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# **New and advanced materials**

**Future of Manufacturing Project: Evidence Paper 10**

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# **New and advanced materials**

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# **Chemistry input into the manufacturing of novel materials and future trends in food manufacturing**

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# **Section A: New and advanced materials**





















and synthetic biological and biomimetic approaches to new materials, such as those currently being explored for synthetic spider silk (Vollrath and Knight, 2001; Porter, Guan and Vollrath, 2013).

Large-scale manufacturing of bio-derived materials presents some interesting aspects: the front-end of the supply chain is familiar with mass production (harvesting) and the large scale movement and storage of raw materials, but is completely unfamiliar with materials-related specifications, and the yield of useable materials from bio-feedstocks for structural applications at large-scale is not yet well-understood.

## 3. Materials for energy

One of the greatest challenges facing society in the 21st century is the provision of a clean, safe, secure and sustainable energy supply to underpin a reasonable standard of living for the world's population. The materials needed to meet this challenge are considered here in terms of fossil fuel and nuclear power generation, renewable power generation, energy storage, and electricity transmission. Not all technologies and materials are discussed, only those where significant challenges exist or major developments might be expected in the context of materials manufacture.

### 3.1 Fossil fuel and nuclear power generation

Structural materials for land-based gas turbines and steam turbines will evolve incrementally, with most emphasis on extended operating life and increased environmental resistance. The turbine diameter and turbine inlet temperature will continue to increase in order to drive up energy efficiencies, producing a complex competition between generally lightweight materials for the former (titanium alloys) and stronger but usually denser materials (steel and nickel alloys) for the latter. In the aerospace sector, acute emphasis on elevated operating temperature to recover improved fuel efficiencies may herald the widespread use of structural ceramic-based composites in the turbine. The problems in successfully introducing these materials are significant, and will require advances in environmental resistance, understanding of how to design with strongly anisotropic properties, assuring minimised manufacturing defects, and developing new lifing strategies. Although the UK is strong in aerospace materials, UK capability in high temperature ceramic composites should be strengthened for these potentially step-change materials that are being pursued with more vigour elsewhere.

For solid oxide fuel cells to secure a greater role in future energy generation technologies, materials must be developed for extended high temperature environmental resistance including insulators, conductors and in particular, the functional ceramics for the electrodes, which typically contain rare earth elements such as yttrium, cerium and lanthanum. The key for improved electrodes will be the development of composite and multi-layered ceramic based materials that meet the balance of properties for ionic conductivity, electronic conductivity, catalytic activity and tolerance to impurities and defects (Atkinson et al., 2004).

In all high temperature and extreme environments in power generation, protective coatings will continue to play a vital role in extending operating windows and lifetimes, the foremost of which will be incremental improvements in corrosion and oxidation resistance, thermal barrier coatings, tribological and wear resistant coatings. More dramatic improvements in performance maybe enabled by graded and layer-by-layer coatings, and the embedding of nano-scale materials throughout or locally within coatings (for example by atomic layer deposition or variants thereof) that can be used as indicators to signal stress conditions, extent of oxidation, etc.

Materials developments in the oil and gas sector will focus on adapting sensor and structural health monitoring approaches for the aggressive marine and down-hole environment (vibration, high pressure, elevated temperature, corrosion, etc.), with the most valuable opportunities in new materials and designs for high temperature electronics and passive components that enable down-hole telemetry and sensing.



Coatings for corrosion and environmental protection already represent a huge annual investment for the sector and future developments will include smart coating systems and self-healing coatings, which will be challenged in particular by an increasing fraction of deep-water operations where reliable remote operation is paramount. Membrane technology for separation, especially for oil and water separation, but also for a host of other separation requirements offers many new materials-manufacturing opportunities, for example new approaches to produce large area, graded and highly selective separation membranes.

For nuclear fission based power generation, near term efforts will concern life extension supported by developments in non-destructive inspection, and improvements in basic understanding of the damage mechanisms under the combined conditions of prolonged neutron bombardment, corrosion and elevated temperature stress and strain (Materials UK, 2010). Foremost in developing this understanding will be theoretical and modelling approaches, particularly in understanding the inter-play between alloy impurities and their segregation behaviour and embrittling effects of neutron bombardment through the formation of vacancies, dislocations and helium that leads to swelling. Although this is a long-standing problem in nuclear materials, accelerating progress in understanding can be expected by combining advances in high resolution materials characterisation to resolve the earliest, near-atomic scale stages of defect generation, and faster, cheaper and more rigorous simulations. This understanding will be applied in support of plant life extension of the UK's current Generation II power plants, and design and selection of incrementally improved ferrous and other alloys for new build reactors.

The next 40 years is likely to see the progression of advanced fission reactor concepts, generally termed Generation III+ or Generation IV, and Table 1 shows a summary of these design comments, some of the critical operating conditions and the main materials classes proposed (Zinkle and Was, 2013). Materials developments will be incremental in the reactor and cooling systems, but there remains considerable scope to improve the quality assurance and manufacturing reproducibility in material joining techniques, including more use of real-time diagnostics and feedback control, measurement and relief of residual stresses, and new variants of friction welding.

**Table 1: Reactor core environment and materials for light water reactors and advanced fission reactor concepts** (Zinkle and Was, 2013).

System	Coolant	Pressure (MPa)	$T_{in}/T_{out}$ (°C)	Neutron spectrum, maximum dose (dpa)	Fuel	Cladding	Structural materials	
							In-core	Out-of-core
Pressurized water reactor – PWR	Water – single phase	16	290/320	Thermal, ~80	UO <sub>2</sub> (or MOX)	Zirconium alloy	Stainless steels, nickel-based alloys	Stainless steels, nickel-based alloys
Boiling water reactor – BWR	Water – two phase	7	280/288	Thermal, ~7	UO <sub>2</sub> (or MOX)	Zircaloy	Stainless steels, nickel-based alloys	Stainless steels, nickel-based alloys
Supercritical water cooled reactor – SCWR	Supercritical water	25	290/600	Thermal, ~30, fast, ~70	UO <sub>2</sub>	F-M (12Cr, 9Cr, etc.) (Fe–35Ni–25Cr–0.3Ti), Incoloy 800, ODS, Inconel 690, 625, and 718	Same as cladding options, plus low swelling stainless steels	F-M, low-alloy steels
Very high temperature reactor – VHTR	Helium	7	600/1000	Thermal, <20	UO <sub>2</sub> , UCO	SiC or ZrC coating and surrounding graphite	Graphites, PyC, SiC, ZrC, vessel: F-M	Ni-based superalloys, 32Ni–25Cr–20Fe–12.5W–0.05C, Ni–23Cr–18W–0.2C, F-M w/thermal barriers, low-alloy steels
Gas fast reactor – GFR	Helium, supercritical CO <sub>2</sub>	7	450/850	Fast, 80	MC	Ceramic	Refractory metals and alloys, Ceramics, ODS, vessel: F-M	Ni-based superalloys, 32Ni–25Cr–20Fe–12.5W–0.05C, Ni–23Cr–18W–0.2C, F-M w/therm barriers
Sodium fast reactor – SFR	Sodium	0.1	370/550	Fast, 200	MOX or U–Pu–Zr or MC or MN	F-M or F-M ODS	F-M ducts, 316SS grid plate	Ferritics, austenitics
Lead fast reactor – LFR	Lead or lead–bismuth	0.1	600/800	Fast, 150	MN	High-Si F-M, ODS, ceramics, or refractory alloys		High-Si austenitics, ceramics, or refractory alloys
Molten salt reactor – MSR	Molten salt, for example: FLiNaK	0.1	700/1000	Thermal, 200	Salt	Not applicable	Ceramics, refractory metals, Mo, Ni-alloys, (e.g., INOR-8), graphite, Hastelloy N	High-Mo, Ni-based alloys (e.g., INOR-8)

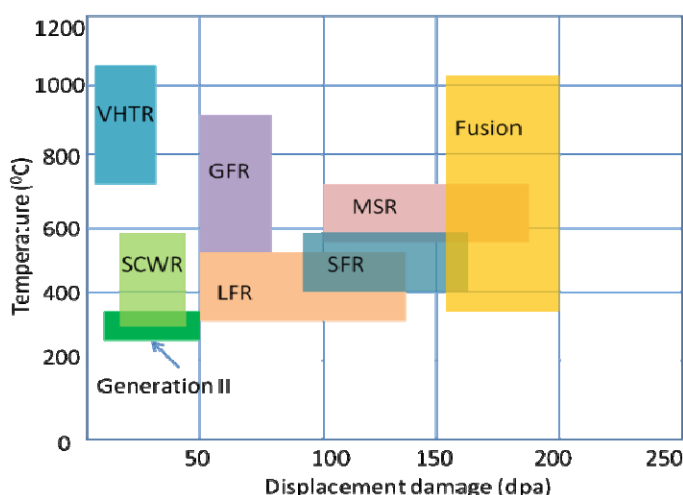
*Abbreviations:* F-M, Ferritic–martensitic stainless steels (typically 9–12 wt.% Cr); ODS, oxide dispersion-strengthened steels (typically ferritic–martensitic); MC, mixed carbide (U,Pu)C; MN, mixed nitride (U,Pu)N; MOX, mixed oxide (U,Pu)O<sub>2</sub>.

Table 1 shows that neutron induced damaged (quantified as displacements per atom due to neutron bombardment) increases from current levels of ~10 dpa up to 200 dpa with new reactor generations, combined with predicted increases in temperature, the combinations of which are also shown in Figure 2.

Of the various current and future materials required to enable these designs in Table 1, oxide dispersion strengthened (ODS) alloys play a key role. In these alloys, superior performance over conventional equivalents derives from nano-sized oxide dispersoids that act at low volume fraction (<1 vol%) to both strengthen and act as sinks for radiation damage. Although these alloys are comparatively well-studied at small scale, scope for further innovation remains: the nano-scale processes that control the critical dissolution and precipitation of the nano-oxide clusters and how they interact with various defects is yet to be fully resolved; perhaps more critically, current ODS alloys rely on powder-based mixing and consolidation methods unsuitable for large scale engineering components. As fission and fusion power plant designers place greater reliance on ODS alloys, this will drive materials-manufacturing innovations for scale-up manufacture in ODS-based alloy engineering components.

Nuclear fusion for energy generation will be advanced by the International Thermo-nuclear Experimental Reactor (ITER) under construction in Cadarache, France. This experimental device will provide performance data that will lead to one or more power generating demonstration projects (termed DEMO) that are planned for operation in the next 40 years. The materials challenges for fusion power are perhaps the most extreme of any structural material application, especially for the plasma reactor vessel itself and the underlying “blanket”. Service conditions involve a combination of high neutron energy, high neutron flux and elevated operating temperature, as shown in Fig. 2. The neutron flux is so energetic that there is transmutation of many commonly used alloying elements, leading to further problems of swelling, loss of properties and induced radioactivity.

**Figure 2: Overview of operating temperatures and displacement damage dose regimes for structural materials\*** (Zinkle and Busby, 2009).



\*Current (Generation II) and proposed future (Generation IV) fission and fusion energy systems. Very High Temperature Reactor (VHTR), Super Critical Water Reactor (SCWR), Lead Fast Reactor (LFR), Gas Fast Reactor (GFR), Sodium Fast Reactor (SFR), and Molten Salt Reactor (MSR)

The reactor plasma facing components (PFCs), experience the most severe combinations of environment. Carbon-carbon composites PFC tiles have performed acceptably in experimental fusion devices but for power generating reactors, the sputter rate of carbon is too high from the inevitable plasma strikes on the reactor wall, and carbon quenches the plasma by radiation; carbon also traps radioactive tritium used in the plasma. Beryllium is an attractive PFC material with low radiative loss, a low tritium retention rate and resistance to transmutation, and is used successfully in experimental plasma reactors (European Fusion Development Agreement, 2013, *ITER-Like Wall Project*), but suffers from a low melting point and toxicity.

As the refractory metal with the highest melting temperature and a high sputtering threshold, tungsten and its alloys are primary candidates for PFC applications. Unfortunately, the high melting point of tungsten and its alloys, their low toughness and comparatively low coefficient of thermal expansion make it difficult to form bulk components. Although there has been progress in using tungsten coatings in fusion devices (Neu et al., 2005), processing-alloy combinations for scalable, reproducible and robust thick tungsten based coatings remain a key material requirement, and this need can be expected to deliver novel materials implementations in the next 40 years.

As host and operator of the Jet European Torus at the Culham Centre for Fusion Energy (CCFE), which was recently upgraded to have an ITER-like wall with a beryllium lined reactor and tungsten divertor (European Fusion Development Agreement, 2013, *ITER-Like Wall Project*), the EU and particularly the UK are well placed to be at the forefront of materials developments for fusion. In terms of wider needs for nuclear materials development, access to neutron sources for materials irradiation tests and the ability to analyse irradiated materials with state-of-the-art is becoming a more pressing requirement.

### 3.2 Renewable power generation

Solar will grow in importance in power generation, especially at the micro-grid scale even in the comparatively non-sunny UK. The extent to which the fraction of solar power generation in the energy mix increases will be subject to the development of new materials and devices that offer higher efficiency at low cost. Single crystal and polycrystalline silicon will continue to dominate photovoltaic technologies in the short term, but thin film technologies based on cadmium telluride and derivatives (that use more abundant and less polluting elements) will advance, but the compelling attributes of flexible, solution or roll-to-roll processed polymer-based solar cells will ensure an enduring strong research focus in this area and major advances in efficiency and reduced cost can be anticipated. Electrochemical/catalytic solar cells that split water to generate hydrogen, colloidal quantum dot, artificial photosynthesis, “all carbon” flexible cells and dye sensitised solar cells (DSSC) will all advance, with organic, DSSC and hybrid organic-inorganic cells offering the most potential for innovations and new low cost manufacturing opportunities (Hoppe and Serdar-Sariciftci, 2004; Hardin et al., 2012). These cells, however; place strict demands on the careful control of the myriad fine-scale interfaces between constituents in order to drive up efficiencies. Ensuring this level of control while being able to manufacture large areas represents both a significant challenge and commercial opportunity.

Wind power, especially off-shore generation, will expand further and materials developments will concern exploiting composite manufacturing routes to embed sensors and actuators within blade structures, to enable a wider window of optimised

performance across the variable wind conditions experienced in service. For example, there are opportunities for blades with active control surfaces for greater aerodynamic flexibility, to retrieve maximum energy from light winds, shed the wind load during strong and potentially damaging winds, and dynamically change the blade shape for gusting flows. Real-time data from sensors embedded in the blades (and elsewhere in the assembly and gearbox) will also be valuable in accurately scheduling preventive maintenance and in estimations of fatigue damage and remaining safe life.

Manufacturing challenges will focus on how to produce larger blades (> 40 m) for the biggest, generally off-shore, installations, with assured quality and lifetime (related to assuring the minimisation of manufacturing defects, especially related to fibre infiltration), with accelerated adoption of out of autoclave processing (Brøndsted, Lilholt and Lystrup, 2005).

While tidal and wave based energy generation systems have many of the turbine-related features of wind based systems, and may appear deceptively simple, the material challenges for long term, low maintenance operation are significant. Not least, the sea surface or sub-surface marine environment is highly corrosive to most large scale structural materials of choice, while fouling due to the progressive accretion of organic material is a further serious problem. Polymeric based composites provide outstanding stability in the marine environment but the scale of wave and tidal based turbine systems, and the very high loads produced in extreme conditions, presents ongoing challenges. Opportunities therefore arise for novel material solutions in terms of anti-fouling and anti-corrosion coatings and treatments, and in the manufacturing of large scale, stiff but lightweight, adaptable composite structures. The UK benefits from a high potential for wind, wave and tidal power, and is therefore strongly positioned for demonstration scale projects and the associated opportunity for data on in-service materials performance.

### 3.3 Energy storage

New energy storage technologies will play a transformative role in the global issues of:

1. Enabling future generations of mass-market portable electronic devices for business and leisure applications, including dramatically enhanced battery life, greater environmental compatibility and transformative designs such as flexible, rollable and transparent devices;
2. Reducing emissions due to fossil fuel based transport against a background of rapidly rising global demand by allowing the use of cleaner hybrid and fully electric vehicles; and
3. Reducing emissions and associated climate effects due to fossil fuel based energy generation by allowing greater use of clean but intermittent energy generation technologies such as solar, wind and tidal power, and storing nuclear power at times of low demand.

#### Portable electronics

The lithium-ion battery has become the most widely deployed high energy density battery technology. The lithium-ion battery is well-suited to portable electronic device applications because it provides a high gravimetric energy density (energy per unit weight) and the manufacturing technology is simple and scalable. Over 3 billion cells are now produced each year.

Since its discovery in 1980, there have been many developments in the Li-ion battery system, including replacing  $\text{LiCoO}_2$  used in the cathode by alternative compounds such as  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , etc., that offer different balances of charging speed, operating voltage, safety and modest differences in energy density. More significant performance enhancements are promised by changes in the anode material, from carbon (graphite) to other materials that allow a higher concentration of lithium ions to be inserted. The most studied alternatives are tin-based (Derrien et al., 2007) and silicon-based (Magasinski et al., 2010) with a theoretical capacity for lithium ion intercalation several times greater than carbon – but because these anodes accept more lithium ions - they suffer far more severe swelling and pulverising effects. Future research will understand how to manage or mitigate these strains to give acceptable lifetimes using scalable nanotechnology approaches (Arico et al., 2005), which will in turn facilitate the cost-effective use of a host of cheaper metal oxides for battery electrodes, such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and others. Similar issues arise in the less mature but higher energy density lithium-sulphur battery system.

There has been little change in battery manufacturing processes, with slurry casting, drying and calendaring used for at least the last 30 years. While this technology is clearly scalable and robust, it is ill-suited to some of the nanotechnology approaches emerging from laboratory science, and produces “monolithic” electrode materials with no potential to engineer discrete or graded properties for enhanced performance. New materials-manufacturing combinations will emerge in the 40 years that facilitate the introduction of more energy dense and/or power dense supercapacitors (similar batteries but involving only fast surface reactions), battery materials that will typically be based on 3D arrangements nanomaterials and thinner, flexible and potentially even transparent storage devices.

### Electrification for transport

Because the lithium-ion battery is a commodity item, in the short term it will continue to be explored for storage sectors outside mobile electronics, especially in transport. In this application, larger voltages and currents are required and so many individual cells (which operate at approximately 3 – 4 V) are connected in series and parallel in topologies designed to produce the required power profile. While it is apparently straightforward to scale-up lithium-ion applications by adding more cells, severe problems have emerged that undermine lithium-ion as the universal battery of choice. For applications in electric vehicles, the two challenges are: (1) lithium-ion automotive battery packs cost ~\$US1000/kWh whereas the target price for viability in mass market vehicles is ~\$US300/kWh, and (2) energy density must be increased by at least a factor of 3 to 300Wh/kg to give a driving range between recharges that is useful to the consumer (King, 2007). Other problems include slow charging times of many hours and battery fires in which the electrolyte ignites during thermal runaway when electrical loads become unbalanced across packs of cells. A potentially attractive route to avoid the use flammable electrolytes, which are an essential feature of current lithium-ion and related batteries, is the use of either safe and environmentally compatible aqueous electrolytes (but which operate at low voltages of ~1V), room temperature ionic liquid (RTIL) electrolytes, or solid electrolytes (Takada, 2013). The research challenge for RTILs and solid electrolytes is to produce safe, cheap electrolytes that are electronic insulators but fast ion conductors, which avoid deleterious interfacial reactions and which can be manufactured on a mass scale.

The high specific energy density of lithium with respect to oxygen (3,840 mAh/g) and a theoretical energy density of 12 kWh/kg similar to that of petrol at 13 kWh/kg makes the

lithium-air system amongst the most attractive for the automotive sector (Peng et al., 2012). Bringing lithium-air batteries to market from their current low technology readiness poses significant materials issues in the choice of cathode materials and catalysts, the avoidance of dendritic deposits at the lithium anode, the stability of electrolytes and catalytic particles, and the design of lithium-air batteries to avoid degradation by contaminants, especially water.

Fuel cells will steadily gather market share in automotive energy storage but with materials research required in cheaper, longer lasting membrane technology to allow penetration into mass markets. Despite on-going challenges in bringing hydrogen fuelled vehicles to the mass market (especially in hydrogen generation and storage infrastructure), its inherent cleanliness as a fuel when obtained using renewable or nuclear electricity to split water over a catalyst will drive continued research and development in both catalysts and storage technologies, where metal-oxide framework materials and other ultra-high surface nano-materials will play an important role.

The UK is well-represented in the basic research capacity for electrochemical energy and hydrogen storage. By international standards, however; the UK lacks larger battery research and manufacturing companies and in the medium term, UK innovations in materials and manufacturing will likely progress by licensing of key intellectual property abroad. However, it is conceivable that in the longer term the UK may be able to leverage against R&D strength to re-attract inward investment.

While not strictly a materials development nor related to the electrification of transport specifically, it should be recognized that the next 40 years will likely see concentrated efforts in the development of synthetic fuels, including the fixing of atmospheric CO<sub>2</sub> into fuel (Pearson et al., 2012). Although such processes will be energy intensive and require advanced catalysts (a key area for future nanomaterials development), energy storage in the chemical bond is extremely efficient and there is a global infrastructure for the storage and distribution of liquid fuels. Acceptance of continuing CO<sub>2</sub> emissions from such carbon containing synthetic fuels may depend on the virtuous use of CO<sub>2</sub> (so that some CO<sub>2</sub> becomes effectively recycled rather emitted only), and manufacture will only be viable where cheap electricity is available.

## Grid-scale storage

Grid scale energy storage technologies are required to allow renewable but variable sources of power generation to be efficiently integrated into the UK grid. By far the largest grid-scale energy storage technology around the world (and also in the UK), is “pumped-hydro” whereby water is pumped uphill at night (typically using excess nuclear generated electricity), which is then used to generate power using hydro-electric technologies during the daytime. However, this daily cycle is ill-matched to the energy storage challenges of matching supply and demand as the fraction of renewable power generation by wind, wave and tidal power on the grid increases, which can operate on cycles of minutes or less, up to many hours or even days.

Demonstrator grid-scale storage projects have again taken commodity lithium-ion technologies and assembled them at large scale, but it appears unlikely that current lithium-ion technology can penetrate large-scale grid storage applications in the long term, not least because of their restricted cycle behaviour (typically a few thousand). Sodium is more abundant and cheaper than lithium, with a gravimetric energy density that is lower but competitive for static grid applications where density is much less of an

issue. Developing from current high temperature sodium-sulphur batteries, ambient sodium-ion batteries with aqueous electrolytes for the grid may follow a similar course to lithium-ion batteries for portable electronics, with families of new anodes, cathodes and electrolytes optimized for the sodium-based and other systems to be discovered and brought to the mass market (Chevrier and Ceder, 2011)

Large scale redox flow batteries are well-suited to grid scale storage but require significant materials innovations to secure widespread commercial use, including more durable and faster ion exchange membranes manufactured cost-effectively at large scale and cheaper electrolytes that do not rely on expensive electrolyte ions such as vanadium (Li et al., 2011).

Other grid-scale storage technologies include fly-wheels, hydroelectric and compressed air, but those which offer the most potential for novel materials developments are superconducting magnetic energy storage (SMES - see later), and thermal storage. As already discussed, thermal storage in the built environment by innovative construction materials will be developed, but this approach can also be used for large scale grid storage applications, especially for longer cycle time, even inter-seasonal storage. Materials developments for thermal storage will involve the development of benign solutions and compounds (non-corrosive, environmental compatibility) with optimised combinations of melting/solidification behaviour, improved thermal conductivity and longer cycling life.

## 3.4 Energy transmission

### Superconductors

Superconductors have no electrical resistance when cooled to very low temperatures and already play a critical role in healthcare where low temperature superconductors (LTS) underpin magnetic resonance imaging techniques and in scientific research development where they are used in nuclear magnetic resonance (NMR). These superconductors are based on NbTi or Nb<sub>3</sub>Sn and require liquid helium temperatures for operation. The impact of superconducting materials in the next 40 years will be immense *if* the development of high temperature superconductors (HTS) that can operate at more easily achieved temperatures at a larger engineering scale can be realised. The primary impact will be low/zero loss transmission of electricity, particularly in high density crowded city environments, as well as potential impacts in large-scale superconducting magnetic energy storage (SMES) for the grid whereby energy is stored in a magnetic field in lossless, recirculating high current devices.

Although superconducting cables of up to 600m have been demonstrated (Materials UK, 2011), the ability to manufacture much longer, high quality cables and to provide affordable long term cable cooling remain significant challenges. The UK is strongly positioned to both lead and take advantage of such developments in HTS, with strength in basic science including modelling, commercial design and manufacturing capability, and large-scale end-users, particularly in suppliers to the medical imaging sector.



## 3.5 Power electronics

Power electronics are an enabling technology for flexible and efficient control of electricity transmission and the incorporation of renewable technologies into the UK grid, providing switching, monitoring and control. Power electronics are also fundamental to managing efficient electrical use in the power-hungry lighting and industrial drive sectors in the UK. For example, industrial electric motors can account for more than 60% of all electrical energy consumption and use of modern power electronics for control could result in a 30-40% reduction in this energy use; applying this across an assumed 50% of end users in these sectors the UK results in a 9% reduction in national electrical consumption (Department for Business Innovation and Skills, 2011, *Power Electronics: A Strategy for Success*).

Key materials developments in power electronics in which the UK can be expected to play a leading role are emergence of silicon carbide and then gallium nitride as the cornerstone of more efficient, higher frequency power semiconductors, and novel thermal management and packaging materials including harsh environment die attach materials, high temperature solders, active cooling systems, dielectrics and other passives, as well as an increasing shift to 3D arrangements of active and passive materials. Here as in many other of advanced materials, much of the value added activity will be in the digital design tools to simulate and optimise these complex arrangements of multi-materials, to process designs ready for manufacture, and then to operate digitally driven, flexible manufacturing cells. The UK has a competitive international research and commercial presence in power electronics with excellent connections between academia and business, and recent significant research funding from RCUK will underpin this capability for the medium term (Engineering and Physical Sciences Research Council, 2012).

## 4. High value markets

Materials for high value markets present many opportunities and only a few can be considered here, selected on the basis of their relative immaturity but high value potential.

### 4.1 Metamaterials

Metamaterials are artificial materials with electromagnetic (EM) properties that are difficult or impossible to achieve with naturally occurring materials. Monolithic, isotropic materials with single valued permittivities and permeabilities at a given frequency, temperature, etc., are arranged in careful architectures that as an ensemble produce a material with contrived, unusual or even negative values of permittivity, permeability and refractive index. The characteristic length scale of this material arrangement should be several times smaller than the wavelength of incident EM wave (Liu and Zhang, 2011). Metamaterials are an enabling technology for complex EM manipulations that can be used to realise concepts such as ultra-low observability, near-perfect absorbance, cloaking, electrically small but efficient antenna, etc. Although there have been practical demonstrations of metamaterials in the visible to microwave domains e.g. (Feng et al., 2013), in general, the theory of spatial transforms that predicts the required variations in permeability and permittivity in space to achieve the most exotic outcomes, has developed faster and further than practical metamaterials and associated manufacturing technology. Many of these demonstration devices are also relatively narrow band and suffer from very high losses away from the design frequency.

Future materials and related manufacturing developments in metamaterials will include: the development of nanocomposites with graded electrical and magnetic composites providing broadband response, arranged in anisotropic architectures using top-down 3D printing and related techniques, or bottom-up self-assembly and clustering (Liu and Zhang, 2011); new inorganic crystalline materials with contrived permittivities and permeabilities derived from inter-penetrating lattices with decoupled magnetic and electrical field responses; and tuneable metamaterials where external magnetic or electric fields, temperature or even light are used to contrive anisotropic properties gradients or variable frequency response.

### 4.2 Carbon nanomaterials, graphene and 2D nanomaterials

Graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. It is the basic building block for graphitic materials of all other dimensionalities (Fig. 3). Individual flakes of pristine monolayer graphene have a blend of properties not previously observed in a single material: massless electron mobility producing a very low resistivity of  $10^{-6} \Omega\text{-cm}$  and robust, anomalous quantum effects, even at room temperature. Although strictly graphene is a monolayer of repeating hexagonally co-ordinated carbon rings, in practice graphene is found as a monolayer, bi-layers, tri-layers, etc. – eventually becoming graphite at about 10 layers.

Graphene can be manufactured by: (1) the physical (mechanical, ultrasound) or chemical (surfactant) cleavage of bulk graphite; or (2) process variants based on growth from the vapour phase on a substrate (chemical vapour deposition). Route (1) is cheaper but produces a more disperse range of graphene properties, while (2) is preferred for

fundamental and electronic studies. In the next decade, graphene prices will fall and there are already relatively cheap suspension-based routes to manufacture, although larger area ( $\gg$  few  $\text{cm}^2$ ), low defect mono- or few-layer graphene will always command a price premium. Where large area low defect sheets are available, valuable commercial opportunities will emerge concerning the integration of graphene into functional devices (transistors, screens, solar cells, etc).

Graphene is being suggested for an ever-widening range of applications, but most effort has focused on electronic applications: fast transistors and efficient emitters in particular. Progress has been swift, but difficulties in market penetration stems from high cost and lack of scalability. In optical devices, graphene is likely to realise its long recognised potential as a thin, transparent and conductive films in touch screens, solar cells, and other applications replacing indium-tin-oxide due to the high cost of indium.

Electrochemical energy storage (batteries, supercapacitors) where carbon is already used widely offers a good near term market opportunity, and graphene's specific niche and advantage over the many other carbon polymorphs may emerge more compellingly. For structural applications, graphene has been shown to produce stiffening and strengthening effects in polymers, which has been argued to be superior to carbon nanotubes (CNTs) for similar loadings. Like CNTs, graphene additions at only low volume fraction simultaneously provide enhanced heat and electron transport.

The immaturity of the graphene research suggests a continuing potential to surprise, and despite significant investment in South Korea, US and elsewhere, the UK remains well-placed to capitalise on maturing ideas and new opportunities, with significant UK and EU investment in research capacity at UK universities. For example, the UK Engineering and Physical Sciences Research Council has invested approximately £90m in UK universities in graphene and carbon Nanomaterials since 2005, while the European Commission has chosen graphene as one of Europe's first 10-year, 1,000 million euro FET flagships (European Union, 2013, *Graphene appointed an EU Future Emerging Technology flagship*). These investments should help secure the engagement of global end-users with UK research, and provide opportunities for small UK enterprises to join an emerging supply chain. However, basic science investments will need to leverage valuable intellectual property positions in manufacturing if exploitation and financial benefit to the UK is to be realised, with overseas nations currently showing much greater appetite for patent protection and scale-up manufacture (Bae et al., 2010; Kobayashi et al., 2013). The surprising and comparative ease with which graphite can be exfoliated to form graphene has spawned accelerating interest in the exfoliation of other 2D, planar materials, many of which have already been realised as flakes of only one or a few several atomic layers thick, including  $\text{MoS}_2$ ,  $\text{WS}_2$  and BN (Coleman et al., 2011). While these materials are not expected to show the range of properties of graphene, intriguing properties probably lie in wait, and particular excitement concerns using this growing family of atomic-scale layered materials as building blocks to be reassembled and interleaved in entirely new, extremely fine arrangements of conductors, semiconductors, insulators, etc. These techniques will rely on exquisite control of the surface properties in solution, as well as delicate and novel characterisation and measurement techniques to understand the resulting hybrid properties.

## 4.3 Electrical materials

A detailed consideration of mass market semi-conductors, passives and related materials is beyond the scope of this review, but materials for organic-based low power displays, polymer based electronics and quantum computation should be mentioned because they are areas of UK research strength and where there is uncertainty - and therefore opportunity - in what might novel materials-manufacturing combinations might emerge. Fundamental materials science studies are steadily improving polymer based electronics and device performance, but capturing the value of this know-how relies on marrying it with new production technologies for the mass market. The fabrication of quantum computers will again require exquisite manipulation and integration of materials at the finest scale and much of the work exploits the diversity of carbon polymorphs such as carbon cages with trapped atoms or molecules (endofullerenes), nanotubes and graphene, while other approaches rely on defects in silicon and other semi-conductors, ion traps and photonics, with basic research in quantum photonics a continuing strength in the UK.

## 4.4 Biomaterials

Growing life expectancy and rapid advances in replacement and transplant surgery have seen a huge increase in implantable medical devices in the last decade, with hip, knee and some spinal joints now being replaced on an almost routine basis. Nonetheless, enormous potential remains for the impact of novel materials in the biomedical and healthcare market.

Near term opportunities concern surface modification developments that not only change the surface mechanical or chemical properties, but where surface geometry and device architecture on different length scales is used to take advantage of the growing understanding of the roll of surface topography in, for example, stem cell differentiation. Combinations of approaches in implantable devices will be enabled by additive manufacture techniques. 3D printing will be used to combine a bioactive tissue or bone scaffolds designed for each patient with a controlled-release active molecular therapy that is embedded in or coated over the entire structure (Reichert et al., 2012).

Responsive materials for targeted drug release concern materials that mimic the high sensitivity and selectivity of natural materials to a biological stimulus in order to release a drug at the right place for the right duration. In this context, the use of nano-particles for molecule delivery has been quickly realised and continues to be promising, although the benefits of these approaches need to be balanced by a rigorous and evidenced-based understanding of other potential biological effects. The behaviour of nano-particles in the body will be strongly governed the surface charge and surface chemistry that can deviate strongly from bulk properties so that extremely localised and potent – and potentially advantageous – conditions can develop in a way not easily measured or understood in terms of bulk materials. The careful surface engineering of particles will allow, for example, intracellular targeting of molecules for virus-free gene therapy (Lee et al., 2012) and improvements in the efficacy of existing therapies by delivering them with greater specificity and local concentration, without systemic side-effects (Farokhzad and Langer, 2009).

In many cases, physical sciences know-how in materials manufacture and control will enable the rapid translation of latest breakthroughs in biosciences, and this will be a significant trend in biomaterials opportunities for the future.

## 5. Cross-cutting themes and recommendations

### 5.1 Design

New and novel materials rarely have intrinsic value and instead it is the way that they are integrated into components and systems, and so enable new designs and deliver improved performance, which provides value. This integration relies on manufacturing processes that strive to realise the new design and forecast performance benefits as fully as possible, within the constraints of cost, number, sustainability, etc. In this way, it is difficult to disentangle materials developments from manufacturing innovations, as each drives the other in a virtuous spiral of improvement towards optimum performance. Thus it should not always be expected that important future materials developments require radically new, discrete materials, but that both new and old materials will be integrated with increasing precision and sophistication, even at the nano-scale, to produce optimised products, devices, components and systems. Much of the value for the UK in future materials will lie in the ability to operate competitively at the intersection of materials science, digital design and manufacture.

### 5.2 Materials modelling and design-led experimentation

The Materials Genome Initiative (MGI) in the United States integrates progress in materials modelling over the last 20 years, afforded by cheaper computing, new algorithms and new materials science understanding, to develop new materials. It is “a multi-agency initiative designed to create a new era of policy, resources, and infrastructure that support U.S. institutions in the effort to discover, manufacture, and deploy advanced materials twice as fast, at a fraction of the cost” (The White House, 2011, *Materials Genome Initiative*). At the core of the initiative are latest materials modelling approaches that allow the practical linkage of simulations operating on a variety of length and time-scales. While lacking such a clear brand or the same multi-agency engagement, similar modelling research is also taking place in the EU and elsewhere.

The MGI points the way to an increasing impact of modelling on materials development in which simulations are integrated with latest analytical techniques, large shared data-sets, and access to cheap high performance computing resources. So far, the role of manufacturing in these concepts and initiatives has not been comprehensively considered and appears as a downstream, not parallel activity. This may represent a weakness in the concept because modelling and analysis approaches to new materials will only meet the commercial cost and productivity goals if manufacturing models and practical realities are integrated fully at an early stage.

Nonetheless, it is certain that materials modelling will have considerable benefit in guiding *design-led experimentation* where the increasing fidelity of predictions will allow a reduced set of critical experiments to be designed and performed that will yield the maximum amount of useful information. Where these experiments can be performed at small-scale by making use of a growing range of fine-scale mechanical (e.g. nanoindentation and related techniques) and *in-situ* test techniques (e.g. electrical measurements during high resolution imaging) that provide data quickly from tiny

volumes of material, there is exciting potential to shorten the design-make-test cycle that paces the timing of a new material deployment, which currently can be typically 20 years for a structural material. While micro-scale or even nano-scale manufacturing techniques (scanning probe assembly, self-assembly, additive manufacture, combinatorial ink-jet techniques, etc) may enable the flexible fabrication of small volumes of new materials for these programmes, these processes are often unsuitable for the subsequent mass production of engineered products based on the new design. Thus there is a need to account for the *future production* manufacturing process in design-led or model-led approaches to new materials.

### 5.3 Additive manufacture

Additive manufacture appears to be fast maturing with myriad commercial machines available and could be a transformational technology for many of the areas described in this review, including 3D electrodes for energy storage, porous graded membranes for filtration and energy conversion devices, anisotropic metamaterials and active biomaterial implants. However, there are currently only a relatively small number of materials that can be manufactured by these processes with final properties approaching those of their conventionally manufactured equivalents. Part of the reason is that the development of the mechanical capability of additive manufacturing (software, positioning actuators and controllers, lasers, etc) has out-stripped the underpinning and critical materials science understanding (micro-structural and residual stress evolution, defects, geometrical control, etc). By comparison with traditional *subtractive* processes such as machining, the manufacturing instrumentation and control in additive manufacture is relatively immature, and this has also slowed down the introduction of new materials into the additive process.

As seen many times in this report, it is the *integration of different* materials by novel manufacturing that is frequently at the heart of low volume, high value manufacture. There is a window of opportunity for UK activities in additive manufacture to push on from using commercial machines restricted to narrow ranges of materials, and instead to develop new approaches to the additive manufacture of *multi-material structures* according to optimised designs, with a higher level of on-line instrumentation and control, and drawing on an improved understanding of the factors controlling shape, microstructure, properties and process yield.

### 5.4 Opportunities and recommendations

The challenges, capabilities and costs of scaling-up basic research in materials and manufacturing need to be knowledgeably and realistically assessed at the outset of research activities so that the early promise of breakthroughs is not forever restricted to the laboratory bench. Access to scale-up facilities is a key part of this, and there are recent Government interventions in this area such as the High Value Manufacturing Catapult that provides access to state-of-the-art pre-production facilities and know-how. However, funding schemes and/or financial incentives to encourage university, company and Government (through the Technology Strategy Board, Research Councils UK, etc.) investments of sufficient size to allow scale-up of the *next generation* of home-grown materials manufacturing ideas and capabilities should be developed. Without this, there is a danger that materials manufacturing research in the UK will become overly dependent on purchasing standardised pre-production machines, usually made outside

the UK. The UK needs to stimulate the ambition and provide the mechanisms to develop and invest effectively in its own niche, high value manufacturing ideas.

Scale-up manufacturing research in new materials should be promoted as offering exciting opportunities for intellectual challenge, imagination and innovation in order to attract the best scientists and engineers and the Engineering and Physical Science Research Council establishment of Manufacturing Fellowships is a first step to building science prestige in manufacturing within the research community. The manufacturability of materials at useful scale must be considered integral to the discipline of industrially relevant materials science and not something separate, performed somewhere else by someone else. This is because often the most valuable knowledge and intellectual property associated with a material only comes to light once scale-up manufacturing is pursued - *learning by doing* is a core aspect of novel manufacturing research. Difficult basic science and engineering issues can emerge only at apparently high technology readiness levels, and sponsors of research in the UK might usefully work together to develop programmes that allow the brightest minds from academy and industry continue to *work together from discovery to deployment*, rather than simply passing materials technology up the technology readiness levels or supply chain.

It is hard to imagine that the UK will ever again generate significant economic opportunities and growth in manufacture of monolithic materials in multi-tonnage qualities and this report has instead emphasised that the most valuable future opportunities will lie at the meeting of new materials, design and manufacture. In almost every case considered in this report, the effective exploitation of a new material will rely on an associated, parallel manufacturing development, and the UK's activities in these areas in the science base and in industry need to be more closely aligned if the UK is to maintain an internationally competitive position in advanced materials.



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**Section B: Chemistry input into the  
manufacturing of novel materials  
and future trends in food  
manufacturing**

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# Executive summary

## Chemistry input into the manufacturing of novel materials

The choice of priority areas for the future of chemistry in the manufacture of novel materials can be predicted based upon the recent expansion of some areas and the prediction of potential problems, shortages and security of supplies for the future. This has led to the identification of four main themes. *Secure and renewable “green” energy sources and feed stocks for industry* the former includes biofuels derived from plant based oils (biodiesel) and from the fermentation of biomass e.g. ethanol and biogas. In terms of chemical resources for the manufacturing industry there will be interest in biobased bulk and fine chemical sources such as platform chemicals derived from the breakdown of plant materials and pharmaceuticals isolated from vegetable sources. Security of supplies will be helped by investment in improved *recycling* for the recovery of scarce materials. The ever increasing interest in nanotechnology has highlighted a theme involving *chemical modifications of nanomaterials* for use in medicine; particularly for applications in the health area. For all of these themes there is a clear need for the development of *new and more efficient reactors*.

## The future of food manufacturing

The food and drink industry represents in excess of 15% of manufacturing turnover and employment in the UK and is likely to retain a significant part of the future of manufacturing. A major theme will be contributions to public health including *extension of shelf life* and much more involvement in issues such as *food functionality*. As with all manufacturing *sustainability* is becoming a major issue and this will require lower energy consumption, reduced water usage and better waste management. Emerging areas in food manufacturing include *active packaging* involving the use of antimicrobial materials or those capable of removing moisture and oxygen to avoid spoilage and *intelligent packaging* to monitor food quality e.g. in terms of registering storage conditions or indicating the spoilage or ripeness of fruit. Emerging trends in food manufacturing include the development of additives to compensate for flavour losses due to reduced salt or fat in food and the search for new sources of protein such as insects and tissue culture.

# I. Key areas for chemistry in the future of materials manufacturing

The choice of priority areas for the future of chemistry as a discipline was reviewed in 2009 in a paper from the Royal Society of Chemistry entitled “Chemistry for Tomorrow’s World: A roadmap for the chemical sciences” [RSC, 2009]. In this paper seven priority areas were identified as Energy, Food, Future Cities, Human Health, Lifestyle & Recreation, Raw Materials & Feedstocks and Clean Water & Air. While all of these remain of importance some are more directly relevant to the longer term future of materials manufacturing. In this report a modified list of priorities is presented in which new and future technologies are specifically targeted.

## I.1 Natural resources providing renewable energy and feed stocks to industry

It is now well accepted that there is a diminishing world supply of non-renewable primary mineral resources such as oil and rare metals. Therefore when we try to predict trends in materials manufacturing it is inescapable that there will be a move towards reduced reliance upon such resources and a move towards more extensive recycling/recovery (see section 2 below) together with a greater usage of renewable feed stocks. The latter is often described as “green technology” in that it is aimed at conserving the natural environment and resources; it also includes sustainable energy generation. In terms of renewable resources for materials manufacturing there is a great need for innovation to enable a greater use of plant-based alternatives for existing compounds which will involve a considerable input from chemistry.

The prospect of establishing a secure and renewable source of materials for the chemical industry involving green technology is extremely attractive [Anastas, 2010]. For this reason attention has been increasingly focussed on biomass as a rich feedstock and a versatile and important resource. Laboratory and pilot plant research has shown that this is a real opportunity for the future of manufacturing [Jering, 2010]. Within this very broad area of R&D two main themes can be identified:

- *Biofuels* from plant based oils (biodiesel) and from the fermentation of biomass e.g. ethanol and biogas
- *Biobased bulk and fine chemicals*: biopolymers and chemical coproducts from biofuel production e.g. glycerol. Pharmaceuticals and nutraceuticals from the extraction of plants.

### Biofuels obtained directly from natural resources

The decline in deposits of fossil fuels and climate change has stimulated worldwide interest in renewable and sustainable energy alternatives. The price of oil, environmental pollution and energy security have made renewable fuel a high priority. It is estimated that over 2 billion tonnes of waste biomass is generated in the EU annually of which over half is suitable as a feedstock for biofuel production [RSC, 2010; EBTF, 2012]. It is important to recognise that the term “biofuel” applies to a range of materials obtained from plants that can be used to replace fossil fuels e.g. ethanol obtained through fermentation, plant derived combustible chemicals and biodiesel from lipids. Chemistry



will play a vital part of the extraction and refinement process as the source of raw materials for biofuels widens and the technologies required for production change.

Historically there are three types of biofuel recognised based upon their origin:

**First-generation biofuels** were made from sugar, starch, or vegetable oil but these are now out of favour because of the extent of the farming area needed to grow the raw materials required e.g. palm oil plantations replacing natural forests or food crops.

**Second-generation biofuels** are produced from sustainable feedstock (cellulose, hemicellulose or lignin) and so are more acceptable than the above since they do not threaten food supplies and biodiversity. These biofuels are produced from agricultural and forestry waste (e.g. straw, wood, and grass) together with crops grown on marginal land.

The problem with such material is that it comprises of lignocellulosic materials which are only useful as fuel when broken down into smaller chemical molecules. Current chemical technologies are energy intensive [Sun & Cheng, 2002]. The most common method is steam explosion in which chipped biomass is treated with high-pressure saturated steam and then the pressure is rapidly reduced. This makes the materials undergo an explosive decompression breaking the lignocelluloses into smaller molecules. Another method is acid hydrolysis under heat and pressure which can also be combined with steam explosion. Biological breakdown is also possible but this takes a long time and so is less attractive for industry. The chemicals derived from these processes can be blended with petroleum-based fuels for use in existing internal combustion engines or used directly in vehicles with slightly adapted internal combustion engines.

The chemical products from the breakdown of lignocellulose can also be used to produce ethanol through fermentation or to provide platform chemicals for industry. A special interest group has been dedicated to this involving the Chemistry Innovation and Biosciences Knowledge Transfer Networks the Royal Society of Chemistry (RSC) and the Institution of Chemical Engineers (IChemE) [Chemistry Innovation, 2009]. Within this chemistry will play a key role in developing novel separation technologies, such as membranes and extraction technology to retrieve valuable components from biological media, and in developing pre-treatment methods for biomass component separation.

**Third generation biofuels** are the latest group of biofuels to receive attention and are derived from the extraction of lipids (oils) from microalgae. In common with all of the sources relying upon extraction of lipids from plant material the value of this source of biofuel depends upon an economic balance between the energies required for the extraction and concentration of the lipids and the value of the final product. In the case of algal sources the release of oil from the biomass in the extraction step is more difficult than from other plant material due to the robustness of the cells containing the lipids.

In the production of biofuel from any vegetable oils the first step is extraction of the crude mixture of triglycerides. This material does not burn efficiently and a further chemical step is needed to convert the extracted oil into fatty acid methyl esters (FAME) which can be used as fuel. Although this process of trans-esterification dates back 100 years, the efficiency and scale must be improved if oils derived from vegetable material are to play a major part in replacing fossil fuels [Leung, 2010].

### ***Main trends/requirements for biofuel production from natural resources***

- Improved thermochemical processes and catalysts for the breakdown of lignocellulose feedstock
- New and more efficient technologies for the extraction of lipids from green biomass
- New methods and catalysts for transesterification
- Better technologies for the production of platform chemicals from biomass

### **Biofuels obtained via fermentation processes**

Ethanol and biogas are the two major biofuels obtained from fermentation, sometimes termed digestion. The industrial production of ethanol normally utilises moderately more expensive substrates such as sugar cane juice and corn-starch. However many micro-organisms have the ability to bioconvert low cost materials and green waste into industrially useful chemicals. A really promising source and valuable target is the fermentation of pre-treated i.e. partially degraded, lignocellulose waste (see above) to ethanol.

Biogas is generated from the fermentation (anaerobic digestion) of biomass from sewage, agriculture or municipal waste. It is composed of a mixture of components the main one of which is methane. For many years raw biogas has been used as a fuel for industry but it can be refined to biomethane, a purer and cleaner biofuel. Biomethane itself is a true raw material for manufacturing since with the correct catalysts it can be oxidised to methanol as a bulk chemical precursor to a range of industrial compounds.

Although the production of biogas for fuel is not a new concept there are two factors that restrict the development of this technology. The first is that the production rate of the gas itself from either sewage or waste biomass is slow and the second is the need to find better methods to refine the produced gas into high grade methane (biomethane). With these two in place it is possible to use the product as an energy source in a national grid, as a fuel for vehicles or as a bulk chemical resource for industry [NNFCC, 2013; National Grid, 2013]

### ***Main trends/requirements for biofuel production via fermentation processes***

- New methods for promoting/accelerating the activities of microbes and enzymes for fermentation to yield ethanol and other chemical feedstocks.
- New technologies that exploit biomethane from waste.
- Improved catalysts for the conversion of biomethane into methanol and other feedstocks
- New catalysts and biocatalysts for breaking down lignocellulose into organic feedstocks for industry

### **Fine and bulk chemicals**

Medicinal and aromatic plants provide an inexhaustible resource of raw materials for the pharmaceutical, cosmetic and food industries. In these days of refined analytical procedures the active components of such plants can be identified and extraction technologies developed for their isolation. The drive towards green technologies and an increasing public demand for “healthy” lifestyles has lent weight to the search for fine chemicals and nutraceuticals from algae and crops. An emerging area of interest as a source of nutraceuticals are the solid waste materials from industries such as wine

making or olive oil production [Tuck, 2012]. The generic name for such waste is pomace and it is a valuable source of fine chemicals but it mainly used as feed supplements for cattle or simply dumped in landfills. There are many useful chemicals in such material e.g. pectin for the food industry from apple pomace and antioxidants as pharmaceuticals from wine pomace. In the UK this is not yet regarded as important but in Europe, possibly because of the greater volume of material from the wine and olive industries as a resource, it is under active investigation [Galanakis, 2013]. Even after extraction of the fine chemicals the residual biomass will still be suitable for animal feed.

The development of second generation biofuels (see above) also offers the possibility of new chemical sources which can be used as building blocks for industrial materials.

### ***Main trends/requirements for fine and bulk chemicals***

- The establishing of optimum extraction methodologies (or processes) to produce good yields under safe, non-destructive and easy to monitor extraction conditions.
- Development of better pre-treatment technologies to improve the handling and storage of biomass

## **1.2 Recycling and recovery of materials**

The re-use of resources is now a subject of intense interest and in future years will be critical to the continuation of some of the UK manufacturing base. This is a rather different problem from that of general waste recycling which is already well established in terms of paper and glass. The emerging areas are plastics/polymer recycling to counteract the loss in petrochemical based raw materials [Hopewell, 2009] and precious metal recovery from a variety of sources as world mining resources become more problematic [EU-Enterprise and Industry, 2011].

There are two approaches to plastic recycling (a) the sorting and reprocessing of domestic and industrial waste and (b) the design of manufactured plastic components to allow relatively easy disassembly for targeted components of value. It is the latter which has promise for future manufacturing and has attracted interest in terms of polymers for matrices (and adhesives) that will assemble and dis-assemble on command. Linked to this is the aim to produce polymers with the inbuilt ability to be scanned to determine the structural health of composites (and adhesives). This will allow such plastic composites to be withdrawn from use before failure [SCI, 2013].

In the long term it is obvious that world resources in terms of precious metals and minerals will reduce. There is currently an urgent need to recover and recycle such materials and this will only increase. One source is from printed circuit boards which contain a range of precious metals including gold, silver, palladium and sometimes platinum. After a European Commission report on critical raw materials [EC, 2010] the Joint Research Centre (JRC) of the European Commission carried out an in depth analysis of the use of raw materials, especially metals, in the six priority low-carbon energy technologies of the Commission's SET-Plan: nuclear, solar, wind, bio-energy, carbon capture and storage and electricity grids. The study Critical Metals in Strategic Energy Technologies [Moss, 2011] reveals that five metals commonly used in these technologies – neodymium, dysprosium, indium, tellurium and gallium – show a high risk of shortage. Europe depends on imports for many of these, for which there is rapidly increasing global demand and limited supply, often concentrated in a few countries with associated political risks. Furthermore, they are not easily recyclable or substitutable. A

large-scale deployment of solar energy technologies, for example, will require half the current world supply of tellurium and 25% of the supply of indium. At the same time, the envisaged deployment of wind energy technology in Europe will require large amounts of neodymium and dysprosium, (about 4% of the current global supply each) for permanent magnet generators, which could only be eased if the supply of such metals in the future is increased, which may not be simple. Virtually the whole European supply of these metals comes from China.

It is clear from this report that there must be strategies put in place to alleviate the predicted shortage of these metals. Options must include the efficient promotion and implementation of the recycling and reuse of materials and an active search for less critical materials which could substitute for those in short supply.

### ***Main trends/requirements for recycling and recovery of materials***

- More emphasis on recycling for precious materials
- Alternative technologies which might alleviate the dependence of UK manufacturing on imports
- More research is needed into polymers for matrices (and adhesives) that will assemble and dis-assemble on command in order to effectively re-use the components.

## **1.3 Nanoparticles (concentrating on application in the health area)**

*Nanoparticles* are normally defined as particles where one dimension is 100 nanometers or less. Because of their size they have an enormous surface area to weight ratio which causes them to be more reactive than the same material in other forms. The study of nanoparticles is of interest to a wide range of different disciplines involving scientists, engineers and medical practitioners. Chemists tend to be involved in the synthesis, materials scientists in properties and biologists/medics with biological interactions. If such groups could find ways of cooperating in those applications within the general domain of health the potential for progress would be enormous. The general problem is that there are few opportunities for broad-based interdisciplinary research within the UK. Much of the existing research funding is targeted towards a main discipline and often there is no real relationship established between say chemists, physicists, biologists and medical practitioners. One way to encourage such collaborations is to bring in new broader research initiatives perhaps linked with more general conferences in which all aspects of the uses of nanoparticle in medicine are addressed.

In terms of future manufacturing these materials are generally high value and with such a broad (and widening) range of applications they are undoubtedly materials for the future [Kang, 2010].

### **Cancer therapy**

Nanomedicine is a rapidly expanding field in which several themes exist mainly targeted at cancer therapy [Wang, 2012]. Nanoparticles themselves are able to attack cancerous cells and have the ability to carry chemotherapy drugs into the cells. Two types of nanoparticle are currently receiving considerable attention, gold [Dreaden, 2011] and magnetic particles [Colombo, 2012]. This range will certainly expand and some of the

newer approaches based on nanoparticles and/or chemotherapy drugs either attached to or encapsulated within soft matter provide great hope [Klibanov, 2010; Pavlov, 2011]. The use of microcapsules as carriers could also remove some of the inherent problems generally associated with anti-cancer drugs which include broad spectrum toxicity and the development of resistance [Wang, 2013].

In terms of manufacturing the question will be whether there will be a reasonable shelf life of some of these new supported nanoparticle materials is sufficient for their complete synthesis. This could well be a major development issue over the next few years.

### Medical implants

Biomaterials for orthopaedic devices are required to assimilate into biological environments according to the function that the device is going to support. Progress observed in the field of biomaterials has been enormous in the last few years and to a large extent driven by higher life expectancy in the population leading to increased need for knee/hip replacements, heart pacemakers etc. Metals used in orthopaedic surgery must display high corrosion resistance *in vivo* to avoid the release of contaminants or particles after implantation and have mechanical properties comparable to the tissue that they replace.

One of the best ways of achieving this is to coat the device with a biocompatible surface. Nanocomposite coatings present interesting alternatives to overcome the above challenges. Zirconia and/or silica nanoparticles incorporated in coatings either by sol-gel or by electro-deposition techniques can be used to increase the barrier effect of the coating which can also be functionalized with CaP rich compounds to stimulate bioactive surfaces [Simchi, 2011; Ballarre, 2012]. Whatever coating is found to have the optimum performance for its purpose it will, of course, need to pass all of the required regulatory/safety approvals.

### Antibacterial coatings

Hospital-acquired (nosocomial) infections are a major financial issue in the European healthcare system. The financial impact of these infections counteract medical advances and expensive medical treatments by increasing the length of hospital stay by at least 8 days on average per affected patient. It has been estimated that in the UK 6.4 % of patients contract a nosocomial infection [Agency, 2012]

In the past one of the most common used metals for antibacterial purposes was silver (Ag). Now some doubt has been cast on its routine use in the form of nanoparticle fabric coating because of some evidence of increased bacteria resistance and the problems of a build up of silver pollution in the environment [Science Daily, 2013]. However antibacterial bandages (and antibacterial hospital fabrics) remain a target for the reduction of hospital acquired infections and nanoparticle coatings are likely to be the best option available [Dastjerdi, 2010].

### Environmental protection

Currently there is a lot of discussion about the potential hazards of the increasing use of nanoparticles and the risk of their escape into the environment. An example of this is the way in which silver nanoparticles, which were perceived as excellent contenders for wide range bacterial disinfection, have drifted out of favour [Faunce, 2010; Tolaymat, 2010].

Two factors have driven this move firstly a build up of bacteria resistance and secondly the problems of a build up of non degradable silver pollution in the environment.

By definition nanoparticles are very small and so their identification and removal from the environment are both a challenge and a concern. Attention is moving towards improving procedures in both of these areas [Tsao, 2011]

### ***Main trends/requirements for nanoparticles and health***

- More interdisciplinary work particularly involving clinicians, biologists, environmental scientists and chemists
- Better analytical methods for the characterisation of nanoparticles and coatings
- Larger scale manufacturing facilities for speciality nanoparticles
- Better environmental analysis for nanoparticle detection
- Improved methods for removal of nanoparticles from the environment

## **1.4 New reactor development**

The drive for any development in chemical reactors has always been process intensification. This is defined essentially as the improvement in the production of a material in terms of time or energy. Nowadays there are additional aims involving the adoption of environmentally friendlier methods leading to the synthesis of chemical compounds and organic or inorganic materials in what is generally termed “Green Chemistry”. Over the next 40 years we would expect that new developments should generally be accompanied by a saving in resources through optimizing reaction conditions and/or introducing new process technologies. Among the newer concepts for reactor developments are:

### **Continuous flow**

Traditional chemical and pharmaceutical manufacturing includes a range of different unit operations e.g. synthesis, work-up, crystallisation, filtration, drying, blending, granulation, filling and compaction. Many of these will be of the batch type where materials are treated as one large volume; in the future there is a need for reliable technologies to convert these to continuous operation i.e. to flow processing. Flow systems have distinct advantages over batch in terms of safety because processing occurs while the materials are pumped through a pipe which is much smaller in volume than a batch reactor. In order to achieve this conversion it will be necessary to improve modelling and control and to achieve a more fundamental understanding of particle structure, properties and processing.

In the case of chemical synthesis flow reactors give better control of the reaction conditions since the mixing zone can be more easily controlled and can be achieved very quickly relative to batch processes. Flow reactors involve continuous, controlled processing and so increase the ‘green’ prospects of pharmaceutical and fine chemical manufacturing. The development of microfluidic reactors suitable for the manufacture of high value, small volume products and the scale up of such systems has received considerable attention [Wiles, 2012]. One of the benefits of such reactors is that scale-up of a proven reaction can be achieved rapidly with little or no process development work, by either changing the reactor volume or by running several reactors in parallel, provided

that flows are recalculated to achieve the same residence times. An example of this is the use of microwaves applied to a flow reactor [Wharton, 2011].

## Sonichemical

Sonochemistry is a term which arrived on the scene in the late 1970's and relates to harnessing the energy of sound through the generation and collapse of acoustic cavitation bubbles in liquids. The microscopic bubbles are produced by power ultrasound and collapse generating "hotspots" of energy that can be used to influence chemical reactions and processes. Sonochemistry can increase mass and heat transfer, activate surfaces, disrupt solids, enhance processes involving impregnation and extraction. Two particularly important applications of ultrasound are in crystallisation and particle engineering [Luque de Castro, 2007].

In recent years there has been a move towards the use of microwaves as well as ultrasound in extraction technologies [Mason, 2011]. Large scale ultrasound and microwave reactors are now available and there are examples of the simultaneous use of microwaves and ultrasound in a single reactor [Leonelli, 2010].

## Microwave

Microwave chemistry has been known since the 1980s and is now widely used in academia and industry. It has the advantages of more energy efficient than conventional methods in a number of applications [Moseley, 2011]. In terms of heating microwaves heat the whole material simultaneously in contrast to conventional heating which begins at the surface and slowly works inwards.

### ***Main trends/requirements for new reactor development***

- There is a trend towards the development of smaller scale flow reactors that can produce larger quantities of product by the harnessing several such reactors in parallel.
- Reactors will be designed that use combinations of two or more energy sources which could involve the traditional forms e.g. heat, pressure or electrochemical but almost certainly will incorporate the more modern developments described above e.g. microfluidics, microwave and ultrasound.
- Traditional reactors will be made more energy efficient.

## 2. The future of food manufacturing

In 2010 the University of Cambridge Institute for Manufacturing estimated that the food and drink industry represented in excess of 15% of manufacturing turnover and employment in the UK. Undoubtedly this sector will retain a significant part of the future of manufacturing and this future will be dictated by the way in which it responds to current trends in processing [IfM, 2010]. In two reviews Campden BRI have addressed the scientific and technical needs of the food and drinks industry 2012-2014 and emerging technologies for manufacturing [Campden BRI, 2011, 2012].

### 2.1 Extended shelf life

In the food industry the extension of shelf life type is clearly important to avoid wastage. From the point of view of the customer, however; it might also be useful to have an equivalent shelf life but with a better quality product. Both of these aims require new or improved preservation technologies and a number of treatments are currently under investigation including pulsed light or pulsed electric fields, ultrasound, high pressure and ohmic heating. The use of microwaves for pasteurisation and sterilisation is attractive and in the future may well provide competition for traditional heat treatment [Tang, 2013]. The challenge for the future is the scale up of microwave treatments; this will almost certainly involve flow systems since microwaves cannot be easily applied to commercial scale batch processing.

Freezing for preservation of food has been used for thousands of years with the quality of frozen food being closely related to the freezing and thawing processes. Both are used on an industrial scale in food manufacturing and are energy intensive. There is a need to intensify them with technologies such as ultrasound for freezing and thawing. New developments in microwaves and radiofrequency heating show promise for thawing.

Surface contamination of food, particularly *Campylobacter* in poultry, presents a serious problem for disinfection when there is a drive towards reducing water usage for processing, washing etc. Therefore lactic acid sprays and the use of pulsed light in UV tunnels are currently used. Linked to this is the need for clean food preparation surfaces in conjunction with developing new anti-fouling surface coating technologies to minimise energy requirements for cleaning

The move towards reducing water consumption in the food industry (see below) leads to the question of how to sterilise dry (or low water content) foods such as grain, dried fruit, vegetables or nuts [Lay, 2013]. In such situations UV irradiation or possibly ozone gas can be used to remove bacterial pathogens and prevent food spoilage.

There is a growing need for a greater understanding of the mechanisms involved in the inhibition of food degradation and chemical stabilisation technologies available to counteract degradation that could be included in formulations.

New and improved technologies are required to permit real-time screening and sensors for rapid diagnostics to detect contaminants and ensure food authenticity and traceability. This will include detection of chemicals, allergens, toxins, veterinary medicines, growth hormones and microbial contamination of food products and on food contact surfaces.



### ***Main trends/requirements for extended shelf life***

- New methodologies for rapid sterilisation of liquid foods without affecting flavour
- Efficient methods of sterilising the surfaces of solid foodstuffs
- More efficient freeze/thaw technology
- Better diagnostic tools for contamination
- Greater understanding of the mechanisms of food spoilage

## **2.2 Food functionality and health issues**

As a result of both government and consumer pressure there will be an increasing emphasis on the manufacture of more healthy food products. This will require a fuller understanding of the links between health and diet in terms of specific food and drink components, functional and personalised foods, bioactives, food and drink structure and energy content.

With more demand from nutritionists for further reductions in the fat and salt content in food the challenge to manufacturing is becoming greater. Fat and salt are not only important for texture and flavour but are also key constituents to aid processing. Salt is a key ingredient in bread and processed meat. There is a real need to find replacements for these two ingredients which will facilitate processing while retaining the organoleptic properties (relating to taste and other senses) of the product.

Food manufacturing will then need to respond to the need for formulations in terms of specific groups in the general population. Such moves are already in place for vegetarians and those suffering from diabetes and Coeliac disease.

Spurred on not only by government and public support for healthy products, but also as a marketing tactic, food manufacturing is also moving towards the development of functional foods e.g. those that can help with the lowering of cholesterol levels, improve heart function and/or reduce cancer risk [Flynn, 2012]. These are already targets through the addition of plant stanol (Benecol), natural antioxidants and fortification with fibre [Nicoletti, 2012]. In a similar area is the inclusion of probiotics in yogurt formulations [Katan, 2012]

A number of health issues relate to preservatives and additives currently in use which appear to have adverse effects such as allergies in some consumers. An example of this is the use of sulphites as preservatives in wine where a replacement is required. Similar problems have been found with some artificial colorants although most of these have been solved

### ***Main trends/requirements for food functionality and health issues***

- Greater research into the health implications of food particularly processed food
- New processing technologies required to solve problems incurred by reductions of salt or fat in food
- Specific additions, preferably natural, to improve nutrition
- Research into foods designed for customers with health issues e.g. diabetes

## 2.3 Sustainability in food manufacturing

Sustainability is a key aim for food manufacturing and can be defined according to the DEFRA Food Industry Sustainability Strategy as “to enable all people throughout the world to satisfy their basic needs and enjoy a better quality of life without compromising the quality of life of future generations” [DEFRA, 2006]. The future for food manufacturing will involve lower energy consumption, reduced water usage and better waste management. Overall there will be a need for processes to become energy efficient and one line of research here is improvements in heat recovery [Carbon Trust, 2012].

Reductions in the use of water are key in the future of food manufacturing as supplies become limited so an integral part of the strategy is “Reduced Water Technology”. This involves the conservation of water involving the development of new methods for the efficient use, purification and cost effective recovery of water in food processing. This would reduce water wastage, with the long term aim being to develop water-neutral factories. This leads on to the concepts of dry food factories together with the search for dry disinfection and preservation methodologies [Rosegrant, 2002].

One problem is to disinfect surfaces on worktops and in machinery using less water. To achieve this; a combination of antimicrobial and low-fouling surfaces would be ideal. Low friction surfaces are certainly a possibility. Recently a nanotechnology coating known as LiquiGlide has been developed and one application is to give a slippery coating to the inside of the bottle, making it almost frictionless so that the ketchup slides out like water [Liqui-Glide, 2012].

A method of minimising waste from manufacturing is through the better use of co-products and by-products a process generally termed waste valorisation. This can be by the extraction of valuable constituents e.g. antioxidants from pomace and bioethanol production through fermentation (see 1.1). It is also important that care should be taken to ensure that there is nothing re-useable or valuable in the waste after these processes. It is also possible to increase the value of lower quality products by the addition of high quality constituents e.g. flavouring added to olive oils [Chandrasekaran, 2012].

New methods are required for the safe but energy-efficient methods of waste disposal. More efficient anaerobic treatment plants are needed to process farm, abattoir and retail waste, thus generating renewable energy from biomass in the form of biogas (see 1.1.3). There is also a problem with supply chain waste accentuating the need for the development of sustainable packaging, which is biodegradable or recyclable and compatible with anaerobic digesters. These might include flexible thin films made from corn starch, polyacetic acid or cellulosic materials, which can withstand the chill-chain, handling and storage. Linked to this there is a need to reduce the amounts of metal in cans for food and drink.

An important long term consideration about the use of biodegradable versus bio compostable packaging is that all councils have the same regional facilities for recycling. At the moment some packaging can be recycled in one council district but not in others.

### ***Main trends/requirements for sustainability in food manufacturing***

- Reduction in water usage
- Reduction in wastage of materials in packaging

- Valorisation of lower quality food products
- Positive moves for recycling acceptable to customers and nationally compatible with the facilities at local authority waste treatment centres
- More widespread use of digestion/fermentation of waste materials to generate energy

## 2.4 Active and intelligent packaging

For the future of food manufacturing “active packaging” will be essential [Imran, 2010]. At the moment inserts are used in some packaging to absorb moisture but one might expect future developments to include anti-oxygen scavengers and lighter weight packaging. It might also be possible to develop anti- microbial packaging perhaps involving a film coated with a chemical to prevent microbes growing within the pack.

The concept of “intelligent packaging” is relatively new but possibilities exist developing and using intelligent packaging to monitor food quality and spoilage or the ripeness of fruit by including microsensors. Sensory packaging could show that the product has been kept in wrong conditions at some point in its travel e.g. reached too high a temperature when it is a chilled product [Pereira de Abreu, 2012].

### *Main trends/requirements for active and intelligent packaging*

- Active packaging technologies incorporating e.g. bactericides or oxygen scavengers
- Intelligent package labelling including sensors enabling customer to trace history of product e.g. length of time since packaging or environmental conditions during storage.

## 2.5 Future trends in food manufacture

### Reduced transportation costs

One way of lowering the price of food to the consumer is to reduce the cost of transport of the food items from the manufacturer to the retailer. This can be achieved if a dry mix is delivered that can be rehydrated and cooked at the retail outlet. This approach is already in place in some types of in-store bakeries and could be expanded within this field. In the drinks industry the transportation of concentrates for dilution at point of sale is another example of improved transport economy.

### Encapsulating flavours and scents

Flavours are valuable but often expensive ingredients in any food formulation. They are usually delicate and volatile and so preserving them is a concern of food manufacturers. Encapsulation facilitates the addition of flavours, particularly to dry products such as instant beverages and bakery mixes [Madene, 2006]. It can also provide protection against oxidation and other degradative reactions. Another possibility is that it may prove an alternative to added salt e.g. adding an aroma of cheese which emerges only when cut or chewed. This is also a method of hiding unpleasant odours as in the case of fish oils.

## New sources of protein

The problem of sourcing meat protein will become difficult with a growing population and so alternatives are being actively sought [Asgar, 2010; Gleadle, 2011]. Suggested sustainable sources include:

- new protein sources from vegetable sources as an alternative to quorn (mycoprotein)
- tissue culture and the so-called “artificial meat” could certainly be a secure solution for growing demand.
- insect protein from insect farms
- fish protein from aqua culture

## 3D printing

Manufacturing specific shapes and geometries for food products could involve 3D printing techniques [Lipton, 2010]. A variety of materials has been used to demonstrate food printing including chocolate, cheese, poultry and seafood. If required the printed products could be slow cooked or deep-fried. In the immediate future applications for such technology are most likely to be in the domestic kitchen or restaurant but if the technology advances then manufacturing might become a reality.

### ***Main trends/requirements for future trends in food manufacture***

- Reduction in transportation costs using dried mixes or concentrates for reconstitution and cooking at point of delivery
- New additives to compensate for flavour losses in reduced salt or fat products
- New sources of protein e.g. insects, tissue culture

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