

FUTURISTIC TRENDS IN CHEMICAL, MATERIAL SCIENCES & NANO TECHNOLOGY

Abstract

Materials science has broadened from its historical roots in metallurgy and solid-state physics to underpin many aspects of physical and engineering science, through to the mechanical behavior of complex engineered products in extreme environments. This field of science investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. In this chapter, is to provide an overview of the various types of materials, with a focus on synthetic methodologies and relationships between the structure of a material and its overall properties. Each chapter will feature a section entitled “Important Materials Applications” that will describe an interesting current/future application related to a particular class of material. Topics for these sections include fuel cells, limb implants, solar cells, “self-healing” plastics, and molecular machines (e.g., artificial muscles). In the future, nanotechnology could also enable objects to harvest energy from their environment. New nano-materials and concepts are currently being developed that show potential for producing energy from movement, light, variations in temperature, glucose and other sources with high conversion efficiency.

Keywords: Biomaterials, Polymer, Composites, Sustainable Resources, Energy Materials, Energy Storages, Portable Electronics, Energy Transmission, High Value Market.

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I. MATERIALS CHEMISTRY

Life in the twenty-first century is ever dependent on an unlimited variety of advanced materials. In our consumptive world, it is easy to take for granted the macro-, micro-, and nanoscopic building blocks that comprise any item ever produced. We are spoiled by the technology that adds convenience to our lives, such as microwave ovens, laptop computers, digital cell phones, and improved modes of transportation. However, we rarely take time to think about and appreciate the materials that constitute these modern engineering feats.

The term material may be broadly defined as any solid-state component or device that may be used to address a current or future societal need. For instance, simple building materials such as nails, wood, coatings, etc. address our need of shelter. Other more intangible materials such as nanodevices may not yet be widely proven for particular applications, but will be essential for the future needs of our civilization. Although the above definition includes solid nanostructural building blocks that assemble to form larger materials, it excludes complex liquid compounds such as crude oil, which may be more properly considered a precursor for materials.

A general description of the various types of materials is illustrated in Figure 1.1. Although this indicates sharp distinctions between various classes, there is often ambiguity regarding the proper taxonomy for a specific material. For example, a thin film is defined as having a film thickness of less than 1 mm; however, if the thickness drops to below 100 nm, the dimensions may be more accurately classified within the nanoscale regime.[1] Likewise, liquid crystals are best described as having properties intermediate between amorphous and crystalline phases, and hybrid composite materials involve both inorganic and organic components.

The broadly defined discipline of materials chemistry is focused on understanding the relationships between the arrangement of atoms, ions, or molecules comprising a material, and its overall bulk structural/physical properties. By this designation, common disciplines such as polymer, solid-state, and surface chemistry would all be placed within the scope of materials chemistry. This broad field consists of studying the structures/properties of existing materials, synthesizing and characterizing new materials, and using advanced computational techniques to predict structures and properties of materials that have not yet been realized.

1. Historical Perspectives: Nanoscale (fullerenes, nanotubes, nanofibers, dendritic polymers, nanoparticles, inorganic-organic nanocomposites, nanoelectronic devices) Although the study of materials chemistry is a relatively new entry in both undergraduate and graduate curricula, it has always been an important part of chemistry. An interesting timeline of materials developments from Prehistoric times to the present may be found in Appendix A. By most accounts, Neolithic man (10,000–300 B.C.) was the first to realize that certain materials such as limestone, wood, shells, and clay were most easily shaped into materials used as utensils, tools, and weaponry. Applications for metallic materials date back to the Chalcolithic Age (4,000–1,500 B.C.), where copper was used for a variety of ornamental, functional, and protective applications. This civilization was the first to realize fundamental properties of metals, such as malleability and thermal conductivity. More importantly, Chalcolithic man was the first to practice top-down materials synthesis (see later), as they developed techniques to extract copper from oxide ores such as malachite, for subsequent use in various applications.

Metal alloys were first used in the Bronze Age (1,400–0 B.C.), where serendipity led to the discovery that doping copper with other compounds drastically altered the physical properties of the material. Artifacts from the Middle East dating back to 3,000 B.C. are found to consist of arsenic-doped copper, due to the wide availability of lautite and domeykite ores, which are rich in both arsenic and copper. However, due to arsenic-related casualties, these alloys were quickly replaced with tin–copper alloys (bronze) that were widely used due to a lower melting point, higher hardness, and lower brittleness relative to their arsenic forerunner.

The Iron Age (1,000 B.C.–1,950 A.D.) first brought about applications for iron-based materials. Since the earth’s crust contains significantly more iron than copper (Table 1), it is not surprising that bronze was eventually abandoned for materials applications. An iron silicate material, known today as wrought iron, was accidentally discovered as a by-product from copper processing. However, this material was softer than bronze, so it was not used extensively until the discovery of steel by the Hittites in 1,400 B.C. The incorporation of this steel technology throughout other parts of the world was likely an artifact of the war-related emigration of the Hittites from the Middle East in 1,200 B.C. The Chinese built upon the existing iron-making technology, by introducing methods to create iron alloys that enabled the molding of iron into desired shapes (i.e., cast iron production). Many other empirical developments were practiced in this time period through other parts of the world; however, it must be stated that it was only in the eighteenth and nineteenth century A.D. that scientists began to understand why these diverse procedures were effective.

Table 1: Natural Abundance of Elements in the Earth’s Crust

Natural Abundance of Elements in the Earth’s Crust	
Oxygen	46.1%
Silicon	28.2%
Aluminum	8.2%
Iron	5.6%
Calcium	4.2%
Sodium	2.4%
Magnesium	2.3%
Potassium	2.1%
Titanium	0.57%
Hydrogen	0.14%
Copper	0.005%
Total	99.8%

Figure 1 presents the major developmental efforts related to materials science, showing the approximate year that each area was first investigated. Each of these areas is still of current interest, including the design of improved ceramics and glasses, originally discovered by the earliest civilizations. Although building and structural materials such as ceramics, glasses, and asphalt have not dramatically changed since their invention, the world of electronics has undergone rapid changes. Much new architecture for advanced material design are surely yet undiscovered, as scientists are now attempting to mimic the

profound structural order existing in living creatures and plant life, which is evident as one delves into their microscopic regimes.

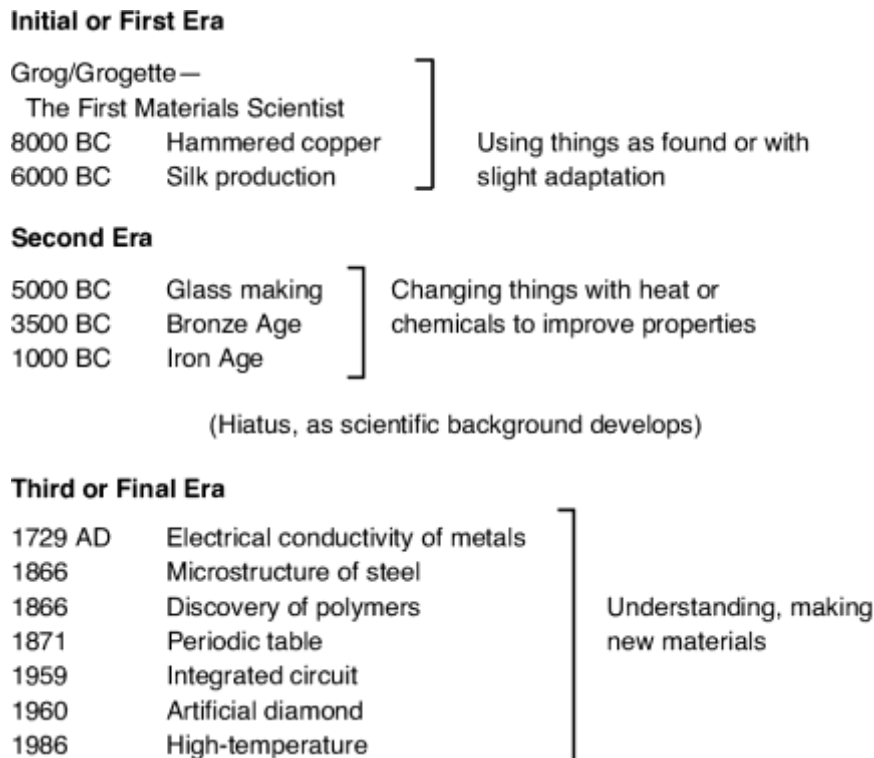


Figure 1: Timeline of Major Developmental Efforts Related to Materials Science

As society moves onto newer technologies, existing materials become obsolete, or their concepts are converted to new applications. A prime example of this is related to phonographs that were commonplace in the early to mid-1900s. However, with the invention of magnetic tape by Marvin Camras in 1947, there was a sharp drop in record usage due to the preferred tape format. The invention of compact disk technology in 1982 has driven the last nail in the coffin of records, which may now only be found in antique shops and garage sales. The needles that were essential to play records no longer have marketability for this application, but have inspired another application at the micro- and nanoscale regime: atomic force microscopy, more generally referred to as scanning probe microscopy.

This materials characterization technique uses a tip, analogous to the record needle that was once used in phonographs, to create images of the surface topology of a sample— even including the controlled placement of individual atoms. Hence, even though the needs and desires of society are constantly changing, the antiquated materials that are being replaced may still be of benefit toward the design of new materials and technology.

The early world of materials discovery consisted solely of empirical observations, without an understanding of the relationship between material structure and properties. Each civilization had specific needs (e.g., materials for shelter, clothing, warfare), and adapted whatever materials were available at the time to address these desires. Although

this suitably addressed whatever issues were of societal concern at the time, such a trial-and-error manner of materials design resulted in slow growth.

Interestingly, until the nineteenth century, the practice of chemistry was viewed as a religion, being derived from alchemical roots that focused on a spiritual quest to make sense of the universe.[3] The alchemists searched for a number of intriguing discoveries including the keys to immortality, a “philosopher’s stone” to transform base matter into higher matter, methods to synthesize gold (or transform any other metal into gold), and magic potions to cure diseases. However noble these pursuits were, they remained unaccomplished due to the lack of an underlying chemical theory to guide their experimentation. In addition, their trial-and-error methodology involved only qualitative characterization, and it was extremely difficult to control the reaction conditions, making it virtually impossible to repeat the exact procedure a number of times.

As a result, from 1,000 B.C. to 1,700 A.D., only a few new substances were discovered which later turned out to be elements such as copper, iron, and mercury. Although this foundation resulted in the development of many experimental techniques of modern chemistry, it is not hard to see that true progress toward new material design may only be accomplished through foresight, based on an intimate understanding of specific relationships between the structure and property of a material. However, as you will see throughout this text, even with such knowledge, many important materials discoveries have been made by accident—the result of an unplanned occurrence during a carefully designed synthesis of an unrelated compound.

- 2. Considerations in the Design of New Materials:** The development of new materials is governed by the current societal need and availability of resources. However, the adoption of a material depends primarily on its cost, which is even observed by changes in the chemical makeup of currencies through the years. Coins currently comprise worthless ferrous alloys rather than high concentrations of metals such as gold, silver, copper, and nickel that comprised early coins. When a new technology or material is introduced, there is almost always a high price associated with its adoption. For example, consider the cost of computers and plasma televisions when they first became available—worth tens of thousands of dollars!

The market price of a device is governed by the costs of its subunits. Shortly after the invention of germanium-based transistors in the late 1940s, the price of an individual transistor was approximately US \$8–10. However, as germanium was substituted with silicon, and fabrication techniques were improved, the price of these materials has exponentially decreased to its current price of one-millionth of a penny! This has allowed for an unprecedented growth in computational expediency, without a concomitant increase in overall price.

There are two rationales for the synthesis of materials- “top-down” and “bottom up”; Figure 2 illustrates examples of materials synthesized from both approaches. Whereas the transformation of complex natural products into desirable materials occurs primarily via a top-down approach (e.g., gemstones from naturally occurring mineral deposits, etching features on silicon wafers for chip production), the majority of synthetic materials are produced using the bottom-up approach. This latter technique is the easiest to visualize, and is even practiced by children who assemble individual LEGO™ building

blocks into more complex architectures. Indeed, the relatively new field of nanotechnology has drastically changed the conception of bottom-up processes, from the historical approach of combining/molding bulk precursor compounds, to the self-assembly of individual atoms and molecules. This capability of being able to manipulate the design of materials from the atomic level will provide an unprecedented control over resultant properties. This will open up possibilities for an unlimited number of future applications, including faster electronic devices, efficient drug-delivery agents, and “green” energy alternatives such as hydrogen-based and fuel cell technologies.

The recent discovery of self-repairing/autonomic healing structural materials is an example of the next generation of “smart materials.” Analogous to the way our bodies are created to heal themselves, these materials are designed to undergo spontaneous physical change, with little or no human intervention. Imagine a world where cracks in buildings repair themselves, or automobile bodies actually appear in showroom condition shortly following an accident. Within the next few decades, these materials could be applied to eliminate defective parts on an assembly line, and could even find use in structures that are at present impractical or impossible to repair, such as integrated circuits or implanted medical devices. This is the exciting world that lies ahead of us— as we learn more about how to reproducibly design materials with specific properties from simple atomic/molecular subunits, the applications will only be limited by our imaginations.

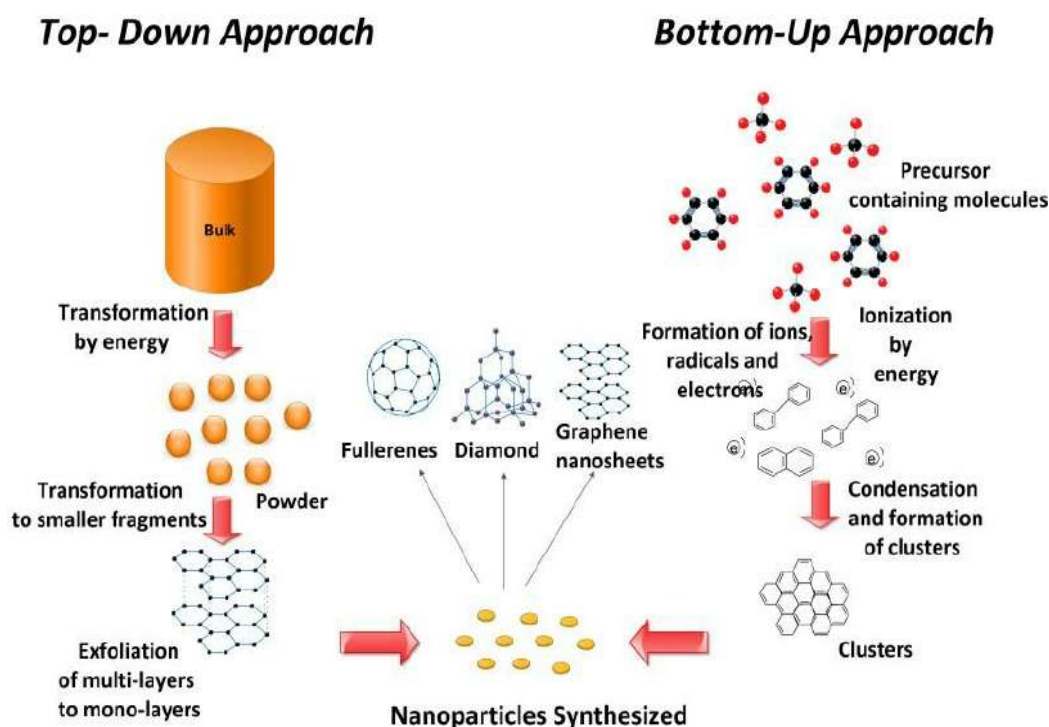


Figure 2: Illustrations for the “Top-Down” and “Bottom-Up” Approach to Materials Synthesis

- 3. Design of New Materials Through A “Critical Thinking” Approach:** Although it is essential to use critical thinking to logically solve problems, this method of reasoning is not being taught in most baccalaureate and post baccalaureate curricula. Unfortunately, the curricular pattern is focused on memorization and standardized-exam preparation.

Further, with such a strong influence of television, movies, and the Internet on today's society, the practice of invoking a deliberate flowchart of thought is not generally applicable. From the MD that must properly diagnose an illness, to the lawyer that must properly follow logic to defend his/her client, critical thinking skills is a necessity for any career path. These skills are also very applicable for the design of new materials- the topic of this textbook. Figure 3 illustrates one example of a critical thinking flowchart that could be applied for the design of a new material.

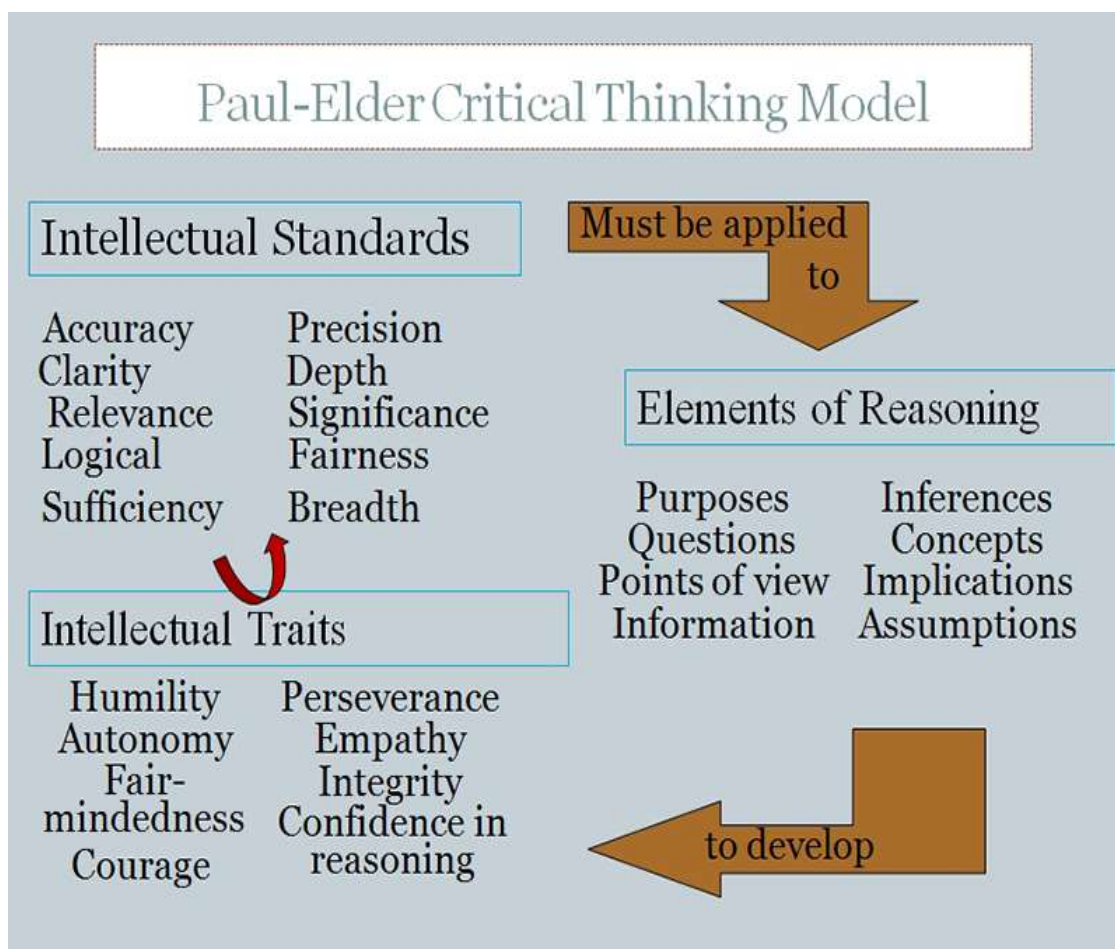


Figure 3: An Example of a Critical Thinking Scheme for the Design of A New Material

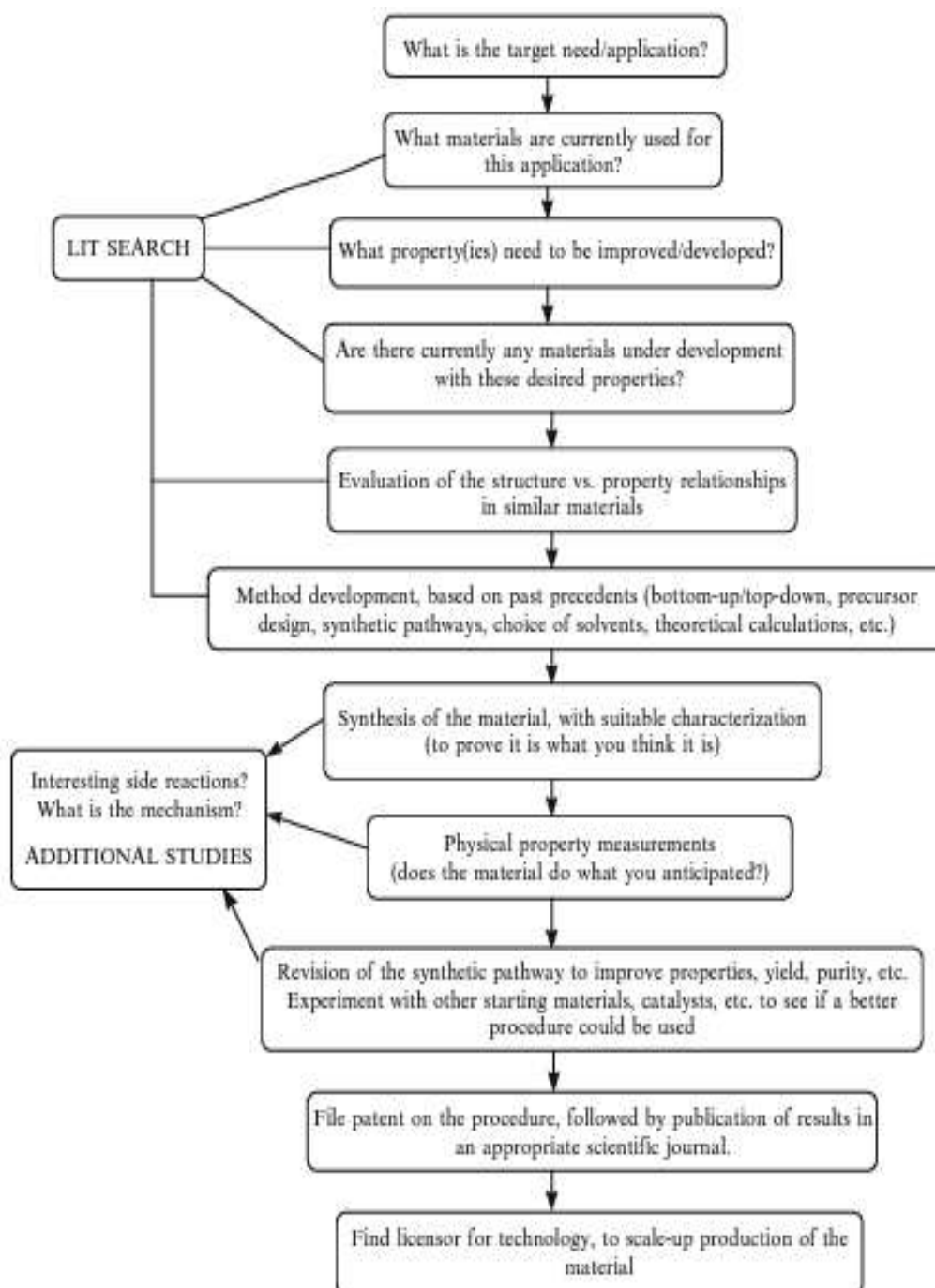


Figure 4: An Example of A Critical Thinking Scheme for the Design of A New Material
 Although there are many possibilities for such development, the following are essential components of any new development:

- Define the societal need, and what type of material is being sought. That is, determine the desired properties of the new material.
- Perform a comprehensive literature survey to determine what materials are currently being used. This must be done in order for the new product to successfully compete in the consumer/industrial market. It is essential to search both scientific (e.g.,

<http://www.pubs.acs.org>– for all journals published by the American Chemical Society) and patent literature (e.g., <http://www.delphion.com>), so that extensive research efforts are not wasted by reinventing something that already exists.

- It should be noted that any exercise in critical thinking will result in more questions than originally anticipated. This is illustrated in the flowchart above, where one will look for interesting products/reactions, and begin to think about the mechanism of the process. Such a “first-principle” understanding of the process is essential in order to increase yields of the material, and scale-up the technology for industrial applications.
- After the new technology is protected by filing patents, publication in scientific literature is also important to foster continual investigations and new/ improved materials. Top journals such as Nature, Science, The Journal of the American Chemical Society, The Chemistry of Materials, Advanced Materials, Nano Letters, and Small publish articles every week related to new developments in the most active areas of science. In recent years, the number of materials-related papers has increased exponentially. The continual compounding of knowledge fosters further development related to the synthesis, characterization, and modeling of materials. However, this may only take place as active researchers share their results with their worldwide colleagues.

The objective of Materials Chemistry is to provide an overview of the various types of materials, with a focus on synthetic methodologies and relationships between the structure of a material and its overall properties. Each chapter will feature a section entitled “Important Materials Applications” that will describe an interesting current/future application related to a particular class of material. Topics for these sections include fuel cells, limb implants, solar cells, “self-healing” plastics, and molecular machines (e.g., artificial muscles).

The classes of materials listed below will be covered in this edition, with a thorough description of how their atomic and molecular subunit architectures affect properties and applications. Without such an appreciation of these relationships, we will not be able to effectively design new and improved materials that are required to further improve our way of life.

- Metals
- Semiconductors
- Superconductors
- Glasses and ceramics
- Magnetic materials
- Soft materials, such as polymers and composites
- Biomaterials
- Nano structural materials
- Thin films

The field of engineered biomaterials will be treated more explicitly in this second edition. Medical breakthroughs have not only extended the life expectancy of humans (currently 78 years in the U.S.), but have resulted in a way of life that would

have seemed impossible just a few decades ago. The market for materials that interact with the body is now a \$12 billion industry. Accordingly, the use of orthopedic and dental implants, bone grafts, coronary stents, and soluble sutures are now commonplace throughout the world. As one would expect, significant research has been devoted to designing the best materials for medical implants that would afford a specific function, with the longest lifetime possible. Throughout this book, we will discuss design aspects for a variety of biomaterials that properly balance structure/functionality and biocompatibility.

The definition used herein for a biomaterial is a biocompatible material or device that is placed within a living system in order to perform, augment, or replace a natural function. Common applications for biomaterials include implants (e.g., artificial limbs), devices (e.g., pacemaker), or components (e.g., contact lenses) placed into a body, or the use of a material to deliver a chemical compound directly to the site of treatment, known as a drug delivery agent. Prescription and over-the counter drugs are now widely used for everything from mild headaches to advanced cancer treatment. The drug industry is now a staggering \$350 billion-per-year business, with rising costs for drug development that must be passed onto the consumer.

Any field of chemistry must make use of extensive characterization techniques. For instance, following an organic synthesis, one must use nuclear magnetic resonance (NMR) or spectroscopic techniques to determine if the correct compound has been produced. The world of materials chemistry is no different; characterization techniques must also be used to verify the identity of a material, or to determine why a certain material has failed in order to guide the developments of improving technologies. Hence, characterization techniques will also be provided in this text, which will illustrate the sophisticated techniques that are used to assess the structures/properties of modern materials. Since common techniques such as UV-visible absorption spectroscopy, atomic absorption/emission spectroscopy, infrared spectroscopy, mass spectrometry, and NMR are covered in a variety of other textbooks,[5] Materials Chemistry will focus on the techniques that are frequently used by modern materials chemists, such as:

Surface/Nanoscale Analysis (Partial List)

- Photoelectron spectroscopy (PES)
- Auger electron spectroscopy (AES)
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Energy-dispersive spectroscopy (EDS/EDX)
- Secondary ion mass spectrometry (SIMS)
- Scanning probe microscopy (SPM)
- X-ray absorption fine structure (XAFS)
- Electron energy-loss spectroscopy (EELS)

Bulk Characterization

- X-ray diffraction (XRD)
- Thermogravimetric analysis (TGA)
- Differential scanning calorimetry (DSC)
- Small-angle X-ray scattering (SAXS)

II. NEW AND ADVANCED MATERIALS

1. Introduction: Materials science has broadened from its historical roots in metallurgy and solid-state physics to underpin many aspects of physical and engineering science, spanning calculation and measurement of the nature of bonding in materials, through to the mechanical behaviour of complex engineered products in extreme environments. In UK industry, there has been a progressive shift from companies that supplied primarily distinct materials classes such as metals, polymers or ceramics, etc., to enterprises that supply finished components and systems into medical, energy, aerospace and many other sectors that rely on novel integration of the latest materials developments. In this vein, rather than consider classes of materials, the review approaches the future trends of new and novel materials in terms of three broad industrial and societal needs: (1) sustainability and materials security, (2) materials for energy, and (3) high value markets. These broad areas correspond to the current UK Technology Strategy Board materials priorities (Technology Strategy Board, 2013), and although these may change with time, they provide a broad and convenient structure in which to consider future materials innovation.

2. Sustainability and Materials Security

- **Lightweight Materials:** There have been sustained efforts since the 1970's oil crises to reduce weight in transport systems in order to realise improved energy efficiency. These efforts have been pursued in parallel with more efficient fossil fuel combustion (petrol, diesel fuel, aviation fuel, etc) engine technologies.

Aluminium and magnesium alloys, carbon and glass fibre reinforced epoxy composites, and metallic and composite foams currently used only in niche, high value vehicles will increasingly find applications in high volume car manufacture. This penetration will not be enabled solely by new materials (of which recyclable and out-of-autoclave, quickly processed thermoplastics are likely the most significant), but rather by increased sophistication in design and simulation of hybrid structures for lightweight, safety and crash-worthiness. These structures will contain many types of material, each optimised for its specific geometrical, mechanical and other requirement, manufactured using faster, scalable multi-material joining and assembly processes (Cantor, 2008).

The competitive pressure exerted by penetration of aluminium alloys into chassis and body applications in the automotive sector has provided a virtuous stimulus for incremental developments in steels for light weighting (Cantor, 2008); new hybrid and composite structures will exert similar pressure on aluminium and magnesium based components. The increasing use of electric based vehicles, most likely through increasing penetration of electric-petrol hybrids (King, 2007) will not ease the pressure for light weighting since the associated engine and powertrain technologies arguably place even more demands on reduced vehicle weight to provide acceptable performance (especially range). However, this increasing hybridisation of materials for reduced weight will create a tension with the increasing requirement for disassembly and easy segregation of materials, for example, in the context the end of vehicle life responsibilities of manufacturers (European Union, 2000, Directive 2000/53/EC).

In the aerospace sector, a similar competition between lightweight technologies has led to structural composites now constituting up to 50% or more of the un-laden airframe weight at the expense of metallic alloys; in turn, the development of a new lightweight aluminium alloys has been stimulated so that the composite fraction in civil airliners is unlikely to increase further. Future airframes will comprise therefore highly optimised and intricate mixtures of aluminium alloys and composite materials, in hybrid materials systems along with titanium alloys.

There is intense international competition in lightweight automotive, airframe and other technologies but the UK is strongly placed through companies such as Jaguar Land Rover, McLaren, GKN, Airbus and others, where sophisticated design, simulation and manufacture of hybrid lightweight structures will increasingly be the most valuable part of the manufacturing supply chain, rather than the materials themselves.

As in other areas of structural composites (e.g. wind power, see below), lightweight composite structures also offer new opportunities unavailable in monolithic materials, such as the ability to exploit the way in which polymeric/epoxy based composites are manufactured as a means to introduce or embed materials alongside the reinforcement (typically long fibres) or matrix (typically epoxy-based) phase to realise additional function. Various embedded sensing and actuation elements have been demonstrated e.g. for strain measurement (Balta et al., 2005) or control surface actuation (Kennedy et al., 2004), as well as self-healing capabilities (White et al., 2001). Subsequent decades will see many of these approaches mature into production technologies, firstly on remotely piloted platforms. In this way, the distinction between structural and functional elements will become blurred, with material hybridization likely occurring from the nanoscale, such as functional particles in coatings to control surface, radar or other properties, up to the platform scale with imaging, other sensing and energy storage capabilities embedded within the composite structure.

Smart textiles research is at the earliest stage and concerns materials that function as textiles but have additional functionalities such as extreme hydrophobicity, sensing, actuation, energy harvesting and storage, data storage, and communication (Jost et al., 2011). Examples of potential applications of this technology include military garment devices, biomedical and antimicrobial textiles, and personal electronics. Although smart textiles might be considered new, discrete materials, they are hybridised materials at the micro- or nano-scale in which the incremental nature of the manufacturing processing e.g. weaving allows incorporation of additional materials and devices into the finished product. Although some demonstrator textiles and garments have been produced, they lack the robustness for consumer products and are at the very earliest technology readiness level. Nonetheless, the UK's strength in advanced high value, low volume textiles know-how suggests design and manufacturing opportunities in smart textiles will be a valuable future opportunity.

- **Materials with Reduced Environmental Impact Through-Life:** Replacement of materials which have been deemed harmful to the environment or hazardous to health

under directives such as the European Union Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation (European Union, 2006, Regulation (EC) No. 1907/2006) creates opportunities for new materials. Products using or containing metals such as hexavalent chromium, lead, cadmium, bismuth and others, plus a range of organic and other chemicals must be adapted or replaced, and this trajectory of materials replacement will continue for the foreseeable future. Near term developments will focus on novel surface treatments primarily for metals such as aluminium that remove harmful chemicals from the production process and/or final product. Medium and longer term trends will concern the advent of cheap and scalable nanotechnology, for instance in the form of nano-scale materials such as nano-tubes, particles, flakes and wires embedded in various matrices, and which will in turn mandate informed use of these materials (Health and Safety Executive, 2013). Development of new experimental techniques for the generation of objective data needed to inform understanding of the environmental effects of nanomaterials is itself an important opportunity for nano-science and nano-materials research, which are a strengths in the UK science base. Construction materials are produced and used in the UK in large quantities and contribute significantly to CO₂ emissions and hence they have a major part to play in meeting the UK's environmental targets in CO₂ reduction (Materials UK, 2009).

There is a need for materials with lower environmental impact in their production, end-use and recyclability, and this generates opportunities for cross-sector technology transfer e.g. the penetration of lightweight materials and mechanically efficient hybrid structures into the 11 New and advanced materials: Section A building sector, including 3D truss and node structures in hybrid materials, offering outstanding load carrying capability at minimum material use. Metals are generally the most recyclable materials and driven by likely further increases in commodity prices, further improvements in the fraction of metals recycled “closed loop” within the UK should be pursued. However, metals are also amongst the most readily corroded and degraded materials and the development of high performance coatings and surface technologies for metallic systems is often an integral part of creating high value added components and systems. It is likely that future developments will include coatings with increased functionality, such as biocidal as well as corrosion resistant coatings, polymer based coatings systems that can generate electricity (solar, mechanical harvesting), or surface treatments to control emissivity, acoustic properties and even electromagnetic compatibility to improve wireless communications in high building density environments. Structural materials will also take on additional functions, such as thermal energy storage for example by inclusion of micro-spheres of phase change materials to absorb heat during the day through a phase change reaction, and to release heat as the ambient temperature falls (Sharma et al., 2009). Cost will always be a constraint on new technologies in the construction sector, but an increasing shift to offsite, mass production techniques will facilitate the integration of embedded functionalities into structural materials for construction.

Concerns surrounding the safe disposal and increased recirculation of packaging materials, and avoiding their release into the environment, will increase in the next few decades and innovative solutions will emerge in biodegradable packaging, with the most pressing needs to increase the biodegradability of plastic packaging materials. These materials will be developed, for example, by fermentation

of plant sugars and oils in large scale microbial factories. Products will be robust in everyday use but designed to be sensitive and easily broken down by targeted enzymes in the waste stream environment (Apelian, 2007).

Smart packaging concepts are now well developed, such as dynamic food freshness indication (integrated sensing and display), embedded radio frequency identification (RFID) tags, temperature control (integrated sense and actuation), anti-counterfeit function (embedded holograms, circuits), embedded energy harvesting, etc. However, alongside regulatory and disposal issues (where biodegradable organic based electronics will be enabling), more capable manufacturing technology (scale, flexibility) and reduced cost are required. Although currently at the earliest technology readiness levels, this will be best achieved by using roll-to-roll techniques capable of keeping pace with mass-scale packaging production.

- **New Materials Technologies and Processes to Support Increased Recirculation of Materials:** The world produces 37 million tons of aluminium and over 2 billion tons of steel every year, accounting for 6-7% of the total global CO₂ emission (Metz et al., 2007). A life cycle assessment for the aluminium industry (Green, 2007) suggested that the production of 1kg of primary aluminium, when all the electricity generation and transmission losses were included, required 45kWh of energy and emitted 12kg of CO₂, whereas 1 kg of recycled Al required only 2.8kWh (5%) and produced 0.6kg CO₂ (5%). Once Al has been obtained, major energy is also required to convert it to a final product, which increases with the extent of mechanical work and complexity of final product shape. Although 12 New and advanced materials: Section A aluminium requires particularly large amounts of energy for its primary extraction, high energy needs and CO₂ emissions are also associated with obtaining all the important engineering metals for alloys (iron, nickel, titanium, magnesium, copper), and their conversion to products.

Therefore, potential energy and emissions savings of recycling will drive up recycling rates further which must be enabled by better segregation at source and by use of high volume segregation technologies (Apelian, 2007). A critical aspect of metal recycling, and the virtuous move to closed loop recycling of metals at a national scale, is the ability to introduce recycled material back into high value products without degradation of properties. Materials standards, often specified in terms of alloy chemistry, maintain a reliance on a high fraction of primary metal in the production of components. However, future years may see a relaxation of chemical tolerances because of an increase in the use of novel and more carefully controlled processing to achieve the same performance from less “clean” feedstocks. Critical to this shift will be a greater understanding of the undermining effects of currently perceived deleterious elements (e.g. embrittlement of aluminium alloys by build of iron and silicon concentrations) and the development of new, more tolerant processing techniques.

The increasing penetration of polymers – especially thermosets such as epoxy-based materials - into large scale structural applications, usually in the form of composites, presents difficult environmental challenges: both matrix and fibre (especially carbon based fibres) require large amounts of energy in their fabrication

(Morgan, 2005), and the resulting materials' inherent environmental stability limits disposal options, especially within a tightening legislative framework (Pickering et al., 2006). Techniques (mechanical, thermal, hybrid) that extract fibres from the matrix while maintaining an acceptable fraction of their virgin properties must be developed, and the key challenges are the development of new markets and products for recovered fibres of sufficient volume and return, and acceptable disposal or re-use of the matrix residue. Alongside metals and composites, perhaps the biggest challenges and opportunities in materials circulation relate to electronic materials. The amount of electronic equipment has increased continuously for at least the last two decades and will likely continue; at the same time there has been a reduction in electronic equipment prices facilitated by massive consumer demand and product volumes, which have led to a drastically reduced lifespan for most electronic equipment (Tanskanen, 2013). Similarly to directives controlling end of vehicle life and requirements for their disposal, the disposal of electronic goods is increasingly regulated (European Union, 2003, Directive 2002/96/EC). As shown in Figure 1 for a mobile phone, much of the materials in electronic waste has low inherent value (ferrous, plastic) and the potentially valuable materials (indium, rare earths) are present only in low concentrations, usually much less than 1% by weight. Therefore efficient and commercially practical recovery and recycling/reuse of the more valuable materials becomes critically dependent on concentrating the fraction electronic waste, separately from other types of waste. Securing this segregation is primarily an issue of consumer behaviour (Tanskanen, 2013). Two intriguing trends may emerge in the future: the development of designs and materials that allow the consumer to disassemble goods before disposal, and the mining of non-segregated waste in very large, existing waste sites. 13 New and advanced materials: Section A
Figure 1: Example of the material content of a mobile phone in wt.%. (Tanskanen, 2013)

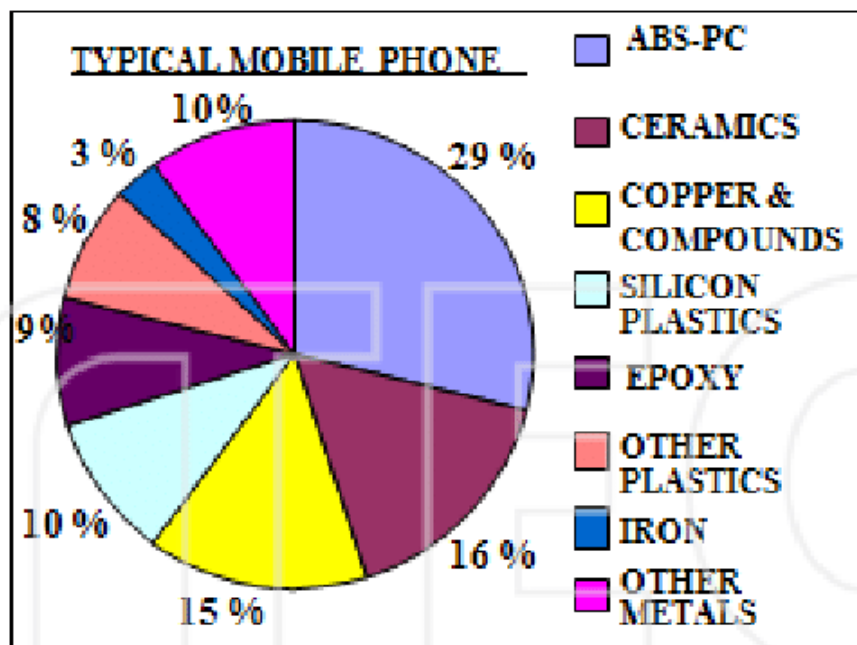


Figure 5: Example of the Material Content of A Mobile Phone in Wt.%

- **Materials for Sustainability of Resources: Bio-Derived Materials:** An approach to circumvent the problems of materials that are increasingly difficult to dispose, or those materials whose price is strongly linked to a limited natural supply (such as rare earth metals), or where the entire security of supply is vulnerable, is to replace them with materials derived from sustainable sources or materials that are readily bio-degraded after use. This has proved easier in theory than in practice but rising costs of disposal and increasing and volatile prices of some metals suggests that the motivation for developing sustainably derived materials will only strengthen in the coming years. Most progress has been made in finding alternatives to petro-chemically derived materials that suffer strong price volatility, such as matrices and fibres for structural composites derived from more sustainable bio-feedstocks, including hemp and flax for the fibres, and cellulose, starch, lactic acid for the matrix (Mohanty et al., 2000). Arguably, the design of composites based on bio-derived materials will require more finesse and know-how than their petro-chemical counterparts since the bio-derived material properties usually have inferior properties.

The last 10 years has seen an order of magnitude increase in the number of scientific publications concerned with biocomposites, with a huge diversification of potential biofeedstocks providing the matrix and the fibre. The automotive sector presents possibly the greatest opportunities for biocomposites, offering massive volumes to retrieve economies of scale, and where carbon fibre supply cannot meet forecast need. The construction sector also offers significant market opportunities for structural applications in relatively lightly loaded sections, especially those under compression. To meet these and other market needs, the next decades will require continued improvements in matrix and fibre property and reproducibility, design understanding (including interfacial design between fibre and matrix and integration of biocomposites into hybrid structures with conventional materials) and environmental stability (partly enabled by the use of coatings), especially fire resistance. Other opportunities include the use of genetic engineering of materials for bio-feedstocks to maximise the yield of useful constituents, 14 New and advanced materials: Section A 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.

- **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 interplay 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, 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.

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 Thermonuclear 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".

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, ITERLike 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.

- **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 anticorrosion 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.

- **Energy Storage:** New energy storage technologies will play a transformative role in the global issues of:
 - 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;
 - 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
 - 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 LiCoO_2 used in the cathode by alternative compounds such as LiFePO_4 , LiMn_2O_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 TiO_2 , Fe_2O_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 CO₂ 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 CO₂ emissions from such carbon containing synthetic fuels may depend on the virtuous use of CO₂ (so that some CO₂ 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.

- **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 Nb₃Sn 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 realized. 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. 24

- **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.

- **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.

- **Carbon Nanomaterials, Graphene and 2D NanomaterialsP:** 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 $10^{-6} \Omega \cdot \text{cm}$ 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, bilayers, 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 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 wellplaced 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 MoS₂, WS₂ 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.

- **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.

- **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

- **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 realize 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 optimized 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.

- **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 multiagency 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 datasets, 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 modeling 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 modeling 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.

- **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.
- **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 standardized 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 quantities 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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- [1] There is often a “grey area” concerning the best definition for small particulate matter. In particular, most structures are automatically referred to as “nanoscale materials,” fueled by the popularity of the nanotechnology revolution. However, the most precise use of the “nano” prefix (e.g., nanoparticles) is only for materials with architectural dimensions (e.g., diameters, thicknesses, etc.) of less than 100 nm; intermediate dimensions between 100 and 1,000 nm should instead be referred to as “submicron.”
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- [3] For a thorough background on alchemy, refer to the following website: <http://www.levity.com/alchemy/index.html>
- [4] Balata golf ball covers may be fabricated from sap extracts of balata/bully trees in South America to produce a thin, resilient material. It is worth mentioning that balata-based materials are now produced artificially.
- [5] Most sophomore organic chemistry undergraduate textbooks provide a thorough coverage of these techniques, including the interpretation of example spectra. For more specialized books on solid-state NMR and MALDI-MS, see (respectively): Duer, M. J. Introduction to Solid-State NMR Spectroscopy, Blackwell: New York, 2005 and Pasch, H.; Schrepp, W. MALDI-TOF Mass Spectrometry of Synthetic Polymers, Springer: New York, 2003.

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