# Chemistry of Advanced Materials

## AN OVERVIEW

Edited by

Leonard V. Interrante
Mark J. Hampden-Smith

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# CHEMISTRY OF ADVANCED MATERIALS

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# PREFACE

The purpose of this book is to introduce the concept of "materials chemistry" to the broader chemistry and materials science communities. This book may also be useful as a text or supplemental reading in graduate or advanced undergraduate courses in materials chemistry. In the introductory chapter, we have attempted to define materials chemistry and to outline its long history in the context of the development of what we now call "chemistry" and "materials science and engineering" (MS & E). Taking the broad perspective of materials chemistry as "chemistry related to preparation, processing and analysis of materials,"[1] it is apparent that "materials chemistry" has always been an integral part of chemistry and that a substantial fraction[2] of the chemistry workforce could be described as "materials chemists." Although this label is not always applied to the wide range of activities that constitute the component subjects of materials chemistry, many individuals who refer to their main area of interest by using such labels as, "polymer science," "surface science," "solid state chemistry," etc., could also be considered as "materials chemists." While quite different in orientation, approach and focus, all of these different areas of materials chemistry have a common goal: the generation, study and/or application of a "material." Most definitions of "materials"[3] connect substance with function and utility. As opposed to "chemicals," whose utility lies primarily in their consumption, materials are generally useful because they can be used repeatedly or continuously for an application that does not irreversibly convert them to something else. In this sense materials and their use underlie every aspect of human activity. Whether one considers the practical aspects of living and functioning in a society or the more aesthetic side of life, it is hard to imagine life without materials.

Chemistry and chemical processes have always had a major role to play in the development and use of materials. However, these processes have become so well integrated into technology or other disciplines, such as metallurgy, that many chemists no longer think of them as part of the subject matter of chemistry. Yet, individuals who have received their academic training in chemistry or chemical engineering are becoming increasingly involved in R & D activities whose main purpose is the development, modification or application of materials. The applications of materials, often derived from an understanding of materials chemistry, have a major impact on our lives, including our economic security. For example, current generations of energy storage devices (batteries), displays, electronic components, information exchange devices, sensors and medical technologies are benefiting from a better understanding of the relevant materials chemistry. We hope that this book will serve to remind chemists and chemical engineers about their intimate connections with MS & E and to inform them about recent progress in applying chemistry and chemical concepts to this area. We also hope that it will convey to the broader MS & E community a sense of the excitement in the field and the opportunities for new materials technologies that materials chemistry continues to offer.

Chapters 2–11 highlight some of the areas of materials chemistry research that are currently being pursued by chemists, chemical engineers and materials scientists worldwide. This survey is intended to illustrate the breadth and scope of materials chemistry research. The general progression is from molecular materials toward extended inorganic solids; however, the focus of most of the chapters is primarily the approach employed to obtain the material or its end application. We end with a chapter that emphasizes the connections between materials chemistry and biotechnology. Each chapter has been written by experts in these areas who have been asked to provide a general overview of their subject suitable for non-experts with a basic background in chemistry. While by no means complete in its coverage of materials chemistry, we feel that this book demonstrates the scope and the importance of this subject as an area of research and as a source of new technology for the 21st century and provides a valuable resource for those receiving training in this area.

LEONARD V. INTERRANTE
MARK J. HAMPDEN-SMITH

## REFERENCES

1. L. V. Interrante, "Materials Chemistry–A New Subdiscipline?", MRS Bulletin, January 1992, p. 4.
2. "National Materials Policy," Proceedings of a Joint Meeting of the National Academy of Sciences–National Academy of Engineering, Natl. Acad. of Sciences Press, Washington, D.C. (1975) p. 125.
3. "The Random House Dictionary of the English Language, The Unabridged Edition." J. Stein and L. Urdang, eds., Random House, N.Y. (1969) p. 884 ["materials: the articles or apparatus needed to make or do something"]; "Materials and Man's Needs," Supplementary Report of the Committee on the Survey of Materials Science and Engineering, National Academy of Sciences, Volume 1, "The History, Scope and Nature of Materials Science and Engineering," Washington, D.C. (1975).

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CHAPTER 1

# Introductory Terms and Concepts

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## 1.1 MATERIALS CHEMISTRY: INTRODUCTION

Stone, bronze, iron; civilization has been defined by Man's relationship with materials. The utilization of materials for feeding, clothing, and protection not only distinguished human beings from other animal life but ensured the survival and ascendancy of our species. Materials have now become so thoroughly ingrained into society that they are often overlooked or underappreciated. When we turn on a light switch, the fact that we are effectively employing hundreds of different materials is hardly apparent to the casual observer. From the glass, metals, and polymers that make up the light bulb to the wires that connect it, via switches and meters, to the power plant that generates the electricity, we are intimately dependent on a wide range of materials which we ordinarily take for granted.

It is clear that materials have had a profound influence on the cultural, socioeconomic, demographic, and geographic development of society. The definition of *materials* as "substances having properties which make them useful in machinery, structures, devices and products" clearly connects materials with function and, through that function, utility.[1] *Chemistry* has been defined as "the study of the composition, structure, and properties of substances and the transformations by which substances are changed into other substances."[2] It is logical that the effective integration of materials

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science with its macroscopic perspective, and chemistry, which focuses on atomic- molecular-level interactions, could provide the opportunity to understand and control the fundamental connections between structure and function from the molecular level to a macroscopic scale. This understanding could lead to improved composition, structure, or synthetic methods and enable the development of new types of advanced-performance materials which have superior properties and performance.

## 1.2 MATERIALS CHEMISTRY: PAST[3, 4]

Historically, the earliest ages of civilization are classified by the key materials that were in use at that time: stone, bronze, and iron. The later industrial age was characterized by the production of materials on a large scale for commercial purposes. In most cases the utility of the material was of primary importance, although there are also many examples of the aesthetic application of a material being the primary origin of its value (e.g., gold and silver as ornamentation, a symbol of wealth, or a medium for trade).

Prior to the discovery that metals could be obtained from rocks by certain (chemical) processes, all metals were relatively rare. Even when the technology for extracting copper and bronze from their ores was developed, the fact that these ores were not widely available presented significant limitations on the widespread use of these metals. It was not until the technology for extracting iron from its much more widely distributed and abundant ores became available that metals became the material of choice for many more practical applications. Clearly, metals have been among the most influential materials in the early development of civilization, and chemistry has been intimately involved in their production.

The role of chemistry in the production of metals is illustrated by the case of iron. Unlike gold or copper, iron is not available in elemental form in nature but must be isolated from iron ore (iron oxide) by chemical means. When iron ore, $Fe_2O_3$ (hematite), is heated together with a source of carbon, the following reactions can occur:

$$3Fe_2O_3 + 11C \rightarrow 2Fe_3C + 9CO \tag{1}$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \tag{2}$$

The $Fe_3C$ (cementite, a hard, brittle material) and iron (relatively soft and malleable) form a composite material known as (carbon) steel. When the concentration of carbon in this steel is too high, the high proportion of cementite in the composite leads to a product that is not very useful, due to its brittle nature. This led to repeated folding, heating, and beating, resulting in removal of some of the carbon as well the silicate "slag," and oxidation of the surface of the iron to black iron oxide, FeO (hence the name *blacksmith*). The iron carbide and iron oxide react to give iron metal,

$$Fe_3C + FeO \longrightarrow 4Fe + CO \quad (3)$$

which, combined with the remaining cementite, give carbon steel its useful properties.

Of course, not only were these specific reactions unknown to early humans, but the basic concepts on which they are based were far from human understanding. Steel, as with all early materials, was developed by an entirely empirical process. As the understanding of the basic chemistry improved, and as the microstructural consequences of the thermal and physical processing became recognized, various refinements of the steelmaking process occurred, leading to the production of carbon and alloy steels with improved properties and therefore higher value.

This example of the successful enhancement of an important materials technology through a better understanding of the chemistry involved is illustrative of the advancement experienced by many material technologies in the late nineteenth and early twentieth centuries as our understanding of the basic science underlying these technologies increased. Other examples can be cited in which advances in chemical understanding, coupled with advancements in analytical methods, led to substantial improvements in materials technologies. These include the dye industry, where the development of synthetic dyes made colored fabrics readily available to most people, and the fibers and plastics industries, which were built on advances in polymer synthesis (see Section 1.3). Thus it is clear that chemistry has always been intimately involved in the development of materials for technology and that a basic understanding of this chemistry was often essential for the optimal (or even successful) production of the material.

Despite its intimate connection with materials, as chemistry became an independent branch of science in the late nineteenth and early twentieth centuries, its study in universities became increasingly disconnected from the technology of materials synthesis and processing. Such "applied" subjects as the chemistry of the earth (geology), of metals (metallurgy), and ceramics were separated off to form new departments in the 1930s to 1950s. In many universities, the study of materials became viewed as an activity more appropriate for engineers, or at least applied scientists, than for "chemists." Few, if any, universities in the United States in the mid-twentieth century undertook to instruct chemistry students in the basic science of materials. In industry, however, chemistry continued to play an important role in the development of new materials and in materials processing, where a growing understanding of the chemical processes involved contributed to the rapid pace of progress. A particularly good example of this key role of chemistry in the production of new materials is provided by the development of synthetic polymers, which started in earnest early in the twentieth century.

Historically, natural organic polymers, in the form of wood and other plant fibers, were among the first materials to be used by humans. The use of wood as a structural material continues to the present, although it is becoming increasingly common to combine wood with synthetic organic polymers so as to provide materials of enhanced utility and/or decreased cost (e.g., particle board and plywood). Perhaps even more important than the structural application of wood was its conversion into paper. This key technology was a contribution of the Chinese that was transmitted westward by the Arabs in the period A.D. 750–800.[4] Even now, the central role of paper as a medium for recording and transmitting information is only gradually giving way to plastics, ceramics, and semiconductors in the form of CDs, magnetic recording media, and integrated circuits.

Among the first natural polymeric materials to attract scientific interest were silk and cobwebs. Robert Hooke (1665) noted the interesting properties of silk and spiders' webs, some of which have properties that are yet to be duplicated in synthetic polymers. The first significant impact of chemistry on the development of useful synthetic polymeric materials came in 1839, when Charles Goodyear found that the elastic properties of natural rubber could be improved, and its tackiness eliminated, by heating it with sulfur. While this discovery was in the process of development into a commercial product, cellulose nitrate, another product resulting from the chemical conversion of a natural material, was discovered and eventually became the basis for both gun cotton and cellophane film. These polymeric materials can be characterized as semisynthetic because they are derived from natural polymers. The first commercial development of fully synthetic polymers came in the early part of the twentieth century, when Leo Baekeland produced Bakelite, a thermoset polymer derived from the reaction of phenol with formaldehyde. However, real progress in synthetic polymer production came only after the development of a scientific understanding of macromolecular structure, bonding, and reactions starting in the 1920s with the work of Hermann Staudinger and continuing into the 1950s with the work of Herman Mark, Kurt Meyer, Wallace Carothers, and Paul Flory.[5] This revolution in synthetic materials production continues to date and is marked by the introduction of such commercial products as nylon, rayon, teflon, and lexan, product names (among many others) that have become part of the vocabulary of modern technology and society. Now organic polymers are part of our everyday life in such a wide variety of forms because they can display the largest spectrum of properties of any class of materials, from nonstick coatings on pots and pans to recording media.

The development of new inorganic materials followed a similar pathway of first using natural materials (such as rocks, minerals, and metals) directly and then later, through experimentation, learning to modify natural substances chemically so as to obtain new materials not known, or not readily available, in nature. An early example of this approach, which undoubtedly preceded the deliberate extraction of metals from their mineral sources, was the development of ceramics, such as pottery, glass, and later, hydraulic cement. The term *ceramics* has now expanded to include virtually all inorganic engineering materials other than metals and semiconductors, where both the material type and its characteristic physical properties provide a basis for its classification.

## 1.3 MATERIALS CHEMISTRY: PRESENT

### 1.3.1 Classification of Materials

In most textbooks of material science and engineering, materials are classified into broad categories, based on both their chemical constitution and their typical physical properties.[6, 7] Solid materials are generally grouped into three basic categories: metals, ceramics, and polymers. In addition, there are two other groups of important engineering materials: composites and semiconductors. *Composites* consist of combinations of two or more different materials, whereas *semiconductors* are distinguished by their unusual electrical characteristics. In addition to this classification based on their structure, bonding, and properties, materials have increasingly come to be classified by their function [e.g., electronic, biomedical, structural, and optical (and nonlinear optical) materials].

*Metallic materials* are usually combinations of one or more metallic elements. Metals are characterized by the existence of large numbers of delocalized electrons; that is, these electrons are not bound to particular atoms. Many properties of metals are directly attributable to these delocalized electrons. Metals are generally good conductors of both electricity and heat and are not transparent to visible light; a polished metal surface typically reflects light and has a lustrous appearance. Furthermore, while metals can be quite strong, they are generally malleable and easily formed into desired shapes, making them particularly useful for structural applications.

*Ceramics* are compounds formed between metallic and nonmetallic elements; important examples include the oxides, sulfides, nitrides, and carbides. The wide range of materials that fall within this classification includes most of the natural minerals of the earth, such as the silicates, oxides, carbonates, and sulfides, as well as glasses and glass ceramics. These materials are typically insulative to the passage of electricity and heat and are resistant to degration at high temperatures and harsh environments. Ceramics are hard but very brittle. These materials are used in structural, optical, and electronic applications.

*Polymers* or *molecular materials* include the familiar plastic and rubber materials. They are typically comprised of macromolecules that range from linear polymers having amorphous or quasicrystalline structures to extensively cross-linked networks. In recent years, this class of materials has been effectively expanded to include virtually all types of materials that are comprised of discrete molecules (i.e., molecular materials). In addition to solids comprised of small molecules or molecular ions, this category of molecular materials would logically include certain liquids, such as the silicones (which are used as lubricants and dielectric fluids), along with those that exhibit long-range order, such as liquid crystals, Langmuir–Blodgett (LB) films, and self-assembled monolayers. Moreover, when one considers that wood (or plant fiber), in all forms from paper to structural components, can also be placed in this category, this is clearly one of the largest and most important of the material categories. Polymers and most other molecular materials typically have low electrical and thermal conductivities, are lower in strength than metals and ceramics, and are generally not suitable for use at high temperatures. Thermoplastic polymers in which the long molecular chains are not rigidly connected have good ductility and formability; thermosetting polymers are stronger but more brittle because the molecular chains are tightly linked. Polymers and other molecular materials are used in many applications, including dielectrics in electronic devices, displays, lithography, recording media, fibers for clothing, and in food and other product packaging.

*Composites* are combinations of different materials. Fiberglass is a familiar example, in which glass fibers are embedded within a polymeric matrix. A composite is designed to display a combination of the best characteristics of each of the component materials. Fiberglass acquires strength from the glass and flexibility from the polymer. Most natural materials, such as stone, concrete, and wood are also logically placed in this category. Many of the recent materials developments in aerospace engineering and sports equipment have involved composite materials where advantage is taken of the combination of high strength and light weight.

*Semiconductors* have electrical properties that are intermediate between the electrical conductors and insulators. Furthermore, the electrical characteristics of these materials are extremely sensitive to the presence of minute concentrations of impurity atoms, the concentrations of which can be controlled over very small spatial regions. Semiconductors have made possible the advent of integrated circuitry that has revolutionized the electronics and computer industries over the last 50+ years.

### 1.3.2 The Role of Chemistry

Chemistry is intimately involved in the generation and processing of materials from each of the various categories listed above, as well as in their environmental degradation by both natural and unnatural causes. In the case of metals, most are derived from ores by chemical reduction of their oxides or silicates or by oxidation (and then reduction) of their sulfides. This historical, and largely empirical, application of chemistry in the generation of metals has benefited in more recent times from an understanding of the basic chemistry involved in these processes (e.g., the oxygen furnace in steel production) as well as the corrosion processes that are experienced by many metals during their useful lifetime. The fact that some of these metals act as poisons toward biological organisms when discarded extends even further the need to understand and control the basic chemistry and biochemistry of metallic substances.

The role of chemistry in ceramic processing is somewhat less obvious but equally profound, as most ceramic materials undergo extensive purification and/or processing involving chemical reactions prior to their consolidation as powders. Even their consolidation and their use as powders often requires the addition of organic polymers and surfactants as binders and dispersing agents. In recent years, chemistry has become increasingly involved in the processing of ceramics in special forms; examples include the preparation of powders with well-defined particle sizes, size distributions and shapes; fibers; films; and membranes. Here methods such as spray drying, vapor-phase synthesis, sol-gel processing, chemical vapor deposition and infiltration, and polymer precursor pyrolysis are finding increasing use in various applications.

As with metals, semiconductors are not found in nature in the purity or even the chemical form that is required for most applications in electronics. Silicon, the mainstay material of the electronics industry, is derived from silica by reduction and then further purified by distillation as silicon tetrachloride before being converted back to the element and then zone refined and crystallized by physical processes. The role of chemistry by no means ends here, as processes such as oxidation, doping, patterning, and etching are all either largely or entirely chemical in nature.[8] One additional chemical process that is making an increasing impact on the processing of semiconductors is chemical vapor deposition (CVD), where everything from the actual growth of the semiconductor material (including Si) to the application of insulators and metallic conductors to its surface can be accomplished.

Apart from a few natural materials, the polymers currently in use as materials are all the end products of chemical processes. Even in those cases where natural products such as wood, paper, or cotton are employed, chemical processes are usually employed at some stage in the conversion of the natural material to a more useful final product (e.g., bleaching, dyeing, and painting). Synthetic polymers, derived from natural materials such as hydrocarbons (petroleum), are used increasingly in place of natural fibers in fabrics as well as in a wide range of other products, creating a new set of problems when it comes to the disposal or reuse of the product.

In general, it is becoming widely recognized that the entire enterprise of materials fabrication and processing is intimately interconnected with both the material's origins and its ultimate disposal or recycling. As a result, no new method for extracting or processing a material can be considered without some understanding of the real costs of obtaining it, as well as its eventual fate after its useful lifetime as a material in a product has ended. The concept of a total materials cycle has been used in this context (Fig. 1.1) to indicate the intimate relationship between our continuing need for new

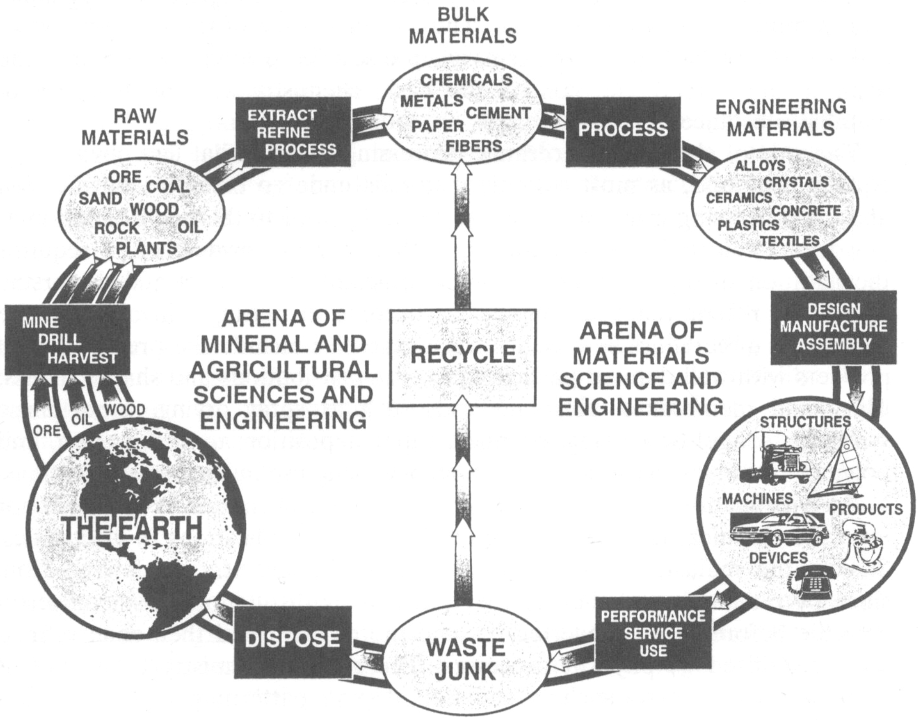


**Figure 1.1** The total materials cycle.

materials and the effects of materials development on the environment and on the diminishing supply of basic raw materials.[9a] Indeed, it is irresponsible, if not impossible, these days to bring a new material into the marketplace without consideration of factors such as the supply of the material and the true costs of its development in terms of the potential impact on the environment. As stated in a U.S. National Academy of Sciences report on materials science and engineering published in 1974, "it is vital to learn how to move materials carefully around the materials cycle, from production of raw materials to use and eventual disposal, in ways that minimize strain on natural and environmental resources."[9a] Considering the fact that the processes included in this cycle are typically chemical processes, chemists have an important role to play in the continuing efforts to understand the fundamental nature, and the practical consequences, of these processes.

The role of chemists in the solution of fundamental materials science problems is becoming more important with time. Recent examples of the role of materials chemists in key materials discoveries include (1) the synthesis of