sigma = \delta (h^2 + k^2 + l^2)$$

where $\delta = 1$ if $h^2 + k^2 + l^2$ is odd and $\delta = 0.5$ if $h^2 + k^2 + l^2$ is even, thus in cubic systems $\Sigma$ is always an odd number (35, 36). For example, the $\Sigma 9(221)$ GB shown above is defined by the (221) Miller index of the surfaces which are scanned to give this boundary, i.e. $(2^2+2^2+1^2) = 9$, which is odd so $\delta = 1$ and thus this is written as $\Sigma 9(221)$. The other GBs studied here are defined in the same way.

3. Methodology

Initial GB structures were generated as outlined above using METADISE with shell model interaction potentials for both CaF$_2$ (37, 38) and CeO$_2$ (39). These structures were then expanded to at least 30 Ångström (Å) in the x-direction, 22 Å in the y-direction (parallel to the GB) and 76 Å in the z-direction (perpendicular to the GB). Each simulation cell contained two identical GBs as illustrated in Figure 3, with each grain having a depth of at least $\sim 35$ Å.

Molecular dynamics simulations were then carried out to determine the average GB structures. The interaction potential used for the molecular dynamics simulations is known as the dipole polarisable ion model (DIPPIM) (40), implemented in the polarisable ion model aspherical ion model (PIMAIM) code (41). The DIPPIM consists of four elements: charge-charge interactions, short-range repulsion, dispersion interactions and polarisation. This is a highly accurate, polarisable, potential, in which the dipoles are solved self consistently at each molecular dynamics step. This leads to a highly accurate description of the dipoles on ions in the simulation which is of particular importance when simulating highly polarisable ions such as F$^-$ and O$^{2-}$. The data used to fit the DIPPIM potentials

![Fig. 2. (a) The PES scan used to identify the minimum energy $\Sigma 9(221)$ GB; (b) the $\Sigma 9(221)$ GB in pure CeO$_2$ before optimisation; (c) the $\Sigma 9(221)$ GB in pure CeO$_2$ after optimisation. Cerium atoms are shown in green with oxygen atoms in red](image-url)
used in this work were calculated using ab initio methods (2, 42, 43). The use of ab initio data allows for non-equilibrium details on the PES to be accounted for which leads to a highly accurate, transferable interatomic potential.

Often interatomic potentials for fluorite materials are derived from equilibrium experimental data or are formed using interatomic potentials from a range of different sources resulting in inconsistent, non-transferable potentials which may have difficulties taking effects of different coordination environments into account, i.e., surfaces and interfaces. Such interatomic potentials are usually better suited to static lattice simulations as opposed to molecular dynamics simulations. In previous work on the surfaces of CeO$_2$ (44) we have shown that the DIPPIM provides an accurate description of extended defects and the effect of such defects on ionic transport.

The simulation cells were heated to 1473 K for 500 ps in order to simulate annealing of the GB structures, they were then cooled to 573 K for 500 ps and finally simulated at 300 K for 500 ps. Temperature scaling was carried out (at all three temperatures) every 0.025 ps before data collection for analysis began. Final GB structures were generated by averaging over the frames of the trajectory at 300 K. The DIPPIM potential parameters used for CaF$_2$ were previously derived by Pyper and Wilson et al. (42, 43) and those for CeO$_2$ were obtained by Burbano et al. (2). All steps of the simulation were carried out using the isothermal-isobaric ensemble (NPT). CaF$_2$ simulations utilised a timestep of 5 fs and a short-range cut-off of 14 Å and in the case of CeO$_2$ simulations had a timestep of 4 fs and a short-range cut-off of 11 Å. The GBs which were simulated for CaF$_2$ were Σ3(111), Σ5(210), Σ5(310), Σ9(221), Σ11(332), Σ13(320) and Σ13(510); and for CeO$_2$ are Σ3(111), Σ5(210) and Σ9(221).

4. Results and Discussion

Here we present the average predicted structures obtained for GBs in fluorite structured materials and compare these with TEM images obtained from experimental studies. As the F$^-$ and O$^{2-}$ ions present in CaF$_2$ and CeO$_2$ are difficult to image due to their low atomic masses we only compare the cation structures obtained with the aforementioned TEM images. First, we discuss the CaF$_2$ structures followed by those found for CeO$_2$. To the authors’ knowledge there are no experimental studies of GB structures in CaF$_2$ so those found in this study are compared to those of other fluorite materials (CeO$_2$, ZrO$_2$ and YSZ).

4.1 Calcium Fluoride Grain Boundaries

The average cation structure of the Σ3(111) GB in CaF$_2$ is shown in Figure 4, alongside the structure identified by Feng et al. for CeO$_2$ using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) (45, 46). The structure obtained from our predictive method presented here shows excellent agreement with the experimental structure. Other studies of the Σ3(111) GB in fluorite structured materials (ZrO$_2$, YSZ, CeO$_2$, uranium dioxide (UO$_2$)) show similar levels of agreement with our predicted structure (12, 47–49).

In Figure 5 the average cation structure of the Σ5(210) GB in CaF$_2$ is presented with the HAADF STEM image of the CeO$_2$ identified by Feng et al. and Hojo et al. (46, 50). The agreement seen here is less striking than that observed for the Σ3(111) GB. Other examples of the Σ5(210) GB in CeO$_2$ (51, 52), UO$_2$ (48) and YSZ (10, 13, 31) show very...
similar structures which are also comparable to those predicted here.

The $\Sigma 5(310)$ GB structure is compared to a HAADF STEM image of the $\Sigma 5(310)$ GB in CeO$_2$ in Figure 6. The STEM image was obtained by Tong et al. (52). Again, the structure is extremely comparable with the experimental structure shown here as well as those appearing in the literature for UO$_2$ (32, 48), YSZ (10, 31, 53–55) and other studies of CeO$_2$ (49).

The $\Sigma 9(221)$ GB in CaF$_2$ is given in Figure 7. This is compared to the HAADF STEM image of the $\Sigma 9(221)$ in CeO$_2$ studied by Feng et al. (46). The comparison between our predicted structure and that of Feng is excellent. Other studies have identified this GB in fluorite materials (YSZ (10, 47), UO$_2$ (48), CeO$_2$ (56)) which give the same level of agreement.

Studies of the $\Sigma 11(332)$ GB are far less common than others studied here with the only available comparison being that of Feng et al.’s CeO$_2$ structure (shown in Figure 8), which displays a high level of agreement with our predicted structure (46).

The final structure studied for CaF$_2$ was the $\Sigma 13(510)$ GB. In Figure 9 our predicted structure is compared with that of Dickey et al., whose $\Sigma 13(510)$ GB in ZrO$_2$ was observed using high Z-contrast STEM (57). As for the previous GBs studied here the level of agreement is extremely good. In addition to the structure from Dickey et al. other fluorite materials (YSZ (10, 58) and CeO$_2$ (39, 45)) are equally comparable to that shown here.

4.2 Ceria Grain Boundaries

In the case of CeO$_2$ three GBs were investigated: the $\Sigma 3(111)$, $\Sigma 5(210)$ and $\Sigma 9(221)$. These three GBs were selected as they span a range of stabilities and therefore will be important going forward to study dynamic properties of these interfaces and because there are TEM images of these GBs in...
CeO$_2$ available for comparison (9). The levels of agreement observed for CaF$_2$ are also seen for CeO$_2$ in Figure 10, Figure 11 and Figure 12. The primary difference is that for CeO$_2$ the structures are being directly compared to experimental results for CeO$_2$, which likely accounts for the improved agreement observed for the ∑5(210) GB over that seen for CaF$_2$.

5. Conclusions

We have presented a computational method for the prediction of the structure of mirror tilt GBs in fluorite structured materials. This method utilises interatomic potentials which are derived from first-principles data meaning the process is entirely predictive. The excellent level of agreement with existing experimental data on the structures of fluorite GBs highlights the power of the method. The ability to accurately predict these structures is an important first step into the computational investigation of the properties of these materials, which is key to future materials and device optimisation. The method presented here can be extended to the prediction of interfaces in different materials, interfaces of different types (i.e. twist GBs) and even heterointerfaces.

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Aoife C. Plunkett obtained a BA (Mod) in Nanoscience, Physics and Chemistry of Advanced Materials at Trinity College Dublin in 2015. In 2017 she completed an MSc by research titled ‘Diffusion Within Fluorite Structured Materials and the Effect of Defects’ in the group of Professor Graeme Watson also at Trinity College Dublin.

Graeme W. Watson is a Professor of Theoretical Chemistry at Trinity College Dublin. His research interests include solid state materials and the effect of point defects, dislocations, surfaces and grain boundaries on their properties. These include reactivity, oxide and proton diffusion, electronic conductivity and thermal conductivity which are all important in a range of functional materials.
**Introduction**

A select group of researchers are profiled here, all of whom are involved in the design and characterisation of materials for electrochemical energy storage and conversion devices. These include a broad range of battery types, fuel cells, supercapacitors, photovoltaics and devices for the production, storage and utilisation of hydrogen.

Many are pioneering the use of advanced techniques for characterising energy materials, enhancing our understanding of the fundamental kinetic, structural, electronic and magnetic properties which distinguish materials as being well suited to a particular application. Some are also developing novel techniques for accurately assessing properties which are currently not easy to measure, for example: Sam Cooper and Ainara Aguadero’s work on isotopic labelling for the quantification of surface exchange and solid-state diffusivity of battery and fuel cell materials.

The performance and function of an energy material is often strongly linked to its microstructure, both in terms of its homogenised bulk properties and certain forms of heterogeneity. Understanding this link is key to enhancing manufacturing methods, through the processing of materials to component and device construction, by tailoring materials for optimum performance in the target device. Experimental techniques are complemented by computational models, providing important insights into physical and chemical processes happening at the nanoscale.

Once reliable assessment techniques are established, it will be possible to screen materials rapidly and build up a database of material properties. This high-throughput screening and a variety of machine learning tools will accelerate the identification of novel functional materials, composites and synthesis techniques for a specific purpose. A comprehensive materials library with powerful data mining capabilities can also provide diagnostics for materials from a degraded device, aiding our understanding of the mechanisms behind device ageing and failure.

Some of the research groups covered here have developed expertise in synthesising new energy materials, with provable success in controlling the resultant materials’ properties. They make use of composites, incorporating nanostructures and other exotic ingredients to introduce specific properties to an already stable and reliable base material, as well as a range of innovative techniques, such as electrospinning, to control microstructure.

The researchers presented here engage with energy research across a range of scales, from the development of atomistic mechanisms all the way up to techno-economics and policy. Beyond this, they are also all active in areas beyond energy, including sensors, catalysts and memristors, as well as the development of new experimental techniques and synthesis routes.

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**About the Research**

1. **Electrochemical Energy Storage**

The most exciting aspects of Sam’s current research focus around two main topics within the realm of materials for electrochemical energy...
storage and many of these projects are undertaken in collaboration with various members of Imperial College London’s Electrochemical Science and Engineering group.

Firstly, he is using isotopic methods to characterise the surface exchange and bulk diffusivity of electrode active materials, in collaboration with Ainara Aguadero. Similar methods were deployed with great success to understand oxygen ion transport and surface exchange for fuel cell systems (1, 2). However, battery materials present specific challenges, in particular room temperature operation and moisture sensitivity, which require these methods to be redesigned. Sam’s group is currently trialling four distinct approaches to this problem, which is a major undertaking, but the potential rewards, in terms of high throughput screening of cathodes and electrolytes, are significant.

Secondly, he is looking at the analysis and design of electrode microstructures, in collaboration principally with Nigel Brandon, also at Imperial College London. X-ray and ion beam three-dimensional (3D) imaging techniques are pushed to their limits by multiphase, nanoscale battery materials, but the last few years have seen significant progress in their application (3, 4), in particular for investigating unusual microstructures (5, 6). Sam has previously focused on developing open-source software to allow the community to standardise their analysis approach (5, 6), but more recently he is working on machine learning techniques and multiphysics parametric studies to generate design rules.

In addition to his material research, Sam collaborates with Billy Wu at Imperial College London on device level characterisation to understand the state of health and optimum designs for battery cells and packs. Simplified cell models typically do not incorporate mechanisms to capture cell-to-cell variation, and yet this is known to be a key feature limiting the performance of battery packs, especially in the context of potential second-life applications. By implementing novel thermal voltammetry methods (7), combined with multidimensional cell grouping, they are looking to overcome this complexity with a data-driven approach. Finally, Sam is using recurrent neural networks to predict trends in the grid-scale market to accelerate the implementation of next generation electrochemical energy storage.

Much of this work is currently being funded by the Faraday Institution’s Multiscale Modelling project, as well as a variety of Faraday-associated Innovate UK projects, including: Advance Battery Life Extension (ABLE), IMProving Power bAttery Cooling Technologies (IMPACT) and A holistic battery design tool: From materials to packs (Mat2Bat).

2. Optimisation of Ion-Dynamics in Electrochemical Systems

Ainara Aguadero

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Ainara’s current research focuses on the study and optimisation of ion-dynamics taking place in electrochemical systems, with a special focus on solid state devices, including secondary batteries, fuel cells, electrolyzers and memristors. The common aim is the analysis of how the different ion dynamics affect the performance and degradation of these systems. In order to reveal this, her group uses a combination of structural, electrochemical and chemical characterisation techniques. More specifically, they use surface-sensitive analysis and isotopic labelling to reveal and differentiate different ion kinetics taking place at the bulk as well as at the surfaces and interfaces of materials.

One of the biggest topics of research focuses on development of solid state batteries, in which Ainara studies the effect of processing on lithium dynamics (8, 9) and seeks to understand the origin of dendrite formation (10, 11). Her group is also developing new isotopic labelling methods to evaluate the bulk diffusivity and surface exchange kinetics of Li in different battery materials. This work takes place in collaboration with Sam Cooper from the Dyson School of Engineering at Imperial College and will be used to correlate battery performances with variations in the Li kinetics, for instance in systems with dynamic interfaces and cation inter-diffusion processes (12).

Another important area of research is the development of fast oxygen conductors (13) and the study of the potential topotactic redox capabilities of oxides (14) and their applications for fuel cells, electrolyzers, hydrogen production, memristive switching or catalysts (15). This work takes place in collaboration with John Kilner and Stephen Skinner at Imperial College London and with universities in the UK, Europe and elsewhere.

Finally, in the area of surface analysis techniques, the group has a strong background in the study of energy materials using secondary ion spectroscopy and low energy ion scattering (16). At the moment, the group is also developing a unique, worldwide facility called Hi5 (strategic equipment grant EP/P029914/1) with a plasma ion source and dual positive and negative ion detection capabilities for in situ characterisation (T, bias) of electrochemical devices, from the nm to the mm scale. Hi5 will be housed in the Department of Materials at Imperial College London.

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3. Chemistry and Physics of Materials
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Chandra’s research activities in the broad areas of chemistry and physics of materials seek to understand charge-carrier dynamics, ion-diffusion, charge-transport and light-matter interactions in solids and metal-organic frameworks for renewable energy. Against this backdrop, shape-controlled synthesis was successfully extended to battery materials via a colloidal route, producing phospho-olivines in the form of thin platelet crystals, which in the case of lithium iron manganese phosphate has led to a fine-tuning of metal redox energies due to cation intermixing (17) and in the case of lithium iron phosphate with an etched surface, enabled ultrafast battery charging (17). Using hierarchical carbon pre-patterned structures, ultra-flexible Li-ion battery design capable of offering fold radii down to 0.5 mm was proposed (18). By integrating solar cell materials such as organic dyes (19) and organo-halide perovskites (20) in Li-ion cell configuration, new design principles of photo-rechargeable batteries are being advanced. Lastly, by exploiting epitaxial growth relationships, bi-functional oxygen cathodes made of iron oxide nanoparticles and carbon nanotubes are shown to regulate the morphology of discharge products, enabling a fully reversible Li-air battery (21).

Current research into the development of next generation Li-ion batteries with value added features (mechanical pliability and shape-conformity) are supported by The Royal Society.
4. Sustainable Materials

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The research interests in Magda’s group are in sustainable materials, in particular porous carbon and hybrids produced from available resources such as bio- and plastic waste and abundant metals (i.e. iron, manganese and nickel). Her group produces carbon and carbon hybrids using hydrothermal processes which allow scale-up and continuous processes. They can produce up to 1 kg carbon per day and can control exactly the morphology, pore structure, pore size and shape required for each application. They have a great degree of control over the degree of graphitisation, ranging from hard carbons to soft graphitic carbons.

The group applies designer carbon materials to energy storage and conversion technologies, for example as anodes for sodium-ion batteries, electrodes in supercapacitors, cathodes in lithium-sulfur batteries and as electrocatalysts in fuel cells, electrolyzers and metal-air batteries. They pay a great deal of attention to understanding the fundamentals involved in structure-function relations using advanced characterisation tools applied ex situ and operando such as: small angle X-ray spectroscopy (SAXS), small-angle neutron scattering (SANS), X-ray absorption near edge structure (XANES), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI), working collaboratively with experts in these areas.

The group is well-funded and formed of around twenty researchers, with funds from EPSRC, the European Union, Innovate UK, the Royal Society, the British Council, the Royal Society of Chemistry (RSC) and industry. Their publications are highly cited and recognised internationally with 18,000 citations from 160 publications, five patents, ten book chapters and one edited book. The Principal Investigator, Professor Titirici, has been recognised internationally with the RSC Corday Morgen Prize, the IOM Rosenheim Medal, the Chinese Academy of Science President Award and an Honorary PhD from Stockholm University, Sweden.

5. Computational Modelling of Fundamental Processes

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Pooja’s research group, based at Loughborough University’s Department of Chemistry, focuses on computational modelling of fundamental processes in complex materials at the atomic or quantum scale. Their multiscale modelling approach combines inter-ionic potential-based methods and density functional theory (DFT) simulations in synergy with experimental groups and industry.

This requires a good understanding of the structural, electronic, magnetic and transport properties which are crucial in identifying novel functional materials for sustainable energy and catalytic applications. The nature of defects in inorganic solids as well as their effect on electronic and transport properties is also important, not
only in understanding the key structure-property relationships, but also in the next phase of materials design with enhanced performance. In addition to this, a sound understanding of nanoionic properties can yield a wealth of materials with significant technological impact.

The computational methods range from atomistic potentials-based methods, where the forces are dominated by the long-range electrostatic interactions, but also includes short range, van der Waals attractions, electron-electron repulsions and polarisability, to DFT at varying levels of theory. Molecular dynamics is also used to study the transport properties as a function of time and temperature.

Further to this, expansion towards more sophisticated time dependent density functional theory and embedded cluster methods is being pursued.

The areas of research within the group are wide-ranging with a focus on the next generation energy storage systems, thin film photovoltaics, fuel cell materials and, more uniquely, fingerprint detection and, more uniquely, fingerprint detection materials and biomarker detection.

Pooja has received funding from several EPSRC grants and her current collaborations include: Professor Laurence Hardwick (University of Liverpool, UK); Professor David Scanlon (University College London, UK); James Cookson (Johnson Matthey Plc, UK); Professor Olle Eriksson and Biplab Sanyal (Uppsala University, Sweden); Professor Frank Tietz (Forschungszentrum Jülich, Germany) and Professor Michael Walls (Centre for Renewable Energy Systems Technology (CREST), Loughborough University, UK).

Acknowledgements

Jacqueline Edge, Department of Mechanical Engineering, Imperial College London, UK is thanked for preparing the text.

References

Further Reading

"Nanostructured Materials for Next-Generation Energy Storage and Conversion: Fuel Cells"

Reviewed by Rob Potter

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Introduction

This Springer volume focuses on the design, characteristics and development potential of proton exchange membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) technologies for both stationary and portable applications. The contents are organised into three themes: (a) energy policy and electrical power (Chapters 1–3); (b) optimisation of fuel cells (FCs) through design and synthesis of novel catalysts (Chapters 4–8); (c) optimisation of FCs through modelling and simulation (Chapters 9–18). The book forms a useful compendium of research activities across the globe that gives the reader a general overview rather than an in-depth treatment of any one area. The layout and presentation are of the usual Springer high standard with clearly visible graphs and illustrations; the book was compiled in 2018.

Energy Policy and Electrical Power

Chapter 1, ‘Fuel Cell Technology: Policy, Features, and Applications – A Mini-Review’ by S. Bashir (Texas A&M University-Kingsville, USA) et al., starts with a comparative analysis of the energy policies of presidents Eisenhower and Trump with lots of facts and figures regarding historical energy use and energy vector types. The text covering fuel cells is PEM-centric (no SOFC or phosphoric acid fuel cell (PAFC)) and battery vehicles are not included in the discussion.

Chapter 2, ‘Concept of Hydrogen Redox Electric Power and Hydrogen Energy Generators’ by K. Ono (Kyoto University, Japan), argues that particular bipolar electrode configurations and power supply arrangements in coupled electrolyser or FC systems can improve overall efficiencies markedly over existing setups. Ono maintains one can treat the system as a combination of electrostatic energy and electrical to chemical energy conversion. I found the reasoning difficult to follow, perhaps because there are considerable conceptual challenges faced in dealing with electrostatic terms in highly condensed phases (see e.g. (1)). Unfortunately, no experimental data are presented to support the claims by Professor Ono.

Chapter 3, ‘Evaluation of Cell Performance and Durability for Cathode Catalysts (Platinum Supported on Carbon Blacks or Conducting Ceramic Nanoparticles) During Simulated Fuel Cell Vehicle Operation: Start-Up/Shutdown Cycles and Load Cycles’ by M. Uchida (University of Yamanashi, Japan) et al., is a comprehensive work on the mechanistic details of degradation mechanisms and with proposed mitigation protocols. Different supports are looked at, not just carbon. We are reminded of the importance of understanding the practical challenges of stack design and operation.
in respect of membrane electrode assembly (MEA) degradation mechanisms. Degradation tests are based on voltammetric cycling to mimic start-up and shut-down automotive duty cycles. Perhaps not surprisingly, platinum dissolves and aggregates and carbon corrodes and different accelerated ageing protocols give different results. This is very important in the commercial world – you may not agree with the customers’ tests, but they are the ones your product will be judged by!

**Design and Synthesis of Novel Catalysts**

Chapter 4, ‘Metal Carbonyl Cluster Complexes as Electrocatalysts for PEM Fuel Cells’ by J. Uribe-Godinez (Centro Nacional de Metrologia, Mexico) offers a general introduction and good summary of work in the field on catalysis preparation for PEMFC systems. Carbonyl complexes can be heat treated to produce metallic-like clusters and here the author looks at rhodium, iridium and osmium species with a heat-treatment regime up to 500°C in either nitrogen or hydrogen or thermolysed by redox in a suitable solvent. Unfortunately, there are no mass or specific surface area activity-based data so although a comparison with a 30 wt% Pt on XC72R catalyst is made, it is difficult to assess specific-area based catalytic activity.

Chapter 5, ‘Non-Carbon Support Materials Used in Low-Temperature Fuel Cells’ by X. Cao (Soochow University, China) et al. Traditional carbon supports used in FCs are prone to degradation through oxidation and many attempts have been made to find substitutes that can offer competitive performance, durability and cost. The authors give us a survey of the state-of-the-art. However, it is clear that carbon is favoured as a support (for good reason) and is unlikely to be substituted in the near term for low-temperature FCs.

Chapter 6, ‘Noble Metal Electrocatalysts for Anode and Cathode in Polymer Electrolyte Fuel Cells’ by S. Sharma and C. M. Branco (University of Birmingham, UK) is potentially a vast subject to tackle and the chapter covers the basics of what is understood about the performance-morphology related aspects of precious metal catalysts for PEMFC electrocatalysis. There is a particular emphasis on the oxygen reduction reaction (ORR).

Chapter 7, ‘Nanomaterials in Proton Exchange Membrane Fuel Cells’ is written by Y. Zhang (Harbin Institute of Technology, China) et al. In this chapter the PEM emphasis is a little more on direct methanol oxidation than the previous chapter and there is a shift of emphasis towards zero-dimensional, one-dimensional and two-dimensional materials. Carbon features explicitly in the form of nanotubes and graphene.

Chapter 8, ‘Nanostructured Electrodes for High-Performing Solid Oxide Fuel Cells’ by H. Ding (Colorado School of Mines, USA), reviews solution-based, ion infiltration methods of catalysing surfaces in electrode structures. Solution impregnation is well-known in the catalysis industries in general and it is no surprise that it has been adopted with enthusiasm by the SOFC research and development community. Much of the know how has been developed through traditional empirical methods and this chapter reviews progress in the field for a wide variety of catalysts from base and precious metals to complex oxides.

**Modelling and Simulation**

Chapter 9, ‘Modelling Analysis for Species, Pressure, and Temperature Regulation in Proton Exchange Membrane Fuel Cells’ is written by Z. Wang (Texas A&M University-Kingsville, USA). The model emphasis is on understanding the controlling factors in flooding of the MEA under steady-state conditions. The construction of the conservation equations for momentum, mass, species, charge and energy are given in some detail.

In Chapter 10, ‘The Application of Computational Thermodynamics to the Cathode-Electrolyte in Solid Oxide Fuel Cells’ by S. Darvish and M. Asadikiya (Florida International University, USA), the authors use the calculation of phase diagrams (CALPHAD) modelling approach with an emphasis on perovskite and fluorite structural motifs. A comprehensive summary of the materials challenge for SOFC materials when used as electrolytes and cathodes is presented. Complexity is added wherein multiple phases can form due to reaction of the components with gaseous impurities either in the air supply or through, for example, carbon dioxide cross-over from the anode. The CALPHAD approach allows for a workable description of the important defect chemistry of the complex oxides to be predicted together with ionic and electronic conductivities.

In Chapter 11, ‘Application of DFT Methods to Investigate Activity and Stability of Oxygen Reduction Reaction Electrocatalysts’ by X. Chen (Southwest Petroleum University, China) et al., the authors describe the use of density functional
theory (DFT) to model and understand the behaviour of PEMFCs at the catalyst level with a focus on the ORR. Not surprisingly, the oxygen binding energy to (pure) metal surfaces is an activity descriptor of choice and its simplest exposition is in the well-known volcano plot which has platinum and palladium close to the apex. More sophisticated approaches consider the energetics of binding of the key intermediates and a mapping of the associated potential energy surface. As well as metallic-type catalysts, some metal-centred, macrocyclic moieties are also investigated for activity. Finally, the stabilities of these various types of ORR catalysts are considered.

Chapter 12, ‘Hydrogen Fuel Cell as Range Extender in Electric Vehicle Powertrains: Fuel Optimization Strategies’ is written by R. Álvarez and S. Corbera (Universidad Nebrija, Spain). As the title suggests, the purpose described in this chapter is to optimise strategies for combining battery and FC power units for range extension. There is a useful summary of the current ‘competitive posturing’ between the various proponents of battery and FC-powered vehicles. A MATLAB®/Simulink® vehicle model, coupled with the use of genetic algorithm routines, has been developed to examine the interplay of the electrical and mechanical components of the system over selected drive cycles. Importantly, the FC in this case study is used to maintain the charge of the lithium ion battery rather than as an alternative power source for coupling to the drive-train directly.

Chapter 13, ‘Totalized Hydrogen Energy Utilization System’ by H. Ito and A. Nakano (National Institute of Advanced Industrial Science and Technology (AIST), Japan) describes a hydrogen-based energy storage system utilising a reversible FC/electrolyser coupled with a metal hydride tank with fluctuating renewable electrical power inputs and heat and electrical power outputs (combined heat and power (CHP)). The heat flow from the system can be both positive and negative i.e. used for cooling or heating. The prototype demonstrator is a ten cell PEM-type stack with <1 kW output. The totalised hydrogen energy utilisation system (THEUS) was run continuously for three days on a fixed duty cycle and data collected and analysed.

Chapter 14, ‘Influence of Air Impurities on the Performance of Nanostructured PEMFC Catalysts’ by O. A. Baturina (Naval Research Laboratory, USA) et al., discusses the practical issues associated with using PEMFC units in the real world with different environments where air-borne pollutants or atmospheric conditions can pose a risk to the proper functioning and longevity of the PEMFC. An example shown is the dramatic and irreversible drop in cathode performance when exposed to low levels of compounds such as hydrogen chloride and bromomethane vapour. The various poisoning mechanisms are discussed together with possible mitigation strategies.

Chapter 15, ‘Solid-State Materials for Hydrogen Storage’ by R. Pedicini (Institute for Advanced Energy Technologies, Italy) et al., gives a general introductory review covering physisorption and chemisorption-based materials. The authors describe the often conflicting requirements that need to be met for a successful hydrogen storage material, such as the storage capacity, the kinetics of release and uptake and the resilience to mechanical degradation after many duty cycles. More novel, polymeric or inorganic hybrid materials are considered including polyether ether ketone-ketone-manganese dioxide (PEEK-MnO₂) composites and the use of more esoteric materials such as mixed metal oxides from volcanic ash.

In Chapter 16, ‘Stress Distribution in PEM Fuel Cells: Traditional Materials and New Trends’ by J. de la Cruz (CONACYT-INEEL, Mexico) et al., the authors remind us that as PEMFC stack technology advances, more attention needs to be focused on the mechanical and electrical engineering aspects of cell components such as the bipolar plates and membranes to optimise performance, manufacturability, durability and cost.

Chapter 17, ‘Recent Progress on the Utilization of Nanomaterials in Microtubular Solid Oxide Fuel Cell’ is written by M. H. Mohamed (Universiti Teknologi Malaysia) et al. Effective extension of the electrode-electrolyte-reactant interface in FCs presents material and electrode processing challenges. Micro-tubular SOFCs (MT-SOFCs) are a recent development for engineering porosity in the ceramic anode and cathode where the more traditional pore formers are substituted and supplemented using tailored hollow fibres. Inevitably, there is a compromise to be had in terms of ensuring good densification of materials to minimise ohmic drops while enabling reactant and product transport to function adequately at higher current densities. The authors present a brief review of progress in both medium and higher temperature SOFC systems.

Chapter 18, ‘Nanostructured Materials for Advanced Energy Conversion and Storage Devices:
Safety Implications at End-of-Life Disposal’ is written by S. Bashir (Texas A&M University-Kingsville, USA) et al. It is increasingly important for manufacturers to demonstrate that they have considered and mitigated against environmental damage that may arise from the disposal of products at end of life. The conclusion from this work using iron oxide nanoparticles as a test probe of materials entering the environment is that best practice should use a combination of life cycle assessment (LCA) and risk assessment (RA) methodologies.

Conclusion

In summary then, this volume brings together an interesting collection of articles covering mainly hydrogen PEM and SOFC technologies that will help build a more balanced understanding of the commercialisation and technical challenges arising from catalyst behaviour through to stack design.

Reference


The Reviewer

Rob Potter worked for Johnson Matthey, UK, for over thirty years on a range of topics including fuel cells, solar cells, photoelectrocatalysis and thermoelectrics, before retiring in July 2019. He completed his PhD in electrochemistry at the University of Southampton, UK, in 1986.
Microemulsions were used to develop a catalyst with high selectivity towards ethylene and ethane while maintaining considerable methane (CH$_4$) conversion. The use of this technique to produce lanthanum nanoparticles was studied under different conditions. Temperature was shown to have the most significant effect on the final material properties providing a minimum crystallite size at 25°C. The morphology observed for all the samples was flake or needle like materials containing nanocrystallites. To obtain the catalytically active materials a thermal treatment was needed and this was studied using $\textit{in situ}$ X-ray diffraction (XRD). This analysis demonstrated that the materials exhibited significant changes in phase and crystallite size when submitted to thermal treatment and these were shown to be difficult to control, meaning that the microemulsion synthesis method is a challenging route to produce La nanoparticles in a reproducible manner. The materials were tested for oxidative coupling of methane (OCM) and no correlation could be observed between the ‘as synthesised’ crystallite size and activity. However, the presence of La carbonates in the materials produced was deemed to be crucial to ensure an adequate OCM activity.

1. Introduction

There has been significant interest in converting gas, in particular CH$_4$, into liquids (gas to liquid (GTL)) (1). Nowadays, two main GTL processes are used: (a) syngas production followed by Fischer-Tropsch (FT) synthesis (2, 3); and (b) liquifed natural gas (LNG) (4, 5). However, these processes require huge investments and their economic viability generally requires them to be carried out at very large scale (6), preferably exceeding 1000 tonnes per year. Therefore, they are mainly employed when low priced natural gas is available, typically in large quantities. As of today, the interest in exploiting small reservoirs has increased significantly, particularly because the gas from such reservoirs is often simply burnt as no other conversion technologies are available or commercially viable. On the other hand, interest in biomass and waste conversion (7) is increasing and this will require processes that are economically viable at small scale.

The development of small GTL plants based on FT is already happening with the use of microreactors and improved catalysts (6). On the other hand, efforts in finding new ways of producing liquids from gas are continuing. An example is the direct production of ethylene from CH$_4$ by oxidative coupling (8–10). Ethylene is one of the largest-volume petrochemicals and the building block for a vast range of chemicals from plastics to antifreeze...
solutions and solvents (11). Ethylene is currently mainly obtained from energy-intensive steam cracking of a wide range of hydrocarbon feedstocks.

OCM was first investigated in the early 1980s by Keller and Bhasin (12). In 1985, Lunsford (2) showed that, starting from CH₄, lithium/magnesium oxide (Li/MgO) could give a 19% yield for C₂, with ethylene as the main C₂ species. Since then, many catalyst combinations have been investigated for OCM with the highest obtained C₂ yields in the range 25–30% (13, 14). The most common catalyst formulations have been oxides based on alkaline earth metals doped with alkali metals and rare earth metals doped with alkali or alkaline earth metals (3). Several studies have shown that the activity of the OCM catalyst is affected by catalyst structural properties, such as morphology (15, 16). Also basicity and oxygen ion conductivity, which have been identified as key parameters for this reaction, are influenced by catalyst structural properties, such as particle size (17–19).

In parallel to catalyst development and considering the challenges encountered in finding catalysts able to perform OCM economically, efforts have recently been directed to the reactor design. There have been a number of different approaches to novel reactor design, the common factor being the use of membranes. In particular, for OCM, the use of membranes has been of interest because of its perceived ability to control the oxygen concentration in the gas phase and, therefore, decrease the undesired over oxidation (20, 21). Johnson Matthey has been involved recently in four European projects working in OCM: CAtytic membrane REactors based on New mAterials for C₁-C₄ valorization (CARENA), MEthane activation via integrated MEMembrane REactors (MEMERE), Adaptable Reactors for Resource- and Energy-Efficient Methane Valoration (ADREM) and Oxidative Coupling of Methane followed by Oligomerization to Liquids (OCMOL). The first two, CARENA and MEMERE, have been dealing with the use of membranes for this reaction. CARENA, a four-year Seventh Framework Programme for Research and Technological Development (FP7) carried out between 2011 and 2015, aimed at investigating the use of relevant process intensification and catalytic membrane reactors to transform light alkanes (C₁–C₄) and CO₂ to added-value products. Currently running is MEMERE, a four-year EU Horizon 2020 project that started in 2015 aimed at the conversion of CH₄ to ethylene using a membrane reactor with integrated air separation. Additionally, the use of non-thermal plasma reactors is also being evaluated for OCM (22, 23). ADREM, a four-year EU Horizon 2020 project, is looking at using innovative reactor types for CH₄ activation processes including a plasma reactor for OCM.

OCMOL, a five-year FP7 project, aimed to integrate energetic coupling of OCM and CO₂ reforming in a heat exchange reactor that was used to recycle CO₂ produced by the OCM reaction. The integration of OCM with other well-known processes to produce fuels or chemicals is another interesting approach and, indeed, this integration seems to be more important than the actual catalyst performance. A new follow up project, Methane oxidative conversion and hydroformylation to propylene (C123), has recently started and will be looking at transforming CH₄ into C₃ products via OCM which will simultaneously provide an optimum ratio of ethylene, carbon monoxide and hydrogen for its further hydroformylation into propanal or propanol. Ultimately, propanol can be dehydrated into propylene; either by an integrated approach as part of the hydroformylation step or through a stand-alone approach. Siluria Technologies, Inc, USA is promoting a catalytic process that can transform natural or shale gas into transportation fuels and commodity chemicals in an efficient, cost effective, scalable manner using processes that can be seamlessly integrated into existing industry infrastructure. This process is based around two basic chemistries: OCM and ethylene to liquids. In particular, nanowires are used for the OCM reaction.

Although process integration and reactor design were key for the OCMOL project, understanding on how to improve the catalyst performance to obtain higher selectivity towards ethylene and higher CH₄ conversion is still relevant as this will positively impact the process economics. The activity of the materials for OCM is closely related to their properties and it is well known that different properties are expected when comparing nanoparticles against the bulk material (24). Indeed, preliminary work has shown that nanomaterials with different morphologies could enhance the OCM performance at low temperatures (19). The present paper presents a summary of the work carried out within OCMOL around process integration and more particularly elaborates on the systematic study of the use of differently sized La-based nanoparticles for OCM which was a main focus of the catalyst development work in OCMOL carried out by Johnson Matthey.
Flame spray pyrolysis (FSP) and microemulsion were the two methods investigated to produce La-based nanoparticles and results from the latter method will be presented and compared to data previously reported on the materials prepared by FSP (25).

2. Oxidative Coupling of Methane Followed by Oligomerization to Liquids Project

2.1. The Process

The aim of OCMOL was to create a laboratory scale demonstration of the production of liquid fuels using process intensification via cutting-edge microreactor technologies to integrate the exothermic OCM and endothermic reforming (RM). Oligomerisation of ethylene from the OCM step was employed to obtain liquid fuels. Another interesting characteristic of the process concept was the recycle of the undesired products and unreacted \( \text{CH}_4 \) that aimed to be converted to syngas in the RM reactor, driven by the heat produced by the exothermic OCM. The syngas would then be converted to liquid fuels via oxygenate synthesis and oxygenate conversion to liquids. A schematic of the process can be seen in Figure 1.

This process not only presented challenges on the catalysis side but even more so on the engineering side. A combination of several reactions and separations was required including OCM, ethylene oligomerisation to liquids, membrane separation, pressure swing adsorption, \( \text{CH}_4 \) dry reforming, oxygenate synthesis and oxygenate to liquids conversion to establish an economically viable process. High throughput methodologies were employed to more quickly overcome the challenges related to each of these steps and allowing, ultimately, to propose a green integrated chemical process with near zero \( \text{CO}_2 \) emissions.

An advanced process simulation toolkit and high tech microengineering technology were developed to aid the progress of the project. Separate units were used and subsequently ‘virtually’ integrated. The use of process simulation tools together with an economic evaluation of the integrated process resulted in several recommendations for improving the competitiveness of the OCMOL process. A life cycle analysis performed during the project indicated that the carbon footprint was smaller compared to the conversion of natural gas to synthetic diesel via FT synthesis. Remaining challenges were identified, such as the limited ethylene yield of the OCM process and, correspondingly, the significant contribution of RM to the overall product formation in the process. Considerable recycle streams resulted in a large capital expenditure required for the separation section.

2.2. Oxidative Coupling of Methane – Lanthanum-Based Nanoparticles

As mentioned above, the activity of materials for OCM is closely related to the catalyst’s structural properties. Some preliminary work can be found in the literature regarding the effect of particle size in OCM. Farsi et al. (27) showed that Li/MgO nanoparticles had higher \( \text{CH}_4 \) conversion and \( \text{C}_2 \) yield than a conventional Li/MgO catalyst. Noon et al. (28) obtained high \( \text{C}_2+ \) selectivities with lanthanum oxide-cerium oxide (\( \text{La}_2\text{O}_3\text{-CeO}_2 \)) nanofibres obtained by electrospinning. The shape of the nanoparticles was also shown to be important by Huang et al. (29), their study showed that \( \text{La}_2\text{O}_3 \) nanorods were more active and \( \text{C}_2 \) selective at low temperatures than \( \text{La}_2\text{O}_3 \) nanoparticles. On the other hand, La-based materials have been extensively studied for OCM and they have been identified as some of the best catalysts for this reaction (30, 31).
The present work more particularly elaborates on the systematic study of the particle size effect of La-based nanoparticles for OCM which was the main focus of the catalyst development work in OCMOL carried out by Johnson Matthey. Catalyst development for OCM was aimed at allowing the development and understanding of two different preparation methods for La-based nanomaterials: FSP and microemulsion. The two methods were chosen because of their versatility when preparing nanomaterials and with the aim of obtaining La-based materials with different particle size. FSP allows the control of particle size and phase as a function of the conditions used. Similarly, the microemulsion technique has been used extensively to prepare oxides with different particle size and allows a finer control of the particle size (32–34). La-based materials have been shown to be active for OCM (35–40), particularly the variant containing 1% strontium/La$_2$O$_3$ (16, 41, 42). Hence, the latter material was chosen as one of the standard materials for benchmarking between the OCMOL partners. The preparation method of the La-based materials has been shown to influence the material properties and, hence, their ultimate performance. Choudhary et al. (36) found that the catalyst precursor and calcination conditions used to prepare La$_2$O$_3$ affected the surface properties, basicity, base strength distribution, activity and selectivity in the OCM. A comparison of the reactivity of phases was performed by Taylor et al. (43) showing that the starting phase influenced the activity and selectivity, despite La$_2$O$_3$ being the final phase following reaction, as the carbonates are not stable under OCM reaction conditions (44).

FSP is a flame aerosol technology for the production of nanoparticles where the precursor is a liquid with high combustion enthalpy (>50% of total energy of combustion), usually an organic solvent. The research group of Sotiris E. Pratsinis at ETH Zurich, Switzerland was the first to develop the technique (45). Since then many others have followed, leading to the production of a wide range of materials and equipment of varying type and complexity. Johnson Matthey has developed its own FSP facility which produces a range of nanopowders. Depending on the material, it has a capacity to produce up to 100 g h$^{-1}$ of nanopowder. FSP produces nanopowders by spraying a liquid feed, metal precursor dissolved in an organic solvent, with an oxidising gas into a flame zone. The combustion of the spray produces nanomaterials with different properties that can be controlled at a high rate (46, 47). This can be achieved by modifying the process parameters and the feed composition.

During OCMOL the effect of process parameters such as oxygen dispersion and feed composition were investigated for the production of La-based nanoparticles. FSP was shown to be a versatile method that allowed tuning of its properties, not only the particle size but basicity and phase. The materials produced were tested for OCM and higher C$_3$ yields were obtained with materials of higher basicity. A mixture of lanthanum oxycarbonate (La$_3$O$_2$CO$_3$) and La$_2$O$_3$ exhibited better OCM performance than La$_2$O$_3$ only (25).

On the other hand, microemulsion has been extensively used to produce nanoparticles due to the ability of this technique to control the particle size (33, 48). Different types of microemulsion are known, such as water in oil and oil in water. The different systems lead to the formation of reverse micelles in the first case and micelles in the second. These mixtures of oil and water are naturally unstable but can, nevertheless, be stabilised by the addition of suitable surfactants in the right proportion. By positioning themselves at the oil-water interface, these surfactants decrease the interfacial energy and help establish a thermodynamically stable solution from the naturally unstable but can, nevertheless, be stabilised by the addition of suitable surfactants in the right proportion. By positioning themselves at the oil-water interface, these surfactants decrease the interfacial energy and help establish a thermodynamically stable solution from the unstable oil and water mixture by creating very small stabilised droplets (<10 nm diameter) (49).

In diluted systems these molecules are present as monomers, however when their concentration exceeds a certain threshold, the critical micelle concentration (CMC), they aggregate to form micelles. At intermediate concentrations, microemulsions with both aqueous and oily continuous domains can exist as three-dimensional (3D) interconnected sponge-like channels, also known as bicontinuous microemulsions.

3. Microemulsion
3.1. Experimental

A reverse micelle method modified from the method described by Chandradass et al. (50) to prepare lanthanum aluminate (LaAlO$_3$) was used to prepare the La-based nanomaterials. The microemulsion was prepared by mixing 100 ml of cyclohexane and 40 ml of Igepal-520 under magnetic stirring. Once the desired synthesis temperature was achieved 5.6 ml of an aqueous lanthanum nitrate solution was added using a pump (24 ml min$^{-1}$). Finally, 2.5 ml of the precipitating agent, ammonia (35%), was added dropwise after 1 h. When the base was added the mixture became white and it was left...
under constant stirring for 22 h. The final solid material was obtained by centrifugation for 30 min at 4000 rpm, the temperature during centrifugation was kept under 20°C. The sample was washed with ethanol and centrifuged (15 min at 4000 rpm) three times. The material was dried at room temperature. The effects of two synthesis variables were assessed: the synthesis temperature (7°C, 15°C, 25°C, 30°C, 40°C, 50°C and 60°C) and the water:surfactant (W:S) ratio (from 4 to 16). The addition rate of the reactants and the stirring speed were kept constant. A schematic of the procedure is shown in Figure 2. It was divided into three stages: (a) microemulsion, (b) dried material and (c) final powder. A summary of the results obtained for each of these stages is presented in this work.

The solid materials prepared by microemulsion were characterised by physisorption with subsequent fitting to the Brunauer-Emmett-Teller (BET) equation, XRD and high-resolution transmission electron microscopy (HR-TEM). Surface area analysis was performed using a Quantachrome AUTOSORB-1 apparatus using nitrogen as the adsorbate. Prior to analysis, samples were outgassed at 150°C under vacuum for approximately 24 h. XRD data were acquired with a Bruker AXS D8 Diffractometer using copper Kα radiation and collected from 10° to 130° 2θ with a step size of 0.02°. Ratios of the identified phases and their crystallite sizes were determined by Rietveld refinements using total pattern analysis solution (TOPAS) (51). The in situ XRD was performed in the same diffractometer in parallel beam mode with Anton Paar XRK 1000 sample chamber and the data collected from 10° to 80° 2θ with a step size of 0.036°. The investigated temperatures ranged from ambient to 900°C. Samples for transmission electron microscopy (TEM) analysis were ground between two glass slides and dusted onto a holey carbon coated Cu TEM grid and a FEI Tecnai F20 transmission electron microscope was used to examine the samples at a 200 kV accelerating voltage. Dynamic light scattering (DLS) was measured using a Zetasizer Nano ZS from Malvern Panalytical.

OCM testing was performed with a high throughput reactor comprising eight quartz reactors (internal diameter = 4 mm, outside diameter = 8 mm). The reaction mixture consisted of CH₄, O₂ and N₂. Contact time, defined as catalyst weight divided by the CH₄ flow (W/FCH₄), was of 2 kg s mol⁻¹. CH₄:O₂ ratio = 2:1, 10% N₂ (internal standard) and a temperature program of: 650°C, 750°C, 650°C, 850°C and 650°C were used to test 0.04 g catalyst (particle size: 250–355 μm). The ramp to the different temperatures was performed under N₂ and the first measurements were taken after 2.5 h. The temperature was controlled with a thermocouple located in one of the reactors containing quartz wool, which was used as a blank reactor to assess the transformations due to gas phase reactions only. A Varian CP-4900 Micro-GC was used to analyse N₂, CH₄ and hydrocarbons containing up to nine carbon atoms. However, the discussion in the present work strongly focused on the C₂ products as only traces of C₃ were observed, in particular at high O₂ conversions. The carbon balance typically amounted to about 90%.

### 3.2. Characterisation

The use of different synthesis temperatures during stage two had no effect on the phase obtained, La(NO₃)(OH)₂·H₂O (see Figure S1 in the Supplementary Information). This phase differs from the ones obtained using FSP, in which
La$_2$O$_3$ and carbonates were formed. Therefore, the samples produced via microemulsion needed an extra thermal treatment to obtain the active phases (stage three). Although no change was observed with respect to the phase composition, the crystallinity of the samples was affected by the synthesis temperature as can be seen in Table I. The results are in accordance with the surface areas which decrease with the increase in synthesis temperature in the range from 25°C to 60°C. The temperature has been reported to exhibit an effect on the micelle formation, i.e., higher temperatures reduce the interfacial tension between the oil and water which enhances the diffusion of the water into the oil phase and increases the number of smaller sized droplets (52, 53). Therefore, when increasing the temperature, a decrease in particle size would be expected, however, the opposite effect was observed which can be attributed to the particles not being single crystals. The particles are constituted of multiple diffraction domains with different orientations and the temperature might help the growth of these domains (Figure 3).

The samples produced by modifying the W:S ratio were also shown to be poorly crystalline materials when studied in stage two and also consisted of LaNO$_3$(OH)$_2$·H$_2$O (see Figure S2 in the Supplementary Information). The crystallite size increased with W:S, as determined by XRD (Table II). The surface area measured agreed with this observation. This effect can be logically explained because, when higher amounts of water are used (higher W:S ratio), bigger micelles are created. Indeed the effect of the W:S ratio has been shown in previous reported work to be one of the most defining synthesis variables for the particle size in microemulsion (48, 54). An example of this effect is described by Lisiecki et al. (55). These authors investigated the effect of the W:S ratio on the preparation of colloidal copper particles which were achieved using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as a surfactant, isooctane or cyclohexane as the solvents and an aqueous solution of hydrazine to reduce the Cu. The increase in particle size when increasing W:S ratio could be observed for the two different solvents.

The morphology of the materials obtained by microemulsion was very different from that obtained using FSP. The latter produced sphere like materials between 10–40 nm, while aggregates ranging from around 0.1 µm to 10 µm were observed for the samples prepared by microemulsion (Figure 4). These were shown to be flakes or needle like materials with different shapes which was confirmed by tilting the sample at different angles (Figure 5). This shape could be due to either aggregation after surfactant removal or it could be due to the colloidal nature of the synthesis mixture and the ability for these systems to form other shapes (56, 57).

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>Temperature, °C</th>
<th>Surface area, m$^2$ g$^{-1}$</th>
<th>Crystallite size*, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME-T7</td>
<td>7</td>
<td>10.0</td>
<td>38.0</td>
</tr>
<tr>
<td>ME-T15</td>
<td>15</td>
<td>10.0</td>
<td>21.0</td>
</tr>
<tr>
<td>ME-T25</td>
<td>25</td>
<td>31.5</td>
<td>13.0</td>
</tr>
<tr>
<td>ME-T30</td>
<td>30</td>
<td>40.4</td>
<td>15.0</td>
</tr>
<tr>
<td>ME-T40</td>
<td>40</td>
<td>30.5</td>
<td>19.3</td>
</tr>
<tr>
<td>ME-T50</td>
<td>50</td>
<td>21.6</td>
<td>24.2</td>
</tr>
<tr>
<td>ME-T60</td>
<td>60</td>
<td>10.1</td>
<td>31.5</td>
</tr>
</tbody>
</table>

*Crystallite size of lanthanum nitrate hydroxide hydrate
To determine the origin of the flake or needle like morphology dynamic light scattering (DLS) analysis was performed on the microemulsions with and without the La precursor in the stage one at the W:S ratios used previously. The micelle size determined with DLS for the microemulsions without the La precursor in stage one followed the same trend observed previously for the materials obtained in stage two (Table II and Table III). A decrease of the W:S ratio resulted in an increase of micelle size. Unfortunately, the microemulsions containing the La precursor (stage one) could not be analysed with the Malvern Panalytical Zetasizer Nano ZS. This was due to the microemulsion becoming cloudy with the presence of the La precursor and not allowing the light to travel through the cuvette. The microemulsions were shown to be stable over time. Therefore, the flake or needle like morphology might be due to a non-spherical micelle shape. Although, the aggregation of spheres due to low stability of the nanoparticles once removed from the microemulsion cannot be eliminated.

Table II  Surface Area and Crystallite Size for Fresh (Stage Two) Samples Prepared Using Different W:S Ratio

<table>
<thead>
<tr>
<th>Catalyst name</th>
<th>W:S ratio</th>
<th>Surface area, m² g⁻¹</th>
<th>Crystallite size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME-W/S4</td>
<td>4</td>
<td>37.5</td>
<td>15.0</td>
</tr>
<tr>
<td>ME-W/S5</td>
<td>5</td>
<td>32.6</td>
<td>16.6</td>
</tr>
<tr>
<td>ME-W/S8</td>
<td>8</td>
<td>17.1</td>
<td>17.4</td>
</tr>
<tr>
<td>ME-W/S16</td>
<td>16</td>
<td>17.1</td>
<td>21.7</td>
</tr>
</tbody>
</table>

*Crystallite size of lanthanum nitrate hydroxide hydrate

Fig. 4. TEM images for the samples prepared at different temperatures: (a) 7°C; (b) 15°C; (c) 25°C; (d) 30°C; (e) 40°C; (f) 50°C; (g) 60°C

Fig. 5. Images of the sample ME-W/S4 being tilted to 60° with steps of 20°: (a) 0°; (b) 20°; (c) 40°; (d) 60°
As already mentioned, the samples prepared using microemulsion needed an extra thermal treatment to obtain the active phase for OCM, La$_2$O$_3$ and carbonate. Therefore, the effect of the thermal treatment on these samples to transform them into stage three materials was investigated using in situ XRD on the samples ME-T25 and ME-T60 (Figure 6 and Figure 7) as they represent the extremes of the crystallite sizes obtained for these materials. In this analysis, the evolution of phase and crystallite size was monitored during thermal treatment under two different atmospheres, air and N$_2$. The starting phase for both samples was different.

While both contained La(NO$_3$)$_3$(OH)$_2$•H$_2$O, ME-T60 also contained La$_2$(OH)$_3$. The order of appearance of the phases was the same for the two samples, i.e., La(OH)$_2$NO$_3$, unassigned phase, Type Ia La$_2$O$_2$CO$_3$ and La$_2$O$_3$. The unassigned phase was determined to be constituted of a mixture of carbonates and nitrates as a loss of CO$_2$ and NO was observed at 340°C using mass spectrometry-thermogravimetric analysis (MS-TGA). The temperature at which each of these phases appeared depended on the starting sample and atmosphere. Not only the transition temperature between phases was different between the two samples, ME-T25 and ME-T60, but also the evolution of the crystallite size was different. These results showed that the systems are complex and further experiments should be done to understand the effect of the thermal treatment.

3.3. Oxidative Coupling of Methane Kinetics Performance

To carry out OCM testing, the samples were treated at 700°C for 2 h under a N$_2$ flow. Under these conditions Type Ia La$_2$O$_2$CO$_3$ or mixtures of Type Ia La$_2$O$_2$CO$_3$ and La$_2$O$_3$ were predicted to be the main phases and these are preferred as they have been shown to be beneficial for OCM activity (25). The XRD analysis for these materials after the thermal treatment can be seen in Figure 8 and Type Ia La$_2$O$_2$CO$_3$ mixed with La(OH)$_3$ or pure La(OH)$_3$. The OCM activity of these samples was evaluated at 650°C, 750°C and 850°C, see Figure 9. As expected, an increase in the CH$_4$ conversion and ethylene:ethane ratio and a decrease in the C$_2$ yield are observed with increasing temperature. The overall observed activity is comparable to that of the benchmark catalyst, i.e. 1% Sr/La$_2$O$_3$. The size differences observed between the samples prepared at different temperatures do not reflect on the activity. As already mentioned, morphology was also shown to play a role in the OCM activity. However, it appears not to be the determining factor for the materials investigated in the present work. They all exhibit a flake like structure while the samples prepared by FSP are spherical and

<table>
<thead>
<tr>
<th>W:S ratio</th>
<th>Average micelle size$^a$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.277±0.111</td>
</tr>
<tr>
<td>5</td>
<td>3.687±0.188</td>
</tr>
<tr>
<td>8</td>
<td>4.791±0.428</td>
</tr>
<tr>
<td>16</td>
<td>7.199±0.916</td>
</tr>
</tbody>
</table>

$^a$The analysis was done after 22 h of stirring in all the samples except for sample ME-W/S5, which was stirred for 67 h. The effect of stirring time was also studied. Bigger average micelle size was observed for the samples stirred for longer time. However, this difference was not significant. (Average micelle size for the microemulsion with W:S = 4 after 9 days was 2.697 ± 0.0135 nm)
no significant difference can be observed when comparing their activity, see Figure 9. Instead the phase could be playing an important role as the activity for the microemulsion samples is comparable to the activity obtained for the FSP materials where higher amounts of Type Ia La$_2$O$_2$CO$_3$ and Type II La$_2$O$_2$CO$_3$ were observed. Characterisation of the spent catalyst could not be performed due to the small amounts of catalyst used during testing. However, the phases present after the thermal treatment and before testing for some of the samples are La carbonates. For some others La(OH)$_3$ is the only phase after thermal treatment, however this is expected to form carbonates by reacting with CO$_2$, atmospheric or from the reaction. Therefore, again the high activity could be linked to the presence of La carbonates or to the capacity of the catalyst to be converted to La carbonate.

Studying the effect of particle size, phase and morphology independently on the OCM activity has been challenging. While gaining an understanding of the catalyst properties on the activity has the potential to achieve higher OCM activities, it is important to consider that the integration of OCM with other technologies could overcome the unsatisfactory results. Process integration that includes the OCM reaction could be the solution to achieve natural gas valorisation in an economically viable manner.

4. Conclusions

Synthesis of La-based nanomaterials using the microemulsion technique yielded flake like materials which contained nanocrystallites. The synthesis temperature has the most pronounced effect on the ultimate material properties. A minimum crystallite size was observed at 25°C, however this did not affect the final OCM activity. Other phenomena such as those occurring during the thermal treatment play an important role for the catalyst activity for these materials.

In situ XRD analysis demonstrated that the materials exhibit significant changes when submitted to thermal treatment to yield the final, catalytically active materials. The changes were difficult to control, rendering the microemulsion synthesis method a challenging one to produce La nanoparticles in a reproducible manner. Alternative techniques, such as FSP, seem much more promising in this respect. In terms of OCM activity, the presence of La carbonates in the materials used was crucial. This work has put in evidence the challenges encountered when trying to study the material properties, such as phase,
particle size and morphology, independently from each other.

Optimisation of the OCM catalyst is a challenge and we believe the solution to achieve natural gas valorisation in an economically viable manner would be a process that integrates OCM. An example is the European project currently running, C123.

Acknowledgements

The work was undertaken within the context of the project ‘Oxidative Coupling of Methane followed by Oligomerization to Liquids (OCMOL)’. OCMOL is large scale collaborative project supported by the European Commission in the Seventh Framework Programme for Research and Technological Development (GA n°228953). For further information see the OCMOL website.

Cristina Estruch Bosch would like to thank Eli Van de Perre and the analytical department at Johnson Matthey for their assistance during this work, in particular to Edd Bilbe and Hoi Johnson for the XRD work.

References


Fig. 9. OCM results for the samples synthesised at different temperatures by microemulsion and then calcined at 700°C for 2 h under N₂: (a) CH₄ conversion; (b) O₂ conversion; (c) C₂ yield; (d) ethylene:ethane ratio. Also included for comparison the best sample prepared by FSP (25)
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Guy B. Marin is professor in Chemical Reaction Engineering and founding member of the Laboratory for Chemical Technology (LCT) and the Center of Sustainable Chemistry (CSC) at Ghent University. He co-founded the spinoff AVGI in 2015. The investigation of chemical kinetics, aimed at the modelling and design of chemical processes and products all the way from molecular up to industrial scale, constitutes the core of his research. He co-authored two books, "Kinetics of Chemical Reactions: Decoding Complexity" with G. Yablonsky and D. Constales (Wiley-VCH, 2nd edition 2019) and "Advanced Data Analysis and Modelling in Chemical Engineering", as well as more than 600 papers in high impact journals and is co-inventor in four filed patents. He is co-editor of the Chemical Engineering Journal and member of the editorial boards of Industrial & Engineering Chemistry Research, Current Opinion in Chemical Engineering and the Canadian Journal of Chemical Engineering. He is member of several international scientific advisory boards and ‘Master’ of 111 projects of the Chinese Government for overseas collaborations in his field.
TechConnect World Innovation Conference and Expo 2019

Commercialising research in advanced materials and sustainable manufacturing

Introduction

The TechConnect World Innovation Conference and Expo event has been held annually for the past 20 years and has alternated location between Boston, USA and California, USA. The 2019 conference was held in Boston between the 17th and 19th of June 2019 and attracted over 3000 participants from across all pillars of the ecosystem. The conference will be held in Washington DC, USA for the first time next year.

The aim of the conference is to connect top applied research and early-stage innovations from universities, laboratories and startups with industry end users and large corporates across the following themes, each with their own parallel stream:

- Advanced materials
- Advanced manufacturing
- Energy and sustainability
- Electronics and microsystems
- Biotechnology, medical, pharmaceutical and consumer
- Artificial intelligence (AI), machine learning, informatics and modelling
- Personal and home care, cosmetics, food and agriculture

There were also two poster sessions over the three days and a large exhibition space with over 250 exhibitors showcasing and demonstrating their novel technologies and inventions.

Commercialisation of R&D

The keynote panel discussion ‘Inspiration to Innovation Commercialization of R&D’ took place on day one of the conference. The panel consisted of Alex Fensore (Sherwin-Williams, USA), Emily Riley (Energizer Holdings Inc, USA) and Chris van Buiten (Lockheed Martin, USA). There was discussion about needing both incremental and transformational innovation at different stages and in different places across an organisation and bespoke approaches and processes in place to run and manage each type effectively.

All panel members emphasised the importance of starting incremental innovation from capturing internal and customer unmet needs, followed by looking to see what capability is already in place or can be easily sourced to solve the problems and then collaborating externally to fill any gaps where necessary. There was less of a consensus on how to succeed at transformational or disruptive innovation.

The panel's top tips for innovators were:

- Understand what your customer needs
- Know what you want to be great at – then work out how to get there
- Be bold and be brave.

Innovation Spotlight: Composite Materials, Films and Coatings

One of the highlights of each of the sessions was the Innovation Spotlight slot. During this time each of the sponsoring companies has an opportunity to pitch to the innovators in the room and describe the company, its vision, ethos and goals and especially the types of challenges they are facing and where they are looking for new advanced materials. The innovators in the audience found these slots particularly useful to guide the areas to target their future research. If an innovative solution can be matched with a known problem that a large company is facing, then the route to commercialisation for the technology can be made easier.
Then followed a number of seven minute selected pitches from university technology transfer offices or startups looking for seed funding, licensing partners or commercialisation partners. Among the pitches in the Advanced Materials Innovation Spotlight (sponsored by AGC, USA and Magna, USA) were a selection summarised here.

‘CompPair Technologies’, A. Cohades (Laboratory for Processing of Advanced Composites, EPFL, Switzerland) (1). Composite materials are formed by combining materials together to form an overall structure with properties that differ from those of the individual components. They are used for a wide range of applications from wind turbine blades or aircraft wings to boat hulls and masts, surfboards and buildings. High performance and lightweight composites that are composed of fibre and resin can be susceptible to damage by fatigue or exposure to dust or projectiles, even small impacts can cause microcracks, which leads to bigger cracks and potentially catastrophic part failure. CompPair has developed a ‘prepreg’: a fibre-based repair agent that is incorporated directly throughout the composite materials on production and remains dormant in the part until activated to enact self-repair of the composite. The healing process requires only moderate temperatures of 70–85°C, easily achieved with a hand-held heat source and takes only one minute. The incorporation of the repair agent uses existing manufacturing routes and assets, maintains the mechanical performance of the original material and can extend the equipment’s lifespan by up to three times. The company is looking to trial its repair additives in new composite materials.

‘Enabling New Technology for Anisotropic Conductive Films’, P. M. Lindberget, CondAlign, Norway. CondAlign has a patented technology for producing a range of conductive films with anisotropic properties known as anisotropic conductive films (ACFs). Anisotropic materials can be described as having directionally different material properties. For instance, the material can be insulating in one direction and electrically conductive in another. The films are usually comprised of conductive particles and a polymer matrix. The mechanical properties of the films are mainly given by the matrix, while the conductive properties are defined by the particles. An electric field is used to structure and align the filler particles in a liquid matrix (Figure 1). When applying the electric field, electric dipoles are induced in the particles causing chain formation. The alignment occurs due to electrophoresis, therefore it is also possible to align non-electrically conductive or magnetic particles. CondAlign has demonstrated production of films with a wide range of different parameters. It is demonstrated in roll to roll production, making the process scalable and cost effective. The process is material independent and is applicable to a wide range of applications.

‘Surface Coating for Reduction of Aerodynamic Noise and Vibrations’, C. Smith (Texas Tech University, USA). Flow separation is a phenomenon considered to be responsible for increased vibration and drag along with higher energy consumption in vehicles. The team at Texas Tech University have focused on solving this problem using passive control via bio-inspired surfaces. Using a material analogous to the denticles on a shark’s skin, they have developed a passive microscale fibrillar coating that significantly reduced flow separation. This micro-texture energises the fluid adjacent to the body by creating local suction and blowing, delaying separation and giving a smaller wake leading to reduced noise and vibrations. A feature of shark denticles is the asymmetric geometry (Figure 2) (2). The denticles are created initially through a process of etching and casting, however once a mould is made it can be used almost indefinitely allowing for cost-effective scale up. Initially focusing on wind turbine blades, they managed to achieve 30% drag and noise reduction and are looking for partners to co-develop solutions for specific applications where noise and vibration reduction are important.
With much in the news currently about plastic waste, the team at NUS has created a cost-effective approach to fabricating recycled polyethylene terephthalate (rPET) aerogels from waste PET fibres obtained from plastic bottles. The high surface area rPET aerogels were fabricated through hydrogen and ester bonds formed between polyvinyl alcohol (PVA) and the rPET fibres and acetal bridges from a glutaraldehyde (GA) cross-linker. The rPET fibres were fully immersed in sodium hydroxide (NaOH) solution to produce carboxyl and hydroxyl groups on their surface. This was heated in an oven for 1 h at 80°C to accelerate the hydrolysis process. They were washed thoroughly with deionised (DI) water to remove all the remaining NaOH before immersing them into the mixture of PVA, GA and DI water. The pH of the reaction media was controlled at pH 3 by hydrochloric acid (37%) to accelerate the cross-linking reaction. The resulting mixture was sonicated for 30 min at 220–230 W for homogenisation and removal of bubbles. The cross-linking reaction was carried out in the oven for 3 h at 80°C and then placed into a freezer for 6–8 h until the sample was frozen. The frozen sample was placed into the freeze dryer for 48 h to remove all the solvent and produce the rPET aerogel. Full details can be found in their publication (4).

The GA cross-linker can improve the interactions between the rPET fibres and the PVA cross-linker. It also reinforces the rPET-PVA fibre matrix by improving its stability and mechanical properties during the curing process (Figure 3). The aerogels are very versatile and can be given different surface treatments to customise them for different applications. For example when the surface contains terminal methyl groups, the aerogels can absorb large amounts of hydrocarbons very quickly making them highly suitable for oil spill cleaning. When the surface is coated with an amine group the material can absorb carbon dioxide from the environment. The surface chemistry can be adapted to be able to incorporate the aerogels into lightweight, breathable personal masks that filter out pollutants such as nitrogen oxides and carbon monoxide in places where air quality is of concern. Aerogels also have incredibly poor heat transfer properties, which makes them ideal for using as insulation. When coated with fire retardant chemicals, the material can withstand temperatures of up to 450°C but weighs only about 10% of the weight of traditional thermal lining, this would allow safety equipment such as coats for firefighters to be made much lighter, safer and cheaper and at the same time helping in the global fight against plastic waste.

Awards: Thin Films, Sensors and Coatings

Each year the TechConnect Review Panel identifies and ranks the top 15% of submitted technologies based on the potential positive impact the submitted technology will have on a specific industry sector. Some of the 2019 award winners are listed below.

Click Materials Corp, Canada, is expert in thin film technologies for coating highly efficient catalysts for reduced power consumption and smart glass. It is commercialising electrochromic window technology that is expected to be >50% lower cost than incumbent technologies. Smart windows provide variable tinting capabilities that significantly reduce energy requirements, improve employee productivity and enable the connected smart home.

Chemeleon, USA, is developing a platform technology for a novel chemical sensor with high sensitivity and specificity. The initial application includes a smart colorimetric sensor that can be embedded in drinkware to help consumers become aware of food and drink safety to protect them from date rape drug facilitated crime. It enables instantaneous on the spot detection of many other potential contaminants.
analytes such as volatile organic compound (VOC), explosives or nerve agents and it can also be extended to detect specific biomarkers to enable clinical diagnosis.

Inhibit Coatings Ltd, New Zealand, uses novel silver nanofunctionalisation to produce highly antimicrobial coatings. Silver is a well-known antimicrobial agent effective against over 650 different microorganisms. The novel nanotechnology allows very low biocide concentrations (<0.1%) and exhibits an extremely low leaching <0.1 ppb cm$^{-2}$ over a period of one week fully immersed. This low leach rate and biocide concentration gives rise to robust coatings with a very long antimicrobial lifetime that withstands wash cycles without compromising the physical properties of the resin system.

**Conclusions**

The overarching themes across all the streams of the conference were about making things better, smaller and cheaper but importantly also more safely, efficiently, ethically and sustainably: using greener solvents and processes, finding alternatives to conflicted starting materials and having a minimal impact on the world’s natural resources by considering recycling and cradle-to-cradle lifecycles at the start of the projects. This looks like a trend that is thankfully set to continue with many of the companies and institutions presenting referencing the United Nations Sustainable Development Goals in their drivers and business models.

**References**


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**The Reviewer**

Debra Jones joined Johnson Matthey in the Technology Centre, Sonning Common, UK in 2004 with a degree in Chemistry from the University of Birmingham, UK. She has worked across a range of sectors including Fischer Tropsch catalysis, automotive catalysis, solar thermal hydrogen production and natural gas purification. Debra currently works in the corporate innovation team and looks after Johnson Matthey’s Open Innovation activities, looking for new technologies and opportunities for Johnson Matthey to collaborate externally, particularly with startups and small to medium enterprises.
“Nanocarbons for Energy Conversion: Supramolecular Approaches”

Reviewed by Harry Macpherson

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Email: harry.macpherson@matthey.com

Introduction

Carbon in its oxide and hydrocarbon forms is the cause of the energy and transport sectors’ biggest headache: climate change, so it is fitting that allotropes of this most versatile element look so promising to play a part in the modernisation of energy conversion. Naotoshi Nakashima (Kyushu University, Japan) brings together a collection of chapters showcasing some impressively creative nanoscience, predominantly from Japan, as part of Springer’s Nanostructure Science and Technology series. On reading, one is left with the impression that these fascinating materials will surely play some part in the coming decarbonisation of the economy.

Nanocarbons, as the name implies, are the allotropes of carbon that take the form of molecules of nanometre dimensions. The archetypal nanocarbon is graphene – a single layer of sp² hybridised atoms arranged in a two-dimensional hexagonal lattice. Nanotubes are essentially rolled up sheets of graphene, while fullerenes are essentially graphene sheets curled up into spheroids. Other nanoscale carbons, such as nanoporous carbon, carbon black and carbon foams are also discussed.

Nanocarbons for Fuel Cells

A large portion of the book is dedicated to the role of nanocarbons in fuel cells (FCs), so it is worth giving a brief overview of FCs and the associated functions of nanocarbons. FCs share features with both internal combustion engines and batteries. Like an internal combustion engine fuel is oxidised, producing exhaust gas, and like a battery chemical energy is converted to electrical energy. In the case of the popular proton exchange membrane fuel cells (PEMFCs) the fuel is commonly hydrogen, which is split into protons and electrons at the anode. Electrons are forced to flow through an external circuit because the electrodes are separated by an electrically insulating proton conducting polymer membrane such as NaFion™. Protons move through the membrane to the cathode where they react with oxygen and electrons that have travelled through the external circuit to form water. The overall reaction is the oxidation of \( \text{H}_2 \) to \( \text{H}_2\text{O} \).

FC performance is largely determined by materials performance. Looking in more detail, at the anode side \( \text{H}_2 \) diffuses through the gas diffusion layer (GDL) to reach the catalyst. The GDL is often composed of carbon fibres which allow electrons to flow from the catalyst to the current collector and \( \text{H}_2 \) to diffuse between them to the catalyst. Platinum nanoparticles catalyse the splitting of \( \text{H}_2 \) into protons which are transported across the proton exchange membrane to the cathode and electrons which are transported along carbon fibres to the current collector.
Carbons are crucial to the performance and cost effectiveness of FCs, especially as catalyst supports where their high specific surface area enables a low Pt loading for a given power density and their conductivity provides a pathway for electrons to move between the Pt catalyst and the conducting fibres. FC performance can be greatly enhanced by improving the surface properties of nanocarbons for better gas accessibility and distribution of Pt nanoparticles. Their conductivity has a significant effect on power density and their chemical and thermal stability has a large influence on FC durability.

**Carbon Nanotubes**

On the topic of FCs, some particularly interesting work on multiwalled carbon nanotubes (MWCNTs) as catalyst supports for H₂ PEMFCs by Naotoshi Nakashima and Tsuyohiko Fujigaya of Kyushu University, Japan, can be found in Chapter 1. The authors first address the difficulty of dispersing Pt nanoparticles onto nanotubes due to the lack of binding sites for deposition. Oxidation of the nanotubes is one method of introducing hydrophilic groups for binding, however this reduces the nanotubes’ electrochemical stability. To get around this problem the authors present a protocol for wrapping MWCNTs with conjugated polymers which bind to the nanotube surface through π–π interactions and on top of which the Pt catalyst can be more easily deposited. Chapter 1 also features durability tests of membrane electrode assemblies (MEAs) using polymer wrapped nanotubes as compared to polymer wrapped carbon black. Nanotube MEAs are found to maintain a significantly higher activity after several thousand cycles of durability tests compared to carbon blacks due to the inherent structural stability of the polymer wrapped pristine nanotubes.

Chapter 2, which is also written by Nakashima, follows on nicely from the first, exploring polymer wrapped nanotubes as catalyst supports for direct methanol FCs. A significant problem for direct methanol PEMFCs is methanol crossover where methanol diffuses through the Nafion™ membrane to the cathode where it reacts with O₂, poisoning the Pt catalyst. While alternative transition metal cathode catalysts are more methanol resistant because they suppress its oxidation this is counterbalanced by lower oxygen reduction reaction (ORR) activities than Pt. Nakashima presents a solution to this problem by coating the polymer wrapped Pt decorated nanotubes with an outer layer of poly(vinylphosphonic acid) (PVPA) polymer, which increases methanol tolerance by the proposed mechanism of preferentially blocking diffusion of the larger molecule while only slightly reducing O₂ accessibility. The PVPA is also found to reduce carbon corrosion of nanotube and carbon black catalyst supports.
Another highlight on the topic of FCs is the review by Matsuhiro Nishizawa of Tohoku University, Japan, of carbon nanotube (CNT) based enzymatic biofuel cells in Chapter 15. Enzymatic biofuel cells are FCs in which an enzyme takes the place of Pt nanoparticles as the electrocatalyst. At the anode, the enzyme oxidises fuels such as fructose or glucose and generates electrons that are carried to the current collector by a conducting carbon support. At the cathode O₂ is reduced to H₂O by another enzyme. An advantage of biofuel cells is that the incredibly high selectivity of the enzyme means impure fuel feeds can be used and there is no need for a separator, making the overall design simply a pair of enzyme functionalised electrodes exposed to solutions containing fuel and O₂. The simplicity of the design makes them suitable for miniaturisation for use in implantable electronic devices. CNTs are presented as promising enzyme support materials due to their biocompatibility and high specific surface area. Previous attempts to immobilise enzymes onto nanotube electrode structures have created nanostructure films before enzyme modification. However, Nishizawa reports a method by which enzyme modification precedes film production so that the nanotubes pack ideally around the enzymes. This is achieved by adding an enzyme solution to a CNT forest which shrinks to a near hexagonal close packed structure on drying, entrapping the enzymes between the nanotubes and resulting in superior activity compared to previous production methods.

**Materials Characterisation**

A fantastic piece of FC material characterisation work is presented in Chapter 5 by Somaye Rasouli and Paulo J. Ferreira working at the University of Texas at Austin, USA. They describe the technique of identical location transmission electron microscopy (TEM) as a way to understand the mechanism of Pt nanoparticle growth on CNTs in PEMFCs. One of the main causes of performance decline of PEMFCs is the instability and coarsening of Pt nanoparticles on carbon supports, which reduces the total surface area of active catalyst. The authors proposed four possible mechanisms of coarsening: Ostwald ripening, particle migration on the carbon support and coalescence, particle detachment and particle dissolution and reprecipitation. While the ideal way to investigate the mechanism would be to do in situ TEM and concurrent voltage cycling on a MEA, the release of moisture into the vacuum chamber precludes this. Furthermore, accelerated stress tests on MEAs make it difficult to tease apart the contribution to performance decline from different components. In order to study specifically Pt nanoparticle instability Arenz et al. first deposited the nanotube supported catalyst onto a gold TEM grid, initially observed the foil to define an area of interest, cycled the grid in a three-electrode electrochemical cell and then re-characterised the identical area of interest by TEM. It was found that carbon corrosion of nanotubes in voltage cycling in which carbon is lost as carbon dioxide, converting the hexagonal lattice to heptagon and pentagon rings, causes the Pt nanoparticles to move across the nanotube surface, possibly to reduce interfacial energy. As the nanoparticles move on the nanotubes they make contact with each other before coalescing to form larger particles.

**Nanocarbons in Hydrogen Production**

Aptly, the complementary theme of the role of nanocarbons in H₂ production is explored in Chapters 9 and 19. In Chapter 9 Yutaka Takaguchi and Tomoyuki Tajima of Okayama University, Japan and Hideaki Miyake of Yamaguchi University, Japan, describe a new category of H₂ evolving photocatalysts based on semiconducting single walled carbon nanotubes (s-SWCNTs). Nanotubes can be metallic or semiconducting, i.e. have or not have a band gap, depending on the rolling angle between the axis of the tube and the crystallographic directions of the rolled graphene sheet. The productivity of H₂ from photocatalysts can be improved by expanding the range of active wavelengths from ultraviolet to near infrared (IR). The new category of nanotube based photocatalyst reported promisingly shows H₂ evolution under near IR radiation. However, s-SWCNTs are seldom used for this application due to the high exciton (electron-hole pair) dissociation energy, the fact that nanotubes form bundles that allow excitons to be transferred between tubes and also because they are difficult to disperse in H₂O. These problems are addressed rather ingeniously through the fabrication of a coaxial cable composed of an s-SWCNT covered with a layer of C₆₀ fullerenes, which are themselves functionalised with a hydrophilic dendron moiety which readily complexes with Pt, the cocatalyst for H₂ evolution. The cable is made simply by sonicating the nanotubes in a H₂O solution of the amphiphilic fullerodendron, which self assembles around the nanotubes due to n–n interactions. This hydrophilic dendron moiety makes the nanotubes more easily dispersible in H₂O, while
the nanotube-C_{60} heterojunction formed improves exciton dissociation. Furthermore, the problem of bundle formation is resolved by the isolation of the nanotubes from each other.

**Lithium-Ion Batteries and Solar Cells**

The FC’s biggest competitor in the race to decarbonise transport – the lithium-ion battery – may also benefit from the use of nanocarbons in future. Of particular interest is the review of nanocarbons as alternatives to graphite in anode materials written by Seok-Kyu Cho and Sang-Young Lee of Ulsan National Institute of Science and Technology (UNIST), South Korea and JongTae Yoo of Korea Institute of S&T Evaluation and Planning (KISTEP, South Korea in Chapter 18. The main advantage of these materials is that they could potentially have significantly higher Li capacities than graphite. For example, the capacity of C_{60} fullerenes was shown by Armand et al. to be 12 Li atoms per fullerene. However, this was only realised once the problem of reduced C_{60} dissolving in liquid electrolyte was worked around by substituting for a polyethylene oxide-based gel polymer electrolyte. Theoretical calculations of the Li storage potential of nanotubes show them to have capacities much greater than graphite, however these have yet to be realised experimentally. The authors conclude that the gap between theory and experiment motivates more work to better understand the lithiation mechanism of nanotubes.

The book covers the potential roles of nanocarbons in several aspects of the future decarbonised economy, covering power generation from H\textsubscript{2} and production of H\textsubscript{2}. Chapter 20 covers the applications of nanotubes in grid energy generation from solar cells with an emphasis on CNT-silicon solar cells and CNT based perovskite solar cells. Feijiu Wang and Kazunari Matsuda of Kyoto University, Japan and Nagoya University, Japan provide a clear overview of the general principles of solar cells, which nicely sets the context for the chapter. Perhaps most intriguing is the ability of semiconducting SWCNTs to generate multiple excitons from one photon, meaning they may be able to surpass the Shockley-Queisser limit on the maximum efficiency of single junction solar cells, which assumes one exciton per photon. While there are many applications for nanotubes, from hole transport layers to transparent conducting electrodes, the authors point to a significant barrier to commercialisation: the presence of metallic nanotubes in the mixtures used for studies, which increase contact resistance due to their difference in work function and band gap.

**Conclusions**

This book covers a very broad range of applications for nanocarbons and while much of the underlying chemistry and materials science transfers between chapters, it is unlikely that any single reader would be familiar with all the concepts covered. The reviewer would recommend this book for any researchers working with carbon nanomaterials, particularly nanotubes, as well as researchers working with PEMFCs. Overall, an interesting read that reminds the reader of the impressive versatility and seemingly endless applications of carbon nanomaterials.

**Reference**

1. CFA213FCE, 'Transport of Gases, p+ and e– in PEMFC', 23rd May 2013

**The Reviewer**

Harry Macpherson has been working as a Materials Scientist in Johnson Matthey, UK, since 2017 on the development of platinum group metal industrial products. Before that he worked on synthesising endohedral fullerene derivatives for quantum information processing in the Carbon Nanomaterials Group at the University of Oxford, UK.
Introduction
The Oxford Battery Modelling Symposium was held in Oxford, UK, from 18th to 19th March 2019. The conference was specifically designed to gather mathematicians, chemists and engineers within the battery modelling community. It was very well received and brought together 170 participants with worldwide representation from academia, research organisations and industry involved in modelling at different scales (atomic length-scale, continuum and control-oriented modelling). This review will focus on eleven talks presented in the four sessions and organised as follows:

- Atomistic to continuum modelling
- Continuum modelling
- Continuum to control modelling
- Control-oriented modelling.

Atomistic to Continuum Modelling
Electrochemical processes can be modelled using a continuum approach (that relies on material specific parameters, sometimes difficult to measure) or from first principles. As electrochemical processes are thermally activated, in 'Connecting Electronic Structure to Phenomenological Continuum Models of Electrochemical Processes' by Anton Van der Ven (University of California Santa Barbara, USA) it was shown that temperature and entropy play a key role for understanding the physics and the properties of materials. As such, a statistical mechanics approach is beneficial, although computationally very demanding. Van der Ven introduced the open-source software Cluster Approach to Statistical Mechanics (CASM) developed in his group and available from GitHub (1). In CASM, for a certain material, the thermodynamic and kinetic properties obtained from density functional theory can be fed into continuum models to realise fast and computationally undemanding first-principle multiscale simulations for dynamic processes such as electrochemical processes. This tool can be used to predict thermodynamic and kinetic properties of various classes of materials (such as layered, olivines, spinels and alloys), see Figure 1 (2).

In literature both accurate first-principle methods and continuum theories are available to predict the properties of materials and interfaces. However, rigorous ways to connect the two approaches are still lacking. In ‘Mind the Gap – Towards an Atomistic Understanding of Battery Materials Interfaces’, Denis Kramer (University of Southampton, UK) described strategies to build continuum models starting from first principle calculations and their application to crystallisation. The coverage effect in the size-stabilisation of nanocrystals during electrochemical processes and the crystallisation process of manganese(IV) oxide polymorphs have been discussed (3). Finally the effect of Li$^+$ ions in the stabilisation of some MnO$_2$ polymorphs was described in this framework.

In ‘Modeling Porous Intercalation Electrodes with Continuum Thermodynamics and Multi-scale Asymptotics’ by Manuel Landstorfer (Weierstrass Institute for Applied Analysis and Stochastics, Germany), a description of the procedure for modelling porous cathodes was provided. For such electrodes three scales can be identified (the double layer scale, the macroscopic porous media scale and the microstructure scale). Landstorfer started...
by describing the metal-electrolyte interface and electron transfer in the double layer through a non-equilibrium thermodynamic continuum model (4). The model was scaled up to electrode particle scale and treated with a matched asymptotic expansion method. Finally, Landstorfer discussed a third scale: the macroscopic porous media scale. He introduced homogenisation techniques for the prediction of transport properties at porous scale. This multiscale methodology was applied to model thermodynamic properties, diffusion processes and the open circuit potentials of intercalation cathodes for Li-ion batteries with different chemical composition and porosity.

**Continuum Modelling**

'Electrochemical Energy Storage' by John Newman (University of California Berkley, USA) was a keynote lecture on mathematical modelling approaches for the design of batteries. Newman introduced various methodologies (such as continuum modelling, (kinetic) Monte Carlo and molecular dynamics) and their application to the modelling of intercalation electrodes and electrolytes in Li-ion batteries. He showed how these tools can improve understanding of the electrochemical processes as well as of failure mechanisms taking place in battery materials, helping to design high power and high energy battery materials.

Bob McMeeking (University of California Santa Barbara, USA) presented a model for the redox kinetics at an interface between a solid electrolyte and a Li metal anode in ‘Redox Kinetics, Interface Roughening and Solid Electrolyte Cracking in Solid State Lithium-Ion Batteries’. This model was based on the extension of the Butler-Volmer equation through the inclusion of the effect of the mechanical stress across the anode-electrolyte interface. This method was applied to the investigation of the morphological stability of the interface between the Li anode and the solid electrolyte for various current densities and solid electrolyte resistivities. Moreover, the extended Butler-Volmer equation was used to model the evolution of cracking in ceramic solid electrolytes caused by Li insertion into pre-existing defects on the electrolyte surface. The model showed how the pressure generated by Li insertion into the flaw causes the propagation of cracking in the solid electrolyte and consequent Li dendrite growth. Finally, the extended Butler-Volmer equation was used to identify the maximum Li pressure and critical lengths ($a_1$) of defects within a series of ceramic electrolytes to avoid the propagation of Li dendrites ($a_1 = 2 \mu m$ for Li$_2$La$_3$Zr$_2$O$_{12}$ (LLZO)) (5).

**Continuum to Control Modelling**

The kinetics and uniformity of Li insertion reactions at the solid-liquid interface govern the rate capability and lifetime of Li-ion batteries. Martin Bazant (Massachusetts Institute of Technology, USA) presented a model for the prediction of phase transformations of intercalation materials in ‘Control of Battery Phase Transformations by Electro-Autocatalysis’. The approach was based on a thermodynamic framework for chemical kinetics applied to charge transfer (namely, the Marcus and extended Butler-Volmer equations) (6).

Reaction-driven phase transformations are common in electrochemistry, when charge transfer is accompanied by ion intercalation or deposition in a solid phase. The model allows rationalisation
of phase separation of Li-rich and Li-poor islands for low discharge rates that affect the stability and cyclability of Li-ion batteries. The model also proved that high discharge rates favour the formation of solid-solution phases through an electro-autocatalytic mechanism, later experimentally confirmed for lithium iron phosphate (LFP) (7). The model can be extended to the investigation of electrodeposition, corrosion, chemical intercalation, precipitation and cell biology.

Göran Lindbergh (KTH Royal Institute of Technology, Sweden) presented an extended physics-based porous electrode model accounting for particle surface stress that was used to describe ageing of nickel manganese cobalt oxide cathode (LiNi$_{x}$Mn$_{y}$Co$_{z}$O$_{2}$, NMC) with composition $x = y = z = 0.33$ (namely NMC111). In ‘An Extended Porous Electrode Model for NMC111 in Lithium-Ion Batteries’ the performances of NMC111 were experimentally investigated via a galvanostatic intermittent titration technique and two models were used to fit the experiments: (i) a standard pseudo-two-dimensional (P2D) model; and (ii) an extended surface stress P2D model that included a stress factor depending on the Li concentration gradient in the material. Model (ii) could accurately extract transport, kinetic, thermodynamic and stress properties for the whole spectrum of operative conditions (low and high charge-discharge rates, temperature and external pressure). Although the standard model works well for low potentials (less particle surface stress), the porous electrode stress model predicts the ageing of NMC at high potentials (high surface stress).

‘Physically-Informed Models for Improved Cell Design and Operation of Lithium-Sulphur Cells’ by Monica Marinescu (Imperial College London, UK) was a lecture about the necessity of using physically-informed models to predict the mechanisms and performance of batteries. The accumulated experience on physically-informed models for Li-ion was used as a starting point for engineering Li-S batteries. Modified equivalent circuit network models were used for Li-S batteries modelling in order to take into account phenomena like shuttling, dissolution and precipitation. Moreover, simple physics-derived zero-dimensional (0D) and one-dimensional (1D) continuum models for the prediction of open circuit voltage and of the effects of mass transport on discharge, degradation mechanisms and capacity fade for commercially-sized Li-S batteries were presented (8–10).

Control-Oriented Modelling

Gregory Plett (University of Colorado, Colorado Springs, USA) delivered a keynote lecture titled ‘Physics-Based Reduced-Order Models of Lithium-Ion Cells for Battery Management Systems’ about physically-informed control models. Plett reviewed the standard physics-based model particularly focusing on how this model could be converted to a physics-based reduced-order model (PBROM). Battery-management systems provide a continuous estimate of state-of-charge, state-of-health, available energy and available power of battery packs. Traditional computational methods rely on empirical equivalent circuit models of the batteries. These models are computationally fast and robust. However, although accurate for many tasks, they cannot predict the internal electrochemical state of the cell. On the other hand, physics-based models that provide good predictions of the internal electrochemical state are too complex to apply to battery-management systems, which are heavily parametrised and have robustness and convergence issues. PBROM is a method that, while reducing the computational requirement of physics-based models, retains their prediction accuracy and can be used for battery management systems.

In ‘Decoding the Electron Swelling for Advanced Battery Diagnostics’ Anna Stefanopoulou (University of Michigan, USA) presented a conjugated experimental and computational control model to account for battery degradation. Since standard control models do not account for swelling and ageing, during the talk Stefanopoulou introduced experimental apparatus to probe battery degradation and convert the observables (measured terminal voltage and surface temperatures) into parameters to implement control models to predict swelling and ageing (11). In particular, observations of the cell swelling during charging were used to estimate the loss of active material and loss of Li inventory in the anode, which is useful for avoiding Li-plating during fast charge.

The last talk was delivered by Scott Trimboli (University of Colorado, Colorado Springs, USA). The ‘Model Predictive Control using Physics-Based Models for Advanced Battery Management’ was a lecture on the model predictive control (MPC) developed in collaboration with Plett. Starting from the PBROM, Trimboli showed the mathematical implementation of MPC. MPC is an effective real-time control strategy that employs a ‘look-ahead’ approach to foresee dynamic behaviours in
the battery pack before they happen. This approach can be coupled with the ability of PBROM to enforce hard constraints on internal electrochemical variables (precursors to degradation or unsafe operation conditions), making MPC appealing for advanced battery management, where safety, lifetime and improved performance are crucial (12).

Conclusions
The Oxford Battery Modelling Symposium aimed to bring together the battery modelling community. It was well attended and the 12 talks as well as the 25 posters were high quality. The four sessions of talks were successfully organised to provide a full overview of the current state of the art in Li-ion and next generation battery modelling, spanning from first-principle investigations to control-oriented approaches.

References

The Author
Giulia Mangione is a Research Scientist in the Battery Materials team of the Catalysts and Materials department at Johnson Matthey, Sonning Common, UK. Her current research interests include the computational design of high-performance materials for Li-ion and next generation battery technologies.
Factors Affecting the Nucleus-Independent Chemical Shift in NMR Studies of Microporous Carbon Electrode Materials

The factors influencing the nucleus-independent chemical shift (NICS) of aqueous electrolyte species adsorbed on polymer-derived activated carbon were investigated in this systematic study. The observed NICS was found to be influenced by the carbon structure and the behavioural and chemical properties of the electrolyte species. Measurement of these effects demonstrates differences in the adsorption behaviour of different ions in the absence of an applied potential. For instance, as pore size decreases, so does the local concentration of spontaneously adsorbed alkali ions. This research could potentially enable greater understanding of the mechanism of charge storage in capacitive devices at the molecular level.

Fe³⁺ Reduction During Melt-Synthesis of LiFePO₄

5 kg batches of LiFePO₄ (LFP) were melt synthesised in an induction furnace from coarse Fe₂O₃ (509 µm). Graphite from the crucible was an effective reducing agent. The Fe²⁺ content and reaction kinetics were improved via the addition of metallic Fe, which is also shown to improve the lifetime of the graphite crucible. To avoid agglomeration of the Fe powder due to the presence of a eutectic in the LiPO₃-Fe₂O₃ system, a pre-mixing step is required. A Fe²⁺ content of 0.325 g g⁻¹ was observed when fine Fe³⁺ (142 µm) was used with CO as the reducing agent at half the holding period at 1150°C, which can be attributed to improved contact between the suspended Fe³⁺ and the CO reducing gas.

Chemical Speciation and Mapping of the Si in Si Doped LFP Ingot with Synchrotron Radiation Technique

The performance of lithium-ion batteries is significantly affected by small changes to the structure of LFP. The authors aimed to understand the effect of silicon-doped LFP prepared using a melt-synthesis process by utilising XAS and XRF mapping as characterisation methods. By using these methods, the non-uniform nature of prepared ingot samples could be better evaluated. With comparison to SiO₂ and amorphous glass phases formed as impurities in Si containing undoped samples, the XAS of Si-doped LFP indicate subtle changes in the local structure surrounding the dopants. Studies of this kind on the structure of modified LFP will help with the design of materials for Li-ion batteries.

Visualization of the Secondary Phase in LiFePO₄ Ingots with Advanced Mapping Techniques

The electrochemical performance of LFP in lithium-ion batteries is influenced by impurity phases. Detection of such impurity phases is essential to improve the quality of LFP as a cathode material. The origin of the impurity and secondary phases can be understood through visualisation of the impurity and secondary phase distributions.
immersed in the bulk LFP crystal. EDS and Raman techniques were used to observe the low melting lithium phosphate phase in the LFP ingot. Further exploration into the LFP materials after carbon coating was achieved through micro XRF mapping. This technology has high sensitivity, which ensured that the secondary phases were clearly defined.

**Melt-Synthesis of LiFePO$_4$ Over a Metallic Bath**


An Fe$^{3+}$ precursor was used to study silver and tin charged metallic baths for purification of the melt-synthesis of LFP. Samples prepared by the Sn bath delivered up to 156 mAh g$^{-1}$ of LFP, whilst Ag bath samples delivered 161 mAh g$^{-1}$ of LFP. XRD patterns of the Ag LFP samples were also cleaner than those produced by the Sn bath. Ag oxides and Ag compounds were not present. It is suggested that future studies should focus on investigating Ag baths as a potential contaminant trap for the melt-synthesis of LFP.

**Synthesis of ZIF-8 Based Composite Hollow Fiber Membrane with a Dense Skin Layer for Facilitated Biogas Upgrading in Gas-Liquid Membrane Contactor**


A composite hollow fibre membrane with an aminosilane-modified zeolitic imidazolate framework-8 (mZIF-8) based dense skin layer was designed and synthesised. The ZIF-8 nanocrystals were modified by the introduction of (3-aminopropyl)triethoxysilane. This enabled the ZIF-8 nanocrystals to bond with PDMS chains for further hydrophobic enhancement, with a contact angle of 130º. This was competitive in comparison to the control membrane. The mZIF-8 based composite membrane also demonstrated enhanced biogas upgrading performance and long-term stability. Biogas upgrading performance in gas-liquid membrane contactor applications could be improved by using mZIF-8 based composite hollow fibre membranes.

**Hydrogen Production from Sucrose via Aqueous-Phase Reforming**


Hydrogenation and aqueous phase reforming techniques were used to produce hydrogen from commercial sucrose. The aqueous sucrose solution was hydrogenated in a trickle bed reactor over 5 wt% Ru/C to produce a technical sorbitol/mannitol mixture. The mixture was compared to a commercial sorbitol in aqueous phase reforming over a Pt/C catalyst. The mixtures demonstrated similar selectivity towards the gas-phase products and little difference in the distribution of products retained in the liquid phase. The Pt/C catalysts displayed low efficiency regarding hydrogen production at an industrial level. It is suggested that future work should focus on increasing the amounts of hydrogen generated per mole of converted sugar alcohols.

**Crystal Chemistry and Antibacterial Properties of Cupriferous Hydroxyapatite**


Solid-state and wet chemical processing were used to produce copper-doped hydroxyapatite with the composition Ca$_{10-x}$ (PO$_4$)$_6$[Cu$_x$(OH)$_{2-2x}$O$_2$] (0.0 ≤ x ≤ 0.8). The impact of synthesis route and mode of crystal chemical incorporation of Cu on the antibacterial efficacy against *Escherichia coli* and *Staphylococcus aureus* strains was investigated. Studies revealed that the substitution site of Cu into the hydroxyapatite framework is mainly controlled by the synthesis method and heat treatment process. Finer particle sizes and greater specific surface areas were observed in the wet chemical material, thus leading to superior efficacy. In comparison to undoped hydroxyapatite, Cu-doping increases antibacterial efficiency by 25% to 55%.

**A Robust and Precious Metal-Free High Performance Cobalt Fischer–Tropsch Catalyst**


Synthetic transportation fuel production commonly uses slurry-phase Fischer-Tropsch catalysis. However, due to the hydrothermal and mechanical reaction conditions of such processes, the catalyst used is exposed to extreme stress. Therefore, the authors demonstrate the synthesis, characterisation and catalytic performance of a robust cobalt-based Fischer-Tropsch catalyst. An inert alpha alumina support and an appropriate cobalt addition were combined to form a mechanically and hydrothermally stable material, which is easy to reduce without precious metal additives. The material demonstrated excellent selectivity and good activity in slurry-phase testing over 1000 h.

**Proton Chelating Ligands Drive Improved Chemical Separations for Rhodium**


In comparison to all elements used for technological applications, rhodium extraction has the worst carbon footprint and, unlike other elements, there are also no commercial extractants for Rh. Solvent extraction could improve current practices; however, the chemical separation stage is complicated by the presence of mixed speciation states following acid chloride leaching. Using a variety of experimental and computational techniques, the dianion \([\text{RhCl}_5(\text{H}_2\text{O})]^{2-}\) was shown to transfer to the organic phase in a process involving the formation of an outer-sphere assembly with the diamidoamine reagent \(N-n\text{-hexylbis}(N\text{-methyl-N-n-octylethylamide})\text{amine} \) (Figure 1). The detailed knowledge gained from this work will be beneficial to the design of Rh extractants and has implications for sustainable metal extraction from both recycling and traditional mining.

High-Selectivity Palladium Catalysts for the Partial Hydrogenation of Alkynes by Gas-Phase Cluster Deposition onto Oxide Powders


The bulk and fine chemical industries rely on the selective hydrogenation of alkynes, with good selectivity to the desired product being of particular importance. In this study, a gas-phase cluster deposition method onto conventional support powders was used to prepare palladium catalysts. These catalysts are shown to be as active and selective as those prepared via conventional methods such as impregnation. Good selectivity was observed for both support materials used. The catalysts prepared by gas-phase cluster deposition are shown to contain less-active interfacial sites.

Inelastic neutron scattering (INS) spectroscopy was used to study the reaction between propene and an activated sample of ZSM-5 at 140 K, 293 K and 373 K. The formation of linear alkyl species is observed when propene oligomerises within the zeolite at 293 K, with no evidence to show branched product formation. This selective formation is attributed to confinement within the zeolite pore structure. The reaction at 373 K yielded the same spectrum as that observed at 293 K, suggesting that oligomerisation process is complete at 293 K. The influence of zeolite crystallite size on the product composition in technically relevant olefin oligomerisation reactions was considered.
Introduction

“Process Systems Engineering for Pharmaceutical Manufacturing” is an ambitious reference comprising 24 chapters covering process systems engineering (PSE) methods and case studies of interest to engineers working in pharmaceutical process development, model development, process simulation, process optimisation and supply-chain or enterprise optimisation. Business model optimisation, including optimisation of clinical trials and supply chain, are topics covered in Chapters 1 and 21–24. Continuous manufacturing of drug product (downstream) is a key theme covered in Chapters 6 and 16–20, while process control, flowsheet modelling and key unit operation modelling are covered in Chapters 5, 7, 8–11 and 13–15. Of particular interest is the topic of small molecule upstream development and workup solvent selection and optimisation discussed in Chapters 3–4, with case studies involving separation solvent selection presented for ibuprofen, artemisinin and diphenhydramine in Chapter 4.

Chapter 2, ‘The Development of a Pharmaceutical Oral Solid Dosage Forms’ submitted by Rahamatullah Shaikh, Donal P. O’Brien, Denise M. Croker and Gavin M. Walker (University of Limerick, Ireland), provides a summary of solid oral dosage form development, covering solubility and dissolution kinetics, pKa, excipient types and the standard formulation processes of direct compression as well as wet and dry granulation and capsule filling. This chapter is recommended reading for anyone not familiar with formulation of drug tablets as it provides a well-organised summary helpful in understanding the types of processes modelled in the chapters on continuous manufacturing, flowsheet and unit operation modelling as it relates to drug product.

I have organised this review according to general topics covered rather than by sequential order of the chapters.

Business Model and Optimisation

Chapter 1, ‘New Product Development and Supply Chains in the Pharmaceutical Industry’, contributed by Catherine Azzaro-Pantel (Université de Toulouse, France), introduces the pharmaceutical supply chain and summarises the product life cycle of a drug starting from discovery through clinical trials, registration and commercialisation. This chapter provides a concise summary of clinical trial phases, pre-launch and launch activities and is recommended reading for those not familiar with the pharmaceutical business model and drug development process (Figure 1).

Chapter 21, contributed by Brianna Christian and Selen Cremaschi (Auburn University, USA), covers ‘Planning of Pharmaceutical Clinical Trials Under Outcome Uncertainty’. The authors reference an increase in attrition rates in clinical trials and...
state “the time from discovery to product launch of a drug is around 10–15 years with an average research and development (R&D) cost of about $2.6 billion per drug” as motivating factors driving the need for better clinical trial optimisation. This chapter provides details of a “perfect information” deterministic mixed-integer linear programming model (MILP) problem including constraints. By using an innovative heuristic modification to the stochastic programming model a five order of magnitude improvement is reported.

Chapter 22, ‘Integrated Production Planning and Inventory Management in a Multinational Pharmaceutical Supply Chain’ contributed by Naresh Susarla and Iftekhar A. Karimi (National University of Singapore) presents a MILP model for a complex supply chain and provides a strategy to optimise inventory, resources and production schedules in the supply chain to maximise profit. The intent of the model is as a tool for decision making for “production planning and scenario analysis in a multinational pharmaceutical enterprise”. To mitigate risk associated with the complex, multinational network of supply, drug inventories of 180 days are not atypical. However, high levels of inventory come at a cost. A change introduced in the supply network may have impact on inventories, lead-times and dependencies as impacted by other portions of the supply network. In this chapter the authors describe their approach to this optimisation problem. While looking at the authors’ formulation of their case study problem, the value of working with fewer strategic suppliers in a vertically integrated supply network is evident in that it will minimise the complexity, delay and cost associated with a complex network. A takeaway from this chapter is that pharmaceutical companies can anticipate improved access to software tools to compare the impact of supply chain alternatives as research is translated into commercial software offerings.

### Process Analytical Technology

Chapter 12, ‘PAT for Pharmaceutical Manufacturing Process Involving Solid Dosages Forms’ contributed by Andrés D. Román-Ospino and Ravendra Singh (Rutgers, The State University of New Jersey, USA), Vanessa Cárdenas and Carlos Ortega-Zuñiga (University of Puerto Rico, USA), presents near-infrared (NIR) calibration models and chemometrics. For those not skilled in process analytical technology (PAT) and analytical determination, this chapter is very informative and provides comparison of various methods for analytical data fitting to determine blend uniformity for real-time control of continuous pharmaceutical processes. Principal component analysis (PCA), partial least squares (PLS) and multivariate curve resolution alternating least squares (MCR-ALS) are presented as suitable techniques for multiple parameter determination where linear regression or classical least squares methods are not suitable. Layering of talc and lactose as a specific case study in non-homogeneity is discussed in this chapter. Finally, a process example utilising Unscrambler® X Process Pulse II (Camo Analytics AS, Norway) and NIR (Viavi Solutions Inc, USA) is presented where Unscrambler® X software is utilised to generate and upload a calibration model generated via methods presented in the chapter. In the example the NIR data processing system is
interfaced to a DeltaV™ distributed control system (Emerson Electric Co, USA) to provide real time process control of a tableting process.

Chapter 19, ‘Monitoring and Control of a Continuous Tumble Mixer’ contributed by Carlos Velázquez, Miguel Florian and Leonel Quiñones, (University of Puerto Rico, USA), presents a case study for the mixing of naproxen sodium with excipient using a continous mixer designed by Velázquez. The PAT technology implemented for this case study employed the use of NIR in conjunction with Unscrambler® X in a PAT implementation similar to that described in Chapter 12. The closed-loop control dynamics for the experimental mixer are evaluated. A finding from the study is that a different control scheme is required for very low dosage active pharmaceutical ingredient (API) vs. higher dosages. The authors identified flowrate control of API addition at very low dosage as variable due to poor powder flow properties as well as limitations of the NIR methods employed in low dosage applications.

Chapter 9, ‘Crystallisation Process Monitoring and Control Using Process Analytical Technology’ contributed by Levente L. Simon (Syngenta Crop Protection AG, Switzerland), Elena Simone (University of Leeds, UK) and Kaoutar Abbou Oucherif (Eli Lilly and Co, USA), introduces quality by design (QbD) and reviews online analytical techniques available for crystallisation monitoring and control which include attenuated total reflectance Fourier-transform infrared (ATR-FTIR), Raman spectroscopy, acoustic spectroscopy, conductivity measurement, refractive index measurement, turbidity measurement, focused beam reflectance measurement (FBRM) and particle vision and measurement (PVM).

Automated direct nucleation control (ADNC) along with polymorph determination and control via Raman and attenuated total reflectance ultraviolet (ATR-UV) spectroscopy are presented for batch and continuous crystallisation processes. The ADNC method involves heating and cooling cycles to control crystal count as measured by FBRM to a specified target. In the batch implementation, after initial nucleation, the system automatically heats to dissolve fines and heating and cooling cycles proceed until the crystallisation endpoint (low solution concentration). An advantage of this method is that from PAT data collected, the metastable zone width (MSZW) and solubility curves may be constructed. Since solubility curves are not required prior to running ADNC experiments, this method is useful for process development.

An interesting adaptation of the ADNC method to a two-stage continuous mixed-suspension mixed-product removal (MSMPR) crystalliser system is an innovation by Yang et al. (1) where heating and cooling is performed on the jacket of a wet mill while the MSMPR crystalliser is maintained at constant temperature. The MSMPR with wet mill achieves both form control and FBRM particle count control under continuous flow operation.

**Continuous Drug Product Manufacturing (Downstream)**

Chapter 5, ‘Flowsheet Modeling of a Continuous Direct Compression Process’ contributed by Seongkyu Yoon, Shaun Galbraith, Bumjoon Cha and Huolong Liu (The University of Massachusetts Lowell, USA), summarises the scope of individual unit operation models for continuous powder blending, powder feeding (and potency control), tablet press, feed frame and tablet compaction. The authors highlight both a population balance model (PBM) as well as a stirred-tanks-in-series modelling approach to blending. The value of the modelling is in being able to accurately predict the response of perturbations on key quality attributes of finished tablets. An accurate system-wide process model allows implementation of both feedback and feedforward (predictive) control methodologies which can be developed and tested offline, provided that the underlying unit operation models are accurate. Modelling will facilitate development of continuous direct compression (CDC) processes and control schemes for CDC, where elimination of granulation results in simpler, less expensive processes.

Chapter 6, ‘Applications of a Plant-Wide Dynamic Model of an Integrated Continuous Pharmaceutical Plant: Design of the Recycle in the Case of Multiple Impurities’ submitted by Brahim Benyahia (Loughborough University, UK), takes the continuous methodology described in Chapter 5 a step further by integrating the chemical synthesis steps (upstream) with the formulation and tableting steps (downstream) into a single continuous flowsheet. Of interest is the impact of wash-factor (i.e. wash volumes) and recycle (purge ratio) on the quantity of in-specification product produced. The recycle of wash streams is not often performed in batch API but in continuous processing this recycle provides potential for optimisation and cost savings. The evaluation of
wash factors and their limits as potential critical process parameters (CPP) is performed following a model-driven QbD approach. In the case study presented, plant dynamics are compared for both full purge and full recycle purge ratios.

**Process Control**

Chapter 11 ‘Process Dynamics and Control of API Manufacturing and Purification Processes’ submitted by Maitraye Sen, Ravendra Singh and Rohit Ramachandran (Rutgers, The State University of New Jersey, USA) introduces a hybrid model predictive control/proportional-integral-derivative (MPC-PID) controller in which a single model based controller coupled with one PID temperature controller replaced four separate PID controllers in a continuous API/pharmaceutical intermediate process comprised of crystallisation, filtration, drying and excipient blending operations. PBM and discrete element method (DEM) methods were utilised to model the process while PCA was used to generate a reduced-order model for use by the model predictive controller. Various control schemes can be tested and optimised entirely in silico allowing investigations of system or controller response to transient conditions and process upsets to be investigated. The authors used MATLAB® (MathWorks Inc, USA) to fit data resulting from process simulations to transfer functions useful for model predictive control. gPROMS® (Process Systems Enterprise Ltd, UK) was utilised for PBM calculations and EDEM® (DEM Solutions Ltd, UK) was used to simulate the DEM model.

Chapter 13, ‘Model-Based Control System Design and Evaluation for Continuous Tablet Manufacturing Processes (via Direct Compaction, via Roller Compaction, via Wet Granulation)’ contributed by one of the editors of the volume, Ravendra Singh (Rutgers, The State University of New Jersey, USA), is a review of model-based control for a formulation process which includes blending, granulation, roller compaction, milling and tabletting. For the case study in Chapter 13, a PBM is employed in gPROMS®, but this time for the roller compactor. Unlike the example in Chapter 11, the API crystallisation, isolation and drying steps are not included as API is taken as the input and blended with excipients prior to granulation.

Chapter 7, ‘Advanced Multiphase Hybrid Model Development of Fluidized Bed Wet Granulation Processes’ submitted by Ashutosh Tamrakar, Dheeraj R. Devarampally and Rohit Ramachandran (Rutgers, The State University of New Jersey, USA), implements a hybrid computational fluid dynamics (CFD)/DEM approach to model the coupled behaviour of fluid flow and collisions. The authors transfer data from their CFD-DEM model to a PBM to provide resulting distributions from the granulation process. The DEM-CFD-PBM approach considers residence time in the spray zone, particle collision frequency, aggregation, attrition, particle temperatures and fluid/particle velocities. Residence time in the two zones (spray zone and drying zone) is impacted by fluid flow within the zones and the passing of particles between zones as modelled via CFD-DEM. Results from the CFD-DEM runs are exported to the PBM to investigate sensitivity to inlet gas temperature and gas flow rate. Excellent fit of experimental data from the fluid bed granulator is achieved.

Chapter 15, ‘Advanced Control for the Continuous Dropwise Additive Manufacturing of Pharmaceutical Products’ was contributed by Elçin Içten (Amgen Inc, USA), Gintaras V. Reklaitis and Zoltan K. Nagy (Purdue University, USA). In this chapter the authors describe a system and control methodology for the generation of solid oral dosage forms via a drop on demand (DoD) additive manufacturing technique involving dropwise deposition of API as solvent solution or as solvent/polymer melt (see Figure 2).

The DoD system is particularly useful for generation of personalised medicine for highly potent (low dosage) products. The authors present a control scheme based on image analysis of each drop and investigate various cooling profiles for the substrate (tablets). The authors present a polynomial chaos expansion (PCE) surrogate model for prediction of crystallisation, total dosage and product attributes as a function of drop attributes and cooling profile. The PCE model provides a QbD approach for predictive performance of the tablets’ release profile.

Chapters 16–18 present case studies for automation of continuous pharmaceutical process plants where process control is the focus. Chapters 17 and 18 have a bit of redundancy with Chapter 13 as all three chapters are based on a series of published articles by one of the editors of the volume, Ravendra Singh. Chapter 18 is focused on formulation without granulation but with a control scheme to control tablet hardness by controlling tablet press punch depth and real-time measurement of bulk density is used in a feedforward control scheme. Detailed discussion of the control hardware, sensors and control algorithms for the pilot plant is presented.
in Chapter 17. Process modelling allows complex system dynamics, interactions and control schemes to be investigated and optimised in silico, as enabling technology in the development of robust continuous drug manufacturing processes.

**Small Molecule Upstream**

Chapter 3, 'Innovative Process Development and Production Concepts for Small-Molecule API Manufacturing', contributed by John M. Woodley (Technical University of Denmark), summarises innovations in process systems engineering used to facilitate process development and optimisation. After a viable process model is developed, 'virtual experimentation' may be used to better focus benchtop experiments. Alternative routes and separation schemes can be evaluated if physical property data is available. The CAPEC-PROCESS Industrial Consortium (now the Process and Systems Engineering Centre (PROSYS)) at the Technical University of Denmark has contributed to the generation of physical property estimation methods to address this need.

The author describes use of template processes in which processes under development are fit to a template scheme based on conditions known to work for similar processes. For instance, a reaction step is evaluated against a process template for which simulation and laboratory models already exist (Figure 3). The sufficiency of the template is tested and then the process is optimised using modelling tools already developed for the template process. The author notes that while the template process approach may only be adaptable to 80% of process candidates, for those processes which are adapted, existing knowledge may be leveraged in the development of the new process. Process templating is a powerful tool in the application of PSE models for process integration and intensification and may be useful in evaluating process scheme alternatives.

![Diagram: Conventional development vs Template approach](https://doi.org/10.1595/205651319X15680343765046)

**Fig. 3.** Concept of template process to accelerate process development. Copyright (2018). Reprinted with permission from Elsevier
when an API synthetic scheme involves multiple transformations.

Chapter 4, ‘Plantwide Technoeconomic Analysis and Separation Solvent Selection for Continuous Pharmaceutical Manufacturing: Ibuprofen, Artemisinin, and Diphenhydramine’ contributed by Samir A. Diab, Hikaru G. Jolliffe and Dimitrios I. Gerogiorgis (University of Edinburgh, UK), provides an evaluation of continuous separation steps vs. their batch separation counterparts. The authors noted that for the three continuous API processes evaluated by others, the evaluations had focused on performing the chemistry steps continuously and had not implemented continuous separation steps. As shown in Figure 4, the authors present a continuous liquid-liquid extraction (LLE) separation scheme as a replacement for the batch scheme found in the literature for ibuprofen (IBU). In addition, the authors evaluated additional solvents including n-heptane, cyclohexane, methylcyclohexane and isooctane and found many of the solvent choices to be suitable when a continuous LLE process is used vs. a continuous process. Using process modelling, the efficiencies of separation, the quantities of solvent and an economic comparison of alternative solvents are presented. For a continuous IBU extraction using heptane, the authors project capital savings of 58% and operating savings greater than 50% vs. the batch process utilising diethylether. The case studies presented in this chapter are based on process simulations performed by the authors and not on actual laboratory data. While it does not validate a final solvent choice, the use and conclusions based on simulation data highlight the value of a modelling-based approach to selecting workup or extraction solvents with environmental, flammability and regulatory suitability.

Conclusions

"Process Systems Engineering for Pharmaceutical Manufacturing" is a diverse collection of reviews and case studies, most of which were published previously. While this book provides an excellent summary of process modelling and computing with a view to the increased importance of robust simulation tools in pharmaceutical process development and manufacturing, more recent
journal publications may provide additional or more in-depth information on the current state of specific technologies or algorithms described in the book. It is also evident that much of the key work in these areas has yet to be done. One topic missing from discussion in the book is the advent of quantum computing and the potential quantum computing presents in solving optimisation problems in process systems engineering. I would look forward to seeing an additional volume added to the series as the technology develops.

References


The Reviewer

Michael Hamlin joined Johnson Matthey in November 2016 as Assistant Director, Processes Engineering at Johnson Matthey’s Devens Research Centre in Devens, MA, USA where he leads the engineering group working to establish a particle engineering capability in Devens. Prior to joining Johnson Matthey, Mike worked in engineering roles in both fine chemicals and contract pharmaceuticals for more than 20 years. Mike received a BS degree in Chemical Engineering from Bucknell University in Lewisburg, PA, USA.
Intensified Liquid-Liquid Extraction Technologies in Small Channels: A Review

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Solvent extraction is a key separation process in several industries. Mixer-settlers and agitated or pulsed columns are mainly used as liquid-liquid contactors. However, these units require large solvent inventories and long residence times, while flow fields are often not uniform and mixing is poor. These drawbacks can be overcome with process intensification approaches where small channel extractors are used instead. The reduced volumes of small units in association with the increased efficiencies facilitate the use of novel, often expensive, but more efficient and environmentally friendly solvents, such as ionic liquids. The small throughputs of intensified contactors, however, can limit their full usage in industrial applications, thus robust scale-up strategies need to be developed. This paper reviews promising intensified technologies for liquid-liquid extractions based on small channels. In particular, extractions in single channels and in confined impinging jets are considered. The increase in throughput via scale-out approaches with appropriate manifolds is discussed, based on the use of many channels in parallel. The combination of small channels and centrifugal forces is exploited in counter-current chromatography (CCC) systems where many mixing and settling steps are combined within the contactors. Scale up is possible via centrifugal partition chromatography (CPC) configurations.

1. Process Intensification

Process intensification (PI) is a design framework which aims to create smaller, safer and more efficient processes. There have been many reviews on process intensification and attempts to define it since its inception over 20 years ago. Process intensification approaches often involve the reduction in the size of the process units to increase heat and mass transfer rates and, in multiphase processes, to manipulate and control the flow patterns and increase the interfacial areas. The benefits of operating in small scale units stem from the thin fluidic films and the decreased diffusion distances, which increase the heat and mass transfer rates resulting in homogeneous concentration and temperature fields. Residence times can be shortened, thus avoiding side reactions, increasing selectivity and reducing waste. The decrease in length scales also increases the importance of surface or interfacial forces over inertial, viscous and gravitational ones; as a result, flow patterns in two-phase systems tend to be regular. Channel walls with different wettabilities can be fabricated to separate two-phase mixtures or impose certain patterns in the channels. The large interfacial area-to-volume ratios benefit mass transfer, while the large channel surface-to-volume ratios improve heat transfer. Flows are laminar in
many cases and, combined with the regular flow patterns, can be modelled more easily. The small volumes reduce the risks of handling hazardous materials, while accidents are better contained. Intensification is often linked to continuous flow processing. The homogeneous conditions in channels facilitate monitoring and allow modularity where the process steps are separated by controlling, for example, the temperature or the addition of reactants along the channel.

Processes involving two immiscible liquids are widespread industrially and intensification has already been shown to benefit emulsifications (1–3) and reactions including hydrogen peroxide oxidations and (trans-)esterifications (4, 5). Among two-phase liquid processes, extractions are commonly used for the separation of materials in, among others, the pharmaceutical (proteins, antibiotics in aqueous two-phase systems), energy (uranium in nuclear spent fuel reprocessing; carbon dioxide or hydrogen sulfide removal) and mining (copper and precious metals) sectors (6, 7). Industrially, extractions are carried out in mixer settler units or pulsed columns which suffer from inhomogeneous and not well-characterised flow fields and large inventories. Intensified approaches have already been applied in the extraction of bio-based chemical precursors (8, 9), transition metals (10) including platinum group metals (11), lanthanides (12, 13) and actinides (14, 15), acetone in toluene-water systems (16–18). Because of the improved efficiency and reduced volumes of the small units, the amount of solvent required is reduced; this paves the way for the use of novel, efficient but sometimes expensive solvents (such as ionic liquids). In addition, external fields such as centrifugal, magnetic and ultrasonic can easily be applied to improve mixing, separation or reaction rates. The majority of the intensified demonstrations are in single channels. For industrial applications it is necessary to increase throughput by increasing the number of channels, which is presently a major challenge.

In what follows, liquid-liquid extractions in intensified small-scale contactors are reviewed. These include extractions in single channels and in confined impinging jets cells as well as approaches to increase throughput via scale out, where many parallel channels are combined with appropriate manifolds. Developments on the use of centrifugal forces to enhance separations in small channels in CCC systems are discussed. The combination of intensified technologies with novel ionic liquid solvents is also considered.

2. Extractions in Small Channels

When two immiscible liquids flow together in small channels, many flow patterns can form, ranging from segmented to annular and dispersed flows, as can be seen in the example in Figure 1. Parallel flows, where the two liquids flow in continuous layers next to each other, can also occur, usually by modifying either the wetting properties or the geometry of the channel walls. The segmented, plug or slug flow pattern has been extensively studied because it appears for a wide range of phase flow rates and has been linked to high mass transfer rates. In this pattern, the dispersed phase moves as drops with size larger than the channel diameter (plugs) separated by slugs of the continuous phase (see Figure 1). Usually, there is a thin film of the continuous phase between the plugs and the channel wall. As the film is usually very thin, axial dispersion is limited. In addition, within each phase, circulation patterns are established which improve radial mixing (see Figure 2). As a result, a plug-flow reactor configuration establishes with improved radial and decreased axial mixing that ensures uniform residence times for the reactants.

In the small channel contactors, the flow characteristics and the mass transfer performance are closely related. The plug and slug lengths
determine not only the interfacial area but also the mixing characteristics within the two phases. Apart from the flow rate ratio and the properties of the two phases, the plug and slug lengths depend significantly on the geometry of the inlet. Plug lengths have been reported by many investigators (19, 20) but there is no single model to predict them a priori.

Interfacial areas can be calculated from the measured plug and slug lengths and shapes of the front and back ends of the plugs. It has been found that the specific interfacial area (interfacial area per unit volume of the contactor) depends on the channel diameter, the flow rate ratio, the total velocity and the inlet geometry. Interfacial areas ranging from 2760 m$^{-2}$ m$^{-3}$ to 4800 m$^{-2}$ m$^{-3}$ in 0.5 mm, 0.75 mm and 1 mm internal diameter (ID) channels have been reported by Kashid et al. (21), whilst Li and Angeli (13) measured specific interfacial areas up to 8500 m$^{-2}$ m$^{-3}$ for smaller channels of 0.2 mm ID, using high-speed imaging. In larger channels, with a diameter of 4 mm, the specific interfacial area decreased to values up to 880 m$^{-2}$ m$^{-3}$. The circulation times within the plugs or slugs can be calculated when the velocity fields in the phases are known. Velocity field measurements have been carried out with particle image velocimetry (PIV) (22) or predicted from computational fluid dynamics (CFD) simulations (23). The results have shown that mixing is improved as the velocity increases and the plug and slug lengths decrease.

Segmented flow contactors have been used for many liquid-liquid mass transfer and reaction operations. In the case of fast reactions, the overall rate of the process is primarily controlled by the rate of mass transfer and microreactors have been shown to intensify processes. A typical example is the transesterification reaction of vegetable oils to produce biodiesel, where yields over 90% can be achieved under 30 s residence time in 240 µm hydraulic diameter channels (24). Regarding liquid-liquid metal extractions, combined with ionic liquids as the solvent phase, microchannels have been applied to the separation of uranium (25) and europium (13) for spent nuclear fuel reprocessing and for analysis in nuclear waste management. Channel sizes between 0.2 mm and 2 mm were used and extraction efficiencies >80% were achieved in <30 s. Pedersen et al. (26) achieved separation >90% of titanium-45 for use in positron imaging in less than 15 s in 0.75 mm perfluoroalkoxy (PFA) tubing.

The overall volumetric mass transfer coefficient for a solute being transferred from the aqueous to the organic phase is given by Equation (i) (15):

$$k_l \alpha = \varepsilon_{aq} \frac{1}{\tau_2 - \tau_1} \ln \left( \frac{C_{aq,eq} - C_{aq,init}}{C_{aq,eq} - C_{aq,fin}} \right)$$

where $\varepsilon_{aq}$ is the volume fraction of the aqueous phase, $C_{aq,eq}$ is the concentration of the solute in the aqueous phase at equilibrium, $C_{aq,init}$ is the concentration of the solute in the aqueous phase at residence time $\tau_1$ and $C_{aq,fin}$ is the concentration of the solute in the aqueous phase at residence time $\tau_2$.

High-value precious metals such as platinum and palladium have also been extracted using intensified contactors. Yin et al. (11) and Kriel et al. (27, 28) extracted high-value metals (Pt, Pd) using parallel flow contactors. These metals are often found in mixtures at low concentrations (for example, from spent automotive catalysts) and their extraction may not be economic using conventional devices. In particular, Kriel et al. (27) demonstrated the extraction, scrub and stripping processes in flow channels with overall recovery rates over 95%. By modelling the flowsheet of spent nuclear fuel reprocessing using intensified extractors for the first time, Bascone et al. (29) showed important reductions in solvent use and in radiolytic degradation.

To increase throughput, large channel sizes should be considered that still preserve the benefits of small-scale operations, such as thin fluid films and enhanced heat and mass transfer rates. The extraction efficiencies and the volumetric mass transfer coefficients for channels between 0.5 mm and 4 mm ID were measured by Tsoulidis and Angeli (25) and $k_l \alpha$ as high as 0.06 s$^{-1}$ were found, even at the largest channels. The $k_l \alpha$ increased as the channel diameter decreased. In smaller channels, however, the pressure drop increased and the throughput decreased. There is, therefore, a trade-off between mass transfer performance, throughput and energy requirements which needs to be carefully considered when designing plug flow separators.
To integrate the small channel extractors with the rest of the process, the separation of the two phases at the end of the channel should be considered. In small channels, wettability and interfacial effects are important and have been successfully implemented for the separation of the organic and aqueous phases. Separators with side channels or membranes that are preferentially wetted by the organic or aqueous phases have been tested. Currently, however, there are few commercially available options (for example, Zaiput Flow Technologies, USA); for parallel processing with many channels (see Section 4 below) the separator capital costs would scale linearly with the number of channels. Alternatively, gravity separators can still be used for systems with high throughput and sufficient density difference (>0.1 g cm\(^{-3}\), (30)). In gravity settlers, however, the mass transfer between the phases can continue and diminishes the benefits of well-controlled conditions of the small channel.

3. Intensified Impinging Jets Cells

An alternative option for increasing throughput in small channels is to increase the velocities of the two fluidic streams in an impinging jets inlet configuration. In recent years, there has been a renewed interest in using confined impinging jets reactors (CIJR) for many applications, such as crystallisation (31), nanoparticle synthesis using liquid precipitation (32), micromixing (33), extraction (15) and bioreactions (34). The high energy dissipation rates due to collision and redirection of the fluidic jets in the impingement zone make the contactor particularly suited for applications where rapid mixing of the fluids is necessary. When the two jets are immiscible liquids, then the large energy dissipation rates result in the formation of dispersions. A typical configuration of a cylindrical CIJR at 180° nozzle angle is shown in Figure 3(a).

The mixing and dispersed phase size are affected by a number of geometric characteristics, such as main channel (D) and nozzle (d\(_j\)) size, main channel to nozzle size ratio, inter-nozzle distance (Id), nozzle height and impingement angle. The main challenge in developing confined impinging jets contactors for a particular application is the quantification of the effects of the parameters on the resulting drop sizes. There are many studies on impinging jets with miscible liquids, which demonstrate that for improved mixing the two opposing jets should have similar momentum so that they collide in the middle plane (35). Studies of impinging jets in confined spaces with immiscible liquids are very limited. The

![Fig. 3. (a) Typical configuration of confined impinging jets contactor; (b) photograph of dispersion in the impingement zone; (c) drop size distribution in the main channel (Photograph from (35) Creative Commons Attribution (CC BY))](image-url)
drop size has been related to the energy dissipation rate, while the uniformity of the dispersions depends on the geometric design of the contactor, the phase ratio and the intensity of mixing in the impingement zone (36). The energy dissipation rate \( \varepsilon \) can be described as the ratio of the power available due to kinetic energy change (K) at collision over the mixing volume of the impingement zone \( (V_{iz}) \), according to Equation (ii):

\[
\varepsilon = \frac{K}{pV_{iz}}
\]

where

\[
K \propto \frac{m_1u_1^2 + m_2u_2^2}{2}
\]

and \( m_1 \) and \( m_2 \) are the mass flow rates (kg s\(^{-1}\)) of Phase 1 and Phase 2 respectively, \( u_1 \) and \( u_2 \) are the average velocities of Phase 1 and Phase 2, respectively, and \( p \) is the density of the mixture.

The Sauter mean diameter, given by Equation (iv):

\[
D[3,2] = \frac{\sum d_i^n d_i^3}{\sum d_i^n}
\]

(where \( n \) is the number of drops and \( d_i \) is the diameter of the drop \( i \) in the distribution) has been related to the specific energy dissipation rate as follows (37), Equation (v):

\[
D[3,2] = k_0 \varepsilon ^{-a}
\]

The dependence of the average drop size on the energy dissipation in the impingement zone is presented in Figure 4 for two different aqueous/organic phase systems (15). As can be seen, at low energy dissipation values, the drop size depends on the geometry of the system and the fluid properties, while at larger \( \varepsilon \), above 600 W kg\(^{-1}\), the drop sizes converge. Similar results were also found by Siddiqui (2) for aqueous/organic systems in impinging jets contactors with the addition of emulsifiers, while in less viscous systems a stronger dependence of drop size on energy dissipation rate was observed.

It has been found that the dispersions formed in impinging jets have low polydispersity. Tsaoulidis and Angeli (36) reported polydispersity indices (PdI) as low as 0.05, for an oil/water system, for a wide range of jet velocities from 0.17 m s\(^{-1}\) to 6.2 m s\(^{-1}\). Interfacial area-to-volume ratios were significantly affected by the velocities of the jets and the values varied between 2000 m\(^2\) m\(^{-3}\) and 12,000 m\(^2\) m\(^{-3}\). Siddiqui (2, 3) also reported very narrow drop size distributions in a sunflower oil/water emulsification process with surfactants, for dispersed phase fractions up to 10% and drop sizes less than 10 \( \mu m \).

The few mass transfer studies available have also revealed high mass transfer coefficients compared to other contactors as can be seen in Table I. \( k_0 \alpha \) can be one to two orders of magnitude higher than in conventional contactors and two to three times higher than in microchannels. Values are similar to those of centrifugal contactors, however, the specific power input for centrifugal contactors can be two to three orders of magnitude higher when compared to a confined impinging jets cell (16).

The studies revealed that high mass transfer coefficients were obtained at short residence times (<4 s), with values up to 1 s\(^{-1}\). Several parameters were found to affect mass transfer, including geometric characteristics and flow rate ratio. In Figure 5(a), mass transfer rates were calculated for two different main channel sizes i.e. 2 mm and 3.2 mm. It is shown that \( k_0 \alpha \) depend on channel size at short residence times but are independent of the channel sizes at long times. The 3.2 mm channel should then be preferred because it has higher throughput and reduced pressure drop compared to the 2 mm channel. The mass transfer coefficient also increases with increasing collision velocities of the two jets (shown as the sum of the two velocities, \( u_{tot} \) in Figure 5(b)). The velocity of the liquid jets will define the position of the point of impingement (Figure 6) and will affect the uniformity of the flow pattern in the main channel as well as the drop size distribution.

Impinging jets systems have been used for more than four decades now but it is still not possible to determine accurately the effects of the dominant variables including aspect ratio of jet inlets, dead
volume at the mixing section, fluid properties on the drop size and the mass transfer performance of the contactors.

4. Scale Out of Single Channel Contactors

Harmsen (41) identified four hurdles that any PI innovation must address before it can be implemented industrially. These are: (a) risk of failure by combining novel aspects; (b) scale-up knowledge uncertainty; (c) equipment unreliability; and (d) improved safety, health and environmental risks. The main hurdle faced by single-channel contactors is the scale-up uncertainty. Currently, there are no applications of small-channel extractors at large commercial or pre-commercial scales reported in the literature.

Table I Overall Mass Transfer Coefficients (k\(_{L\alpha}\)) in Intensified and Conventional Contactors

<table>
<thead>
<tr>
<th>Equipment</th>
<th>System</th>
<th>k(_{L\alpha}), s(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensified impinging jets</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Confined impinging jets cell</td>
<td>TBP/kerosene-U-HNO(_3)</td>
<td>0.15–1.05</td>
<td>(15)</td>
</tr>
<tr>
<td>Two impinging jets device</td>
<td>H(_2)O-acetone-toluene</td>
<td>0.001–0.19</td>
<td>(18)</td>
</tr>
<tr>
<td>Impinging jets extractor</td>
<td>Butanol–succinic acid–H(_2)O</td>
<td>0.015–0.2</td>
<td>(16)</td>
</tr>
<tr>
<td><strong>Intensified small channels</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microchannels (D = 0.5–4 mm)</td>
<td>TBP/ionic liquid-U-HNO(_3)</td>
<td>0.05–0.3</td>
<td>(25)</td>
</tr>
<tr>
<td>Centrifugal extractor</td>
<td>Aqueous NaOH-(butyl acetate, iso-amyl acetate, hexyl acetate)</td>
<td>0.2–2</td>
<td>(38)</td>
</tr>
<tr>
<td><strong>Conventional contactors</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixer-settler</td>
<td>NPH-TBP-HNO(_3)</td>
<td>0.5–13.3 (x 10(^{-5}))</td>
<td>(39)</td>
</tr>
<tr>
<td>Rotating disc contactor</td>
<td>Toluene-H(_2)O-acetone</td>
<td>4–9.5 (x 10(^{-3}))</td>
<td>(40)</td>
</tr>
</tbody>
</table>

Fig. 5. Overall volumetric mass transfer coefficient, k\(_{L\alpha}\), as a function of residence time: (a) for two different main channel sizes (D = 3.2 mm, d\(_j\) = 0.25 mm, Id = 3.2 mm; D = 2 mm, d\(_j\) = 0.25 mm, Id = 2 mm); (b) for different total jet velocities u\(_{tot}\) (D = 3.2 mm, d\(_j\) = 0.5 mm, Id = 3.2 mm) (data adapted from Tsaoulidis et al. (15))

Fig. 6. Effect of kinetic energy (K) ratio of the two jets on the flow pattern in the impingement zone
While single small channel flow contactors and reactors are highly efficient, the scale-up of the throughput without losing the small-scale advantages remains a main challenge. Scale-up can be achieved by increasing the number of channels operating in parallel (‘scale out’ or ‘number-up’). It is not trivial, however, to reproduce accurately the flow conditions of a single channel in many parallel ones. The challenge is to design a flow distributor within the process-specific maldistribution tolerance of the total flow rate and of the flow rate ratio of the two phases for each channel.

Scale out for single-phase processes requires a flow distributor that can achieve almost the same flow rate and thus residence time, in all channels. Single-phase flow distributors are commonly encountered in multi-tubular reactors, catalytic converters and other honeycomb catalysts. The distributors usually take one of two forms, bifurcation or consecutive manifolds, as shown in Figure 7. The consecutive manifold has a small footprint compared to the bifurcation one. Approaches based on resistance networks have been used to design manifolds that reduce flow non-uniformities among the channels (42).

In the case of multiphase systems, both the residence time and the flow rate ratio of the two phases are critical for the performance of the process and should be constant among the many channels of the manifold. There are two types of two-phase flow distributors: split-combine and combine-split.

![Fig. 7. Schematics of: (a) a consecutive manifold; (b) a bifurcation manifold](image)

![Fig. 8. Multiphase flow distribution strategies: (a) split-combine, where both phases are distributed separately and then brought into contact; (b) combine-split, where the phases are brought together first and then the two-phase flow is split into several channels](image)
5. Counter-Current Chromatography using Ionic Liquid Solvent Systems

A promising intensified separation technology is high-performance CCC. It is a form of liquid-liquid extraction that achieves separation by repeated partitioning of solutes between two immiscible liquid phases, as they interact in a continuous length of coiled tubing under centrifugal and Archimedean forces. The tubing is wrapped around a cylindrical drum (called a bobbin) to form typically a three-dimensional (3D) helical configuration with one or several layers. Within the CCC column, one of the liquid phases is held stationary by a combination of hydrodynamic and hydrostatic forces generated as a result of rotating the column in planetary motion, while the other mobile phase is continuously pumped through the coil and serves to transport the solutes through the system. The J-type CCC is the most commonly used, where the bobbin is mounted on a planetary axis, driven by a central axis so that the column rotates about its own axis while it revolves around the central axis at the same velocity in the same direction (*Figure 9(a)*). The double rotation of the column during its planetary motion produces a variable centrifugal force field. This force field creates a unique mixing pattern in which a series of sequential mixing and settling zones are generated simultaneously along the length of the column. These alternating mixing and settling steps are essential to the chromatographic process as they promote solute transfer between the phases and therefore, separation of species with different partition coefficients.

In the last decade, the use of ionic liquids either as solvents or additives in liquid-liquid extractions has expanded considerably because of their unique properties. Ionic liquids are organic salts that are liquid at room temperature. The stability, phase behaviour and greater solvating power of ionic liquids, together with the ability to design their structure, can increase both the flexibility and performance of separations and allow separations that were not previously considered possible. The combination of the two technologies, ionic liquids and CCC, therefore represents an exciting approach to intensified liquid-liquid separations. However, the use of ionic liquids in CCC is not a trivial task due to their relatively high viscosities, which can introduce significant problems for the majority of traditional CCC machines that are mostly low pressure. To overcome the pressure limitations previously encountered using the CCC technique, AECS-QuikPrep™ Ltd, UK in collaboration with the QUILL Research Centre have reported on the design and construction of a modified high backpressure CCC instrument (*Figure 9(b)*). The high solvating power of ionic liquids allows separations to be run at very high sample loadings which gives rise to high space-time yields for ionic liquid and CCC separations. The ability to custom design ionic liquids allows a greater range of mobile phases to be employed and enables separations

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*Fig. 9. (a) Schematics of the operation of a J-type countercurrent chromatographic column showing the coil layout and motion from as viewed from the front (left) and from the side (right); (b) The inside view of the chromatographic coil in the AECS IL-Prep instrument*
with pH neutral water as the mobile phase, where previously toxic organic solvents (such as acetonitrile), concentrated salt solutions (such as aqueous di potassium phosphate), polymers (such as polyethylene glycol) or acids (such as nitric acid) were used. Scale up can be achieved with the increased capacity CPC instrument (46). Ionic liquids have been applied successfully as a major solvent system component for a wide range of separations (47–49) including:

(a) Inorganic metal salt separations (cobalt chloride from nickel chloride from copper chloride) and more recently praseodymium(III) nitrate from erbium(III) nitrate both with water as the mobile phase

(b) Separation of saccharides such as glucose from sucrose and fructose from sucrose

(c) The extraction of aromatic compounds from alkanes (such as cumene from hexane)

(d) The separation of fatty acid derivatives.

The combination of ionic liquids with CCC has been successfully used in the separation of the anticancer drug lentinan at a scale 10–100 times the scales of earlier separations (50). Lentinan is found in shiitake mushrooms (Lentinus edodes) and is used as an adjunct to therapy in combination with chemotherapeutic drugs such as fluorouracil to modulate the body’s immune system activity. Lentinan naturally exists in water and salt solutions but is easily denatured by solvents. This means that for the isolation and purification process of lentinan, water based solvent systems are required. The conventional purification of lentinan normally involves up to 10 steps. An ionic liquid-based aqueous biphasic solvent system (ABSS) was developed using 1-\textit{n}-butyl-3-methylimidazolium salts [C\text{4}mim]Cl / 2.5 M K\text{2}[HPO\text{4}]\text{aq} (1:1) mixture (51), which allowed lentinan separations on the 1–3 g scale, without denaturing the lentinan. This CCC process used aqueous [C\text{4}mim]Cl as the mobile phase and the lentinan was separated from the [C\text{4}mim]Cl solution by the addition of ethanol to the [C\text{4}mim]Cl phase. The [C\text{4}mim]Cl can be recovered and reused after the lentinan has been precipitated. The ethanol can also be recovered by evaporation allowing it to be reused. This leads to a separation process that does not consume solvents or reagents.

An improved lentinan process has also been developed with a novel ABSS based on microemulsions. Surface active ionic liquids such as 1-dodecyl-3-methylimidazolium di(isooctyl)phosphinate ([C\text{12}mim][DiIOP]), when mixed with water and hexane produce a water immiscible microemulsion phase, which contains 75 mol\% water (Figure 10). The aqueous phase is composed of >99\% water, which allows water to be used as the mobile phase in CCC separations, with the microemulsion as the stationary phase. This greatly simplifies product isolation since the product does not end up mixed with large quantities of involatile chromatography solvent constituents. Also, this approach does not produce any solvent waste (other than water) making this a very green and inexpensive separation to run. The full lentinan process takes the freeze dried hot water extract of shiitake mushrooms (Figure 11(a)) and precipitates lentinan from this crude extract dissolved in [C\text{4}mim]Cl, using ethanol. The precipitated 80\% lentinan (Figure 11(b)) is then purified with the water-microemulsion solvent system shown in Figure 10 to give the off-white 95\% lentinan shown in Figure 11(c) on the 25 g per run scale. Recent industrial uses of CCC and CPC instruments are in the refining of galantamine from daffodils (for example, BioExtractions (Wales) Ltd, UK) or the red spider lily (52), the purification of cannabinoids and metal ion separations associated with the nuclear industry.

6. Conclusions

Liquid-liquid extractions are widely used for the separation and purification of many compounds. Small channels (up to 4 mm in diameter) and a combination with external fields, such as
centrifugal forces, can significantly intensify the process by reducing residence times, improving extraction and extraction efficiencies and reducing the amount of solvent required. Mass transfer coefficients up to 1 s\(^{-1}\) have been measured in the impinging jet contactors. These characteristics have made possible the implementation of novel and often expensive solvents such as ionic liquids with significant improvements to the separation. Droplet-based flows (dispersed or plug flow patterns) in particular have been shown to enhance mass transfer and increase interfacial areas. However, the throughputs are small and scale out would be required before they can be applied to industry. On the other hand, the fast mass transfer rates and well-characterised flow patterns render small channels suitable for analysis and for research on new extractants. Impinging jets have increased throughputs and can produce dispersions with narrow size distribution and large interfacial areas. CCC devices with alternating mixing and settling steps allow separation of species with different partition coefficients and have been used to optimise solvent systems and conditions for separations. High throughputs can be achieved with the increased capacity CPC which has simpler rotor design and fewer moving parts compared to CCC (46, 53).

At small scales, the contactor geometry significantly affects the flow and mass transfer characteristics. Possibilities are open for novel contactor designs that exploit interfacial and wettability effects to establish desirable flow patterns and enhance mass transfer. For the commercial application of the technology in production, robust scale-out designs for two-phase systems need to be further developed and the sensitivity of their performance against flow maldistribution needs to be tested.

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References

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