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Future directions in solid state chemistry: report of the NSF-sponsored workshop

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Abstract

A long-established area of scientific excellence in Europe, solid state chemistry has emerged in the US in the past two decades as a field experiencing rapid growth and development. At its core, it is an interdisciplinary melding of chemistry, physics, engineering, and materials science, as it focuses on the design, synthesis and structural characterization of new chemical compounds and characterization of their physical properties. As a consequence of this inherently interdisciplinary character, the solid state chemistry community is highly open to the influx of new ideas and directions. The inclusionary character of the field's culture has been a significant factor in its continuing growth and vitality.

This report presents an elaboration of discussions held during an NSF-sponsored workshop on *Future Directions in Solid State Chemistry*, held on the UC Davis Campus in October 2001. That workshop was the second of a series of workshops planned in this topical area. The first, held at NSF headquarters in Arlington, Virginia, in January of 1998, was designed to address the core of the field, describing how it has developed in the US and worldwide in the past decade, and how the members of the community saw the central thrusts of research and education in solid state chemistry proceeding in the next several years. A report was published on that workshop (J.M. Honig, chair, "Proceedings of the Workshop on the Present Status and Future Developments of Solid State Chemistry and Materials", Arlington, VA, January 15–16, 1998) describing the state of the field and recommendations for future development of the core discipline.

In the spirit of continuing to expand the scope of the solid state chemistry community into new areas of scientific inquiry, the workshop elaborated in this document was designed to address the interfaces between our field and fields where we thought there would be significant opportunity for the development of new scientific advancements through increased interaction. The 7 topic areas, described in detail in this report, ranged from those with established ties to solid state chemistry such as Earth and planetary sciences, and energy storage and conversion, to those such as condensed matter physics, where the connections are in their infancy, to biology, where the opportunities for connections are largely unexplored. Exciting ties to materials chemistry were explored in discussions on molecular materials and nanoscale science, and a session on the importance of improving the ties between solid state chemists and experts in characterization at national experimental facilities was included. The full report elaborates these ideas extensively.

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1. Introductory overview

1.1. The workshop

The second NSF-sponsored workshop on *Future Directions in Solid State Chemistry* was held at UC Davis, from Friday October 12 through Sunday October 14, 2001. The workshop was attended by approximately 50 scientists, with many different areas of expertise, including the core of solid state chemistry, and areas in related specialties. The participants took part in the workshop out of a desire to help build better bridges and more multidisciplinary collaboration among solid state chemists and scientists in other disciplines. Approximately 20 talks were presented, and there was considerable time for both general discussion and time for discussion in special topic groups.

The goal of the workshop was to articulate the solid state chemistry community's sense of the opportunities and directions it wishes to take in the future. In our first workshop, held in January of 1998, we focused on the core of our discipline. This second workshop focused on the interfaces of solid state chemistry with other disciplines, in both the biological and physical sciences.

One important aspect of the workshop was to elaborate on how we have previously worked at such interfaces, and how we might better exploit them in the future. Discussed were the many ways of interacting across traditional disciplinary boundaries, and in particular the opportunities for forming multidisciplinary collaborations of different types.

There were many potential areas on which to focus a workshop such as this, because solid state chemistry interfaces with many different areas of science. After an initial meeting of the organizing committee, it was decided to focus the workshop on the interfaces between solid state chemistry and: *nanoscale science, biology, theory and condensed matter physics, molecular and macromolecular materials, Earth, planetary, and environmental science, energy storage and conversion,* and *national facilities.* In all these discussions the central role of education was discussed. For each of these topics, a brief general summary is given below.

1.2. Earth, planetary and environmental science

The Earth's surface is part of a complex planet whose history over geologic time and whose ability to maintain habitat for life is governed by physical and chemical processes involving the solid state in minerals, soils, and rocks. The understanding of relatively short-term surface processes, on time scales of years to centuries, is needed to sensibly approach problems of resource management, pollution, and climate change. The understanding of processes occurring at pressures into the megabar range, temperatures of several thousand degrees, and times of millions of years, is necessary to understand the evolution of the Earth and other planets. The solid state chemistry community can both contribute to and benefit from active research in the mineral physics, geochemistry, and environmental science communities. Examples of important areas discussed in this session include the reactivity of mineral surfaces, high pressure phase transitions, solid state approaches to nuclear waste disposal and CO_2 sequestration, and nanoparticles in the environment. Many materials (for example zeolites, spinels, perovskites, clays) are of interest to both Earth science and materials science, and provide suitable ground for mutual interest and interdisciplinary collaboration.

Earth scientists have many areas of commonality with solid state chemists. Earth scientists are concerned with complex and diverse chemical systems, and thermodynamic stability and chemical compatibility over both long and short time scales, and length scales ranging from the atomic, through the nanoscale, to the geological. One particular area of interaction with solid state chemistry can be in the area of mineralogy, where the complexities of mineral crystal structures are unequalled. Such complex mineral structures are not often considered by solid state chemists in their search for functional materials. Solid state chemists and geologists share many common tools, and also often think about the same chemical compounds though from different points of view. Of particular interest to both areas of expertise is compound formation in high pressure, high temperature water or other solvents. This has only recently begun to be extensively exploited in solid state chemistry. The concepts of nanoscale science, of such recent interest to solid state chemists, are presently also of great interest in Earth and environmental science and present a great opportunity for mutual interaction.

1.3. Biology

The study and exploitation of biological processes has not yet had substantial overlap with the field of solid state chemistry. However, given recent developments, there is substantial reason to believe that this will be an area of tremendous future growth. The earliest manifestation of this research—bio-inorganic chemistry—sought to understand the function of metal clusters in enzymes and electron transfer proteins. This field has matured considerably. However, it still begs more fundamental understanding. More importantly, this body of work suggests new opportunities such as mimic of functions of cluster-containing proteins in, for example, energy transduction and catalysis. In parallel, use of metallic surfaces to conjugate proteins and oligonucleotides has resulted in new opportunities for bio-assays, preparation of bio-inspired devices and fundamental studies of biomolecular function. It is obvious that conjugation of biomolecules to a wider variety of surfaces can lead to new functions and new opportunities for hybrid devices. These could include solid-state semiconducting materials and the walls of zeolitic channels. This work also extends to the interaction of materials with whole cells—control of their growth and proliferation can be effected using simple surfaces. Perhaps solid-state materials can further the efforts to couple electronic, electromagnetic and mechanical stimulations to cells and ultimately to tissues. Exploration of these emerging issues was accomplished during the workshop. The overall goal was to appreciate new opportunities at this interface and to assess potential paths for interdisciplinary research in this area.

Increased interactions between biology and solid state chemistry, like between biology and other areas of physical science, are hampered by a lack of a common language and research culture. However, the need for increasing interaction is seen by both sides. The participants in the workshop strongly felt that areas of mutual interest can be further established, and that the development of multidisciplinary education programs is essential. One of the areas of potential common interest is the development of biosensors—in which biological components are joined to microelectronic substrates on order sense or relay signals or to initiate mechanical or biological activity. This area is only in its infancy and is clearly of great potential. The interaction of living cells with solid state materials seems to offer limitless possibilities for the future. The nature of the interface between biological and solid state materials, and the design and manipulation of that interface to enhance function or interaction, are virtually completely unexplored. Finally, biology can impact solid state chemistry by influencing the design of materials to mimic the function of complex biological materials.

1.4. Energy storage and conversion

The development of viable, long-term solutions to meet our energy needs that also maintain the quality of our environment remains one of the most critical challenges facing the scientific community. Solutions to this challenge increasingly depend on electrochemical processes in solids. Photovoltaics, fuel cells, thermoelectrics and batteries are all devices in which energy storage or conversion relies on a coupling of chemical and electrical phenomena within the solid state. Accordingly, advances in energy technology require that fundamental questions of charge and mass transfer through complex solids be answered, and that novel processing techniques be developed to implement strategies for micro-structure and/or crystal structure modification. These themes arise in each of the many energy systems described in this section, specifically, membrane reactors, fuel cells, thermoelectrics, batteries, capacitors, photovoltaics, hydrogen storage media and superconductors.

While each type of energy conversion or storage device faces its own unique challenges, each is in critical need of new materials with improved properties. Thus, a broad-based effort in materials discovery, guided by computational chemistry, and complemented with a similar effort in comprehensive architectural control of known materials is essential. The solid state chemist brings to bear on this problem the unique ability to synthesize new compounds which may exhibit inherently unusual properties, not only leading to improvements to conventional devices, for example, better cathodes for lithium ion batteries, but also rendering entirely new and as-of-yet un-envisioned devices possible. Fundamental advances, however, require the cooperative efforts of experts in fields ranging from solid state chemistry and electrochemistry to solid state physics and materials science to ensure that material behaviour is understood at the most fundamental level while potential new devices are rapidly developed. The present status of those collaborations and future possibilities were discussed.

1.5. Molecular, hybrid, and macromolecular materials

The design, preparation, and study of physical properties of molecular assemblies and polymeric molecule-based materials exhibiting useful magnetic, electrical, or optical properties is a very active area of worldwide research. The quest in this area is not just to obtain molecule-based compounds than can behave like classical materials, but also to produce materials that may exhibit completely new physical properties or those in which several properties are combined. Examples of such systems could be materials showing electrical or magnetic bistability, tunable magnetic ordering temperatures, discrete molecules showing magnetic hysteresis (nanomagnets), and hybrid materials coupling more than one property, e.g. magnetism with conductivity/superconductivity, or magnetism with optical properties. Other interesting phenomena that may be studied are quantum tunneling effects, long-lived photo-optical excited states, and solids with restricted magnetic dimensionalities.

One frontier area in this research field is the evolution of new synthetic strategies to construct molecules at the mesoscale level and to specifically control their organization in solution and/or in the solid state. This includes the formation of thin layers and organized films, or their encapsulation/intercalation, etc., into solids. A second key area is the application of frontier experimental techniques to characterize the resulting materials and allow for the identification of the most interesting phenomena. Finally, it is important to develop suitable theoretical models based on solid-state approaches as well as on molecular orbital approaches (ab initio and density functional theory). The ultimate goal is an understanding of the properties of the materials that will lead to predictions about the nature of interactions in molecular/macromolecular assemblies. All these areas of research have been, and continue to be, of great interest in the study of the solid state chemistry of non-molecular compounds. There is an immeasurable potential benefit to both the solid state chemistry and molecular chemistry communities in greatly increasing the interactions between these two areas of research.

The structural and chemical diversity of molecular compounds is unparalleled in the world of solid state chemistry. Moreover, molecular compounds can be synthesized by rational synthetic strategies that are impossible to implement in the solid state. In light of these attributes, molecular compounds present almost unlimited possibilities for development of new materials with novel and complex physical properties. The potential for fruitful interactions with the solid state chemistry community also appear to be limitless, as molecular chemists become increasingly interested in the synthesis of new compounds with exotic magnetic and electronic properties and the correlation of those properties with chemistry and structure—areas of research that are at the very heart of traditional solid state chemistry. This section describes the potential for interactions in the areas of molecular precursor routes to materials, self-assembled and organic materials, molecular nanomagnets, composite and hybrid molecular materials (such as templated materials) and finally inorganic/organic hybrid materials.

1.6. Nanoscale science and technology

The synthesis and characterization of materials at the nanometer length scale has been an area of increasing vitality and importance in the past five years. New phenomena arise because the size of the resulting materials is on the same order as the fundamental interaction distances that give rise to physical properties. Great opportunities for the investigation of both fundamentally new physical phenomena and enabling new technologies lie ahead. At the heart of the revolution in nanoscale science has been the development by chemists of synthesis and assembly methods for making and manipulating new molecular and extended-structure materials on length scales previously inaccessible through conventional pathways. Sophisticated assembly methods allow for the synthesis and exploration of non-thermodynamic phase assemblages with designed-in physical properties. The potential for the development of new materials with new properties appears almost limitless.

Synthesis of new materials and characterization of their properties is at the heart of solid state chemistry, and solid state chemists have had a significant role in the development of this area of research. The nanoscale science community extends well beyond the borders of the solid state chemistry community, however, and most of the important developments so far have been outside the traditional boundaries of our field. Significant opportunities lie in the further integration of the solid state community into the developments in nanoscale science.

The interactions between nanoscale science and solid state chemistry are strong. Nanoscale science concerns itself with synthesizing and assembling matter at multiple length scales—from atomic and molecular species, to individual nanoscale building blocks such as nanocrystals and nanowires, and then from these building blocks to larger scale assemblies and systems. Solid state chemistry plays an important role in the first step of this process: putting atoms together into ordered 3-dimensional crystal lattices. The manner in which the properties of those crystalline structural units change their properties on changing their physical size into the nanometer regime is of mutual interest to solid state chemists and nanoscale scientists. Described in this section is state of the art knowledge in semiconductor nanoparticles, nanowires, nanotubes, and photonic crystals. The central challenge of the continued development of this field—the assembly of such nanoscale components into systems with unique physical properties or functions, an area of great potential interest to solid state chemists, is described.

1.6.1. Theory and condensed matter physics

Progress in understanding new phenomena in condensed matter physics is best achieved through ingenious synthesis, in-depth characterization, and theoretical analysis of high quality, complex new materials. Through the process of materials synthesis, intimately linked to materials theory and definitive characterization, further new phenomena are dreamed of, pursued, discovered, characterized, and ultimately extrapolated to even more surprising discoveries. High temperature superconductors and quantum spin liquid magnetic insulators provide examples of unexpected properties that emerge only when the systems become sufficiently complex, but this complexity can make further progress very difficult. The solid state chemistry community has the potential to play a much more active role in this process.

Solid state physics and solid state chemistry have long had strongly overlapping interests, and have been growing closer together for a few decades. Many of the materials of intense current interest in condensed matter physics are also of interest to solid state chemists. This section describes materials such as manganites, novel superconductors, multiferroics, dilute magnetic semiconductors, magnetic insulators, half metallic ferromagnets, correlated electron materials, and battery materials, appearing certain to attract growing mutual interest in the near future. The impact of theory, modeling, and computation have been growing rapidly in solid state chemistry, but their potential to change the field profoundly is yet to be fully exploited. Finally, the central importance of new materials to condensed matter physics can hardly be overstated. Great opportunities in materials exploration lie in strengthening ties between solid state chemistry and solid state physics, building more intimate connections, and establishing strong feedback between computation and experiment. Finally, solid state chemists have the potential to impact condensed matter physics deeply through the growth of high quality single crystals and ultrapure materials.

1.7. National facilities

The US has made a considerable investment in synchrotron X-ray and neutron scattering capabilities, as well as other facilities such as the National High Field Magnet Laboratory. They represent a valuable resource for the characterization of new and potentially technologically important materials. However, the use of these facilities by solid-state chemists is not as widespread as it could be. This may in part be because solid-state chemists are not aware of the contributions that such facilities can make to their research. However, it also seems likely that the “activation barrier” associated with central facility use deters many scientists from using them. Our national facilities generally do a good job of serving expert users, but they do not always meet the needs of occasional (and inexperienced) users with good scientific problems. This session examined how we can improve the link between solid-state chemists and the national facilities community. Current and future capabilities that may be of interest to solid-state chemists were described, and possible strategies for improving accessibility and ease of use were presented.

Major research facilities, such as the high field magnet laboratory, and the nation’s neutron and synchrotron X-ray centers, are very important resources for the solid state chemistry community. The participants in the workshop emphasized the importance of using these facilities effectively and productively. This section of the report outlines the variety of such facilities, and suggests some measures to enhance the efficiency and productivity of these facilities. The issues discussed include training and supporting users while they are working at facilities, the effective education of potential users, tailoring the user access process to better meet the needs of the scientific community, the development of new instrumentation, dedicated versus multipurpose instrumentation, and remote access to instruments. A series of recommendations are made that focus on increasing the value of these facilities to the scientific community in general and solid state chemists in particular.

2. Earth, planetary, and environmental science

Alexandra Navrotsky, Peter Burns

2.1. Linking Earth science and solid state chemistry

Mineralogical research largely focuses on the structures, chemistry and occurrences of naturally occurring inorganic compounds. It is, in a sense, inorganic natural products chemistry. Minerals are unique in that they are the subset of inorganic compounds that are sufficiently compatible with their surroundings to persist for geologic time and that have compositions compatible with the elemental abundances and geochemistry of the Earth. Thus it is no surprise that mineralogy has many commonalities with solid state chemistry, especially in the realm of materials characterization. Mineralogists typically are expert crystallographers, and contribute a unique understanding of complex inorganic structures. They deal with diverse chemical systems, and have an appreciation of the interaction between complex mineral assemblages and geologic fluids. Earth scientists deal with time scales and distance scales far more diverse than those accessed by direct human experience or by technological processes.

Many materials are important both in the Earth and in technological applications. Table 1 lists some of these. Furthermore, minerals are the raw materials on which technology depends. The distribution, discovery and mining of ores and other raw materials pose critical technological, social, and political issues. Impending real or

Table 1
Materials of interest to both Earth science and materials science

Material	Nature of interest and application	
	Earth science	Solid state chemistry
Hydrogen	Jupiter and other giant planets	energy storage
Iron	Earth's core	steel industry
Perovskites	Earth's mantle	electronic materials
Iron oxides	environmental science	magnetic recording
Manganese oxides	environmental science	catalysts
Zeolites	environmental science	catalysts
	ion exchange	ion exchange
Clays	environmental science	ceramics industry
	petroleum	structural materials
Silicate melts	volcanism	slags, glasses
Titania	environmental science	paints, solar cells, catalysts

manipulated shortages of such materials (water, oil, chromium, to name some) are important political drivers. The transport, refining, use, and eventual disposal of these ores and their technological products pose equally important social environmental questions. For example, the nuclear fuel cycle must consider the cradle-to-grave (ore body to nuclear reactor to repository) handling of uranium. Solid state chemical issues (the chemical reactions involved) must be considered in the context of geological processes (transport of contaminants by groundwater, long term climate change, volcanism).

Many minerals are crystalline silicates and aluminosilicates, and amorphous and glassy silicates (e.g. obsidian glass) are also found in nature. Thus there is strong overlap of the science of Earth materials with fields such as glass, zeolites, and ceramics. Certain binary oxides, notably those of Si, Al, Fe, Mn, and Ti are important in both technology and nature. There are commonalities between sulfide minerals and semiconductors. Equally importantly, many processes—crystallization, melting, dissolution, diffusion, surface reaction, catalysis—are common to Earth and materials science.

Solid state chemistry and mineralogy share many experimental tools. X-ray diffraction using both laboratory and synchrotron sources is used by both communities, sometimes at common beamlines. The added information obtained from neutron scattering about the positions of light atoms (O and H) and about magnetic order is important to both minerals and materials. Small angle scattering studies reveal mid-range order and heterogeneity in complex ceramic and geologic materials. Vibrational, optical, Mossbauer, and nuclear magnetic resonance spectroscopy are used by both communities. Advances in calorimetry and thermal analysis benefit both. The Earth science and solid state chemistry community share interests in computational and modeling tools for the prediction of crystallographic, electronic, and vibrational properties [1].

Often Earth scientists are the beneficiaries of physical methods developed by the physical sciences. However, the Earth sciences lead technique development and applications in certain areas. The pressure distribution in the Earth is well known, with pressure rising to 3 megabars at the center. The temperature distribution is less well known, and probably locally heterogeneous, but temperatures in the 3000–5000 K range are likely in the core. Thus research at high P and T is critical to the Earth sciences, and the development of shock wave [2,3], diamond anvil cell [4,5,6] and multianvil [5,7] apparatus and techniques has been actively pursued by the mineral physics community. An example of overlap with solid state chemistry is the study of phase transitions in hydrogen [8,9], important to both planetary science (the interior of Jupiter) and to fundamental physics and chemistry. A second example is the geological interest in magnesium silicate perovskite in the mantle. This phase, with silicon in octahedral coordination, may be the most abundant single phase in the planet [5]. Its crystal chemistry, elasticity, defect structure, and transport properties may help define the properties of the lower mantle. Study of these properties, made difficult by its high pressure stability field (>26 GPa), can be aided by the study of analogous ceramic perovskites stable under ambient conditions [10]. Understanding the behavior of these ceramic perovskites can be improved by considering the behavior of $MgSiO_3$ perovskite, a material very much at the extreme end of the stability field for this structure type. Another example is iron, the major constituent of the Earth's core at pressures up to 3 megabars [11].

The chemical analysis of coexisting mineral grains provides a goldmine of information to the Earth sciences. The distributions of major and trace [12] elements and of isotopes [13] between different phases, as well as their overall abundances, provide information on the source regions and pressure temperature history of rocks [14]. To enable these measurements, Earth scientists have developed and utilized specialized instrumentation, including electron microprobe microanalysis (EPMA) [15], the ion microprobe (spatially selective SIMS), and the X-ray microprobe (spatially selective X-ray fluorescence using synchrotron radiation). The processing of samples for trace element and isotopic analysis requires clean room facilities and procedures on a par with those in the semiconductor industry. Very sensitive high resolution mass spectrometric techniques are then used for isotopic analysis. These methodologies are well known to the Earth science community. They can probably be applied fruitfully to solid state chemistry where they have been underutilized.

The fugacities of water, oxygen, carbon dioxide, and other volatile species are important variables in Earth processes. Experimental petrologists have developed means to control and measure these variables during synthesis and phase equilibrium experiments at low to moderate pressures. These methodologies, relatively standard in the Earth sciences, should find wider application in solid state chemistry.

2.2. Nanogeoscience

For minerals, as for other solids, most chemical reactions occur at interfaces: solid–solid, solid–liquid, solid–gas, solid–supercritical fluid. Furthermore, many minerals near the Earth's surface (in soils, sediments, low grade metamorphic rocks) are very fine grained (micron sized or smaller). There is currently great interest in that part of the planet dubbed the "critical zone"—the atmosphere, ocean, land surface, and shallow interior directly affecting and affected by human activities. In the critical zone, nanosized materials abound: dust particles, soil particles, clays, zeolites, oxides and oxyhydroxides. These particles interact strongly with both organic and inorganic constituents and transport both nutrients and pollutants. Minerals interact with life, ranging from bacterial to human.

The dusty surfaces of Mars, asteroids, our Moon, and other moons also may harbor nanoparticles and host nanoscale phenomena. Interstellar dust grains may be nanoparticles. Even in the Earth's deep interior, grain size reduction during phase transformation may lead to transformational plasticity, a nanoscale process. The unity and breadth gained by thinking of these diverse topics as involving similar underlying fundamental issues represents far more than an opportunistic desire to hitch a ride on the nanotechnology bandwagon. Rather, the whole field of geology has much to gain from the growing realization that phenomena at the nanoscale often dominate geologic processes, that these phenomena can be studied using the concepts and techniques of physics and chemistry, and that this molecular level understanding can and must be incorporated into models of geologic processes at the outcrop, regional, and planetary scale. A recent book summarizes many of the issues (Reviews in Mineralogy and Geochemistry: Nanoparticles and the Environment, 2000 [17]).

The examples below illustrate specific topics in which solid state chemistry plays an important part in understanding Earth materials.

2.3. TiO_2 Phases: polymorphism and surface energetics

Titania is an important accessory oxide mineral and is used widely in technology. Rutile is the stable high temperature phase, but anatase and brookite are common in fine grained (nanoscale) natural and synthetic samples. Upon heating concomitant with coarsening, the following transformations are all seen, each under somewhat different conditions of particle size, starting material, temperature, and other parameters: anatase to brookite to rutile, brookite to anatase to rutile, anatase to rutile, and brookite to rutile. These variable transformation sequences imply very closely balanced energetics as a function of particle size. It has been proposed that the surface enthalpies of the three polymorphs are sufficiently different that crossover in thermodynamic stability can occur under conditions that preclude coarsening, with anatase and/or brookite stable at small particle size [16,17]. Previously, using high temperature oxide melt calorimetry for nanocrystalline Al_2O_3, it was shown that γ, the defect spinel phase observed for nanosized particles, is more stable in enthalpy than nanophase α, corundum, the macrocrystalline thermodynamically stable phase [18]. The goal of the recent work summarized here [19] is to gather calorimetric evidence concerning the analogous proposed phase stability reversal for nanocrystalline TiO_2. Such information is essential for understanding fundamental solid state chemistry, for predicting phase equilibria, for controlling nucleation, grain growth, and phase transformation, and thus is fundamental to technological applications. Energetics of anatase, brookite, and rutile have been measured by high temperature oxide melt drop solution calorimetry at 975 K with $3Na_2O \bullet 4MoO_3$ solvent using a Calvet twin microcalorimeter.

Figure 1 shows the transformation enthalpies of nanocrystalline samples (kJ/mol) versus surface areas (m^2/mol). A linear fit for each structure yields both the surface enthalpy (slope) and the bulk phase transformation enthalpy (intercept). Figure 1 represents the enthalpy of nanorutile. Bulk rutile is taken as the reference point of zero enthalpy for all samples. A linear fit using these three nanorutile data is therefore forced through the origin to derive the surface enthalpy of nanocrystalline rutile as 2.2 ± 0.2 J/m^2. Figure 1(b) shows the anatase data. A linear fit yields the surface enthalpy of anatase as 0.4 ± 0.1 J/m^2 and the enthalpy of phase transformation of bulk rutile to bulk anatase as 2.61 ± 0.41 kJ/mol. Figure 1(c) represents the enthalpy of the one nanocrystalline brookite (NB) and the bulk brookite–rutile phase transformation enthalpy (0.71 ± 0.38 kJ/mol) of Mitsuhashi and Kleppa. Attempts to obtain pure brookite of other surface areas, either by direct synthesis or by coarsening the initial brookite sample were not successful. Therefore the linear fit is constrained by only two points. It gives the surface enthalpy of brookite as 1.0 ± 0.2 J/m^2.

Figure 1(d) summarizes the enthalpy of nanocrystalline titania. The intersections of the linear fits of brookite and rutile and of brookite and anatase place a limit on

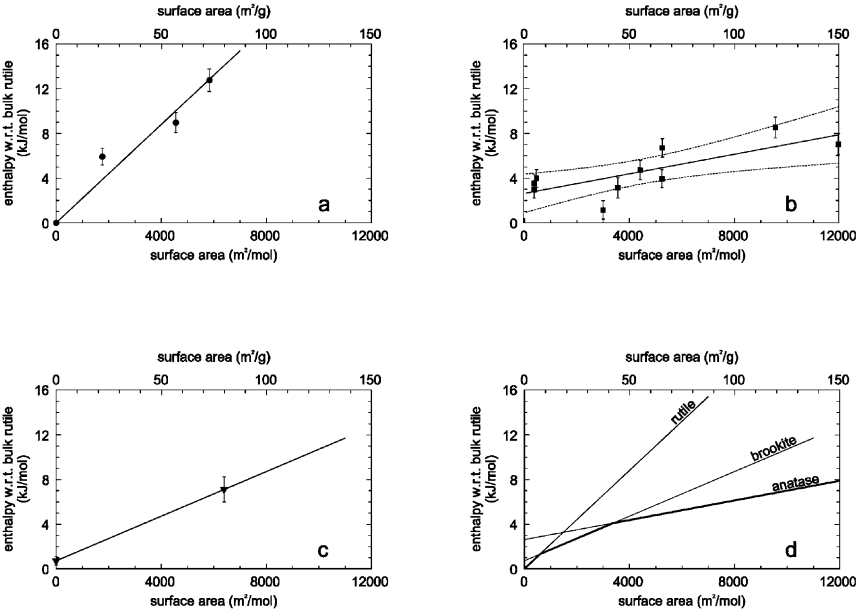

Fig. 1. Enthalpy of nanocrystalline samples with respect to bulk rutile (kJ/mol) versus surface area (m^2/mol) (a) for nanorutile (b) for nanoanatase, dashed curves represent 95% confidence limits for the mean, (c) for nanobrookite (6), and (d) phase stability crossover of titania. The lines are taken from Fig. 1(a, b, and c) and the darker line segments indicate the energetically stable phases, from Ranade et al. 2002 [19] (Reprinted by permission from National Academy of Sciences, USA).

the stability field of various polymorphs. Rutile is energetically stable for surface area <592 m^2/mol (7 m^2/g), brookite is energetically stable from 592 to 3174 m^2/mol (7 to 40 m^2/g), and anatase is energetically stable for greater surface areas. The anatase and rutile energetics cross at 1452 m^2/mol (18 m^2/g). The dark solid lines represent the phases of lowest enthalpy as a function of surface area. The energetic stability crossovers are confirmed.

Of course phase stability in a thermodynamic sense is governed by the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) rather than the enthalpy. Low temperature heat capacity and entropy data are available for anatase and rutile (6), but not for brookite. The data for anatase probably refer to a fine grained (perhaps nanophase) sample, but no characterization is given. Thus the anatase entropy may contain contributions from both bulk and surface terms. The data suggest that rutile and anatase have the same entropy within experimental error (S^0(298 K, rutile)=50.6±0.6 J/mol K and S^0(298 K, anatase)=49.9±0.3 J/mol K). Thus the $T\Delta S$ will not significantly perturb the sequence of stability seen from the enthalpies.

This work can be generalized to other nanophase materials. Zirconia and zinc oxide are important from the materials science point of view. Iron and manganese oxides are important as both minerals and materials. An understanding of the patterns of surface energetics for different polymorphs will give predictive power. Measurements of heat capacities on carefully controlled nanophase samples will shed light on surface entropies. A comprehensive picture involving surface enthalpies, entropies and free energies with the effects of hydration is essential to understanding nanophase stability and reactivity in both natural and synthetic systems, and is thus useful to both Earth science and solid state chemistry.

2.4. Uranyl minerals

Complicated assemblages of fine-grained low-temperature minerals challenge our understanding of mineralogy, both chemically and geologically. The crystal structures of minerals in complex geochemical environments should be related to the occurrences and distribution of the minerals. Recently, with the introduction of synchrotron radiation and CCD-based detectors of X-rays, it has become possible to solve the structures of crystals with an effective volume of less than (20 μm) [3,20,21,22]. Details of the structural relationships of fine-grained low-temperature minerals are now attainable, and should revolutionize understanding and applications of low-temperature mineralogy.

Synergisms between mineralogy and solid state chemistry exist in many areas. One topical example is uranyl (U^{6+}) minerals. Uranyl minerals are extraordinarily complex, and our understanding of this important mineral group lags behind that of almost all other important groups. More than 180 uranyl minerals have been described; these are key to understanding the genesis of uranium ore deposits [23], and are also important in the environment. They form due to the weathering of uranium mine and mill tailings, where soils are contaminated with actinides [24], and will be the main products of alteration of spent nuclear fuel in a geological repository that is oxidizing and moist, such as the proposed repository at Yucca Mountain [25,26]. It is likely that many of the radionuclides contained in nuclear waste forms will be incorporated into the uranyl alteration phases that form in the repository [27,28].

The structural hierarchy of uranyl minerals and inorganic compounds has been established on the basis of the polymerization of those polyhedra of higher bond-valence [29,30](Fig. 2). The majority of inorganic uranyl compounds contain sheets of polyhedra of higher bond-valence, although structures containing finite clusters, chains and frameworks of polyhedra of higher bond-valence also occur. Structural units tend to be complex in uranyl minerals, even when they are of low dimensionality. For example, the chain that is the basis of the structure of the uranyl sulfate uranopilite contains clusters of six uranyl pentagonal bipyramids that share equatorial edges and vertices, with the clusters cross-linked to form chains by sharing vertices with sulfate tetrahedra [31]. In uranopilite, the chains are linked directly by hydrogen bonds, as well as to interstitial H_2O groups.

The majority of uranyl minerals have structures based upon sheets of polymerized polyhedra of higher bond-valence. Tremendous structural complexity exists within the more than 100 sheets observed in inorganic uranyl compounds, and it is difficult to probe the relationships between these sheets. A topological approach has been developed to facilitate understanding complex sheets based on the arrangement of the anions in the sheet [30]. The utility of this approach is that sheets that appear

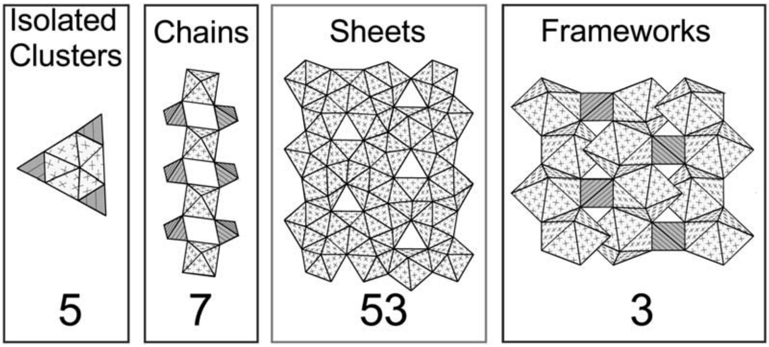

Fig. 2. The structural hierarchy of uranyl minerals based on polymerization of cation polyhedra of higher bond-valence (from Burns, 1999[32] Reprinted by permission of the Mineralogical Society of America, USA).

very different often have the same underlying sheet anion topology. This approach is indispensable when dealing with complex sheets, as it provides the means to relate such sheets to simpler topologies. Most sheet anion topologies from uranyl compounds can be constructed as stacking sequences of five different chains of polygons. Typically, only one or two chain types are needed to construct a given topology [32], and this approach permits comparison of anion topologies. For example, unusually complex sheets of uranyl polyhedra have been found in the structures of the Pb uranyl oxide hydrates vandendriesscheite and wölsendorfite [32,33], with primitive repeat distances of 41 and 56 Å, respectively (Fig. 3). Analysis of the sheet anion topologies using the chain stacking sequence approach reveals that both of these sheets are built of modules of simpler sheets (Fig. 4). In this regard, complex uranyl mineral structures are similar to some other mineral structures such as sulphosalts and complex sulfides.

Recent structural studies of uranyl minerals provide the foundation for development of an understanding of bonding and structural topologies. Bonding potentials

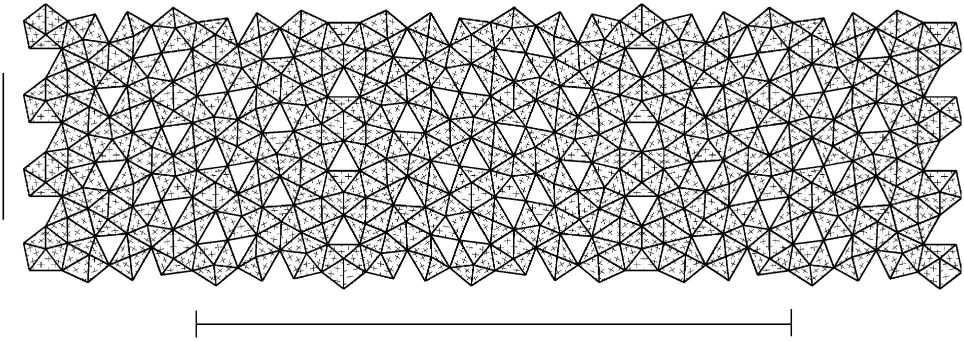

Fig. 3. The sheet of uranyl polyhedra in the structure of wölsendorfite (from Burns, 1999[32] Reprinted by permission of the Mineralogical Society of America, USA).

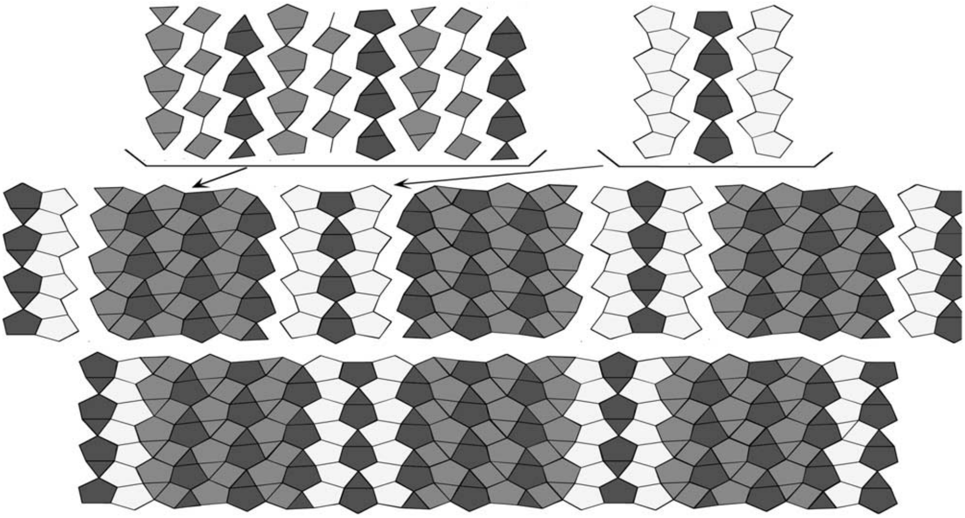

Fig. 4. Development of the wölsendorfite sheet anion topology as a stacking sequence of chains. This approach demonstrates that the wölsendorfite anion topology is composed of modules of the simpler α-U_3O_8 and β-U_3O_8 anion topologies (Reprinted by permission of the Mineralogical Society of America, USA).

for uranyl polyhedra should be established, perhaps using quantum mechanical simulations, although this approach is especially demanding because of relativistic effects involving core electrons on the U atoms. Such potentials may then be used for static energy minimizations and molecular dynamic simulations of uranyl minerals, including crystal surfaces. The relationships between the structural units and interstitial components also need to be modeled, and the role of interstitial components as structure directing agents should be addressed. An understanding of the energetics of complex sheets of uranyl polyhedra is needed, and may provide the basis for development of a method to predict thermodynamic properties of uranyl minerals on the basis of structural connectivity.

X-ray absorption spectroscopy (XAS) permits the probing of oxidation states and local coordination environments about U in minerals [34]. Further development of this approach is warranted in the area of analysis of extended X-ray absorption fine structure (EXAFS) spectra for U^{6+}. The situation is complex owing to the occurrence of U^{6+} in three different coordination environments, and the sharing of uranyl polyhedral elements with a diverse range of oxyanions, including silicate, phosphate, arsenate, carbonate, vanadate, and sulfate. The spectra of U^{6+} associated with mineral and bacteria surfaces can also be difficult to interpret [35,36]. Studies of the EXAFS spectra of several model compounds containing different coordination environments about U^{6+}, and multiple U valence states, will substantially improve the applicability of this technique to complex natural specimens.

Recent advances in characterization of the structures and chemistries of uranyl minerals provide the foundation for studies of their thermodynamics. However, there is a dearth of material and much of what is available are natural intergrowths of phases. Calorimetric studies of carefully characterized synthetic and natural uranyl compounds will further establish the thermodynamic properties of these minerals, and should provide the underpinning for development of methods of prediction of thermodynamic parameters based upon structural connectivity.

2.5. Conclusions

Many materials are important both in the Earth and in technological applications. The distribution, discovery and mining of ores and other raw materials pose critical technological, social, and political issues. Impending real or manipulated shortages of such materials (water, oil, chromium, to name some) are important political drivers. The transport, refining, use, and eventual disposal of these ores and their technological products pose equally important social environmental questions. The nuclear fuel cycle, for example, must consider the cradle-to-grave (ore body to nuclear reactor to repository) handling of uranium. Solid state chemical issues (the chemical reactions involved) must be considered in the context of geological processes (transport of contaminants by groundwater, long term climate change, volcanism). Many minerals are crystalline silicates and aluminosilicates, and amorphous and glassy silicates (e.g. obsidian glass) are also found in nature. Thus there is strong overlap of the science of Earth materials with fields such as glass, zeolites, and cements. Certain binary oxides, notably those of Si, Al, Fe, Mn, and Ti are important in both technology and nature. There are commonalities between sulfide minerals and semiconductors. Equally importantly, many processes—crystallization, melting, dissolution, diffusion, surface reaction, catalysis—are common to Earth and materials science. Geological reactions are governed by surfaces, interfaces, and nanoparticles. The emerging field of nanogeoscience further links solid state chemistry and Earth science. We therefore believe that the potential benefit derived from fostering increased interactions between these fields is very great.

3. Biology

Christopher Gorman, Milan Mrksich, Uli Wiesner

3.1. Introduction

The study and exploitation of biological processes has not yet had substantial overlap with the field of solid state chemistry. However, given recent developments, there is substantial reason to believe that this will be an area of tremendous future growth. The earliest manifestation of this research—bio-inorganic chemistry—sought to understand the function of metal clusters in enzymes and electron transfer proteins. This field has matured considerably. However, it still begs more fundamental understanding. More importantly, this body of work suggests new opportunities such as mimic of functions of cluster-containing proteins in, for example, energy transduction and catalysis. In parallel, use of metallic surfaces to conjugate proteins and oligonucleotides has resulted in new opportunities for bio-assays, preparation of bio-inspired devices and fundamental studies of biomolecular function. It is obvious that conjugation of biomolecules to a wider variety of surfaces can lead to new functions and new opportunities for hybrid devices. These could include solid-state semiconducting materials and the walls of zeolitic channels. This work also extends to the interaction of materials with whole cells—control of their growth and proliferation can be effected using simple surfaces. Perhaps solid-state materials can further the efforts to couple electronic, electromagnetic and mechanical stimulations to cells and ultimately to tissues.

3.2. The relevance of biology to solid state chemistry

Biology shares important relevance with solid state chemistry in two ways: first, lessons from living systems offer new strategies for designing and preparing solid state materials, and secondly, the development of technologies based on biological components (e.g., sensors) require solid state components with specific properties. In the first example, organisms produce a variety of materials that parallel synthetic solid state materials, including single crystalline magnetic nanorods and structural scaffolds based on composites of minerals and proteins. These materials are assembled by self-assembly and protein-mediated pathways (in water and at room temperature) which suggest new strategies for preparing synthetic materials. In the second example, many biosensing technologies require that biological components (proteins, nucleic acids, cells, etc.) be joined to a substrate that can transduce biological activities into electrical signals. There is still a need for solid-state materials that have tailored electrical, optical, mechanical and magnetic properties to realize new biosensor designs.

3.3. Current federal programs and support

The attendees of the workshop discussed the state of current federal support for biological opportunities in solid-state materials. While firm data for federal funding of this area was not available, what follows is a community perspective of the funding portfolio. Research activity in this area has largely been supported by special programs and as minor components of traditional programs. Existing programs, largely funded by the NSF, do not have sufficient budget flexibility to explore biologically oriented approaches in solid-state materials. The NIH has a growing interest in developing technologies that in part rely on solid-state materials—largely focused through the BECON consortium—but this agency has yet to implement programs. A number of special programs, largely within the DoD, have focused on applied aspects of solid-state materials for biotechnologies. While these programs have been important to demonstrating the promise of this emerging field, they are non-recurrent and therefore must be replaced with stable and renewable sources of support.

3.4. Breakdown of scientific opportunities

3.4.1. What does biology bring to solid-state chemistry?

The control of the shape and the size of inorganic materials is an important feature of natural growth phenomena. For biological systems both are the result of long evolutionary optimisation processes and are intimately related to specific functions [37]. In biomineralization, complex morphologies on different length scales are usually obtained through cooperative self-assembly of organic and inorganic species [38,39]. In spite of the considerable success in understanding the mechanisms of self-assembly, it remains a challenge for solid-state chemists and material scientists to mimic such natural pathways and develop simple and efficient routes to advanced materials. In Fig. 5 is a picture of single cellular organisms that use inorganic substances as building material for complex shell structures [40]. Organic molecules serve as structure directing agents for the generation of these shells. Structure direction is exerted on both crystalline (e.g., $CaCO_3$) as well as amorphous (e.g., SiO_2) inorganic materials. Several lessons can be learned from looking at Fig. 5. First of all, structure formation down to the nanometer regime is realized in these shell structures. Second, inorganic materials in the vicinity of cell surfaces have survived billions of years of evolution indicating that these materials have a lot to offer when it comes down to, e.g., issues of biocompatibility.

In natural growth phenomena proteins play a key role. While in the biological sciences a lot of effort is devoted to the detailed understanding of their functions, on the materials science side structural protein concepts are more and more integrated

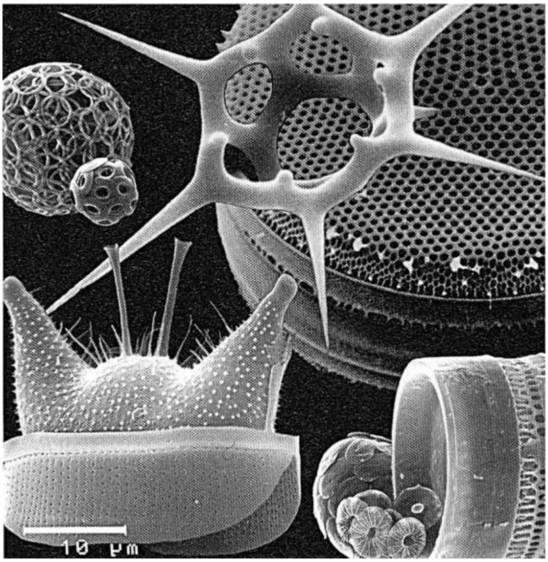

Fig. 5. Single cellular organisms with complex shell structures from inorganic materials[40] Reprinted by permission of Wiley-VCH, UK).

into materials design opening exciting opportunities. As indicated in Fig. 6, block copolymers can be viewed as model macromolecules for the behavior of protein structures. It is thus not surprising that in the recent past these synthetic chain molecules and their self-assembly behavior have found their way into studies of size and shape control of inorganic materials. For example it has recently been demonstrated that block copolymers can be used to control the growth (habit) of anisotropic inorganic crystals [41]. Furthermore, block copolymers have found their way into the design of silica-type mesostructures [42] opening pathways to the preparation of ceramic nano-objects with controlled shape, size, and composition [43] as well as to mesoporous materials [44,45].

In the past organic–inorganic interfaces have been stabilized primarily through non-covalent interactions. Copying a strategy of natural systems, an alternative approach is to actually incorporate parts of the organic molecules, e.g. synthetic polymer chains, into the inorganic structures. Properties can be anticipated for such composite materials that are vastly different from those of the parent organic as well as inorganic precursor materials, thus offering enormous scientific and technological promise for new materials with unknown property profiles [46]. Taking polymers as the organic molecules the future potential of this approach lies in the versatility of the polymer chemistry as well as that of the solid-state chemistry (e.g. sol–gel chemistry) that can be exploited in the materials synthesis. Complex hierarchical structures integrating functionalities from organic as well as inorganic materials might thus become available opening a whole new field to be explored.

Looking at Fig. 6 it is apparent that natural growth phenomena often operate far from equilibrium. In contrast, most materials investigated by the solid state chemistry community today are obtained from processes leading to equilibrium or “close to” equilibrium structures. This has to do with the fact that in natural systems active transport processes are involved in structure formation. As an example, organic templates for inorganic crystal growth might change as a function of time leading to

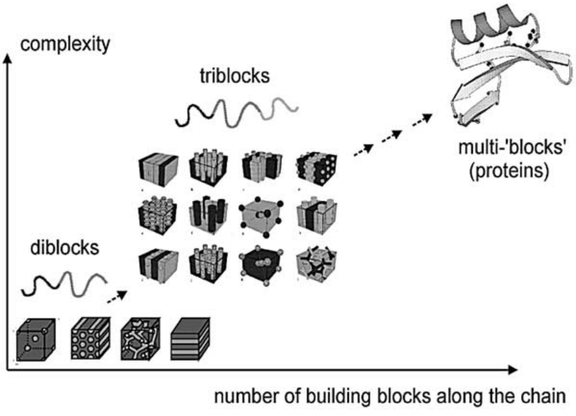

Fig. 6. Complexity diagram for blocked macromolecules[40] (Reprinted by permission of American Chemical Society, USA).

structures difficult to reproduce in the synthetic world. While the study of phenomena like “oscillatory reactions” in chemistry or “self-repair” in biology are well established these concepts have not yet found entry into synthesis strategies in solid state chemistry. The potential benefits are tremendous looking at structural and functional control of solid-state materials from the living world.

While offering tremendous scientific and technological promise, the integration of organic as well as inorganic molecules to novel hybrid materials according to concepts derived from natural systems poses a number of challenges to the solid-state community. Through the reduction of structural features to the nanoscale, surfaces and interfaces become dominant factors in the property control, a phenomenon generally appreciated in nanoscience. The integration of macromolecules (natural as well as synthetic) also significantly increases the importance of dynamical features of such systems. The width of the motional mode spectrum of polymers covers many orders of magnitude. Thus, the importance of techniques like solid-state nuclear magnetic resonance (NMR) spectroscopy, that are able to measure structure, order and dynamics over a broad range of time and length scales are expected to increase [47]. Finally, integration of multiple components with multiple interactions into hierarchical structures often leads to synergistic effects and thus complex behavior. Tackling the multidimensional parameter space of such complex systems with linear techniques is inadequate. Faster approaches as, e.g., provided by combinatorial chemistry, are promising and are expected to lead to significant contributions in the field.

3.4.2. What can solid state chemistry do for biology?

This section outlines opportunities for applying solid-state materials and approaches to problems that traditionally lie in basic and applied biology. These opportunities include those where the methods and expertise common in solid-state materials are important to addressing scientific problems in biological areas and also those where the properties of solid-state materials are important to biotechnologies.

3.4.2.1. Biointerfacial science Many biomedical and sensor technologies require that a material reside in contact with a biological fluid. The complex interactions between man-made materials and components of biological fluids (which principally include proteins) often lead to unwanted interactions with detrimental effects in the particular application. One limitation to understanding these non-specific interactions of proteins with materials has been a lack of analytical methods that have the sensitivity and spatial resolution for characterizing the bio–materials interface. At the same time, many of these techniques are common in solid-state materials—indeed, many have been developed because of the needs in this field—and offer important opportunities to gain a fundamental understanding of the more complex surfaces used in biological environments. There is a substantial opportunity to apply the experimental analytical methods of solid-state materials to elucidate the principles of the bio–materials interface and then guide the design of these interfaces that have controlled properties. Research and development on this frontier is critical to the development of several technologies, including indwelling sensors, tissue engineering and electrical prosthetic devices.

3.4.2.2. Transduction schemes in sensors Biosensors combine a molecular recognition function—for selective binding to the target analyte—with a transduction function that translates binding events ultimately to an electrical output. The most important sensing strategies to date have used either fluorescent or radioisotopic labels to quantitate bound analyte. While these methods are sensitive and time-tested, they have not been easily reduced to microformat (or the analogous lab on a chip formats) that are important to several sensor applications. The hardware required for counting isotope decay and for imaging fluorescence (particularly in confocal mode) are not yet reducible to microformat scales. Indeed, there are a range of opportunities for applying other transduction schemes that more directly couple biological activity at a substrate with a physical activity within the substrate. Many of these strategies—including those that rely on mechanical, thermal, magnetic, plasmon coupling—require solid-state substrates that possess tailored properties. These applications represent an emerging frontier theme in solid-state materials.

3.4.2.3. Hybrid cell-based technologies An emerging theme in engineering is the development of cell-based microtechnologies, which seek to build devices that combine cellular and tissue components with conventional materials processes found in microfabrication. This recent interest is motivated by the realization that the combination of man-made systems and biological systems, which each have unique characteristics, could yield engineered devices with broad new capabilities. The development of cell-based sensors that monitor environments for pathogenic agents have now entered commercialization and represent the possibilities for cell-based engineering. In the near term, a central challenge in these programs is the development of a common framework for designing and building structures having both materials and biological components. This framework must address the development of strategies to integrate the functions of engineered systems—which are based on firm physics and engineering, use inorganic and metallic materials, and are constructed with photolithography and microfabrication tools—and biological systems—which use soft materials in aqueous environments, rely on self-assembly for their construction, and where the design rules are in many cases incompletely understood. Again, the scientific and technical expertise that are common in solid-state materials have a central role to play in this emerging field.

3.4.2.4. Synergistic technologies What new things can these two areas do together that is not specifically based on either of the two? Up to this point, the major concern has been to define interdisciplinary efforts in which either solid state chemistry or biology takes the lead. However, in exploring this boundary, one must also consider activities that are truly synergistic. These are completely new research directions that are not well represented by paradigms in either of the traditional fields. The path for the establishment of new paradigms is difficult to predict. Moreover, it also can be hard to follow—it often requires some time and substantiation by historical perspective before a new avenue can be declared a paradigm. Two examples are provided in an attempt to suggest the potential for true synergy between these fields.

Recently, Montemagno et al. [48] reported harnessing of the F1-ATPase motor found in biology to produce a new type of nano-motor (Fig. 7). By using nano-scale lithography techniques to define anchor points for the F1-ATPase apparatus and by attaching nickel nanowires to the tops of the motor, this biological system could be integrated with these solid-state structures to produce a motor. Biological motors have well-defined modes by which they operate and are powered. Moreover, they are highly efficient. This motor exploits all of these features and extends operation to the motion of nanoscale structures. Rotation of the nanopropeller was initiated with 2 mM adenosine triphosphate and inhibited by sodium azide. This motor could generate ca. 100 pN of force and, over the course of hours it performed with an efficiency of about 80%. To manufacture at the nanometer scale, motors and machines are likely to be required. Biological motors offer efficiency at the right length scale yet require the introduction of other, nanostructured elements to display the types of new functions one could envision wanting.

Another attractive place to exploit the biological apparatus is in energy transduction. Greenbaum et al. have illustrated a biophotovoltaic device in which photo synthetic reaction centers are exploited to generate a photovoltage [49]. This is accomplished via the long-distance charge separation inherent in the photosynthetic process. By attaching these structures to platinum-coated chips, a photovoltage of approximately one volt per molecule can be measured. This hybrid structure suggests opportunities in energy conversion and in computing elements as well (Fig. 8).

3.5. Needed infrastructure

Programs that merge solid state materials with biology require new types of infrastructures. Significantly, user facilities for fabricating structures that are based on conventional micro-fabrication and on biological materials and methods do not yet exist. This need can be met by commissioning ‘dirty fabs’, which contain common tools for microfabrication, deposition, and processing and also allow cells, proteins,

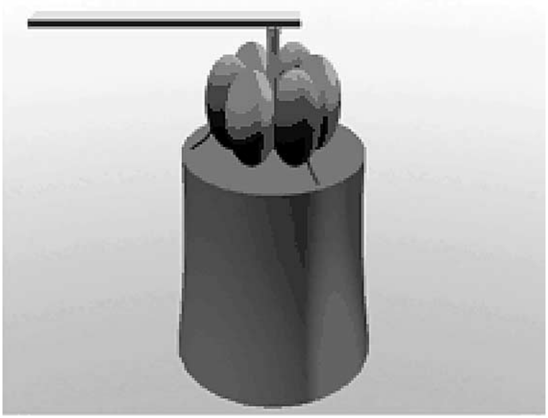

Fig. 7. Nanoscale biological motor[48] (Reprinted by permission from American Association for the Advancement of Science, USA).

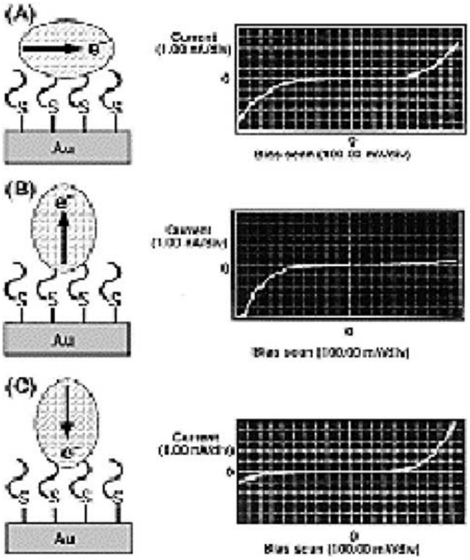

Fig. 8. The orientation of individual PSI reaction centers can be determined by the measurement of the I–V curve. (A) If a PSI is oriented parallel to the electric surface, a semiconductor-like I–V curve with a bandgap of -1.8 eV can be observed. (B),(C) If a PSI is anchored perpendicular [up as in (B) or down as in (C)] to the gold surface, a diode-like (current rectification) I–V curve can be observed. (A) and (B) are examples taken from PSIs anchored on a 2-mercaptoethanol treated gold surface. For illustration purposes, the size of the PSI reaction center is enlarged. It is possibly embedded among the surface molecules so that the negative charge COD groups tug equally at the two positively charged end groups [49] (Reprinted by permission from American Physical Society, USA).

nonconventional organic and inorganic materials to be used. The facilities also require experienced full-time staff members that can maintain the equipment and work with non-expert users on specific projects. This latter point is very significant; many of the users of a dirty fab will not have experience in microfabrication and will not choose to spend several months learning the techniques inherent in microfabrication. A second broad infrastructure need is to support the highly diverse multi-investigator teams that will be necessary to make significant progress in this field. Programs could be modeled after the NSF programs for Institutional research efforts (e.g. NSEC, MRSEC, ERC). In practice, these research centers provide important collaborative environments and support to seed research programs that are then very competitive for more traditional forms of funding.

3.6. Educational objectives

Clearly there is substantial potential profit in the integration of research activities in solid state chemistry and biology. As this represents a new type of activity for both of these communities, one must ask what new educational objectives does this call for? First and foremost, it calls for scientists who are expertly trained in this area. This training can only happen in an environment where students hear about and learn about this kind of interdisciplinary effort. Research activities that promote interdisciplinary interactions and efforts in an academic setting will be a necessary first step. Although the discussion of research and education is often kept separate in these sorts of reports, research is education—particularly in new, interdisciplinary areas.

Naturally, there is also potential profit in re-examination of the traditional curriculum. Learning about interdisciplinary science, however, cannot occur through a completely new curriculum—academic chemists and physicists will not accept a "weakening of training" in their area. Refusal to abridge current courses leads to more courses, which the academic community also doesn't like. Thus, this problem is not simply solved. In redefining and refining an interdisciplinary curriculum, the following two general guidelines are proposed:

1. Develop educational concepts generating students fluent in languages of various communities.
2. Define the central concepts in each field and develop a curriculum that teaches concepts and uses synergistic examples whenever possible to show the parallels developing between the fields.

Is there any model for promoting these types of interdisciplinary educational efforts? Bioengineering departments created over the past decade at many universities provide either a starting point, or a model or a partner for this new kind of education. Such departments are generally relatively new, yet some have acquired enough age that they can provide an initial assessment of agendas that do and do not work. Overall, however, education (which is, in part, research) remains a fundamental challenge.

4. Energy storage and conversion

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4.1. Introduction

World oil reserves can be anticipated to meet world demand for perhaps another 70 years [50]. While this timescale may not evoke an immediate call to action, atmospheric CO_2 levels, deriving primarily from fossil fuel combustion [51], have risen dramatically since pre-industrial times, from 280 ppm to 370 ppm today, and are predicted to reach between 500 and 700 ppm by the year 2100 [52], and thus demand a response from the scientific community. Solid state chemists have much to offer by way of solutions. Indeed, viable, long-term solutions to meet our energy needs while maintaining the quality of our environment will increasingly depend on electrochemical processes within and at the surface of solids. Photovoltaics, fuel cells, thermoelectrics and batteries are all devices in which energy storage or conversion relies on a coupling of chemical, thermal and/or electrical phenomena within the solid state. The direct and elegant coupling of these phenomena, in turn, is responsible for high efficiencies in fuel cells and batteries, and for the ability to use energy sources that might otherwise have been lost, such as sunlight in photovoltaics and “waste” heat in thermoelectrics.

In discussing the broad topic of energy, it is necessary to distinguish between *sources*, both primary and secondary, and *technologies* that serve as either energy conversion devices or energy storage devices, Table 2. The vast majority of our planet’s energy resources are available in the form of fossil fuels, whereas our con-

Table 2
Energy sources and technologies

Energy Sources

Primary	***Secondary***
Fossil/chemical (oil, natural gas)	Chemical (H_2, methanol)
Hydroelectric	Thermal (waste heat)
Geothermal	
Wind	
Solar	

Energy Technologies

Conversion

Technology	**Conversion**
Combustion engine	chemical → (thermal →) mechanical (→ electrical)
Reactor	fossil → chemical
Fuel Cell	chemical → electrical
Photovoltaic	solar → electrical
Photoelectro-chemical cell	solar → chemical
Thermoelectric	heat → electrical
Stirling engine	heat → mechanical (→ electrical)

Storage

Technology	**Interconversion**
Battery	chemical ↔ electrical
Capacitor	chemical ↔ electrical
Electrolyzer[a]	electrical ↔ chemical
Flywheel	electrical ↔ mechanical
Hydrogen storage	chemical

[a] Electrolyzers are considered energy storage rather than conversion devices because their input is electrical energy, which must be generated using some other conversion device.

sumption of energy is primarily in the form of electricity or mechanical work. As will be demonstrated below, solid state materials chemistry can play a critical role in many electricity generating technologies, particularly those which bypass mechanical work as an intermediate step. In addition, energy transmission technologies (involving superconducting electric cables) and fuel stream purification technologies (involving hydrogen separation membranes), also stand to benefit tremendously from advances in solid state materials chemistry.

4.2. Materials and technologies

4.2.1. Membranes: reactors and separators

As our fossil fuel-based energy economy relies to a greater and greater extent on natural gas rather than oil, it is clear that highly efficient means of converting gaseous methane to liquid chemicals, which can be more easily transported, are required. Similarly, means for generating and separating oxygen and/or hydrogen are becoming increasingly important. Over the past decade oxygen ion transport membrane reactors have attracted considerable interest as cost-effective alternatives to conventional methane conversion processes and for oxygen separation. The membrane in such a reactor is comprised of a dense ceramic oxide that has both high electronic and high oxide ion conductivity at temperatures in the range 700°C–1100°C. At the air-side of the membrane, the surface catalyzes the reduction of oxygen [$1/2O_2+2e^- \longrightarrow O^=$]; the other surface catalyzes either the oxygen recombination reaction when the membrane is used as an oxygen separator, or the methane partial oxidation reaction [$CH_4+O^= \longrightarrow CO+H_2+2e^-$]. The overall oxygen transport process is driven by the gradient in the oxygen chemical potential. Analogous reactors/separators can be envisioned based on mixed proton/electron conductors, although relatively few oxides with good conductivity of both protons and electrons have been reported to date. Hydrogen separation membranes are particularly relevant to energy technologies: in PEM (proton exchange membrane) fuel cells that use hydrogen produced by on-board reforming of hydrocarbons, significant process simplification can be achieved by replacing portions of the CO clean-up hardware by a hydrogen separation membrane.

Considerable progress has been made over the past decade in the development of oxygen ion-transport membranes for use in methane partial oxidation. Most are based on defect perovskites (or related structures) containing a variable valence element, e.g. $(La,Sr)(Fe,Co)O_{3-\delta}$ and $SrFeCo_{0.5}O_x$. Relative to conventional partial oxidation routes, such membranes reactors offer very high selectivity, with methane conversion rates of up to 98% and CO selectivities of up to 90% [53]. While these results demonstrate exceptional promise, several challenges remain to be addressed. In particular, the materials implemented to date require relatively high temperatures in order to attain acceptable flux (high diffusion rates, rapid surface kinetics and high electronic conductivity). Moreover, because the specific volume of the membrane material is strongly dependent on oxygen partial pressure, the chemical potential gradient across the membrane leads to severe internal stresses and often failure. The development of oxides with a lesser dependence of chemical bond distances on transition metal valence is thus a significant challenge and opportunity to the solid state chemistry community.

Two main types of inorganic hydrogen membranes have been studied based either on microporous materials (porous silica, zeolites and related) and ion transport systems. The microporous materials separate hydrogen as molecular hydrogen and rely on selective diffusion through pores ($\leq$2 nm) in the solid phase. Ion transport systems, in contrast, require dissociative adsorption of hydrogen at the membrane surfaces and coupled transport of $H^{+}+e^{-}$. Silver–palladium membranes are the most studied of this type but oxides have also been considered. Many proton conducting pervoskites, such as doped barium cerate, exhibit primarily protonic conductivity at temperature below ~500°C, but become mixed proton–electron conductors at elevated temperatures, $>$700°C, and are thus viable for high-temperature membrane reactor applications. Alternatively, dual phase composites of nickel with proton conducting perovskites can be implemented at lower temperatures, as can mixed electronic–protonic conducting transition metal oxides, originally developed for electrochromic applications. At present, microporous systems are limited by their low separation factors at reasonable fluxes, silver–palladium systems are limited for many applications by poisoning, and none of the other systems have adequate fluxes.

In order for the chemical and energy industries to be able to take full advantage of the high selectivities and yield-enhancements offered by membrane reactors in a broad range of reactions, significantly improved membrane materials are required. Strategies are needed for the discovery of new materials that meet the complex performance criteria: fast diffusion rates, rapid surface kinetics, high electronic conductivity, and good chemical and mechanical stability. Accordingly, solid state chemistry, with its historical strength in new materials discovery, has a significant role to play in advancing the field. Experimental synthetic efforts to identify improved membrane materials must be guided by computational efforts, that may be able to explain the properties of synthesized compounds, and uncover promising new directions. Particularly challenging will be to develop a complete theoretical framework for understanding and enhancing surface catalysis by multi-component oxides.

Of the often competing materials properties required for membrane materials, diffusion, conductivity and surface kinetics establish the overall rate at which a desired reaction will occur, whereas chemical and mechanical stability establish the lifetime of the reactor. Reaction rates can often be enhanced by architectural control, and as such do not rely solely on improvements in material properties. For example, thin membranes can bypass limitations in conductivity and diffusion rates, and can even reduce internal stresses, whereas roughened, high-area surfaces can bypass limitations in surface reaction kinetics. Taking advantage of this approach will require novel processing routes to yield supported thin films with controlled surface morphology. The selectivity of zeolitic and other porous materials will also benefit from recent solid state chemistry advances in the fabrication of nanostructured materials with highly controlled pore sizes and pore size distribution.

4.2.2. Fuel cells and regenerative fuel cells as electrolyzers

Fuel cell technology, for both stationary and mobile applications, has the potential to improve energy efficiency and distribution and to reduce the environmental impact of the use of fossil fuels. Among the attractive features of fuel cell technology are: the conversion of chemical energy into electrical energy with high efficiency; the distributed and modular nature; and low environmental impact (no NO_x, low SO_x, no noise, no transmission lines). They will also serve a critical role should the generation of hydrogen from non-fossil sources and a truly closed energy cycle become a reality.

The central component of a fuel cell, shown schematically in Fig. 9, is the ion conducting electrolyte. In the simplest example, a fuel such as hydrogen is brought into the anode compartment and oxygen into the cathode compartment. Hydrogen is oxidized to form protons and electrons at the anode, protons travel through the electrolyte, and then react at the cathode with oxygen and electrons. The flow of ionic charge through the electrolyte is balanced by the flow of electronic charge through the device to which electrical power is provided. Solids in which protons, hydronium ions, hydroxide ions, oxide ions, ammonium ions, and even carbonate ions are mobile are all known, but for fuel cell applications, oxide ions offer perhaps the simplest overall system. This is because direct electrochemical oxidation of a hydrocarbon fuel is possible when oxide ions are transported to the fuel compartment or anode. In contrast, in the case of a proton conducting electrolyte, the fuel is 'stripped' of hydrogen, and the proton is transported to the air compartment or cathode. If hydrocarbon fuels rather than hydrogen are to be utilized as the energy source, at best, excess water is required in the fuel supply in order to convert this fuel to CO_2 and hydrogen, the latter of which is used in the electrochemical process. Hydronium, hydroxide and carbonate ion conductors introduce further complications in fuel cell operation because an otherwise inert species, H_2O in the case of hydronium and hydroxide conductors or CO_2 in the case of carbonate conductors, must be continuously recycled through the system. State-of-the art fuel cell electrolytes are listed in Table 3, along with the fuels typically utilized, the recycled species, and temperatures of operation.

Critical to the function of a fuel cell are the electrodes/electrocatalysts. Within

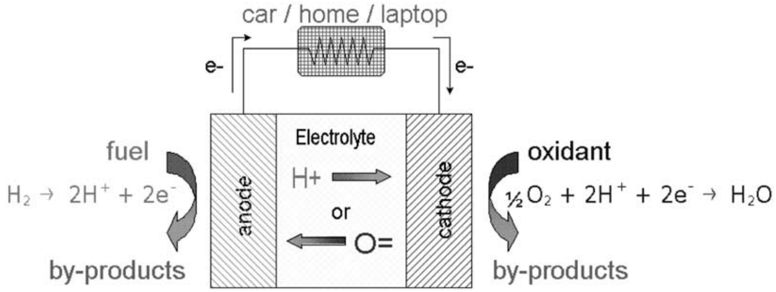

Fig. 9. Schematic of a fuel cell. The overall chemical reaction is $H_2+1/2O_2 \rightarrow H_2O$. Anode and cathode reactions written assume a proton conducting electrolyte.

Table 3
Fuel cell types and selected features [54,55]

Type	Temperature °C	Fuel	Electrolyte	Mobile Ion	Recycled species
PEM: polymer electrolyte membrane	70–110	H_2, CH_3OH	Sulfonated polymers(Nafion tm)	$(H_2O)_nH^+$	H_2O
AFC: alkali fuel cell	100–250	H_2	Aqueous KOH	OH^-	H_2O
PAFC: phosphoric acid fuel cell	150–250	H_2	H_3PO_4	H^+	
MCFC: molten carbonate fuel cell	500–700	hydrocarbons, CO	$(Na,K)_2CO_3$	CO_3^{2-}	CO_2
SOFC: solid oxide fuel cell	700–1000	hydrocarbons, CO	$(Zr,Y)O_{2-\delta}$	O^{2-}	

the electrodes, transport of gaseous (or liquid) species, ions, and electrons must all be facilitated, and at the points where all three meet, the so-called triple-point boundaries, the electrocatalysts must reduce the oxygen and oxidize the fuel, respectively, at the cathode and anode. Thus, the electrodes must be porous, electronically and ionically conducting, electrochemically active, and have a high surface area. It is rare for a single material to fulfill all of these functions, especially at low temperatures, and thus a composite electrode, of which the electrocatalyst is one component, is often utilized. For high temperature solid oxide fuel cells, single component electrodes are possible because mixed conducting ($O^=$ and e^-) ceramics are known and reaction kinetics are relatively fast. For low temperature proton conducting polymer systems, mixed conducting systems are virtually unknown, and slow reaction kinetics require specialized (precious metal) catalysts. Thus composite systems are the state-of-the-art.

There is little question that today’s fuel cell systems are complex and costly because of the design constraints placed on them by the materials (electrolytes and electrodes/electrocatalysts) available. For example, while SOFC systems offer apparent simplicity, they suffer from the requirement of very high temperature operation, necessitated by the low mobility of the bulky oxygen ion through the zirconia electrolyte. High temperature operation, in turn, precludes the use of low-cost metals in the fabrication of non-electrochemical fuel cell components and is one of the primary reasons that SOFCs are not yet commercially competitive. It is likely that major breakthroughs will be needed to lower the operating temperature to 650°C, at which direct hydrocarbon oxidation can still be achieved. Polymer electrolyte membrane fuel cells rely on the relatively facile transport of hydronium ions through hydrated regions of the sulfonated polymer. Their high conductivity enables operation at close to ambient temperatures, which is well-suited to portable applications. The challenges here arise from the sluggish reaction kinetics, precluding the direct use of hydrocarbon fuels other than perhaps methanol. Major breakthroughs in electrocatalysts are required and indeed few dare to propose that heavy hydrocarbons could ever be directly utilized in PEM fuel cells. An additional set of complications arise directly from the hydrated nature of the polymeric electrolyte material. Because the mobile species is hydronium, high levels of humidification are required to maintain high electrolyte conductivity, yet this must be balanced by the need to remove water from the cathode and prevent flooding of the electrocatalyst. Other consequences of utilizing a hydrated polymer as the electrolyte are (1) high rates of methanol diffusion from anode to cathode in a direct methanol PEM fuel cell, and (2) degradation in mechanical properties due to ‘swelling’ upon hydration.

Operated in reverse, a fuel cell can serve to generate hydrogen and oxygen from the electrolysis of water. In principle, a single device can serve both electrolysis and fuel cell functions providing a compact instrument for both energy storage and electricity generation. The major types of electrolyzer that have been developed to at least small pilot scale are [56]: AWE, alkali water electrolyzer; PMWE, polymer membrane water electrolyzer: and SOWE: solid oxide water electrolyzer. While there are several features of electrolyzer operation that are similar to those of fuel cells, there are a number of distinctions. First, the reactions that must take place in the electrolyzer are the complement of those that must take place in the fuel cell, and thus reaction pathways and electrodes are fundamentally different. Second, because the Gibb’s free energy change and hence also the equilibrium voltage associated with the reaction $H_2+1/2O_2 \rightarrow H_2O$ and are decreasing functions of temperature, it is thermodynamically preferable to perform electrolysis at elevated temperatures (under high pressure) but operate (H_2/O_2) fuel cells at reduced temperatures. Third, given that electrolysis is typically aimed at producing hydrogen rather than oxygen, pure proton conducting electrolytes offer the advantage of generating undiluted hydrogen whereas the hydrogen generated from SOWEs must be separated from unreacted water. Much as in the case of fuel cells, wide-scale implementation of electrolyzers faces major obstacles with respect to electrolyte and electrode performance, which in turn negatively impact cost, efficiency and reliability.

These challenges beg for solutions in terms of new materials—new electrolytes free of the difficulties that currently plague state-of-the-art oxide ion conductors and polymeric proton/hydronium ion conductors; and new electrocatalysts that can rapidly break down hydrocarbon fuels and are tolerant to species such as carbon monoxide and sulfur. The traditional strength of solid state chemistry, materials discovery, can thus be exploited. Approaches that have recently shown tremendous promise are inorganic, ‘dry’ proton conductors and ceria-based catalysts for direct electro-oxidation of higher hydrocarbons at temperatures as low as 500°C. The search for new materials must be balanced with careful characterization and fundamental understanding of such phenomena as reaction pathways on the surfaces of complex oxides, surface modifications in the presence of adsorbates and under electric fields, and transport across solid–solid interfaces. It is only with such understanding that thoughtful directions for future research can be set. In addition, architectural control of fuel cell and electrolyzer electrodes is a critical area for major advances. The same material or mixture of materials may lead to dramatically different properties when subjected to different processing routes that lead to different pore sizes, pore size distribution and surface area. The fuel cell community has yet to take advantage of recent breakthroughs in nanoscale fabrication that could lead to engineered electrodes with revolutionary performance.

4.2.3. *Thermoelectrics*

At the heart of thermoelectric (TE) modules are materials with a unique combination of properties: high thermoelectric power, high electrical conductivity and low thermal conductivity. These properties define the thermoelectric figure of merit $ZT=(S^2\sigma/\kappa)T$; where S is the thermopower (or Seebeck coefficient), σ the electrical conductivity, κ the thermal conductivity, and T the temperature. Such a combination of properties, critical to obtaining high device efficiency, is difficult to achieve in a single material because often the properties are interdependent and change at the detriment of each other. This situation creates a great challenge and an exciting opportunity for solid state chemists, theorists and materials scientists to devise creative approaches to optimize all relevant properties. The potential pay-offs for addressing this challenge are substantial, both in the realm of thermal management and thermal-to-electric power generators.

The operation of a thermoelectric power generator is shown schematically in Fig. 10. When a temperature gradient is applied to a thermoelectric (or any) material, the mobile charge carriers at the hot end preferentially drift to the cold end, inducing a voltage, the so-called Seebeck effect. The sign of the Seebeck coefficient depends on the sign of the charge carriers. Consequently, a pair of n-type and p-type “legs” can be placed in parallel with a temperature gradient, but in series with respect to electron flow, and the voltage generated across each leg will be additive. In this manner, power is delivered to a load placed in the circuit from both legs. Other thermoelectric devices, such as coolers and heaters, utilize similar circuitry. Thus, useful thermoelectric materials must not only exhibit high ZT over a wide tempera-

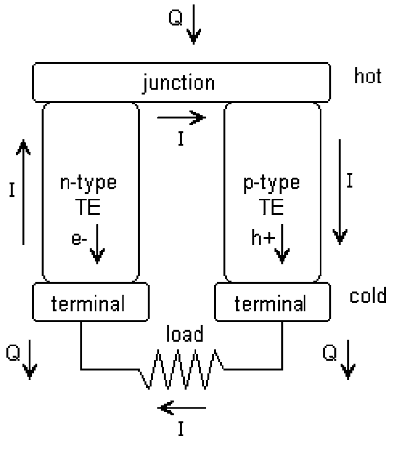

Fig. 10. Schematic of a thermoelectric generator; I=current, Q=heat.

ture range, but must also be compatible with both donor and acceptor doping. Although the two legs could be made of unrelated n- and p-type compounds, complications with material compatibility and device design can arise if the properties (coefficient of thermal expansion, thermal conductivity, electrical conductivity, etc.) of the of the two legs differ significantly.

The advantages offered by thermoelectric devices over alternative approaches to cooling or power generation can be substantial: Thermoelectric modules contain to moving parts and are highly reliable—indeed, TE modules have operated continuously on NASA Voyager 1 and 2 missions since 1977. The size and weight of such devices are often small and their performance is orientation independent, making them particularly attractive for space and flight applications. They have the ability to operate in an electrically "quiet" mode, and can deliver very localized cooling to temperatures below ambient. The temperature control offered by thermoelectric coolers is very precise and constant, well within 0.1°C variability. These features render TE coolers attractive for electronic applications. In addition, the cooling does not require the use of environmentally damaging chlorofluorocarbons. In the realm of power generation, thermoelectric modules offer the ability to convert waste heat, particularly from combustion processes (automotive engine exhaust, utility stacks, etc.) into useful electrical energy, and may play a key role in addressing the nation's energy needs.

While the advantageous features of thermoelectric devices are well recognized, they are not widely available today because of their low efficiencies, which, in turn, is a direct consequence of the low values of ZT in known materials. Even the best thermoelectric materials exhibit (bulk) values of ZT that are only on the order of 1, a milestone that was achieved in the early 1960s [57]. These are materials based on complex semiconductors, with optimized carrier concentration, high effective mass carriers, high carrier mobility, narrow band-gap, and low lattice thermal conductivity [58]. Examples include Bi_2Te_3, PbTe, $Si_{0.8}Ge_{0.2}$ and Zn_4Sb_3. If one is to develop viable thermoelectric devices, much higher values of ZT, up to 2, 3 and even 4, are necessary. Such targets, while they have remained elusive, violate no laws of thermodynamics. Indeed, there is no fundamental limit to the possible value of ZT, and the slow progress of recent years calls for new approaches in thermoelectric materials development.

Unlike many technological, solid-state electronic materials, in which simplicity in composition and structure and extreme crystalline order and purity are sought, thermoelectric materials are more likely to have complex composition, elaborate crystal structure and even disorder, features which may lower lattice thermal conductivity without sacrificing electrical conductivity and thermopower. Moreover, a single material is unlikely to exhibit high ZT over the entire temperature range of interest. Therefore a broad-based and sustained, exploratory synthetic effort, that encompasses many classes of materials and structures (chalcogenides, pnictides, intermetallics, oxides, etc.) and even leads to the development of entirely new families of materials, must be pursued if the challenge of high ZT is to be met. In this context solid state chemistry possesses a central role.

In addition to bulk material approaches, nanoscience many also have a role to play in next-generation thermoelectrics. There are theoretical considerations that predict quantum confinement, which can increase the density of states at the Fermi level, may be another path to systems with high *ZT*. Quantum confinement, using multilayered structures, can also provide interfaces between the layers that selectively scatter or confine phonons (lattice vibrations) to reduce the thermal conductivity. Thin film thermoelectric materials and devices thus offer exciting possibilities. Preliminary results for Bi_2Te_3/Sb_2Te_3 superlattices are very promising, with a reported effective ZT of 2.4 (at room temperature) [59], and efforts must now be directed towards implementing such structures in functional devices and thereby experimentally verifying this concept.

Any exploratory synthetic effort towards new thermoelectric materials must be complemented with a strong computational/theoretical effort, particularly in electronic band structure calculations and interpretation. Several parameters are critical in establishing thermoelectric behavior: actual band-gap, the shape and width of the bands near the Fermi level, the carrier effective masses and mobilities as well as the degeneracy of band extrema (i.e. number of valleys in conduction band or peaks in the valence band). Of the three properties that define *Z*, thermopower is particularly poorly understood. It cannot be predicted, nor do we know how to increase the thermopower of a material without depressing the electronic conductivity. With such understanding, solid state theory can provide invaluable guidance in selecting materials for consideration. The synthetic effort must also be matched by breakthroughs in approaches and methods of screening large numbers of candidate materials reliably and quickly. This necessarily brings together the fields of solid state chemistry, solid state physics, materials science and electrical engineering and close collaboration between scientists from these areas is of paramount importance.

4.2.4. Batteries

Batteries convert chemical energy directly into electrical energy and are the major power sources for portable electronic devices. The miniaturization in electronics during the past decade or so has revolutionized society. The exponential growth of popular portable electronic devices such as cellular phones and laptop computers has created an ever-increasing demand for compact, lightweight power sources. Lithium-ion batteries have become appealing in this regard as they offer higher energy density than other rechargeable battery systems such as lead–acid, nickel–cadmium, and nickel–metal hydride batteries. The higher energy density also makes them attractive for future electric vehicle applications. The higher energy density of lithium-ion cells is due to the higher cell voltages (4 V per cell) achievable by the use of non-aqueous electrolytes compared to the 1 to 2 V per cell achieved with the aqueous electrolyte based cells. The lithium-ion technology has become a commercial reality since the early 1990s as a result of the fundamental solid state chemistry research carried out in the 1970s and 80s on lithium insertion compounds and of the strong interaction between the solid state chemistry and the electrochemical science and engineering communities. Commercial lithium-ion cells are currently made with a layered lithium cobalt oxide cathode (positive electrode) and carbon anode (negative electrode) [60]. Unfortunately, only 50% of the theoretical capacity of the cobalt oxide can be practically utilized and cobalt is relatively expensive and toxic. On the other hand, the carbon anode exhibits large irreversible capacity. Additionally, cathodes with highly oxidized redox couples pose safety concerns. The challenge is to develop inexpensive and environmentally benign cathode and anode hosts of high electrochemical capacity and energy density and good safety characteristics. Solid state chemistry in collaboration with related fields is at the forefront of addressing this challenge.

The limited practical energy density or the unacceptable performance of some of the known lithium insertion hosts are due to the chemical and structural instabilities encountered with them during the charge–discharge cycling. These limitations provide an opportunity for the solid state chemistry community to improve upon existing materials and to explore new directions. The chemical instability originates from an interaction between the electrode surface and the electrolyte and an introduction of significant amount of holes into the oxygen band (oxidation of oxide ions). The structural instability originates from the tendency of the transition metal cations to migrate in the lattice to form thermodynamically more stable phases. Recent experiments suggest that the chemical and structural instabilities could be overcome to some extent by a chemical/surface modification of the electrodes to develop a more stable electrode–electrolyte interface and chemical substitutions to arrest the cationic mobility, respectively. In another direction, amorphous and nanophase materials produced by innovative chemical synthesis processes are found to exhibit exceptionally high capacities compared to the conventional crystalline materials. The origin of this behavior is not well understood and the inherent disorder of these materials makes it challenging to characterize their local chemistry and structure. High surface area materials represent another unique direction, one where local defect chemistry may now influence electrochemical properties. Moreover, the high surface area may lead to an enhanced interaction between the electrode surface and the electrolyte, which in turn is likely to play an important role in the charge storage mechanism. In summary, heterogeneous, nanophase materials offer new opportunities for battery materials. The solid state chemistry community, with its emphasis on structure–property relationships, is well situated to answer some of the key questions regarding these materials, namely the mechanism and kinetics of lithium insertion/extraction—particularly, where and how the ions are located in the lattice.

Overall, the challenge is to (i) develop new insertion host materials with high electrochemical capacity and energy density while preserving good structural and chemical stabilities needed for long-term charge–discharge cycling, (ii) characterize them adequately, and (iii) understand the electrochemical and solid state phenomena occurring in them. Solid state inorganic chemistry will continue to dominate the design and synthesis of new insertion materials. However, materials characterization will be a critical task, particularly in the case of nanomaterials, and strong interaction with related fields such as materials science and engineering and physics can help to make the new materials viable candidates for practical cells and advance the field rapidly with important breakthroughs. Electrochemical science and engineering will continue to have a strong interaction with solid state chemistry as in the past in elucidating interfacial phenomena and advancing the field of battery research.

4.2.5. Capacitors

Devices, particularly portable devices, whose operational features require high peak power, in which bursts of charge are rapidly delivered, frequently turn to power sources in which energy is stored via electrochemical capacitance. Electrochemical capacitors mimic dielectric capacitors in that one electrified plane with excess positive charge is separated in space from another electrified plane with excess negative charge (|+ −|), but in electrochemical capacitors, the electrified planes are electrodes immersed in an ionic medium (electrolyte) in which ions move as necessary to counterbalance surface excess charge at each electrode.

Each electrode in an electrochemical cell thus assembles two planes, or double layers, of electrical charge, as depicted in Fig. 11, in which the negatively charged electrode (left) is charge balanced by an ionic structure dominated at the interface by solvated cations, while the positively charged electrode (right) is charge balanced by an ionic interfacial structure dominated by specifically adsorbed anions. The magnitude of the surface excess charge at an electrode immersed in an electrolyte can be precisely controlled by the applied potential. Just as for an ideal dielectric capacitor, the amount of energy stored in an ideal electrochemical capacitor is directly proportional to the capacitance, which, in turn, is proportional to the area of electrified interface. The amount of charge that can be stored as an electrical double layer typically ranges from $10–40 \mu F/cm^2$. In order to store enough farads of capacitance to be useful in devices, the area of the electrified interface must be $>10^2 m^2$—electrochemical capacitors that store energy electrostatically at such high surface area electrodes are termed supercapacitors.

Multiple physical requirements now come into play in order to design a practical electrode structure in a supercapacitor: high surface areas of a lightweight electrode (to maximize energy density) formed of a solid-state material with high electronic conductivity (to minimize resistive losses which result in heat generation) and excellent chemical stability (to prevent degradation under potential in high-ionic-strength electrolytes) arranged in space such that porous paths permit facile electrolyte approach to the entire high-surface-area electrified interface.

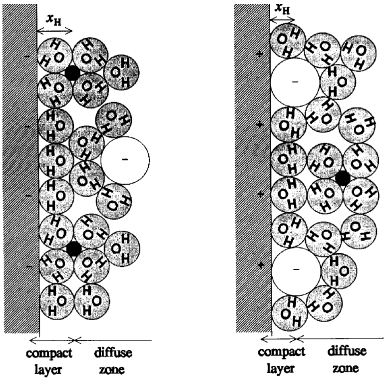

Fig. 11. Formation of electrical double-layers in pseudocapacitors.

Although metals and metal oxides have been explored as electrodes in supercapacitors, commercial devices utilize high surface area ($>1000 m^2/g$), highly porous carbons [61]. Fundamental, although clearly not commercially detrimental, drawbacks to carbon electrodes in supercapacitors arise from the relatively low conductivity of carbon relative to other solid-state conductors (which affects the maximum power a supercapacitor delivers at high frequency), and the long-term chemical stability of carbon relative to many metals, oxides, and ceramics.

State-of-the-art carbon supercapacitors store 50–100F per gram of carbon (or 4-8F/mol). In contrast, thin-film, high-surface-area morphologies of certain conductive oxides and non-oxides can store ionic charge at 150-2000$\mu F/cm^2$. This extra charge per unit surface area arises because both electron and ion charge are transferred into the structure, but the response, nevertheless, appears capacitive, i.e., $\partial Q/\partial V$ is constant over some potential window. This charge-potential (Q–V) response, designated “pseudocapacitance”, differs from that seen upon transfer of electron and ion charge into insertion battery materials in which the charge inserts at a characteristic energy associated with a defined redox process. Pseudocapacitive materials thus offer two means to store energy: as electrical double-layer capacitance and as electron-ion insertion over a broad potential window. Pseudocapacitive materials can store >10-times the energy of supercapacitors [62] and are usually termed ultracapacitors.[1]

The champion pseudocapacitive material to date has been hydrous ruthenium oxide, which stores 720 F per gram of RuO_2 and exhibits excellent metallic conductivity. Ruthenium, however, is scarce and costly, and alternatives are sought. Transition metal oxides need not be the only class of materials examined, although much can be learned from what is already understood, e.g., highly crystalline forms of ruthenium and cobalt oxides express low pseudocapacitance. Pair density functional analysis of the X-rays scattered from $RuO_2 \bullet xH_2O$ show that it is an innate nanocomposite comprising a rutile, electron-conducting RuO_2 network through hydrous, proton-conducting domains, where the fraction of the components tracks the mole fraction of structural water (x).

Recent work by the groups of Smyrl [63], Dunn and Rolison on sol-gel-derived nanoscopic, highly mesoporous, networked charge-insertion oxides has revealed that these architectures store charge in three ways: double-layer capacitance, energy-specific insertion of cations (as would be seen in a standard insertion battery material), and pseudocapacitance [64]. Materials that blend all three mechanisms of charge storage are innately hybrid and should be able to provide future functions now served by the physical/electrical coupling of battery and capacitor in applications that require both high peak power and sustained low power. The ability to store both battery-like and ultracapacitor-like charge is attributed to the disorder present in these nanomaterials [64].

Solid state chemical sciences have a tremendous opportunity to make significant

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[1] Note: carbon-based supercapacitors store a few percentage of their total capacitance as faradaic-derived pseudocapacitance because of redox-active functionalities (usually oxygenates) on the surface of the carbon. Electrodes in ultracapacitors, in turn, store ~10% of their total capacitance as electrical double-layer capacitance.

contributions to the materials of importance in energy storage. For example, a natural extension of carbon-based electrodes is the use of arrayed carbon nanotubes because of their inherently high surface area. While this approach holds promise, it is fundamentally limited by the inaccessibility of the inner walls of the nanotubes to liquid electrolytes. In general, it will be necessary to construct architectures in which the surface area contained within micropores (≤2nm) is minimized, and that accessible through mesopores (2-50nm) or macropores (≥50nm) is maximized. Furthermore, such control must be achieved in materials which are electronically conducting, often amorphous, and, ideally, also capable of charge insertion. Realizing such nanostructured, mesoporous architectures will require better theoretical, synthetic, and characterization approaches to disordered materials. A key challenge will be to "pin" the most active, highest performance physico–chemical state of the material even when exposed to thermodynamic forces (temperature, pressure, electrical potential, photochemical energy) that would otherwise drive re-structuring, crystallization, or densification of the nanoscale material. Another opportunity is the development of nonaqueous electrolytes, which permit larger ΔV, yet maintain rapid response of the ions and take full advantage of the surface area offered by the electrodes.

4.2.6. Photovoltaic and photoelectrochemical cells

Photovoltaic solar cells enable the direct conversion of light to electricity, whereas photoelectrochemical (PEC) cells can convert solar radiation either into stored chemical potential or to electricity. Until about 1975, the only approach for direct solar-to-electricity conversion under serious consideration was through the photovoltaic effect in solid-state semiconductor p–n junctions [65]. Here, p- and n-type materials are brought together to form a electrical contact, Fig. 12, and absorbed solar radiation creates electron-hole pairs in both types of materials. Electrons generated in the p-type region easily migrate across the p–n junction to the n-type region, and similarly holes migrate from the n-type to the p-type regions. This transfer of charge creates an electrical potential and a photocurrent which can then be used to power a load placed within a circuit that closes the loop from the n and p-type regions. The dominant semiconductors studied and under development were, until the mid-1970s, sin-

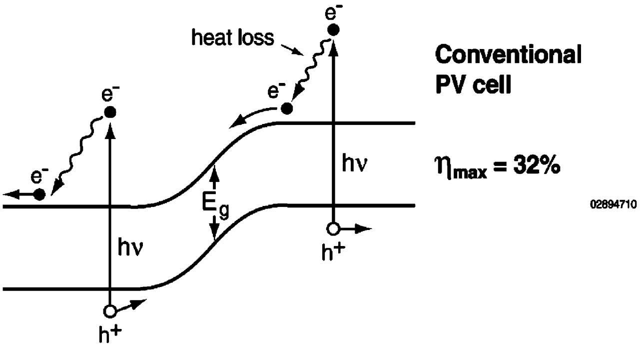


Fig. 12. Operation of a conventional photovoltaic.

gle crystal Si and GaAs. More recently, however, several other approaches have been discovered and investigated; these include: polycrystalline Si, thin film amorphous Si, polycrystalline II–VI thin film solar cells ($CuInSe_2$, CdTe), high-efficiency tandem solar cells ($GaAs/GaInP_2$), organic/polymer solar cells, and “quantum dot” solar cells.

Like photovoltaics, photoelectrochemical cells [66] rely on light-absorbing semiconductor structures that generate and separate electron-hole pairs (for example, see Fig. 13). When placed in contact with an electrolyte, holes generated in an n-type semiconductor will be injected into the electrolyte (for a p-type semiconductor, electrons are injected).

If the circuit is closed via an exterior path, electrons flow through the external circuit to an opposite metal electrode. In the case where the electrolyte is aqueous, water is oxidized at the n-type semiconductor–electrolyte interface (the anode), to produce oxygen and protons, whereas protons are reduced at the electrolyte–metal interface (the cathode) to produce hydrogen. The overall reaction thus results in the splitting of water into oxygen and hydrogen, and is termed photoelectrolysis. Methane, methanol, and ethanol may be formed in a similar manner by the photo-driven reduction of carbon dioxide with water using p-type photoelectrodes. Alternatively, photoelectrochemical cells can be modified to generate electricity rather than stored chemical charge by placing a single redox couple (i.e., a pair of chemical species that accepts and donate electrons) in the electrolyte. The redox couple serves to transport charge across the electrolyte, without inducing a net change in the chemical state of the electrolyte. Another type of photoelectrochemical solar cell is based on dye molecules adsorbed onto nanocrystalline titanium dioxide films in contact with electrolyte. In this case, the light is absorbed by the dye molecules which then inject electrons from its photoexcited state into the titanium dioxide, affecting charge separation and the production of photocurrent and photovoltage. Thus, photoelectrochem-

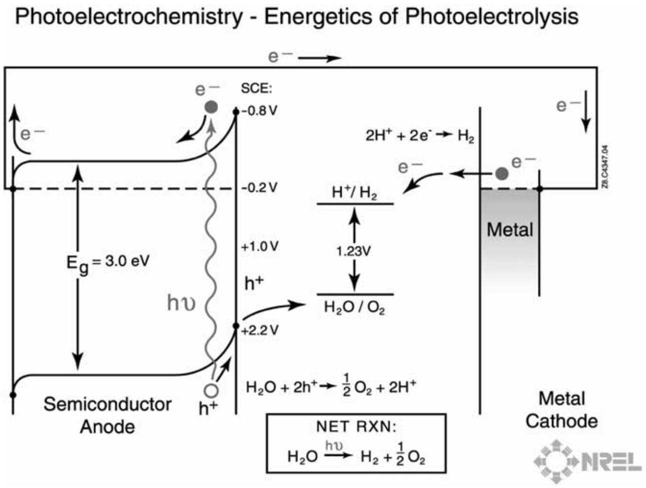


Fig. 13. Operation of a photoelectrochemical cell.

ical solar cells (semiconductor–liquid junctions and dye-sensitized solar cells) are new approaches to solar-to-electric conversion.

Photovoltaics and photoelectrochemical cells are, once fabricated, inherently environmentally benign. The direct conversion of solar energy into electricity by photovoltaics obviates any impact on the carbon cycle or consumption of scarce or environmentally problematic energy resources, whereas photoelectrochemical (PEC) cells can be integrated into closed cycle energy processes. The photo-driven reduction of carbon dioxide with water to form methane, melthanol and ethanol described above represent a form of artificial photosynthesis, analogous to biological photosynthesis that involves the conversion of water and carbon dioxide by green plants into oxygen and complex reduced carbon compounds (biomass). This process is highly attractive because, ideally, any carbon dioxide generated during hydrocarbon consumption is subsequently consumed in photolytic reduction of CO_2. Thus, the build-up of carbon dioxide as a greenhouse gas is mitigated. Solar water splitting similarly relies on an infinite energy source, limited only by the existence of the sun, and is truly non-polluting and free of carbon dioxide emission because only water is produced after the hydrogen is utilized to produce either electricity (via a fuel cell) or heat (via combustion).

The widespread implementation of photovoltaic electricity generation is limited today primarily by the high cost per unit electric power generated. The cost of PV electricity from Si solar cells is presently about 3–4 times that of conventional electricity (fossil, hydroelectric or nuclear). The two most critical factors controlling the cost of PV electricity are conversion efficiency and the cost of the cells per unit area. The ultimate conversion efficiency for unconcentrated sunlight is limited to about 32% in a single band gap threshold absorber in which the photogenerated electrons are in equilibrium with the semiconductor phonons (i.e., the excess photogenerated electron energy above the band gap is converted into heat). The efficiency of present Si solar cells is about 10–12%, and the cost is about \$250 to \$500/m^2. Photoelectrochemical cells are similarly limited by low efficiencies, compounded in some cases by slow reaction kinetics. Additional challenges arise in terms of materials compatibility, photostability, and device longevity.

For the production of ultra-high efficiency solar cells that have thermodynamic conversion efficiency limits of 66% rather than 32%, novel materials and structures need to be discovered and developed. The approaches include: (a) tandem solar cells with multiple band gaps that are optimized for the minimization of thermalization losses; (b) hot electron solar cells that allow the transport, transfer, and collection of hot electrons (i.e. electrons formed by supra-band gap photons) before they thermalize by phonon emission and convert their excess kinetic energy to heat; (c) discovery and development of semiconductor systems that permit photocurrent multiplication by enhancing impact ionization, whereby hot carriers produce one or more additional electron-hole pairs by an inverse Auger process, and (d) use of semiconductor structures that produce midgap bands that allow for two-photon absorption processes, thus sensitizing the system to the near infra-red, producing greater light absorption and higher photocurrent. The possibility of achieving these structures and effects have recently been shown to be enhanced by the use of nanostructures and semiconductor quantum dots, both in the form of semiconductor quantum dot arrays and as isolated quantum dots used instead of dye molecules in dye-sensitized solar cells or dispersed in conducting polymers.

For the development of low cost photovoltaics, efforts must be directed towards: (a) finding, developing, and understanding new organic semiconductors and electron- and hole-conducting polymers that have better electronic properties than present materials; (b) developing new dyes that can extend the response of dye-sensitized solar cells over the whole solar spectrum; (c) developing hole-conducting polymers for dye-sensitized solar cells that can efficiently transport holes from oxidized dyes adsorbed on the nanocrystalline TiO_2 surface to the counter cathode; (d) finding new semiconductor materials that are photochemically stable in liquid junction solar cells; and (e) developing new inexpensive semiconductor materials and processes that allow simple and low cost deposition as effective photovoltaic elements in a PV cell.

For water splitting in a PEC cell, a critical solid state chemistry problem that must be solved is that thus far semiconductors that have been found to be stable (oxides like TiO_2, $SrTiO_3$) have large band gaps (>3 eV) and hence do not absorb visible light and are thus inefficient, while semiconductors that absorb visible light (Si, GaAs, CdSe, CdTe, $CuInSe_2$) and are thus efficient, are not stable in water and photodecompose or photoxidize. New materials must be found that show both good conversion efficiency and long term stability against photocorrosion/photooxidation. An alternative approach for increasing efficiency is to utilize photovoltaic tandem structures in series with conventional electrolysis using metal electrodes. Such systems show very high efficiency for solar water splitting ($>15\%$ in the laboratory), but are expensive. The challenge here is to find inexpensive PV structures that can be optimized for electrolysis of water. Many of the challenges involved in the photoelectrochemical reduction of CO_2 with H_2O are as of yet unknown because the field is very much in its infancy. Nevertheless, it is clear that the reduction kinetics of CO_2 are rate-limiting, and again, photostability must be achieved.

The challenges outlined here represent tremendous opportunities for solid state chemistry in the area of materials for energy storage and conversion. Exploratory materials synthesis, coupled with characterization and computation, are envisioned to lead to major breakthroughs in both efficiency enhancement and cost reduction of photoelectrical and photochemical devices. The research involved is highly interdisciplinary, involving not only solid state chemistry and semiconductor physics, but spanning also physical chemistry, electrochemistry, photochemistry, organic chemistry, inorganic chemistry, and polymer chemistry.

4.2.7. Hydrogen storage

If a hydrogen energy economy, particularly in the transportation sector, is to be developed, it is certain that more effective means of hydrogen storage are necessary. We can classify hydrogen storage schemes into two broad categories consisting of (a) conventional storage, which includes compressed gas and liquid hydrogen storage and (b) sorption systems, which rely on van der Waals interaction (physisorption) or bond formation (chemisorption). Sorption systems would include metal hydride, carbon sorbent, borohydride and alanate storage. For mobile applications none of these candidates has yet to achieve a level of technological maturity or practicality that commercial markets will demand if fuel cell vehicles are to garner an environmentally and strategically meaningful share of the transportation market.

Compressed gas storage will require pressures in excess of 5000 psi or 350 bar in order to meet the mass ratio of fuel to fuel-container target of 6.5 wt%. This is twice the pressure that is presently used in steel tanks that are familiar to us in laboratory and industrial use. While aluminum composite tanks have been developed for this application (with demonstrations to date of about 4 wt% H_2 [67]), reliability and safety issues related to their use have not been fully addressed. In addition, 20% of the energy content of this storage method is consumed during container pressurization. Liquid hydrogen storage systems have also been demonstrated but such systems require 20 K temperature to keep the hydrogen from boiling off and even well-insulated systems experience a 1.7% loss of hydrogen per day [67]. In addition, the energy cost associated with liquefaction of hydrogen are ~1/3 that of the energy content of the fuel itself.

In contrast to compressed or liquified storage, physisorbed or chemisorbed hydrogen can offer the advantages of higher gravimetric and volumetric densities using low burst pressure containers at ambient temperature. Because of the requirements for high gravimetric density, compounds of elements with low atomic number which can reversibly store and release hydrogen are necessary. To date, two classes of materials have been examined, metal hydrides and carbon compounds.

Many elemental metals form hydrides with high hydrogen contents, for example, MgH_2, REH_2 (rare-earth hydride) and $PdH_{0.5}$, however, the temperatures and pressures for reversible storage–release in these materials are unattractive for many applications (1–10 bar, 0–300°C). Hydrides of intermetallic metal compounds in many cases show excellent absorption–desorption behavior, enabling hydrogen to be stored and released over hundreds of cycles around ambient temperature. For example, a $La(Ni,Sn)_5$ material, based on the well-known AB_5 alloy system, is presently being developed for cryo-cooler applications for the Planck mission (2007 launch date). Metal–hydride beds will produce liquid hydrogen for cooling of the detectors on this probe. Unfortunately, the gravimetric density of lanthanum-based alloys is below 2 wt% and their cost is high. Higher mass densities can be attained only with light elements such as Li, Be, B, Na, Mg and Al. In many cases, strong interaction with hydrogen produces a material with high hydrogen content that is better considered an ionic compound than a hydride [67,68]. Examples include MgH_2 (7.7 wt% H_2), $Li_3Be_2H_7$ (9 wt% H_2), and $LiBH_4$ with 18 wt% H_2. As the strength of the chemical interactions and the hydrogen storage capacity increase, the temperatures required to extract the hydrogen also generally increase and cycling performance degrades. Whether this behavior is kinetic or thermodynamic in nature remains to be established (and likely depends on the specific material examined), and yet is of critical importance. If the behavior is limited by reaction kinetics, then surface treatments and catalysts can modify material behavior, as has been observed for alanates. Where thermodynamics are controlling, bulk material properties must be modified by chemical substitutions. Thus, understanding the behavior of intermetallics in the presence of hydrogen is a significant and important challenge for solid state chemistry.

Addressing this challenge, in collaboration with metallurgists and physical chemists, may result in new light-metal alloy systems and render hydrogen-powered fuel cells for automotive and other portable applications a commercial reality.

A carbon-based material would be an ideal sorbent for hydrogen storage. Large surface area activated carbons have long been known as effective physisorbents, relying only on van der Waals interactions between adsorbate and adsorbant. Surface areas of activated carbons between 1600 to 3000 m^2 g provide numerous sites onto which gases can easily adsorb and desorb with well-understood adsorption enthalpies. Interest was renewed in the use of carbons as hydrogen sorbents in 1997 with claims that certain carbon graphite nanofibers could absorb and retain 67 wt% hydrogen gas at ambient temperature and moderate pressures [69] (i.e., up to 23 standard liters or 2 grams of hydrogen per gram of carbon at 50–120 bar). More realistic measurements since then indicate that not more than ~4 wt% can be stored at ambient temperatures and high pressures, and is more likely limited to ~2 wt% [67]. While carbon-based materials may not miraculously solve current hydrogen storage challenges, there remains great value in precisely understanding the interaction of hydrogen with different and very well-characterized carbon nano-structures. Indeed, current discrepancies in the literature may well be attributed to inadequate characterization of the carbon material employed. Tantalizing prospects for hydrogen sorbent by large surface area activated carbons and nanotubes remain, provided adsorption enthalpies can be suitably altered. The challenges of precise control of carbon synthesis conditions and material characterization are ones which require the input of solid state chemists, materials scientists, surface scientists and others, which, when brought to bear on problems of hydrogen storage may not only resolve discrepancies but also bring us closer to a hydrogen energy economy.

4.2.8. Superconductors

For reasons of space and expertise of the panel members some critical areas could not be addressed in depth, but certainly cannot be ignored. These are superconductors for electricity for transmission or mechanical energy storage via flywheels. The completely unanticipated discovery of high-temperature oxide superconductors in the early 1980s, and the even more surprising discovery of mid-temperature superconductivity in MgB_2 in 2000, suggests that additional discoveries are still to be made. The potential impact of superconductors operating above the temperature of liquid nitrogen on energy transmission and storage, and a number of other technologies, cannot be understated. Fundamental studies of crystalline structure in complex materials has advanced the field of superconductivity to its standing today, and continued collaborations with physicists, with expertise in understanding electron–electron interactions, and materials scientists, with expertise in crystal growth and large-scale synthesis, are anticipated to lead to further advances.

4.3. Thematics

There are certain common themes that pervaded the session on Materials For Energy Storage and Conversion. The following discussion identifies some of these themes and their relevance.

4.3.1. Surfaces and interfaces

A good deal of electrochemical science is directed at understanding the role of surfaces and interfaces in electrochemical processes. The continuing interest in nanophase materials means that electrochemical processes in these materials may now be dominated by surfaces and interfaces because of enhanced diffusion, higher defect concentration and disorder. Some indication of the role of surfaces and interfaces is already evident in the high levels of pseudocapacitance observed with mixed electron–proton conducting oxides, the enhanced ionic conductivity of certain nanophase inorganic solid electrolytes and the anomalous lithium capacity observed for transition metal oxide aerogels. It would seem that the challenge for the solid state chemistry community is not only in the synthesis of nanophase materials, but in leading the characterization of the physical and chemical properties of surfaces and interfaces, and in developing a fundamental understanding of their underlying thermodynamics.

4.3.2. Architecture/nanoscale science

The research community for electrochemically-based energy storage systems has long recognized the importance of establishing the proper architecture. A good example is the solid oxide fuel cell where the integration of anode and cathode structures with the electrolyte has become highly refined over the past decade and led to impressive advances in the technology. There is the recognition that the solid oxide fuel cell needs to be an integrated architecture that not only functions electrochemically, but also achieves mechanical and thermodynamic stability at elevated temperature in order to operate successfully. The “Bellcore Battery” is another example of where architecture plays a vital role. In this case, the integration of materials processing and microstructure control has largely defined the resulting architecture. Its impact on lithium battery technology has been dramatic.

The future of architecture is in extending it to the nanoscale. In order to facilitate electron transfer, “wiring schemes” must be established to supplant the traditional approaches that use powder processing. The prospect of developing an electronically conducting network that reaches the nanoscale is certain to lead to better utilization of the electrochemical materials and reactants. Access of reactants with ion and electron conducting phases (e.g. the three-phase boundary in fuel cells) is very much an architectural problem. Future directions in electrochemical architecture are likely to involve carbon nanotubes as a means of creating 3-dimensional wiring harnesses, mesoporous materials with interconnected porosity (e.g. aerogels) which enhance the transport of solvent, reactants or products, and mesostructured materials which use self assembly processes to separate ion conducting and electron conducting regions. In the past, the role of solid state chemistry was largely to create the “building blocks” of electrochemical architectures. In the future, it would seem that solid state chemistry can expand its role through an emphasis on architecture design.

4.3.3. Multifunctionality

The materials used for energy storage and conversion applications are generally multifunctional because of the need to possess the appropriate electrochemical properties under operating conditions. Over the years, solid state chemists have been quite successful in synthesizing electrolytes and electrode materials that exhibit adequate mechanical, thermal and chemical stability. A good example is stabilized zirconia, which is of interest to the structural materials community in addition to being the electrolyte of choice for solid oxide fuel cells. In addition to homogeneous materials, composite approaches have been successfully used to achieve multifunctionality. The advantage here is that one can design materials in which each component satisfies a particular function. This approach has been well demonstrated in the use of cermets (e.g., Ni with stabilized zirconia) and in inorganic gel electrolytes. The latter is a new direction in materials synthesis in that it is an organic/inorganic hybrid material. The organic (polymer or liquid) phase provides ion transport while the inorganic phase provides structural and mechanical stability. It is evident that the composite approach, especially the incorporation of nanophase materials, is well suited for developing a new generation of multifunctional materials for energy storage applications. Carbon nanotubes are clearly such a material; the outstanding mechanical properties of these materials make them ideal for reinforcing lightweight structures while their high level of electronic conductivity makes them suitable for current collection applications. Aerogels are inherently multifunctional. Their nanodimensional porosity gives them extraordinary thermal insulation properties while their high surface area enables them to be used as heterogeneous catalysts, supercapacitors and battery electrodes. It is not clear whether the solid state chemistry community is well suited for the challenges of multifunctional materials. Such materials are likely to need new synthetic approaches that integrate organics and inorganics, nanophase materials and the development of novel processing methods.

4.3.4. Computational materials science—a guide to new materials development

There is a long and successful history in the application of computational methods to energy storage and conversion materials. Over the years, theoretical work has addressed a number of important fundamental topics including cooperative ion motion, order–disorder phenomena and insulator–metal transitions. The future direction here may well be in guiding the synthetic efforts. Combinatorial methods do indeed work and computational approaches that support combinatorial methods could have substantial impact in terms of identifying regions of phase diagrams where experiments should start. Another key advantage is the broad spectrum of materials that can be addressed by computational materials science—from new photovoltaic systems, to thermoelectrics, to membrane reactor materials. There is no question that the solid state chemistry community can make tremendous strides in energy materials by continuing to incorporate computational methods into the discipline.

4.3.5. Characterization tools

The complex structures and interfaces encountered with the new materials require innovative and sophisticated characterization tools. For instance, high resolution transmission electron and scanning electron microscopies with elemental analysis, small angle X-ray scattering, synchrotron radiation, solid state nuclear magnetic resonance spectroscopy, photoelectron spectroscopy, Auger electron spectroscopy, electron energy loss spectroscopy, X-ray absorption spectroscopy, X-ray absorption near edge spectroscopy, Raman spectroscopy, electrochemical characterization techniques, and a variety of physical property measurement techniques will be valuable in this regard.

4.4. Concluding remarks

Advances in energy storage and conversion devices require that fundamental questions of charge and mass transfer through complex solids be answered, and that novel processing techniques be developed to implement strategies for microstructure and/or crystal structure modification. For example, a complete description of electrodes in fuel cells involves gas transport through porous media, ion and electron transport through porous solids, and electrochemical reactions at interfaces. With a complete description it becomes possible to design optimized electrode structures, and with advanced processing techniques it becomes possible to fabricate those structures. Such problems are inherently interdisciplinary in nature, and solving them requires the cooperative efforts of experts in fields spanning from solid state chemistry and electrochemistry to computational chemistry, materials science, surface science, catalysis and solid state physics.

Overall, the challenge is to develop new materials, characterize them adequately, and understand the electrochemical and solid state phenomena occurring in these materials. In this regard, strong interaction with condensed matter physics, materials science and engineering, surface science, chemical engineering, inorganic chemistry, electrochemistry, and computational materials science communities can help to advance the field rapidly and realize important breakthroughs. For example, while solid state inorganic chemistry is able to access high capacity amorphous and nanocrystalline oxide hosts, strong interaction with other disciplines such as physics, materials science, and electrochemistry is needed to adequately characterize these materials and make them viable candidates for practical cells. While theoretical calculations based on computational materials science have been helpful to explain some of the experimental observations, their full potential is yet to be seen. For example, a more reliable prediction of the crystal structures and phase stability for a given composition under various conditions (temperature, pressure, atmosphere, etc.) can guide the synthesis of new materials. The theoretical calculations can also possibly help in predicting the properties of and designing new materials. Once new materials are identified at the university laboratory scale, chemical processing will become an important issue in scaling up and fabrication of practical devices. Interaction with chemical engineering and surface science communities can help in this regard. Electrochemical science and engineering will continue to have a strong interaction with solid state chemistry as in the past in advancing many of the areas of research outlined here.

5. Molecular, hybrid and macromolecular materials

Kim Dunbar, Leonard Interrante, Janet Musfeldt, Ralph Nuzzo, Eugenio Coronado, Dante Gatteschi, Wenbin Lin, Sarah Tolbert

5.1. Introduction

This section of the report centers on a broad class of synthetic materials that are currently the subject of intense interest among scientists and engineers, both from a fundamental and applied perspective. These materials are distinguished by the presence of molecular constituents as a major functional component, or by the use of molecule-based approaches for their fabrication. The materials in the latter category are typically inorganic solids with unusual microstructures or external forms that are best prepared (or sometimes only prepared) by using molecular sources. In the much broader class of materials that incorporate molecular constituents as a major functional component, we find crystalline molecular solids, liquid crystalline materials and macromolecular (polymeric) materials, as well as a wide range of "hybrid materials" that combine, at length scales that range from nanometers to millimeters, one-, two-, or three-dimensional inorganic or coordinate-covalent arrays of molecules or macromolecules. Within this class of so-called "soft" materials reside the well-known thermoplastic and thermoset polymers that constitute a major proportion of the materials that are currently in widespread use throughout modern society and technology. Even in these cases, research on molecular-based materials is continuing to have a large impact on current technology, both through the introduction of new types of specialty materials (e.g., stereoregular polyolefins and various types of co-polymers) and by providing lower cost, or less environmentally sensitive, methods for the production and reuse of current commodity polymers. We shall focus here, however, on materials that have not yet found their way into widespread use in modern technology, but which show significant potential for making revolutionary changes in materials-based technologies. In general, these fundamentally new types of materials have a level of complexity and sophistication in their design and structure that is not found in typical commodity materials and which provides unique properties or property combinations that are needed for a wide range of advanced applications.

5.2. Major goals

The ultimate goal of molecular materials chemistry is to build organic and inorganic structures of increasing complexity and functionality in a controlled fashion. The frontiers of this area include: (a) the control of supramolecular interactions; (b) the use of metal coordinate bonds in the design of functional materials; (c) the development of new methods of fabrication that enable the organization of chemical and organizational structure over length scales that range from the dimensions of molecules to the sizes of macroscopic objects; (d) the control of the properties of self-assembled systems that are far from equilibrium.

In order to solve problems in these frontier areas, chemists must be committed to a systematic approach that involves:

- Using a combination of physical methods and theory to further our understanding of the properties of molecular materials.
- Exploiting synthetic control and principles of molecular design to further our understanding of the correlation between structure and physical properties.
- Applying this knowledge in the design of materials with novel or enhanced properties.
- Devising and assembling hierarchical molecular systems that exhibit complex functional behaviors. Materials of interest include systems that usefully transduce environmental or chemical signals (sensors) or process information (molecular devices and logic systems).

The design, preparation and study of physical properties of molecular assemblies and polymeric materials exhibiting interesting chemical, physical, or spectroscopic properties is a topic of great importance in current and future materials research. The quest in this area is not necessarily to obtain molecule-based compounds than can behave as classical solid state materials, but to produce materials that may exhibit completely new physical properties or types of functionality. The new properties may be a result of quantum confinement (e.g., discrete molecules showing magnetic hysteresis and quantum tunneling—nanomagnets), or a result of having more than one structural element present (e.g., hybrid materials coupling magnetism with conductivity or even superconductivity, or with optical properties). The main challenge in molecular materials research is the development of new synthetic strategies with which to construct molecules at the nano- and mesoscale levels and to specifically control their subsequent organization in solution and/or in the solid state. It is important to prepare these new materials in such a way as to be able to use their properties in devices. This includes the formation of thin layers and organized films, or their encapsulation/intercalation etc., into solids. Since this research encompasses the design and synthesis of materials, their physical characterization, and the theoretical study of the physical phenomena associated with them, it necessarily requires close contact of experimentalists and theoreticians as well as chemists and physicists with complementary expertise.

A second important issue is the development, improvement, and broader dissemination of experimental techniques for the characterization of molecular materials more generally and nanomaterials explicitly. The advances being made in the field of nanoscale materials require significant new investments in the capital infrastructure that supports characterization. The issues of concern in the study of hybrid materials are broadly representative of those affecting the field of solid-state chemistry more generally. The ability to address and develop structural understanding at length scales appropriate to the understanding of advanced materials properties are critically needed. These efforts frequently require the use of advanced instrumental methods of characterization, ones that are neither appropriate for the characterization of either molecules or the extended bulk states of condensed matter systems. Considerable opportunities exist to improve access to such instrumentation and to develop new methods for characterizing nanoscale materials.

We also note that it is vitally important to develop suitable theoretical models and computational methods for predicting and explaining the structural and functional properties of complex molecular materials. The ability to understand organizational, dynamical, and assembly properties of nanoscale systems, for example, requires significant advances in fundamental theory based on methods of statistical mechanics and molecular dynamics. The joining of quantum methods with molecular dynamics offers equal promise, offering a vision that it may well be possible to define the evolution of a system—its most fundamental dynamics—at a level that embraces both the properties of the electronic system and the atoms of which it is comprised. The ultimate goal of these efforts is to achieve an understanding of both the structural, electronic, and dynamical behaviors of the materials at a sufficient level of understanding so as to enable predictive calculations as to their organizational, electronic, magnetic and optical properties in the solid state.

5.3. Specific frontier areas of current and future development

5.3.1. Molecular precursor routes to materials

Research in this area involves the use of molecules (including polymers) to generate a material (or controlled porosity in a material) through a chemical reaction. This research has had a long history of development that includes the use of sol–gel chemistry and related sol–gel processing methods (e.g., supercritical drying) to obtain metal oxides in special forms (e.g., continuous fibers or coatings), microstructures (e.g., aerogels) or phase distributions (composites); the use of volatile (or soluble) molecular precursors for chemical vapor deposition of metals, ceramics and semiconductors; and also the pyrolysis of polymeric precursors as a means of obtaining covalent ceramic materials (e.g., SiC) in the form of coatings, continuous fibers, or as matrices for composites. A variant of the sol–gel process that has found widespread use in technology as a source of synthetic zeolites and other porous materials, uses molecules and molecular assemblies as removable "templates" for the controlled growth of micro- or meso-porous structures (see below). Current research in these particular areas centers on the understanding and control of such processes through changes in the precursor molecular structure or processing method. In addition, the design of new methods for particular applications in electronic processing (e.g. templating or growing nanotubes and nanofibers) and the control of the product microstructure are also highly relevant issues. A recent example that combines several of these approaches involves the use of organic dendrimers to "template" the sol–gel synthesis of a methylsilsesquioxane network, and then the subsequent removal of the dendrimer by heating to produce a material which has closed pores of controlled size. This advanced material offers significant promise for use as a low dielectric constant film in advanced microelectronic circuits.

5.3.2. Self-assembled and organic materials

The properties of complex matter and assemblies follow from structural elements embedded at a variety of length scales. These influences begin at the most microscopic level—that is at sizes associated with their atomic or molecular constituents—and extend upwards through increasingly more complex hierarchies of organization. The organization may arise via a thermodynamically directed assembly or form solely as a result of the temporal evolution of the underlying dynamics of the system. Progress in materials research will come to rely increasingly on our ability to understand, design, and exploit systems exhibiting properties such as these. Considerable progress has been made towards this end. For example, it is now possible to synthesize systems that develop very sophisticated large-scale structures via self-assembly (Fig. 14). Typically, this is a static self-organization and it remains a significant challenge to address (much less design) systems that assemble and perform even elementary functions by dissipating energy. Progress in research on organic materials will involve a very broad set of advances along several lines of inquiry that follow from these ideas. These include: the design of solid-state architectures via rational molecular design and synthesis; the organization of complex assemblies via the exploitation of supramolecular interactions; the organization of hierarchical structures and assemblies using advanced methods of micro and nanofabrication; the design and synthesis of responsive materials; and the development of function-driven assemblies.

Materials that contain molecular building blocks are arguably the most diverse

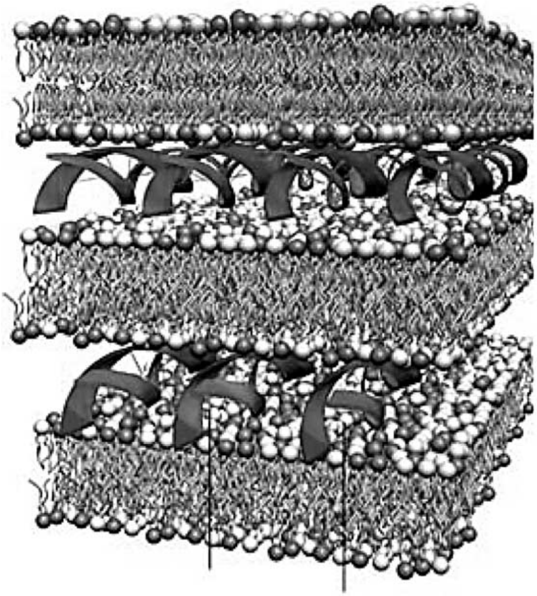


Fig. 14. Mesoscopic structure of DNA-membrane[70] (Reprinted by permission from American Institute of Physics, USA).

and functionally flexible form of solid-state matter. Extended structures, for example, can be made via direct covalent or coordination bonds connected in 1-D (the basis of technologically important linear polymers), 2-D (e.g. ladder polymers or sheet structures), or 3-D (e.g. dendrimers, networks, and gels) (Fig. 15).

Supramolecular materials closely follow examples of the structural habits observed for polymeric materials, albeit in such a way that the longer length scales of the assembly arise without the use of extended systems of covalent bonding; hydrogen bonded assemblies and the diverse mesophases formed by molecular amphiphiles provide elegant examples of the complex structural habits that can be developed in this way (Fig. 16). Materials with molecular constituents can be synthesized so as to impart important structural and mechanical behaviors in ways that exhibit unprecedented levels of anisotropy or effective ranges of engineering-rationalized design. These so-called “soft” materials often exhibit unprecedented levels of functionality: they can serve as insulators or conductors of current; they can provide barrier properties to prevent the contamination of structures by environmental agents or serve as the responsive molecular recognition elements that transduce their presence. Without argument, organic solid-state materials surpass essentially every other structural material on the basis of the value they add to the national economy. When metal atoms are introduced into this setting, the materials are even more diverse and can be tailored for additional properties such as magnetism and novel optical and electrical properties.

There exists significant opportunities for progress in research in this area of interest. The areas of potential impact are so broad that a report of this sort cannot hope to do justice to the entire field but, rather, can serve to suggest the nature of the horizons that lie ahead. A few key areas of current research interest are summarized below.

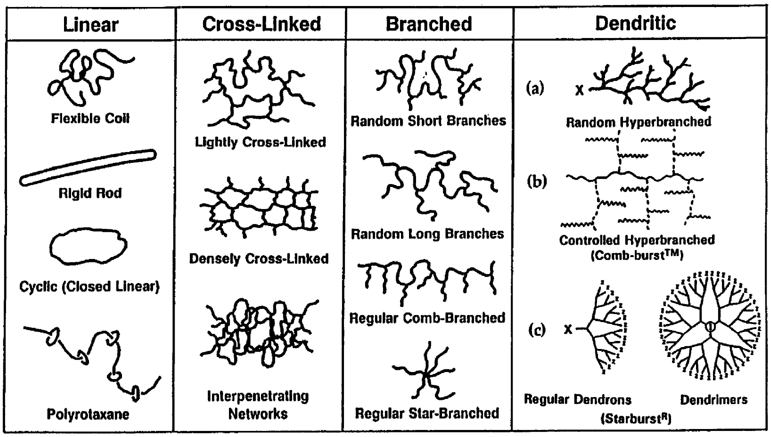


Fig. 15. Molecular building blocks[71] (Reprinted by permission from MRS Bulletin, USA. http://www.mrs.org/publications/bulletin/).

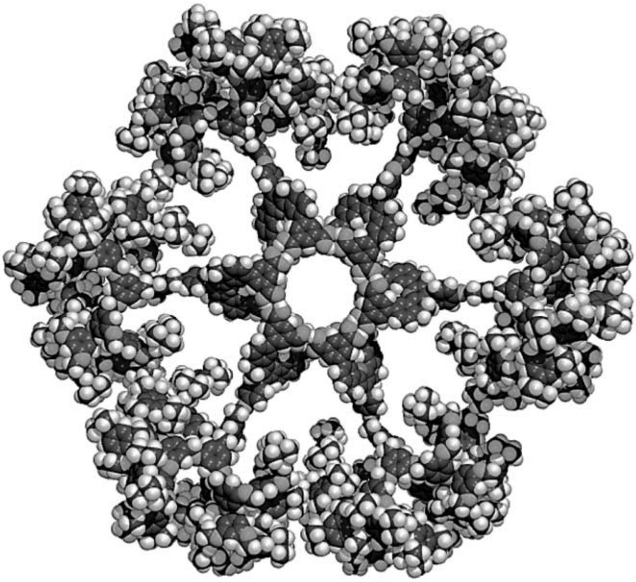


Fig. 16. An elegant example of a supramolecular structure[72] (Reprinted by permission from Amercan Association for the Advancement of Science, USA).

5.3.2.1. Synthesis A dominant area of need in synthesis is the development of methods that enable chemists to address compositional and structural complexity. The dominant paradigm in materials synthesis to this point is the purposeful creation of specific (“designed”) structures, following the belief that structure gives rise to function. Viewed in this way, synthesis is a powerful tool for systematic structure-property studies, enabling one to deconvolute a complex problem and invent new derivatives. Undoubtedly, this approach will continue to be important in the future and will make important contributions. However, preparing and studying materials one-at-a-time has its limits, especially when facing the vast diversity of structures that can be realized in molecular solid-state materials. This problem comes to the forefront when searching for new leads in materials development. Combinatorial methods offer one potential model in this regard. Alternatively, we might learn to link synthesis directly to desired function. *Function-driven* synthesis is a major opportunity and challenge for research in synthesis. Is it possible to create materials whose components are linked through strong yet reversible connections, such that there is continuous assembly and disassembly occurring? Can this be done so as to drive selection and expression of those materials that exhibit desired properties? Can materials be synthesized that are adaptive and/or self-repairing (Fig. 17)? Can an optimal arrangement for a desired optical or electronic property be used to direct the progress of a complex synthesis? Can a synthetic polymer of high molecular weight and significant segmental complexity be prepared so as not to exhibit polydispersity or statistical placements of monomers? The development of such approaches to materials synthesis follows close analogies to processes belonging to other areas

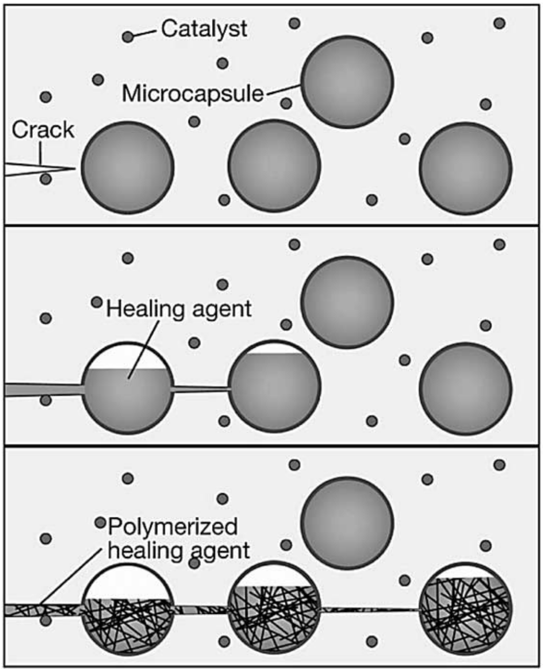


Fig. 17. Autonomic healing of polymer composites[73] (Reprinted by permission from Macmillan Publishers Ltd, UK).

of science, in particular to biology, and constitutes a significant area of opportunity for progress in materials research.

5.3.2.2. Assembly The use of assembly processes to drive the formation of desired organic structures in the solid state has been the focus of considerable attention in research. The prospects for making important advances in the future are significant and should be strongly encouraged. The ability of molecules to serve as the structural elements of a complex assembly system are well understood and finds perhaps no better representative example than that provided by the protein folding problem. Across a range of relevant time-scales, the assembly of these complex molecular machines follows along elementary pathways driven by the minimization of free energy. The complex energy landscape defines the trajectories of the system as it approaches the thermodynamically directed endpoint. These same ideas powerfully inform the use of self-assembly as a method for constructing solid-state materials and structures derived from them. A significant area of need continues to be found in the development of assembly methods that enable the flexible construction of organizational complexity, 3-D objects, or the non-close packing of structural elements (Fig. 18). There also exists a significant need to develop approaches to assembly as a platform technology for micro and nano fabrication that deliver the

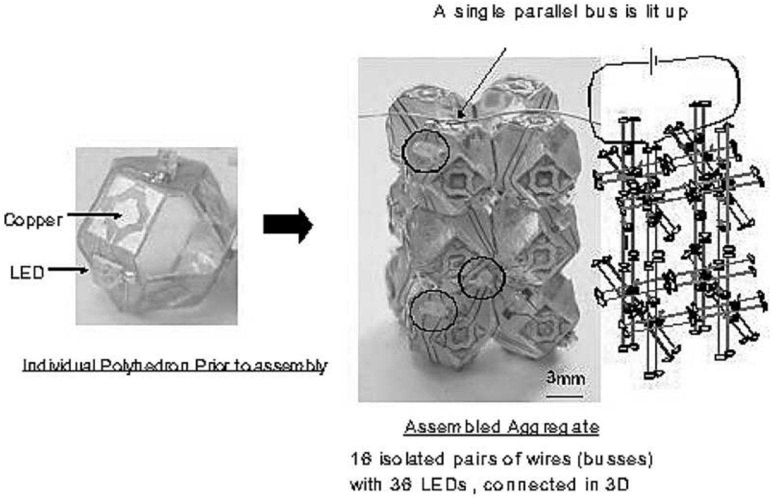


Fig. 18. Functional self-assembly of devices in 3 dimensions[74] (Reprinted by permission from American Association for the Advancement of Science, USA).

degree of structural perfection that is currently realized by state of the art physical processing methods.

Molecular materials play other important roles in assembly processes, namely in their ability to serve as templates and scaffolds for the construction of structures derived from other classes of materials. These ideas are developed in more detail below. It is worth noting here, though, that the utility demonstrated in these applications is one that speaks to the incredible diversity of the phase behaviors developed in organic materials. Molecular materials remain distinguished by their ability to evolve complex mesoscopic organizations that are amenable to manipulation by both synthetic and experimental design across a broad range of conditions, and to synergistically accommodate these behaviors to the purposes of synthesis.

5.3.2.3. Functional properties and structures The prospects for research directed by a focus on the functional properties of organic and metal–organic solid-state materials remains very bright. Molecular systems possess useful optical properties. They have characteristics that render them ideal candidates for the development of new approaches to electronics. They are the structural basis of biological systems and therefore have to be among the central components of technologies that lead to the post genomic revolution of proteomics. Organic materials have found limited applications in some areas, however. For example, they have demonstrated only limited utility in applications where magnetic properties are of interest. In this arena, the combination of organic molecules and metal ions is an area that needs further development. Despite their great success as an active material in LEDs, less progress has been made in developing solid-state devices of other classes based on functional organic materials. Even so, the current literature suggests a rich range of applications in technology. Applications ranging from displays, sensor arrays, to radio frequency

ID systems, as specific examples, appear to be well suited to the properties of organic electronic materials. The development of new patterning methods ideally suited to the integration of organic materials (e.g. soft lithograph) and nano-imprint methods) also offers suggestions of the rich future that awaits further progress in research in this area (Figure 19).

5.3.2.4. Future directions The years ahead are likely to witness considerable advances in the development of a completely new approach to assembly, namely one that removes the constraint of processing under conditions that lie close to equilibrium. A survey of the organizational motifs found in biology illustrates this point. Most of the complex structural, and certainly all of the complex functional, behaviors of biological systems arise because of regulated processes that are highly dissipative. Research has yet to provide good models of how materials processing could mimic this very powerful idea in a general way. There is a pressing need for development in this area.

It should be noted, however, that the contributions that can be made by a more conventional approach to synthesis should not be discounted or given a lesser importance in future research. The importance of the advances being made in conventional synthesis—as illustrated by the phenomenal progress made in the area of dendrimers and block copolymers as two explicit examples—are well understood and argue well for the need to maintain strong program efforts directed along these lines. Examples of the notable progress made in this area include the very recent demonstrations that the self-assembling mesophases derived from block copolymers could hold excep-

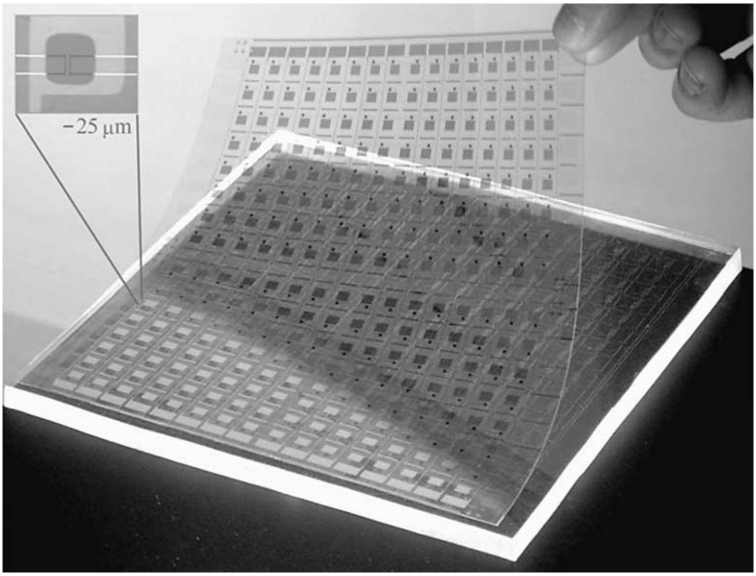


Fig. 19. Organic FET backplane and device structure for a flexible (electronic paper) display [75] (Reprinted by permission from American Association for the Advancement of Science, USA).

tional potential in the area of photonics. These mesophases, for example, can serve as the basis of assembled systems that yield perfect dielectric mirrors and reflectors that can be easily integrated into fiber-based platforms (Fig. 20). These materials also function very well as scaffolds for nanostructured assemblies and have shown utility as precursors to OBG materials. The recent history of the field also documents a major reversal of fortune for methods development related to the synthesis of polymers. Twenty years ago, the case was forcefully made that the prospects for developing commercially interesting homogeneous catalysts for the formation of high polymers were at best nil. This evaluation was clearly shown to be shortsighted and, if it had been followed, would have frustrated the staggering advances made in recent years in metallocene, ROMP, and other coordination-based polymerization methods.

It is very likely that advances in self-assembly and molecular materials chemistry will broadly establish the viability and utility of these materials as functional components in both electronic and optical devices. Molecular materials of advanced design will certainly play a very critical role as well in advances made in the area of biomaterials. These successes will transform the landscape of both information and medical technologies.

5.4. Molecular nanomagnets

The aim of this area is the design of large magnetic clusters which, due to their simplicity, can serve as molecular models for extended magnetic solids or, due to their electronic features, can display unusual magnetic properties (such as magnetic bistability or quantum tunneling of the magnetization). Molecular magnets have been developed over the last 20 years, and important success has been achieved in the field to date. Among the main achievements in the area is the development of an unconventional area that can be described as “magnetic molecules”. These are mol-

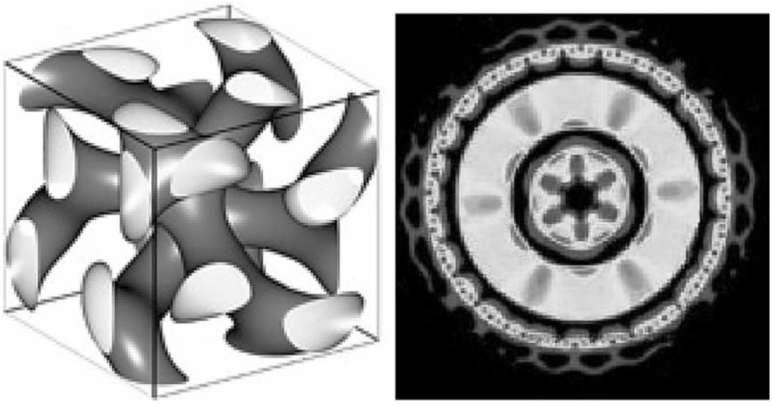


Fig. 20. Examples of advances made in block copolymers. (A) A double gyroid mesophase that is used as a basis for self-assembling OBG materials, and (B) an optical fiber coated with a self-assembling (perfect) dielectric mirror[76,77] ((B) Reprinted by permission from American Association for the Advancement of Science, USA).

ecular systems, comprising a large but finite number of interacting magnetic centers, which can be provided by transition metal, lanthanide ions or organic radicals. The simplest way of thinking of these molecules is to consider them as small pieces of bulk magnets, be they ferro- antiferro-, or ferri-magnets. It is intuitively clear that when there is only one magnetic center, the molecule will behave as a simple paramagnet, and when the number of centers tends to infinite, the molecule will behave like a bulk magnet. The chemical bottom-up approach can therefore answer fundamental questions like “when does the cross-over from paramagnetic to bulk behavior occur?”, “when do typical quantum effects vanish?”, “is there an overlap region for the two regimes?”. A particularly important class of magnetic molecules is the so-called “single molecule magnets (SMMs)” i.e., systems characterized by slow relaxation of the magnetization at low temperature, which become bistable, with magnetic hysteresis analogous to that observed in bulk magnets, but with apparent quantum effects The first molecule to show this property is the one shown in Fig. 21, but several others have now been discovered, and no doubt many more will be unearthed in the coming years, due to the efforts of synthetic chemists. The general requirements for observing SMM behavior are becoming clear: namely, molecules with a large spin ground state and a high magnetic anisotropy of the “easy-axis” type. The latter condition may be met by using several different strategies, for instance by assembling highly anisotropic ions such as Co^{II} and Mn^{III}.

Another important aspect of these molecules is that they can be used to store information by exploiting their quantum properties. Recently a procedure for implementing the Grover’s algorithm using Mn_{12} has been suggested by Leuenberger

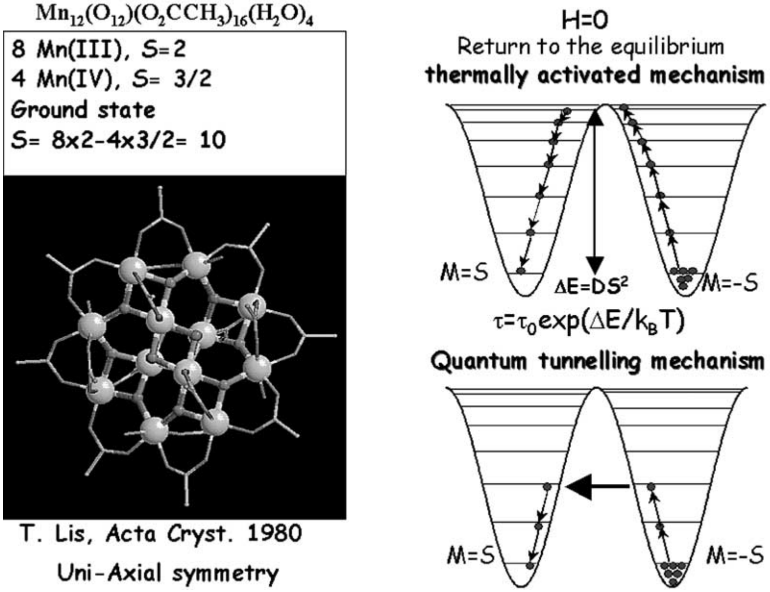


Fig. 21. The cluster molecule $Mn_{12}(O_{12})(O_2CCH_3)_{16}(H_2O)_4$, “Mn12”, the first single-molecule magnet (Dante Datteschi).

and Loss. It must be stressed here that not only SMMs can in principle be used for quantum computing, but also antiferromagnetic molecules also present excellent perspectives.

A related field that has only recently been recognized to be of vital interest in the area of magnetic bistability is that of magnetic 1-D systems. It has been observed that if individual magnetic chains in a crystal are well-separated from one another and if the intra-chain interactions are strong, anisotropic and of the Ising type, then slow relaxation effects of the magnetization are observed, analogous to those observed for SMMs. In this case, the polymeric molecules become bistable due to molecular magnetic hysteresis. It becomes possible therefore to store information in these molecules. (Fig. 22).

5.4.1. Future directions

Some future goals of the field are: (a) to understand the intrinsic factors involved in generating slow magnetic relaxation and associated quantum effects in single-molecule magnets; (b) to develop models to obtain the energy levels and the exchange parameters of the clusters and to understand the factors determining the cross-over from the quantum to the classical regime, and for the coexistence of both types of effects; (c) to synthesize single-molecule magnets with high spin-reversal barriers; (d) to test the data storage capabilities of these improved single-molecule magnets (including development of read/write technology/materials); (e) to fully characterize these systems by magnetic susceptibility, inelastic neutron scattering, high-frequency (GHz) electron paramagnetic resonance, high magnetic field and photoinduced spectroscopies; and (f) to devise procedures for casting films of the molecular units, e.g., by the Langmuir–Blodgett technique.

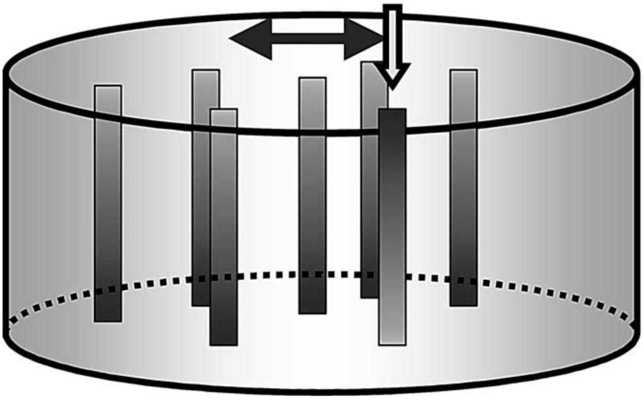


Fig. 22. A schematic depicting the possibility of using magnetic nano-wires for high-density storage media.

5.5. Composite and hybrid molecular materials

Composite and hybrid materials mark an exciting expansion area for solid state chemistry. By combining materials with disparate properties in an intimate manner, it becomes possible to synthesize a single phase with a range of complex functions. Composite solids can be optimized for structural, optical, electronic, or even magnetic properties. The most interesting materials, however, are formed when disparate functions are combined in a single solid phase. Composites can be divided into two classes, viz., those with crystalline or atomic scale order, and those with no order or only nanometer scale periodicity. In crystalline composite materials, the coupling between components can be controlled through their geometric ordering in a well-defined way. Formation of such materials, particularly when the components have very different properties, however, can be difficult. Non-crystalline composites, by contrast, allow components to be mixed at the molecular scale without requiring a perfect "molecular fit" between the components. Such disordered materials can be much easier to produce and as a result a huge range of potential combinations are available. In the sections below we will discuss three classes of composite materials. The first, sol–gel based materials generally have no order (atomic or nanometer scale) but do have nanometer scale dimensions and so allow for intimate mixing of different components. The second class, loosely called intercalation composites, generally have a layered structure, although the periodicity is sometimes lost during composite formation. The final broad class of materials can be described as templated solids. In these materials, very well-defined nanometer scale periodicity can be produced. Because the nanometer scale order is usually not accompanied by atomic scale order, however, a perfect "molecular fit" is not required to form these composite materials. Some specific examples of the enormous range of materials that fall within this broad category of "hybrid materials" are described briefly in the following paragraphs.

5.5.1. Sol—gel based porous materials

Sol–gel processing provides a simple and quick method for combining materials on the molecular or nanometer length scale into intimate composite solids. Solution phase polymerization of a reactive inorganic species is used to produce a disordered nanometer scale inorganic network. Molecular and nanoscale components included in the synthesis solution (both organic and inorganic) can be easily incorporated into the final composite. This type of material has found exciting applications anywhere high surface area or high porosity is needed in a composite solid. Specific examples include the use of sol–gel materials as battery electrodes, optical materials, or molecular sensors. For electrochemical systems, facile diffusion and high surface area can dramatically accelerate the kinetics of the fundamental processes. In terms of optical materials, a wide range of absorbing or fluorescing materials can easily be incorporated into sol–gel solids to produce nearly limitless variability in optical solids. An interesting and unique challenge for sol–gel materials is the production of chemical sensors. The combination of high surface area and good porosity means than a range of binding sites, from proteins to organometallics, can be incorporated into the sol–gel matrix and the molecule to be sensed can rapidly diffuse to the binding site. If analyte binding produces a color change, this can be the basis for a chemical sensor. Efficient electronic detection of analyte binding in these materials, however, is less well developed.

Sol–gel chemistry appears, at this time, to be a rich but fairly mature field. A fantastic array of disordered nanometer scale composite materials can now be made and a huge range of functionalities can be combined in a homogeneous solid. The challenge for this field is to extend the range of materials that can be used. This is particularly difficult because sol–gel frameworks are usually amorphous or nanocrystalline and high temperature crystallization frequently results in phase separation and a loss of porosity and surface area. For applications where amorphous phases are suitable, however, creativity and practical engineering concerns should now control the progress of this field.

5.5.2. Intercalation materials

Many layered materials, such as clays, are produced naturally. When the space between the crystalline sheets is occupied by ions, atomically crystalline solids result. In some cases, however, the sheets of layered materials can be coerced to separate or to completely exfoliate. Such materials then provide a unique basis for the formation of inorganic/organic composite materials. In particular, polymer chains can be intercalated between the inorganic layers, or completely exfoliated sheets can be incorporated in to polymeric solids. Both of these combinations can produce solids with unique functionality. Polymers intercalated between sheets have reduced conformational freedom. This can modify the electronic and optical activity of semiconducting polymers. On the other hand, isolated sheet incorporated into polymer matrices can dramatically alter and improve the thermal and mechanical properties of a polymer matrix. While this class of composite materials is not currently as broad as either the sol–gel materials discussed above or the templated materials discussed below, it is unique in that it combines atomically ordered layers with disordered organic phases in an amorphous or loosely ordered composite material. While the range of materials that has currently been explored is still limited, there is great potential to combine magnetism or superconductivity in the inorganic layers, which relies upon crystalline atomic scale periodicity, with a variety of optical or electronically active organic materials to produce some very complex and exciting composite solids.

5.5.3. Templated materials

Organic templating of inorganic materials on the nanometer length scale is a relatively recent technique that allows the high surface area and large pore volume of disordered sol–gel materials to be combined with true nanometer scale periodicity. In these composites, the same type of solution phase chemistry that is used to produce random network solids is employed, but the reactions now occur in the presence of organic molecules that have a tendency to self-assemble into periodic arrays. The result is an interconnected inorganic framework that surrounds a periodic array of organic domains. While a well-defined nanometer scale structure is produced with these methods, on the atomic scale these materials are generally amorphous or nanocrystalline, much like the sol–gel solids described earlier. The earliest work in this area focused on silica as the inorganic network former and simple surfactants as the structure-directing phase. Through this method, inorganic/organic composites could be produced that mimic the huge range of the structures typically observed in lyotropic liquid crystals. More recent work has expanded in the inorganic network from silica to a wide range of other oxides and now more recently to some non-oxide phases and even to inorganic–organic mixed networks. The template component of such composites has also grown from surfactants, to block-copolymers, and even to arrays of colloids. Periodicities ranging from 3 nm up to hundreds of nanometers can be produced by straightforward variations on the templating process. Optical and electronic components have been included in the structure directing organic phases, and the mechanical properties of the overall periodic solid have been examined.

For many applications, however, the true power of templated composites is not the ability to produce regular inorganic/organic arrays, but rather the ability to remove the organic template completely to produce periodic, porous inorganic solids. Such periodic porous solids are leading to a fantastic array of new composite materials. Catalytic and other molecular binding sites have been grafted to the inner surfaces of these porous solids forming the basis for size and shape selective catalysts, separations supports, and chemical sensors. A range of optical and electronic materials have been incorporated into the pores, including semiconducting polymers, stacked porphyrins, and a variety of other luminescent and absorbing molecules (Fig. 23). In the most exciting of these composites, the unique nanoscale architecture of the composite material modifies the optical or electronic properties of the guest molecule, resulting in a solid phase that could not be produced by simpler techniques such as the disordered sol–gel precipitation described above. For templated materials with larger periodicities, the porous framework itself becomes the optical material as porous solids with periodicities on the order of the wavelength of light can serve as photonic solids.

The field of templated composite materials currently seems virtually limitless. Kinetic control of solution phase reactions allow scientists to produce a periodic array of any solid phase that can be synthesized from solution. The basic principles of electrostatic assembly developed in the complex fluids community have served this field well by providing a framework for understanding the assembly process. As a result, a huge range of amphiphilic organic phases can be exploited to produce complex architectures on many different length scales. A major caveat to the previous statements, however, is the fact that the inorganic network is still generally limited to be amorphous or nanocrystalline. Particularly in materials with periodicities below the ~30 nm length scale, the production of a single crystal inorganic network appears to be forbidden based on surface energy considerations. In addition, the low thermal stability of many organic phases further limits the templating process to solids that can be produced at fairly mild temperatures. Finally, the solution phase assembly process is sufficiently complex that to date, mostly binary and single element inorganic phases have been produced. For example, the production of templated perovskite structures, while exciting for a range of applications, is currently beyond the immediate synthetic horizon.

Fig. 23. Polymers in pores.

This concept of creating pores of a controlled size by templating has also been used to generate structures involving regular arrays of larger size pores. In this case, either an inorganic (typically silica) or organic (e.g., polystyrene) colloid of uniform size (typically in the range of 10–1000 nm) is allowed to self-assemble into a 3-D cubic (or sometimes, 2-D) close-packed network and then infiltrated with a thermosetting polymer or an inorganic network-forming structure which fills the space between the close-packed colloid spheres. Removal of the templating species by dissolving it in a suitable solvent or by pyrolysis then leaves a 3-D macroporous solid with a periodic array of holes or an inverse opal type of structure, which can be left empty (full of air) or filled with a liquid or solid to give a material that shows useful optical properties, or periodic macroporosity. A wide variety of materials, including metals, semiconductors and insulating inorganic solids as well as organic polymers and liquid crystals have been used as either the network-forming solid or the pore filler. Potential applications for these materials include photonic crystals, porous electrodes, thermal insulators and catalysts for large molecule reactions. Yet another variant of “templating” starts with an array of uniform holes of ca. 20–500 nm in an inorganic or organic foil or film (usually created in the film by controlled etching) and then fills these holes (or coats the pore walls) with another material by electrochemical deposition, chemical vapor deposition or liquid phase infiltration.

The resultant composite can be used as is, or treated chemically to remove the template, leaving uniform, nanosized fibers or tubes (including C and BN nanotubes). Both of these different routes to novel nanostructured materials typically employ molecular systems, either for building the network structure or for filling the pores in that structure.

5.5.4. Multiproperty hybrid inorganic/organic materials

Molecule-based materials, i.e., materials formed from molecular building blocks, are providing remarkable examples of materials with interesting magnetic, electrical or optical properties such as ferromagnetism, conductivity and superconductivity, or non-linear optics. One of the most appealing current aims is to explore bi-functionality. In this aspect the potential of the molecular materials compared with the classical inorganic solids is evident. Thus, from a wise choice of the molecular building blocks one can combine, in the same crystalline framework, two properties that are difficult or impossible to achieve in a continuous lattice solid. This new direction in the field of the molecule-based materials opens new possibilities for potential applications in molecular electronics.

The goal of this research area is to obtain hybrid molecular materials formed by two molecular networks so that each network contributes distinct physical properties to the solid. An attractive approach is to employ anion/cation salts or host/guest solids, where each network furnishes distinct physical properties to the solid. We can envisage, for example, the combination of an extended inorganic magnetic layer furnishing the pathway for cooperative magnetism, with an organic molecule that controls the interlayer separation and therefore the interlayer magnetic interactions and properties. In this case the inserted molecules only play a structural role. A more interesting situation is that of inserting between layers an "electronically" active molecule capable of incorporating a second property to the magnetic solid as for example electronic conductivity or non-linear optics. The star materials in this context are those combining magnetic and conducting or even superconducting properties. They are typically formed by segregated stacks of planar radical cations of the type tetrathiafulvalene (TTF) and its derivatives (Fig. 24) that can support electron delocalization, interleaved by magnetic inorganic anions.

There are at least two main reasons that justify the intense effort currently devoted to prepare and physically characterize this type of material. The first one is to investi-

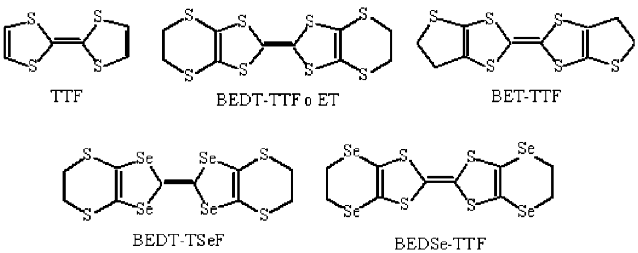


Fig. 24. Some typical organic donors.

gate if a metallic conductivity can stabilize indirect exchange interactions among the localized magnetic moments mediated by the conducting electrons (Fig. 25).

This exchange interaction resembles the so-called RKKY mechanism proposed in the solid state to explain the magnetic interactions in transition and rare-earth metals and alloys. The studies with the molecular materials has led to a new insight, namely intermolecular d–π coupling between the two networks, in contrast with the intra-atomic coupling between the unpaired electrons of the metal (d or f) and the free (mainly s) electron carriers. Furthermore, in molecular conductors the electrons are strongly correlated, while the RKKY model assumes free electrons. A second impetus is that of bringing together in the same crystal lattice unusual combinations of physical properties, as for example ferromagnetism and superconductivity, which have long been considered as mutually exclusive. This, as yet, has not been achieved, but a synthetic metal that is also an ordered ferromagnet has been designed. It is formed by bimetallic $Mn^{II}Cr^{III}$ layers interleaved by molecular layers of organic BEDT–TTF donors and exhibits coexistence of ferromagnetism below 5.5 K and metal conductivity at least down to 0.2 K (Fig. 26). This hybrid system is an example of physical behavior for molecular-based systems that is not possible to design with atomically simple solid-state materials[78].

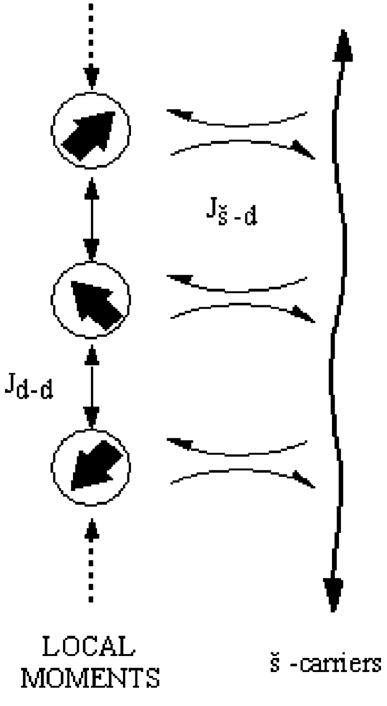


Fig. 25. Indirect magnetic exchange interactions in molecular conductors.

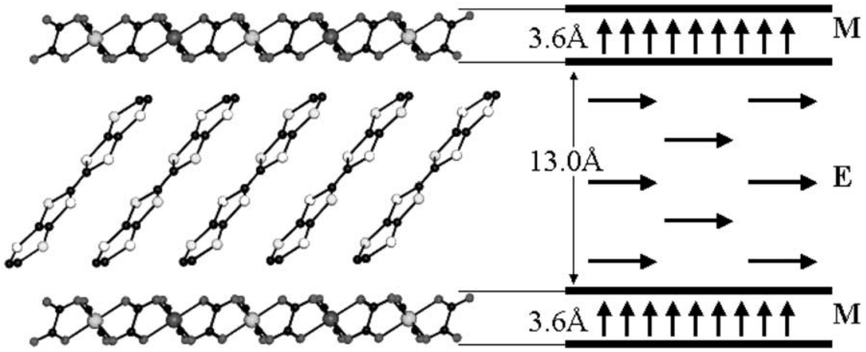


Fig. 26. Structure of $[\mathrm{BEDT{-}TTF}]_3[\mathrm{MnCr(ox)}_3]$, the first molecule-based metal ferromagnet, showing the alternating magnetic (ferromagnetic) and electrical (metallic) multilayers.

5.5.5. Coordination networks

The synthesis of polymeric metal–organic coordination networks with collective properties has received much recent attention, mostly inspired by the rational design of novel material properties via judicious choices of the constituent building blocks. Significant progress has been made in the areas of magnetic, optical, and porous metal–organic coordination networks. Polymeric networks with cyanide bridging ligands based on the Prussian blue structure have been extensively explored, and many systems with T_c above room temperature are now available. Recent efforts on the synthesis of high-spin metal cyanide clusters have afforded novel materials that may find potential applications in single-molecule data storage. Metal–ligand coordination bonds have recently been used to counteract weaker centric non-covalent interactions (such as dipole–dipole repulsive interactions) and form the molecular basis for the rational construction of polar solids. In these metal–organic coordination networks, the control of the acentricity of a solid has been reduced from a very difficult three-dimensional problem to either a choice of ligands of suitable lengths or a much simpler one-dimensional problem. Several of these metal–organic coordination networks exhibit second-order nonlinear optical efficiency exceeding that of technologically important lithium niobate. The ready availability of coordination networks with a variety of chromophoric building blocks will also allow for the elucidation of the origin of optical nonlinearity in (delocalized) inorganic and metal–organic NLO materials. The synthesis of porous metal–organic coordination networks has been the most fruitful; coordination networks with permanent porosity and surface areas as large as 2000 m^2 g have been obtained. It remains to be seen whether these porous materials with their weaker metal–ligand coordination bonds as compared to the bonds in zeolites and MCM-type mesoporous materials will find practical application in the production of commodity chemicals. Chiral porous metal–organic frameworks may find practical applications in enantioselective separations and catalysis (owing to much milder conditions involved in these processes). Several examples of such chiral porous materials have recently appeared that show promise in enantioselective separations and catalysis. The successful synthesis of chiral porous materials with desired chiral environments and chemical functionalities could have a profound impact on chirotechnology and the pharmaceutical industry in particular (Fig. 27).

5.5.6. Future directions

In the area of composite hybrid structures, a main future goal is to extend the range of inorganic and organic phases that can be combined into periodic solids. On the theoretical front, it remains an open question as to what types of phases can be expected to be metastable in a periodic composite material. Is it reasonable to hope that crystalline frameworks can someday be produced, despite the high surface energy required to produce such a nanoporous framework? In isolated nanocrystals, very high surface area crystalline colloids can now be synthesized, but the huge surface area is maintained by isolating the colloids from each other. In a framework material that is intrinsically interconnected, can crystalline materials with complex unit cells be produced without spontaneous transition to a bulk phase? High-level quantum chemistry is perhaps the best way to address this question. Finally, how can one exploit the unique nanometer scale architecture of these composite materials to produce truly new, functional solid phases? This is probably the greatest challenge to the imagination. For applications that simply require high surface area and porosity, the sol–gel porous solids described above are both simpler and cheaper to produce. The unique future of templated materials is the ability to separate guest molecules in identical environments, to put those guest molecules in contact with an optically or electronically inorganic active framework, and to know the spatial distribution of the guest because of the periodicity of the whole material. With this type of control, templated composite materials should lead to a range of exciting solids including the active elements in photovoltaics, LEDs, electrochemical cells,

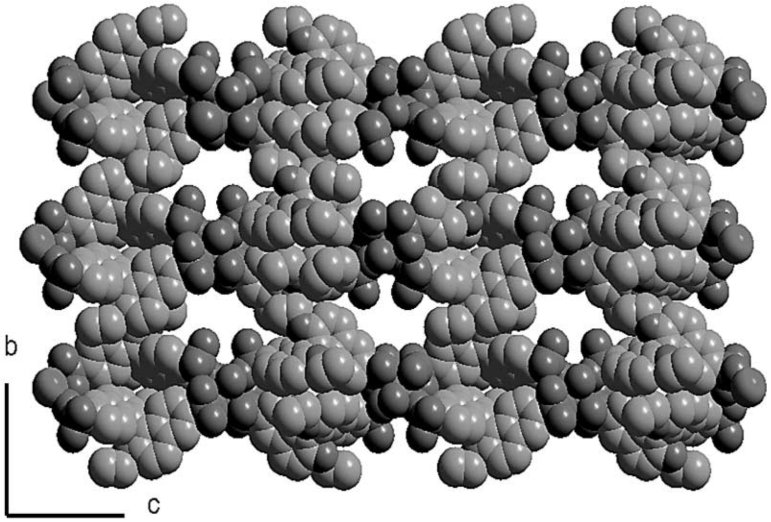


Fig. 27. A space filling model of $[Gd(L\text{-}H_2)(L\text{-}H_3)(H_2O)_4 \cdot 12H_2O$, where L-$H_4$ is 2,2'-Diethoxy-1,1'-binaphthalene-6,6'-biphosphonic acid viewed down the a axis.

lightweight structural materials, and electronically active sensors. The connection to almost every field of solid state chemistry is straightforward and the potential for new applications is outstanding.

In terms of bi-functional (or multifunctional) molecule-based materials, the field is only just beginning to move forward and relevant open issues are whether systems can be designed that for example combine superconductivity with ferromagnetism, conductivity/superconductivity with photochromism, chirality with magnetism, or liquid crystallinity with magnetism and conductivity.

5.6. Conclusions

We have presented a selection of topics that serves to illustrate the vast opportunities for molecular, organic and solid state chemists to collaborate on the synthesis and structural characterization of novel materials. It is obvious that there is great need for strong interactions between the chemistry community, materials scientists and condensed matter physicists in order to characterize physical properties, and provide a theoretical framework for their interpretation.

6. Nanoscale science and technology

Louis Brus, Peidong Yang, Xiaogang Peng, David Norris, Hongjie Dai, Christopher Chidsey

6.1. Introduction: built from the bottom up

From a chemist's point view, nanoscale science is all about actually synthesizing and assembling matter at multiple length scales—from atomic and molecular species to individual nanoscale building blocks such as nanocrystals and nanowires, then from these individual nanoscale building blocks to higher-level functional assemblies and systems. This hierarchical process covers length scale of several orders, from Angstrom (Å) to micrometer (Fig. 28).

Solid state chemistry plays a significant role in the first step of this process: putting different atoms together into ordered 3-dimensional crystal lattices. The evolution of the field of high temperature superconductor cuprates since 1987 is a perfect example. With the recent extensive research efforts into many different types of nanostructured materials, we can now probably all agree upon on one thing, that is, the physical properties (optical, electrical, magnetic and ferroelectric), thermodynamics, and stability of a particular material is not only determined by its crystal structure, but also determined by the size and dimensionality of the materials and interface within. This is especially true for those condensed solids that are covalently or ionicly bonded. Fundamental understanding of nucleation and growth is absolutely critical in the discovery of new bulk phases, and in the growth of specific nanoscale building blocks from known phases.

In the past two decades it has become especially clear that covalent nanocrystals,

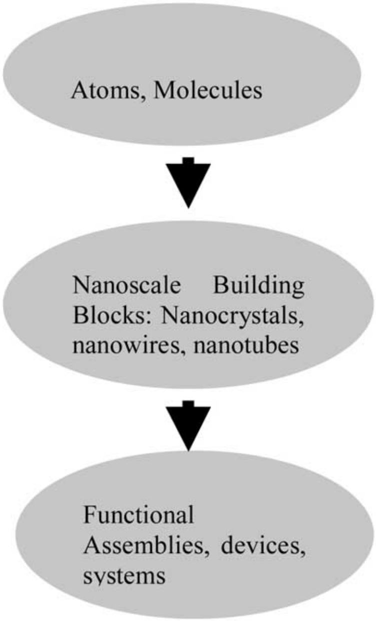


Fig. 28. Illustration of bottom-up process for nanostructures and their assemblies.

nanowires and nanotubes have drastically different physical properties than bulk solids, even when their chemical compositions and crystal structures are identical to their bulk counterparts. Below we describe such nanocrystals and nanowires—stage two in Fig. 28—and we describe issues and efforts to organize nano-components into fundamentally new materials (photonic crystals), and even into designed electronic circuits—stage three in the figure.

6.2. Semiconductor nanocrystals

Colloidal nanocrystals are nanometer-sized fragments of the corresponding bulk crystals. These nanometer-sized “solids” have attracted much attention recently due to their size dependent properties and flexible processing chemistry. As a semiconductor nanocrystal grows in size, bulk electronic properties are approached only slowly because of long bulk electron delocalization lengths resulting from strong covalent bonding. Particles containing many thousands of atoms can show a large three-dimensional quantum size effect, and novel electrical and optical properties.

Nanocrystal synthetic and processing chemistry possesses strong ties to modern solid state chemistry. A successful synthetic scheme should at least produce single-crystalline nanocrystals with close to monodisperse size distribution if one wants to exploit their size-dependent properties. The ability to vary the size and shape of the resulting nanocrystals is an additional measurement of such a synthetic scheme. Presumably, control over the optical and/or other interested properties is also an important concern. Similar to other fields of materials science, scientists working in this field are mostly from device and fundamental physics, physical chemistry, biomedical sciences, etc. Consequently, a successful synthetic scheme should be "user-friendly", or readily adoptable. At present, the success of the synthetic chemistry for colloidal nanocrystals is limited to very few types of materials.

The most developed nanocrystal system in terms of synthesis is compound semiconductor nanocrystals, especially cadmium chalcogenides nanocrystals. For example, CdSe nanocrystals with control over their size, shape and optical quality have become available using safe and inexpensive raw materials with simple synthetic settings. Figure 29 illustrates several transmission electron micrographs of as-prepared CdSe nanocrystals with a variety of sizes and shapes [79,80,81].

Importantly, the development of the synthetic methods for CdSe nanocrystals has been strongly based on the understanding of the nucleation and growth mechanisms [81,82,83,84,85]. In some sense, the synthesis of high quality colloidal nanocrystals must be a well-controlled crystallization process. Since crystallization is poorly understood in general, it is necessary to investigate it systematically in order to develop reliable synthetic chemistry for colloidal nanocrystals. It should be pointed out that crystallization is one of the few key concepts in the field of solid state chemistry. Therefore, understanding of the nucleation and growth of colloidal nanocrystals will eventually benefit the development of solid state chemistry by and large.

The other research topic related to solid state chemistry in the field of colloidal nanocrystals is the interfacial sciences. Since colloidal nanocrystals are thermodynamically metastable species, their surface is often coated by a monolayer of organic

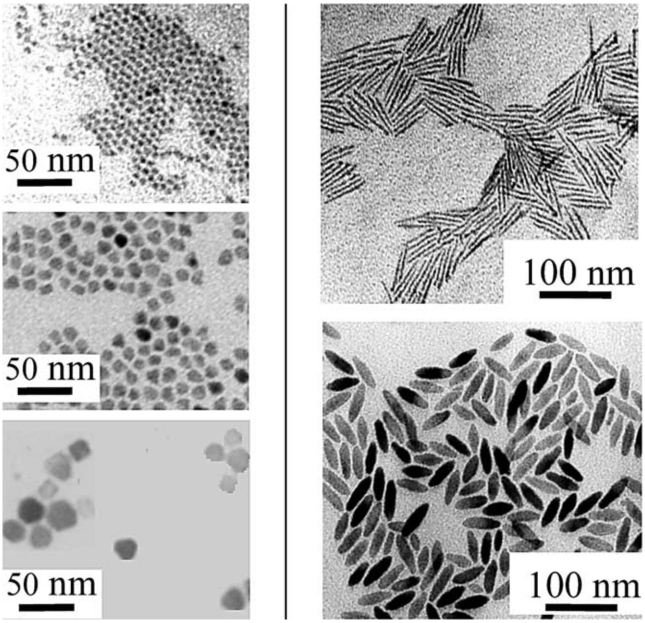


Fig. 29. Transmission electron microscope images of as-prepared CdSe nanocrystals.

ligands. The processing chemistry of colloidal nanocrystals is solely dependent on the interfacial chemistry either at the interface between a nanocrystal and its ligand monolayer or the outer surface of the ligand monolayer. In various fields of solid state chemistry, such as heterogeneous catalysis, self-assembly films, etc., interface or surface also plays an essential role. In general, surface phenomena related to conventional solids need to be addressed using those expensive, not common, and destructive instruments, such as XPS, mass spectroscopy, etc. In general, the related measurements need to be performed in high vacuum, which is often not the working environment of those functional solid surfaces. In comparison to the traditional interface and surface sciences, the interfacial phenomena in the field of colloidal nanocrystals can be investigated by those nondestructive solution phase methods, such as solution NMR, FTIR, UV-Vis absorption, etc. Figure 30 illustrates how to probe the changes on the inorganic nanocrystal core and the surface ligands through these conventional tools [86]. Colloidal nanocrystals as "tiny solids in a liquid" should be good model systems for understanding the interfacial phenomena in the other fields of solid state chemistry.

6.3. Nanowires and nanotubes

Carbon nanotubes, especially single-walled carbon nanotubes (SWNT, typical diameter 1 to 2 nm) represent perhaps the most extreme case of how properties of nanomaterials critically depend on structure and size. SWNTs are formed by rolling a graphite sheet fragment back upon itself so that all carbon atoms at the seam bond covalently; there are no dangling bonds or surface states. Depending on the so-called chirality (the chiral angle between atomic-carbon hexagons and the tube axis), nanotubes can be either metals or semiconductors, even if their diameters are nearly

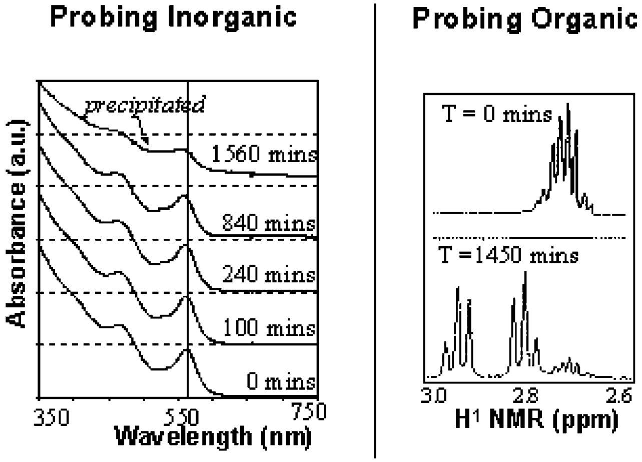


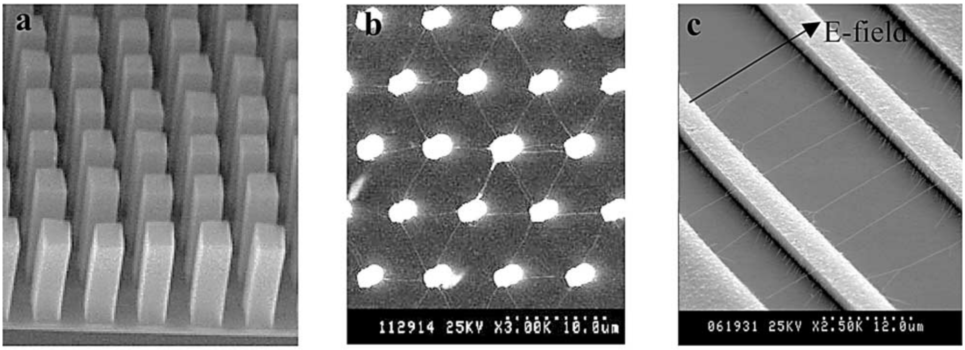
Fig. 30. Photocatalytic and photochemical processes occurred at the interface between CdSe nanocrystals and their hydrophilic thiol ligands were assessed quantitatively by UV–Vis absorption spectroscopy (left) and NMR spectroscopy (right) in solution.

identical. For same-chirality semiconducting nanotubes, the band gap is proportional to the inverse of the diameter. Thus, there are infinite possibilities in the types of carbon-tube ‘molecules’, each having distinct physical properties. Understanding how to synthesize the various types of nanotubes essentially requires an exquisite control of atomic arrangement along the tubes, and is an ultimate challenge to chemists in the nanotube area.

At present nanotubes are grown by carbon chemical vapor deposition (CVD) on nm size transition metal particles (Fe, Co, etc.). Various patterned CVD growth schemes have been devised to synthesize nanotubes from specific sites on surfaces. This is aimed to control the location and orientation of nanotubes, thus obtaining ordered nanotube networks or arrays that can be integrated into addressable electrical or mechanical devices. Multiwalled nanotube towers have been grown (Fig. 31(a)), and the nanotubes in the towers are aligned perpendicular to the substrate due to self-assembly via inter-tube van der Waals interactions. Suspended SWNTs making ordered networks have been synthesized from patterned arrays of silicon pillar structures (Fig. 31(b)), and the nanotubes self orient due to nanotube-substrate van der Waals interactions. Electric fields have also been used to direct the growth of SWNTs (Fig. 31(c)).

To tackle the problem of controlling the nanotube structural parameters, one route is via controlling the structure of catalytic particles and understanding the catalyst–nanotube relationship. Initial progress has been made recently. Discrete iron catalytic nanoparticles with diameters in the range of 1–2 nm are synthesized to grow SWNTs (Fig. 32(b)). The results shed light into how a nanotube grows from a catalytic nanoparticle via carbon supersaturation of iron and precipitation (Fig. 32(a)). The diameter of the particle determines the diameter of the nanotube.

Future challenges include the synthesis of monodispersed catalytic nanoparticles. It is not yet clear if solution phase synthesis methods can achieve monodispersity for 1–2 nm scale particles. The synthesis of suitable high nuclearity molecular clus-



Intra-tube vdW self-assembly of nanotubes

Substrate-tube vdW self-assembly

Assembly by electric field

Fig. 31. (a) Intra-tube vdW self-assembly of nanotubes; (b) substrate-tube vdW self-assembly; (c) assembly by electric field.

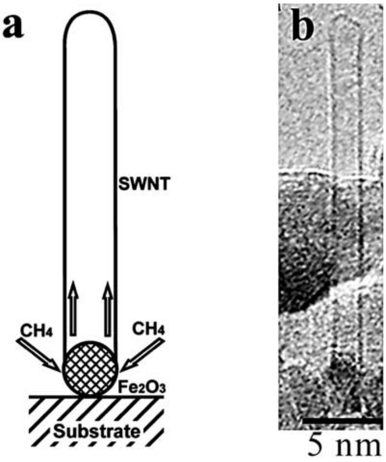


Fig. 32. Growth of nanotube on particle.

ters may offer unique opportunities to the synthesis of nanotubes with well-defined structures. Further, it is necessary to understand the nucleation and initial growth stage of a nanotube, and how chirality is determined by the catalyst particle size, shape and the chemical processes involved in the carbon–nanoparticle mixture. Theoretical modeling/simulation at multiple length scales could provide invaluable guidance to nanotube synthesis and nanoscale solid state chemistry in general.

6.4. ZnO nanowire ultraviolet lasers

An analogous example is provided by the recent successful growth of crystalline wurtzite ZnO in nanowire geometry for an ultraviolet lasing application. This has only been possible by basic understanding and control of the crystal nucleation and growth at nanometer scale dimensions. As a consequence, compositional, size, site, orientational and doping profile control during the nanowire growth have been achieved. Further understanding of the crystal nucleation and growth in solution and gas phase will surely lead us to nanoscale building blocks with excellent monodispersity and increasing complexity (Fig. 33).

6.5. Photonic crystals

Photonic crystals are materials that have a periodic index of refraction. If this periodicity is on an optical length scale, it can modify the optical properties of the material. While this effect has been utilized for decades in one-dimensionally periodic structures (such as interference filters), more recently researchers have investigated more complex three-dimensionally periodic structures. One motivation is to obtain a structure which exhibits a photonic band gap—a range of frequencies for which the photon cannot propagate inside the crystal. If synthesized, such a structure would provide an ideal material to manipulate light and create optical integrated

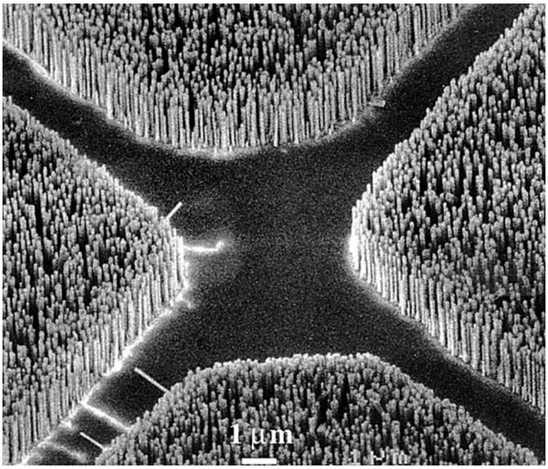


Fig. 33. ZnO nanowires grown vertically from a lithographically patterned substrate. Fundamental understanding of the nanowire growth in gas phase leads to our capability of control of nanowires' compositions, sizes, sites, orientations and doping profiles. This control of nanowire growth enables the successful demonstration of nanowire UV lasers[87] (Reprinted by permission from American Association for the Advancement of Science, USA).

circuits. Unfortunately, photonic band gap crystals have proven extremely challenging to prepare.

One chemical strategy to achieve photonic band gap crystals is to exploit the tendency of monodisperse sub-micron spheres to spontaneously organize on a face-centered cubic (fcc) lattice. The resulting material, referred to as a synthetic opal, then acts as a template into which a semiconductor material is infiltrated. Subsequent removal of the template leads to a 3D photonic crystal, referred to as an inverted opal, which has periodic air-spheres embedded inside the semiconductor. If the refractive index of the semiconductor is sufficiently high (>2.85), such a structure has been predicted to exhibit a band gap. Indeed, recently it has been experimentally demonstrated that self-assembled photonic crystals made from silicon (see Fig. 34) can exhibit a photonic band gap.

While this is a significant achievement for the chemical assembly approach, many applications will require that photonic band gap crystals are prepared from materials other than silicon. A difficult near-term challenge will be to make similar structures from solids that can emit light. This could potentially be achieved with III–V semiconductors (such as GaAs, InAs, GaP) or by utilizing recent efforts to obtain emission from doped silicon. However, success in this area will require clever solid state chemistry to infiltrate the proper solid material into the topographically complex template.

A longer term challenge is to utilize self-assembly approaches to move away from fcc templates to make photonic band gap crystals that have diamond symmetry. Since colloidal spheres naturally prefer to close pack, this is a significant hurdle to overcome. However, since photonic crystals with diamond symmetry should have sig-

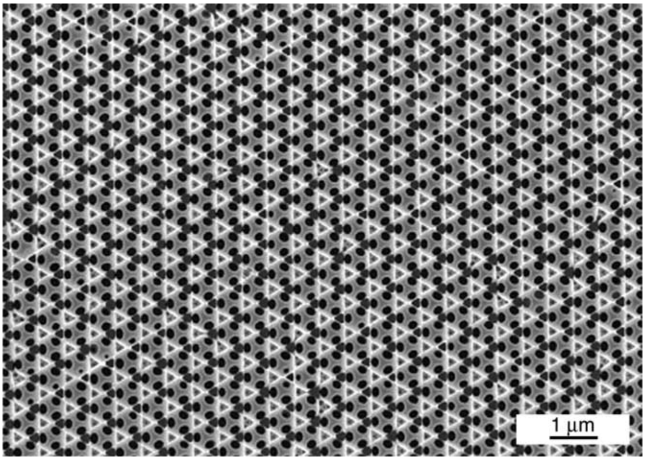


Fig. 34. Silicon inverted opal synthesized by the chemical assembly approach. Such structures have been shown to have a complete photonic band gap. However, for applications, such structures must be induced to efficiently emit light. Solid state chemistry can help achieve this goal (Reprinted by permission from Vlasov et al, Nature 414 (289–293) (2001). copyright Macmillan Publishers Ltd, UK; http://www.nature.com/nature).

nificantly improved properties, such as a much broader photonic band gap that is much less susceptible to defects in the crystal, the ability to make such structures would have an immediate impact. Again, a solution to this problem could come from solid state chemistry approaches.

6.6. Hierarchical integration and electronic systems

A grand challenge resides in the hierarchical integration of the nanoscale building blocks into functional assemblies and ultimately to a system. Unlike the traditional lithographical process, where precise placement of certain elements or devices is embedded in the designing process, the precise placement of nanoscale building blocks on the right place with right configuration, and with exceedingly high densities, represents a daunting task for many of us at this stage. Several techniques are very much at their early stages, for example, the microfluidic assisted nanowire integration process and Langmuir Blodgett nanorod/wire assemblies techniques developed in this lab [88,89].

Putting building blocks into different architectures will surely lead to new functionality, the question of what type of architectures would be needed and be of interest is a pressing one. While those traditional configurations in semiconductor technology (e.g. cross-bar, logic, memory devices) should be important ones to pursue, it should also be borne in mind that they are not the only configurations. New, revolutionary thinking of device architectures (or even radical ones) should be called for as well as grand new assembly schemes. Manipulating the nanoscale building blocks in many ways is critical for the success of the whole nanoscale science and technology.

One additional aspect of nanoscience is the importance of the surface. Surface essentially is everywhere within the nanostructures. Surface states are critical for the electronic, optical properties and, not surprisingly, chemical properties. The key issue is what is exactly happening at the molecular level and causing the changes of properties (e.g. conductivity change in the nanostructure sensing applications). To this end, high spatial resolution microscopy and spectroscopy are needed to elucidate the chemical signature of species on the nanostructure surface. This is another big challenge that needs to be tackled in the next couple of years. The information is very much critical for understanding sensing, catalysis and chemical gating phenomena, to name a few.

In these system and device considerations, electron transfer across solid interfaces is of great importance This is already true for contemporary Si-based transistors. Electron tunneling between the gate electrode and the Si channel region through the nanometer-thick dielectric phases of modern field-effect transistors is now a significant limitation on device performance. In the future, both the channel region and the dielectric phase may be replaced by molecular equivalents to achieve the smallest and most reproducible devices possible within the fundamental limits imposed by the tunneling of electrons between electrodes. In that limit, the tunneling of electrons between the electrodes and the active element(s) of the device will be tailored to optimize the ratio of the signal in the on state to that in the off state while minimizing the time and energy dissipation of each switching or information storage event. A range of studies have been made of the rate of transfer of electrons from electrodes to other materials through well defined interfaces (see for instance [90]) and more recently through single molecules [91]. Recent measurements of electron transfer between gold electrodes and redox species by tunneling through conjugated oligomers with barriers of at least 0.8 eV have shown 10^{10} s^{-1} tunneling rates out to distances of 3.5 nm [92] at which distance the tunneling through saturated bridges would be 1 s^{-1}. To study these effects fully for single molecule electronic elements and to create useful device structures, nanowiring methods must be developed that allow two and preferably three electrodes to be reproducibly attached to single molecule devices. One prospective structure shown here diagrammatically is two crossed nanowires embedded in an immobilizing dielectric with fluid-phase access to the crossing point so that electrochemical etching and dielectrophoretic localization of molecular devices can be used to construct robust and reproducible 3-electrode devices on the nanometer length scale.

This device (Fig. 35) illustrates the many opportunities for solid-state synthesis and characterization on the nanometer length scale. How should one make and position the nanowires? How will the diameter of the nanowires and the curvature of their ends effect the nature of their electronic states? What dielectric phase should be used to embed them and how should that be made? How can porosity be incorporated in the necessary places? How can the resulting nanostructure be electrically addressed from the macroscopic world?

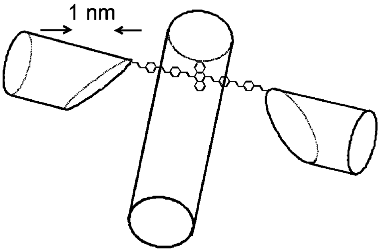


Fig. 35. Nanowire device.

6.7. The future: synergism between nanoscience and solid state chemistry

The fundamental problem in solid state chemistry is the absence of a general methodology for successful synthesis of a proposed new phase or solid state compound. In the examples above, we can see that even partial understanding of nucleation and growth can lead to successful synthesis of new bulk phases, and can lead to controlled growth of specific shapes and sizes with novel nanoscale properties. In understanding how to synthesize and control a solid state compound, it is just as important to understand the surface of the material as the bulk of the material. In complex bulk phases, a deeper understanding of bulk properties (for example, electronic and/or structural phase transitions) can come from an understanding of how these properties evolve as a function of shape, increasing size, and independently modified surface chemistry.

Many of the current synthetic methodologies have their origins in traditional solid state chemistry, while extra efforts have been placed on the precise control of the size and shape of the nanocrystals. The level of control, however, is far from perfect at the present stage. Significant effort should be placed on the monodispersity control of the nanoscale building blocks. It is of course one of the major challenges in the field to synthesize nanoscale building blocks with nearly monodispersed sizes and aspect ratios. In addition, the complexity of nanostructures is far less than those that are accessible to many solid state chemists. Synthesizing nanostructures of multiple components (rather than single element or binary compounds) represents another big challenge. It is fair to expect that increasing complexity in the nanostructure could lead to additional functionalities.

The near term challenges are the synthesis of known phases with control of size, shape, position, orientation and surface termination, as well as the characterization of the electrical, magnetic, optical and chemical properties of the resulting nanostructures. The long term challenges are the integration of multiple nanophases into devices and superstructures on the smallest possible length scale consistent with the physical and system properties desired.

The educational challenge is to broaden the undergraduate and graduate chemistry curriculum to train a generation of chemists prepared to think creatively about materials that are not composed of single homogeneous phases any more and for which the interfaces are much or even all of the material. However, while striving for a broadly educated chemist, education must not just layer more on top of an already bursting curriculum. Ways are needed to cull the huge body of information without just settling for a limited number of special topics courses. Wherever possible broad bases for understanding and well chosen prototype examples must be the subject of courses, because we can no longer afford to go into all areas in detail.

7. Theory and condensed matter physics

Warren Pickett, James Allen, Gerbrand Ceder, Michael Deem, Giulia Galli, David Singh

7.1. Introduction

Some of the most vigorous, highest impact activities of solid state chemistry lie where they are bound to another discipline. Solid state physics and solid state chemistry have always had strongly overlapping interests, centered on several classes of materials (e.g. ferroelectrics). Classically they differed in their approach, solid state chemistry made real space pictures and concepts their focus, whereas solid state physics tended to regard the reciprocal space approach as more productive for their purposes. ‘Bonds’ versus ‘bands’ is actually a very useful way to teach solid state science, as both approaches have their own special importance—when they are not actually describing the same thing. As one simple contrast: the former make crystal structures and their occurrence and regularities more accessible, whereas the latter account naturally for the effective mass of the charge carriers and for Fermi surface phenomena.

These two fields actually have been growing closer together for several decades, although they each still retain their disciplinary identity. More than ever, they share experimental techniques if not quite the same objectives, they share theoretical methods if not quite for the same applications. In this section the connections between these two disciplines will be discussed, to establish where these relationships are at this time, what the near-term opportunities appear to be, and what long-range goals might have the most impact.

7.2. Materials that define the cutting edge

Many of the classes of materials of intense interest currently to condensed matter physicists border and overlap solid state chemistry interests. Work on high temperature superconductors has moderated somewhat in recent years, but intense interest in the underdoped region remains—the phenomena of charge and spin stripes—and the pseudogap feature and possible critical point phenomena remain the focus of activities. The “colossal magnetoresistance” manganites present such a broad range of unusual behavior, including charge, spin, and orbital ordering phenomena that are sensitive to everything (doping level and dopant size, magnetic field, temperature, pressure), that their importance can be expected to continue into the foreseeable future. Buckytubes are investigated strongly because of both scientific importance and possible technological impact.

We consider here only a few classes of materials that appear certain to attract growing activity in the near future. Several of these share the similarity of having "emergent" properties that can only arise when the materials have sufficient complexity—enough degrees of freedom of the proper type to 'house' the properties.

7.2.1. Manganites and related oxides

The rich chemistry and physics discovered over the past decade in perovskite manganites provides an excellent example of the scientific opportunities that arise from the interplay of solid state chemistry, modern physical characterization and theory. This manganite family $(R,D)_{n+1}Mn_nO_{3n+1}$, where R is a trivalent rare earth and D is a simple divalent atom, has been known for more than five decades and was studied by several techniques, including neutron diffraction, beginning in the 1950s. In particular, the magnetic phase diagram of the $n=\infty$ member, $(La,Ca)MnO_3$ was elucidated by Wollan and Koehler. While both end-point compounds are antiferromagnetic insulators, a metallic, ferromagnetic region was found extending from approximately 10%–50% Ca. The exchange coupling responsible for this region was proposed to be a double exchange mechanism involving spin-dependent Mn d–O p hopping.

One could have asked, ten years ago, whether any interesting science was left undiscovered here after the 1970s. The answer turned out to be a resounding yes, as is apparent from the work of the last five years. The perovskite manganites came under renewed scrutiny following the finding of large negative magnetoresistance ("colossal magnetoresistance") in the metallic regime, with promise of practical applications. Motivated by this, the materials were studied again, bringing to bear the full complement of modern solid state chemistry and physical characterization methods as well as first principles calculations that did not exist in the 1950s. These quickly established the basic features of the electronic structure of the metallic CMR phase and important aspects of the origin of the exchange coupling. While the basic origin of the ferromagnetic phase is double-exchange-like, the calculations revealed a complex interplay of lattice, electronic and magnetic degrees of freedom that had not been anticipated.

Advances in solid state chemistry techniques have allowed the synthesis of phase pure crystalline samples with controlled stoichiometries. When studied with high flux neutron, synchrotron X-ray diffraction and other methods, remarkably rich phase diagrams were revealed. As an example, the phase diagram for $(La,Ca)MnO_3$ is shown in Fig. 36. The complexity of the phase diagram reflects the competition of on-site Hubbard and Hund's physics, lattice degrees of freedom (e.g. Jahn–Teller effects), and itinerant electron physics. This picture completely revises the simple phase diagram of the 1950s. What is seen instead is a very rich sandbox for the interplay of precise experiments and modern theory.

Much of these discoveries have emerged because of advances in solid state chemistry—particularly the ability to make very high quality homogeneous, crystalline samples of these oxides, so that precise phase diagrams could be mapped out and

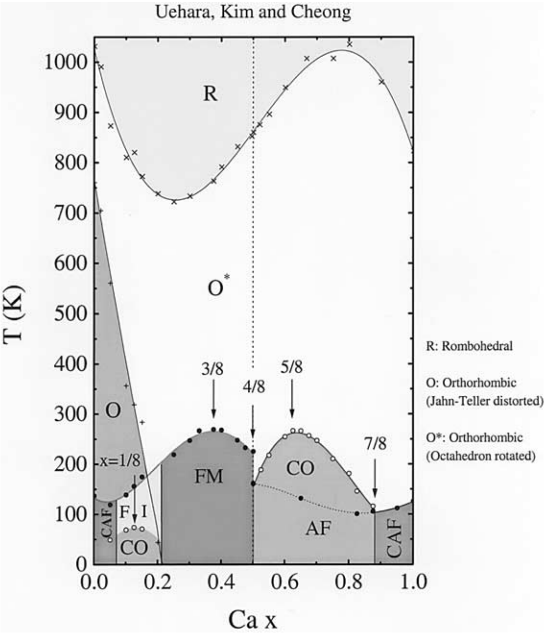


Fig. 36. The phase diagram for $La_{1-x}Ca_xMnO_3$. The end-member, $LaMnO_3$, is found to be an insulator with a strong orthorhombic (Jahn–Teller) lattice distortion, and so-called A-type antiferromagnetism. The exact evolution of the spin order approaching the metallic region (starting around x=1/8) remains controversial, perhaps being dominated by phase separation and/or spin canting. However, despite the presence of the CMR metal and this phase boundary, the rare earth rich side of the phase diagram is relatively simple. The Ca rich side, starting at x=1/2, on the other hand, displays a quite unexpected variety of ground states, depending in detail on the exact divalent and rare earth ions used. The ground states include a wide variety of charge, orbital and spin orderings as well as stripe physics at commensurate carrier concentrations. One example is the so-called CE-phase, which is charge ordered, and consists of orbital ordered one-dimensional ferromagnetic stripes (Reprinted by permission from the author).

the individual phases studied in detail. The need for such a capacity clearly goes beyond manganites. For example, perovskite-derived ruthenates have been known for decades. Only recently, however, have very pure samples been made, and what has been discovered is a unique interplay of lattice couplings, magnetism and unconventional superconductivity. This example also illustrates another trend that should be noted. The discovery of unconventional superconductivity in ruthenates, and most of the high quality samples that are available in this field, like those of the manganites, originate outside the United States. This point, of synthesis of ultrapure, single crystal samples, is addressed below.

7.2.2. Superconductors

Ironically, as the interest in the superconductivity, at least the critical temperature, in HTS materials has waned due to the lack of new discoveries for several years, superconductivity in other areas is causing great excitement. The discovery of MgB_2 was stunning: a simple intermetallic superconductor without d electrons, without a high value of the density of states, and without cubic symmetry (all thought to be crucial for conventional intermetallic superconductors) has a critical temperature T_c=40 K, nearly twice as large of any previous intermetallic material. The underlying mechanism has already been discovered and understood: the interaction of structure and chemistry conspires to move strongly covalently bonded states (B–B bonds in the graphitic layer) to the Fermi level, where they become conducting. They are extremely strongly coupled to the B–B bond stretching mode, and this very strong coupling, of only a fraction of the modes to a part of the Fermi surface, is what drives the remarkable superconductivity. No better superconductors of its type have yet been found (as of late 2001), but this compound has opened the way for the search for good superconductors in classes of compounds that would have been ignored (and have been ignored) heretofore. The synthesis expertise of solid state chemists will be crucial in this search for new superconductors.

One other dogma of superconductivity has been breached: that magnetism is anathema to superconductors. Although a few “superconducting antiferromagnets” have been known since around 1980, the new developments have been stunning. $RuSr_2GdCu_2O_8$, initially appearing to be a ferromagnet that becomes superconducting, has now been shown to be a canted antiferromagnet, but one in which a surprisingly large internal field coexists with a bulk superconducting phase. The barrier was really broken by UGe_2, which becomes ferromagnetic at 50 K, then enters the superconducting state somewhat below 1 K and around 10 kbar, while still a robust ferromagnet. In addition, URhGe and $ZrZn_2$ have been reported to display coexisting superconductivity with ferromagnetism, and the inverse perovskite $MgCNi_3$ is superconducting very near (in the sense of doping) to a ferromagnetic instability.

This coexistence will attract intense interest, both theoretically and experimentally, certainly in the short term but almost certainly for some time to come, because there are so many open questions. Starting from the most basic end: the mechanism of pairing—spin fluctuations, and are the spin waves of the ordered ferromagnet crucial?; the character of the order parameter—triplet in most cases, presumably, but even more exotic possibilities exist, such as superconductivity of carriers of only one spin direction; coexistence and competition of the magnetic and superconducting order parameters; behavior of the ferromagnetic flux (spontaneous vortex phase?) and its reaction to external fields.

7.2.3. Multiferroics

Materials that show the coexistence of two (or more) types of collective electronic phases—ferroelectricity, ferromagnetism, ferroconductivity (i.e. superconductivity)—are called multiferroics. There is increasing interest amongst solid state chemists and physicists in the apparent dearth of multiferroics. Consider the perovskite crystal structure, for example. Some of the most important, and most studied, ferroelectrics include transition metal ions and have this crystal structure. And in the perovskite structure there are numerous magnetic materials, many antiferromagnetic but also several ferromagnetic ones. Both of these classes are mostly oxides. Yet there are very few examples of ferroelectric perovskite oxides that include magnetic ions. One of the simplest examples, in terms of chemical formula, is $BiMnO_3$. It is not really so simple, however, because the polarizability of the Bi^{3+} ion drives a cell-quadrupling distortion that leads to a difficult perovskite superstructure. A fundamental question is to what extent is the ferromagnetism related to the ferroelectric crystal structure? Solid state chemists have much to contribute to such an investigation.

Why there are so few multiferroics is not clear. The ferroelectrics often involve d^0 ions (which are not magnetic) whereas magnetic oxides require d^n ions with $n>0$. Do d^0 ions have a tendency to displace off-center and destroy inversion symmetry (necessary for ferroelectricity) more than d^n ions do? Looked at in the other direction, d^n ions favor Jahn–Teller distortions, which are centrosymmetry-conserving (and hence non-ferroelectric). Or is it possibly more a size issue, or some other chemical reason? The answers to these questions are not known, and it is not even known if these questions are the ones that are important to answer.

It is clear that multiferroics pose some exceedingly interesting and potentially important fundamental questions in materials science. It has been mentioned above that coexisting ferromagnetism and superconductivity, another type of multiferroic behavior, has recently been discovered and poses a large number of fundamental problems. What can also be said is that multiferroics pose extremely interesting candidates for new device possibilities: manipulations of electric polarizations by magnetic fields, manipulations of magnetization of magnetic layers by electric fields, switching on/off of superconductivity by locally-produced magnetic fields—one can reel off a large number of possibilities. Multiferroics clearly provide important near term challenges, and opportunities for strong collaboration, for solid state chemists.

7.2.4. Dilute magnetic semiconductors

The discovery that “dilute magnetic semiconductors” such as $Ga_{1-x}Mn_xAs$ with x near 0.05 (hardly dilute) order ferromagnetically, has put these materials at the leading edge of basic research at the same time that applied scientists work to incorporate them into electronics and spintronics devices. These materials combine the desirable and well understood transport properties of semiconductors with the possibility of using the spin degree of freedom and the ability to control transport with an applied field. The primary mechanism of spin alignment is under intense study, and more than one mechanism may be contributing. This area of study is well funded by several government agencies.

There is a distinct, but perhaps related, set of materials that qualify as (really) dilute magnetic semiconductors. These materials are typified by La-doped alkaline-earth hexaborides (viz. CaB_6) although related effects can apparently arise in off-stoichiometric materials. Curie temperatures are high and can approach 1000 K; the ordered moment, on the other hand, is tiny, of the order of 10^{-4} per unit cell. The electronic structure itself of these materials is under debate; originally seeming to be semimetals, there is now both theoretical and experimental evidence that they are semiconductors with a substantial gap. There are other materials displaying very closely related behavior. CaB_2C_2 and MgB_2C_2 have been reported to display similar weak ferromagnetism at high temperature; even graphite itself shows the same effect.

There is much work to be done to understand how the magnetic defects (understandable, if they are semiconductors) order magnetically at such high temperature.

7.2.5. Battery materials

The growing demand for portable electronics makes production and sales of batteries a multibillion dollar industry. Lithium energy storage batteries are an important technology that is amenable to computational study, because a substantial number of the essential properties can be obtained by quantum mechanical materials computation. The essential properties involve transition metal chemistry, structure, anion chemistry, and their interrelationships determine the operating voltage, efficiency of storage, etc. Although the current level of accuracy provides important understanding, and guidelines for better materials, the calculated voltages are 10–20% too small.

The main challenges are (i) the description of the transition metal chemistry needs improvement, which requires improved treatment of electron correlation, (ii) one needs the free energy rather than just the energy, (iii) Li and vacancy disorder (entropy) is essential in the free energy, (iv) disorder and alloying effects in general are not well enough understood. The experience and expertise of solid state chemists will be an important part of the development of better battery materials. Many general advances in materials computation will assist in meeting these challenges, and funding for code development is a long-neglected need. Better science and materials education at all levels will lead to better prepared students.

7.2.6. Magnetic insulators

Although local moment magnetism in insulators is not as involved as in metals, several examples of unexpected magnetic behavior have been found in insulators in recent years. In several cases this behavior has been discovered in materials that were synthesized by solid state chemists 20–40 years ago, and were of interest then primarily for their structural regularities. Examples include the calcium vanadates [CaV_nO_{2n+1}, n=2, 3, 4], sodium vanadates [viz. NaV_2O_5], and the quadruple perovskites $CaCu_3M_4O_{12}$, M=Mn and Ti. Numerous other examples could be given.

Fundamental questions about magnetic insulators of this type center around (1) the occurrence of unusual ground states, especially in reduced dimensionality systems, and (2) determining what the exchange couplings are, and how they can be obtained. Ground states of interest include “spin gap” states (also called global singlets or quantum spin liquids), spin Peierls states in which magnetic ordering occurs only due to coupling to the lattice which leads to symmetry breaking in the spin Hamiltonian, magnetic ordering due to a small exchange coupling in a system with larger but frustrated interactions, and the “order by disorder” systems in which order arises only out of the quantum fluctuations in a frustrated system. As the materials, and the resulting spin Hamiltonians, become more intricate, the exchange couplings cannot be obtained from susceptibility and heat capacity data as in simple systems, and calculation of the parameters using various forms of electronic structure calculations has become an integral part of the investigation of magnetic insulators.

This field of study will remain vigorous for the near future. In addition to the many facets of frustration in a Heisenberg Hamiltonian, there are single ion anisotropies and non-Heisenberg couplings (bilinear terms, antisymmetric Dzyaloshinski–Moriya terms, etc.) that arise from unusual chemistry of the materials and lead to new physics in the phenomena.

7.2.7. Half metallic ferromagnets

Due both to intrinsic scientific interest and to possible applications in spin electronic devices, half metallic ferromagnets are attracting great interest. These materials are magnetically aligned, with the electrons with one spin polarization (up, say) being metallic while the spin down electrons are gapped at the Fermi level—they are nonconducting. Evidently, they will provide a “spin filter” or “spin rectifier” if spin-flip scattering at interfaces can be controlled. The half metallic ferromagnet really provides a novel state of matter at very low temperature, then as the Curie temperature is approached and exceeded it converts into a paramagnet that is not necessarily distinct from conventional paramagnets.

Half metals provide fundamental theoretical conundrums: with a gap in the minority channel, it costs a finite energy (some fraction of the gap) to create a spin flip excitation. How then does one describe magnons properly in such materials, since they involve intrinsically non-collinear spins on neighboring atoms? There are several other theoretical question about half metals; in fact, it has recently been discovered that the customary theorems in density functional theory, which is the basis for nearly all electronic structure calculations of solids, do not hold in half metals as has been supposed. Although the calculations as performed are valid, there are important theoretical (formal) questions that are raised by half metals.

Experimental verification of half metallic character in ferromagnets has been difficult, due primarily to materials complications. Most of the probes of the half metallic state that have been relied on so far involve transport of an electron through a surface (photoemission) or through an interface (tunneling, Andreev reflection), and in many cases studied so far it has become evident that the materials are different from the bulk near the surface or interface. Since many of the same materials challenges will be present in the incorporation of half metals into spin electronics devices, research on synthesis and characterization of the interfaces of half metals will remain an area of strong activity. Bulk probes of the properties of half metals may become more fruitful as the theory matures.

7.2.8. Correlated electron materials

This category overlaps several of the above-mentioned classes, and includes certainly high temperature superconductors, colossal magnetoresistance manganites, intermediate/mixed valence compounds, and heavy fermion metals. As more is learned about these systems, yet more questions of an apparently fundamental nature arise. The classic approach has been to adopt a model Hamiltonian, whose choice sometimes is not evident, and treat it with perturbative or phenomenological approaches, guided by experiment. Electronic structure calculations have been useful in selected cases, but often they contribute little to the understanding because correlation effects are so large.

This model Hamiltonian approach has been assisted by the extensive experimental work on several members of a given class—for example, the correlated antiferromagnetic metals such as $CeRh_2Si_2$, $CeIn_3$, $CePd_2Si_2$, and $CeRhIn_5$. Still, it is apparent that subtle differences in materials can sometimes cause remarkable differences, and there is a developing effort to include correlations within electronic structure calculations that already include many of the nuances of a material. The vanadate LiV_2O_4 holds a special niche in these systems: it is the only truly heavy Fermion compound in which it is d electrons, rather than f electrons, that become heavy. It is also distinguished in another way: the d electrons provide both the local moment and the itinerant states via which the local moments interact. The LDA+U method "band structure for correlated materials" has been around for a decade and has been exceedingly important in understanding collective order (spin and orbital) in Mott insulators. A dynamic extension, called dynamical mean field theory (DMFT), is appropriate for the description of metals and perhaps heavy fermion phases, and is being applied by several groups with encouraging results. This direction of theory should and no doubt will be continued, and procedures to give it a better theoretical foundation should be a part of future research.

7.3. Theory and modeling: computation as a scientific tool

Theory and modeling is an essential aspect of solid state chemistry, and its impact has been growing rapidly and will continue to increase in impact in the foreseeable future. Computation is now well accepted as the third pillar of scientific investigation, alongside experimentation and formal theory. Computation provides information that is not otherwise accessible; computation in close conjunction with experiment, or with formal theory, results in advances that otherwise could not occur.

Although computation deals with specific numbers, it is worth emphasizing that the first purpose of a computational theory is *understanding*, as it produces the results from the equations of the formal theory and provides an interpretation of experimental observations. A complete feedback loop contains all three pillars. Understanding feeds progress, and understanding enables innovation.

Methods of computational theory and modeling range from *first principles* electronic structure calculations, to their highly parameterized 'tight binding' counterparts, and on to classical potentials for energetics and molecular dynamics studies of large numbers of atoms. There are comparable ranges of methods for other properties (such as for phonons), but we will focus here on the larger area of electronic (and magnetic) structure.

7.3.1. Methods of electronic structure calculations

7.3.1.1. First principles approaches If it is tenable, the preferred electronic structure procedure is to begin "ab initio" using as little as possible information from experiment. Commonly this means taking the known crystal structure, although ab initio implementations of the DFT total energy are quite successful in predicting the most stable structure from within a small set of alternatives. Lattice constants and internal structural parameters can be obtained by minimizing the energy; this is done most efficiently by implementing “linear response” methods whereby forces on atoms are calculated directly (rather than by finite differences).

The study of ab initio methods has burgeoned in the past decade. The impressive list of developments include:

1. extending basis sets (such as adding local orbitals to augmented plane waves) to extend efficiency or flexibility;
2. new types of pseudopotentials, such as the (Vanderbilt) ultrasoft construction;
3. real space approaches: finite element methods and finite differences on grids;
4. treatment of non-collinear magnetism, which is intrinsic in magnets where there is strong spin–orbit coupling, and is probably more important in transition metal magnetism than is currently recognized;
5. improved treatment of correlation: generalized gradient approximation (GGA), meta-GGA that includes dependence on individual orbitals, better treatments of the exchange energy, including phenomenological treatment of exchange and correlation in hybrid functionals;
6. treatment of strong correlations: LDA+U (band theory of strongly correlated materials), LDA++ (inclusion of dynamical effects via perturbation theory), dynamical mean field theory that incorporates many-body treatments of intra-atomic interactions;
7. linear response functions, providing direct calculations of phonon and magnon dispersion curves, forces on atoms and stresses on the unit cell,
8. ab initio spin dynamics for finite temperature simulations of magnetic systems;
9. construction and applications of Wannier functions: recent developments suggest the likelihood that there are several applications (correlated systems, ferroelectrics) where Wannier functions will facilitate progress in the understanding and the computational treatment of electronic processes.

There is much excitement in this field, and each of these items could command its own subsection. In many of the materials classes discussed above, it will require two or more of these innovations to address the fundamental questions.

7.3.1.2. Self-consistent minimum basis approach Self-consistent, minimum basis electronic structure methods will have an important role in the future. While based on the density functional viewpoint, simplifications—and some sacrifices in accuracy—are made, with the gain being that substantially larger systems may be treated realistically. These methods use minimal basis sets, which are necessary to develop intuition anyway, for expanding electron states. Additional approximations are made, ranging from the calculation of the density and the resulting potential to the DFT energy expression itself. Still, the methods include charge self-consistency, which is essential for most systems, and certainly for systems which are not well understood beforehand.

Although there has not been a great deal of effort yet to push these methods to a really large system, it seems realistic to consider applications to 10000 atom systems. The factors in extending them to ever larger systems are: (1) computational power to carry out the calculations, for which (2) further parallel algorithms should help, and (3) verifying the ability to obtain the necessary "computational data" to assist in understanding the systems. For large molecules there is always the question of structure: the energy landscape is complex and may well contain a huge number of local minima that differ little in their energy. Given the approximations that have been accepted in order to treat much larger systems, what are the questions that can be answered? Much study, based on computational results, is needed to address such questions.

7.3.1.3. Parameterized tight-binding methods A few groups have made remarkable progress in producing parameterized tight-binding energy functionals that work well for a specified range of phenomena, once a (large) set of parameters have been determined on simple, related systems using first principles methods. Fit to various carbon systems, the functionals can be used to describe the dynamics of C_{60} buckyballs, for example, although the process of bond breaking and reforming may still require advancements to be useful. The functionals have been extended to many elemental metals, and then on to several binary intermetallics. The promise for these methods is that they will be efficient enough that one can, say, perform relaxation of structures with thousands or tens of thousands of atoms, or one can perform useful dynamical simulations of thousands of atoms. Applications at present are best limited to simulations that do not involve wholesale breaking and reforming of bonds, which in most cases would take the method out of the regime for which it was designed and constructed.

7.3.1.4. Ab initio molecular dynamics: meeting of chemistry and physics The introduction by Car and Parrinello in 1985 of an algorithm to allow the simultaneous movement of electrons and nuclei provided not only an important new computational approach, but it stimulated the development of new algorithms more generally in the field of chemistry, physics, and materials science. The broad interdisciplinary interest in this technique reflects the growing importance of computational studies of the dynamics of materials. This activity has also had to address the importance of how statistical effects and entropy play crucial roles in dynamics.

This area of materials research is only beginning to come into its own. Its impact is being felt in both inorganic and organic materials research, and its enormous potential is difficult to quantify. This will depend on the progress of computational power (which has been at the rate of something like a thousand-fold increase each decade), the further development of algorithms that increase efficiency and lead to evaluation of new quantities, and the increased understanding that feeds back into the process. Larger systems seem to cry out for local basis sets (instead of plane waves) and researchers have been addressing this possibility very seriously with atom-centered orbitals (the SIESTA project is the best example at this time). Other types of local basis sets (wavelets, finite elements, etc.) and local approaches (real space finite differences) also show promise.

7.4. Materials exploration: to optimize, to discover

Carrying the comparisons made above to just one more level, one might say that solid state chemistry has a long and illustrious history in materials exploration, while solid state physics perhaps might rather be characterized in terms of properties exploration. Examples are common in the area of magnetic insulators during the past decade, where solid state chemists fabricated materials such as CaV_4O_9 two decades before their 'quantum spin liquid' (highly correlated but disordered spins) were studied and rather quickly understood. The quadruple perovskites $CaCu_3Mn_4O_{12}$ and $CaCu_3Ti_4O_{12}$ were fabricated around 1980 by solid state chemists, but only recently have their outstanding properties been discovered (CMR above room temperature, high dielectric constant (10^4) in the kHz range, respectively).

The central importance of materials exploration to materials science in general can hardly be overstated. Fairly recent examples include (i) the high temperature superconductors (HTS), where superconductivity was being pursued in a class that had previously been overlooked; (ii) the fullerenes and buckytubes, where the same element that makes diamond settings and pencil lead leads to amazingly high superconducting critical temperatures and to promising nanoelectronic components, and (iii) the transition metal borocarbides (such as YNi_2B_2C), which were discovered only because a pesky impurity (carbon) had not been eliminated. All of these 'accidental' materials, and more, have attracted great attention among materials scientists of all stripes. There is another type of discovery: that of near doubling of the superconducting critical temperature in intermetallics in MgB_2; here the material had been commonly available for decades and had simply not been examined at low temperature.

Strong opportunities in materials exploration lie in forming intimate connections with strong feedback between computation and experiment, two of which we mention here.

7.4.1. Computational theory: methods for design of new materials in solid state chemistry

There is a fundamental lack of tools to manipulate solid state compounds in as deliberate a fashion as needed for the exploration for novel materials. In contrast, "solids" made by crystallization of large, supra-molecular compounds can be tuned quite handily by a change of the supra-molecular host. The ability to control compounds at this level should be one goal of solid state chemists. One example where this is achieved to some extent is in templated materials synthesis. In this example, the template or structure-directing-agent can be modified by organic chemistry means, and this agent will then dramatically affect the form of the final material. Simplistically, one needs more to control than just composition.

7.4.2. Computational theory: high-throughput experimentation

High-throughput experimentation involves a meeting of physics, physical chemistry, and solid state chemistry. Companies such as Symyx hire physicists and physical chemists to design and use the equipment necessary for various parts of materials discovery. They also hire solid state (and organic) chemists. Relatively little academic work has focused on the intellectual framework of high-throughput experimentation. There remains a big gap that academic researchers can help to fill.

There are four challenges in high-throughput chemistry:

- development of sufficiently robust and transferable chemistries;
- development of appropriate screening technology;
- development of database technology to track experimental results;
- development of means to design the libraries.

It is this last area to which theory seems most applicable. This type of thinking is at a high level. Instead of designing the synthesis of a single molecule, one is thinking about the important principles in the synthesis of many molecules; this is meta-synthesis.

What little work (in the solid state context) that has been done to date has concentrated on statistical methods, i.e. large numbers of candidates. There is an important question at the other end: given that a laboratory might be able to synthesize, say, 30 samples rather than 30 million, are there useful principles to guide the choice of samples? Is there a “law of small numbers” or some related useful concept? These questions reflect a need of experimentalists and should be considered in future study.

7.5. Laboratory issues: improvements and needs

Two components comprise experimental materials research: materials synthesis, and probes of the properties. Both aspects of this “experimental method” need continuing attention and well-placed emphasis from time to time. In this section, we briefly address the issue of materials synthesis.

While it might be possible to state that the importance of materials synthesis to solid state chemistry in particular and to materials research in general is self-evident, there are important areas of materials synthesis that are in need of emphasis and encouragement. The areas of single crystal growth and ultrapure material synthesis are becoming increasingly important for several of the materials classes that were discussed above.

Single crystal growth is particularly important in establishing the properties of highly anisotropic materials, the high T_c superconductors provided a clear example of the importance. A more recent example is provided by the CMR manganites. Although they are derived from parent phases that are cubic (or are so in idealized form), they display collective order (Jahn–Teller, magnetic ordering, orbital ordering, charge ordering) that often results in high anisotropic behavior. The main activity in growth of single crystal growth of manganites is in Japan, of ruthenates is in Europe and Japan, and in the coexisting ferromagnet-superconductor UGe_2 is also in Europe and Japan. The US has a few strong centers for synthesis of pure, single crystal intermetallics, but appears to lag in the synthesis of such samples of oxide materials.

There are some specific needs in this area. The first is the recognition of the overriding importance of crystal growth, from the most basic level of the recognition by colleagues in academic departments and laboratories, to the upper levels of funding in government agencies, and the various levels in between. Examples where this capability is crucial in probing the basic chemistry and physics are easy to identify: the alkaline earth hexaborides (viz. CaB_6) whose baffling properties now seem to be dominated by defects, triplet superconductors, such as Sr_2RuO_4 and (most likely) UGe_2, manganites, and many more. It is difficult to get funding and recognition for exploratory materials research, and extra difficult in the specific area of single crystal growth that requires (1) specialized, often expensive equipment, and (2) expertise distinct from probes (characterization) that draws the lion's share of attention. The image furnace provides one of the best methods to grow high purity, single crystal samples of inorganic materials, but there are relatively few available in the US.

7.6. Conclusions

The opportunities for multidisciplinary collaboration among condensed matter theorists and experimentalists and solid state chemists seem almost limitless. Some of the current opportunities have been described above, and many more are expected to develop in the future. It appears at this time that the physics community has a very high interest in facilitating these collaborations and that solid state chemists have a high stake in such linkages.

8. National facilities

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8.1. Introduction

Major facilities, such as the national high field magnet laboratory and the nation's neutron and synchrotron X-ray centers, are very important resources for the scientific community and a major investment for the US taxpayer. It is vital that these facilities are used in an efficient and productive manner to train the next generation of scientists and engineers, and to provide a solid intellectual foundation for tomorrow's science and technology. This report focuses on methods for achieving the highest return on our investment in these facilities and indicates some areas where future investments may be well rewarded. While these ideas were developed with the nation's synchrotron and neutron facilities in mind, most are applicable to any major user facility.

8.2. Synchrotron and neutron facilities in the US

The US has made a very large financial commitment to the construction and operation of both neutron and synchrotron X-ray sources. The hard X-ray needs of the community of scientists and engineers are served by synchrotron sources located at

Stanford (SSRL), Brookhaven National Laboratory (NSLS), Cornell (CHESS) and the Argonne National laboratory (APS). There are also soft X-ray/VUV synchrotron sources located at the Lawrence Berkeley Laboratory (ALS), at Brookhaven National Laboratory (NSLS), in Louisiana (CAMD) and in Wisconsin (ALADIN). These facilities make a significant contribution to the nation's science and technology base. The APS, the most recently constructed hard X-ray facility, enables experiments that are at the cutting edge of what can be done with hard X-rays. It represents an investment of ~\$800 million for the initial construction and an additional several hundred million dollars will have been spent on instrumentation by the time it is fully equipped and utilized.

The nation's investment in neutron scattering facilities is also substantial. There are reactor neutron scattering facilities in operation at NIST in Maryland and at Oak Ridge, Tennessee (HFIR). The NIST facility provides an excellent example of how a modest investment by the NSF in a facility that is operated by another agency can have a big payoff for the user community. Spallation (pulsed) neutron scattering facilities are operated at Los Alamos (LANSCE) and Argonne National Laboratories (IPNS). At present, the US does not have a neutron source competitive with the world's best facilities in the UK (ISIS) and in France (ILL). However, what will be the world's brightest spallation neutron source is currently under construction at the Oak Ridge National Laboratory. This \$1.4 billion facility will enable US neutron users to be fully internationally competitive.

The operation of multiple synchrotron and neutron sources in the USA does not create unnecessary and costly duplication of capabilities. The facilities address different needs within the scientific community, as the demand for instrument time is great and the characteristics of each radiation source are different. For instance, experiments that can be performed at the NSLS or SSRL do not compete for access with measurements that require a very high brightness, and very expensive, undulator source at the APS. There is also considerable merit in having geographically diverse facilities, since being within a reasonable driving distance encourages experimenters to more closely couple their work at major facilities with ongoing activities at home institutions. The resulting synergy is likely to improve overall productivity.

8.3. Science at the major facilities

The nation's synchrotron and neutron sources serve a very diverse set of scientists and engineers. At one facility it may be possible to witness experiments on cement-based materials or residual stress in aircraft components going on at the same time as work with archaeological specimens or pharmaceuticals. One of the great strengths of these facilities is the broad range of science and scientists that they successfully support.

In addition to facilitating a broad range of science, it is vital that the major facilities successfully host scientists and engineers with a broad range of experience levels. Many research areas can benefit greatly from access to major facilities, but not all researchers have prior experience using these facilities. The need for user support is even greater with neutron instrumentation, since most solid-state scientists have experience with lab-based X-ray instrumentation. Carefully nurturing relatively inexperienced users is important if we are to obtain the biggest scientific return from our investment in national facilities.

Solid state chemists represent a small but none-the-less important component of the synchrotron and neutron user communities. Conversely, access to these major facilities is very significant to a major segment of the solid state chemistry community and the importance of these facilities can be expected to increase, as more complex materials are developed. The current significance of these facilities to solid-state chemistry and its interfaces with other traditional disciplines was very well illustrated by the large number of presentations, during the October 2001 “Future Directions in Solid State Chemistry” workshop at U.C. Davis. Presentations scattered through virtually all sections of the workshop included results obtained using synchrotron radiation. In some cases, the inclusion of these results was not explicitly mentioned, demonstrating that major-facility experiments are becoming a routine part of modern solid state chemistry for many research groups.

8.4. Making the most of our investment

The construction and operation of major national user facilities is a considerable investment by the taxpayer in the future of the US scientific enterprise. It is vital that the best possible long-term return on this investment is obtained. The maximum benefit will only be obtained with careful attention to the needs of the users and potential users of these facilities. It is not adequate to simply build and run instruments, there must be a mechanism to ensure that the best possible work is done at these facilities and that the next generation of highly competent scientists and engineers are trained. Experimenters with important scientific problems must be encouraged and trained to use the facilities, barriers to access must be minimized and careful thought must be put into ease of use.

The vitality of the work being performed at national facilities can be maintained and enhanced by encouraging people with exciting scientific problems to make full use of the capabilities of these facilities. As will be discussed in the subsequent paragraphs, there are many barriers to the use of these facilities, due to the need for travel and training, difficult-to-use instrumentation, as well as the delays produced by the facility’s scheduling system. These barriers are most acute for first-time users of facilities.

Travel/funding: one component of this activation barrier is the cost of travel to a central facility. A synchrotron or neutron scattering experiment may take several days or a week to complete and require more than one person to be present due to the need for round the clock operation. This can lead to travel costs of a few thousand dollars for an initial experiment. If these funds were not budgeted in the grant supporting the work because the national facility experiment was not anticipated, it can be very difficult to find the money. This obstacle could be overcome for NSF investigators by providing travel supplements on existing grants to cover unanticipated national facility work.

The geographical diversity of the nation’s major synchrotron facilities aids both low cost physical access and rapid feedback between characterization and materials synthesis. The funds designated for the support of major user facilities should NOT be concentrated in one location. For some types of experiment, cost and ease of access to the experimental facility are very important and the world's best synchrotron or neutron source is not needed. While some innovative measurements do require the latest generation radiation sources, much (but not all) good materials chemistry can be done at older facilities, provided the instrumentation is accessible and usable.

Sample submission/remote instrument access: ease of use is a very significant consideration in ensuring that the best possible work is done at the nation's major facilities. Many very valuable experiments of interest to materials chemists employ relatively simple hardware and do not require constant attention to the instrument. These needs could, in part, be met by offering access to certain types of experiments in a service mode. The sample could be mailed in and the measurement performed by technical staff members that are paid to perform this service. Services of this type are being operated at central facilities in other countries. For example, there is a single crystal diffraction service at the UK's Daresbury synchrotron for small-molecule work. We anticipate that a limited amount of instrument time would be dedicated to service work and the remaining time would be available for experiments employing other access modes. This is an area where a modest investment of NSF resources could benefit a large number of investigators from the chemistry, Earth science and materials communities.

For experiments where considerable user input is required, but complex sample handling operations are not needed, remote access via the internet could lead to a sizeable reduction in travel costs. This mode of operation also provides an opportunity to further train students in an economical fashion. However, prior hands-on experience at the facility is likely to lead to improved productivity while using remote access capabilities. For remote access and instrument control to become a widespread reality considerable development work is required. There are already some working models that can be examined, for example the High Temperature Materials Laboratory (HTML) at Oak Ridge National Laboratory (http://www.ornl.gov/doe2k/hfir).

The implementation of remote access capabilities requires careful consideration of the safety, data security and staffing implications. Frequent remote access may require high levels of staffing for activities such as sample changes. Instruments that are often used from remote locations may require funds for full automation, robots for sample changing, robots for changing sample environment etc. in order to reduce the staffing requirements.

Security is also a barrier when scientists travel to national facilities. Security clearance requirements should be minimized wherever possible and particular attention should be given to the issue of clearance for foreign students as they represent a significant fraction of the science and engineering graduate student population. A common clearance procedure and ID requirement for ALL DOE user facilities would decrease the burden on users. Careful thought also needs to be given to the security issues surrounding electronic access to major facilities as, in the future, it is likely that a significant number of experiments will be performed remotely.

Quick response to need: university users typically gain access to instrumentation at the National Facilities by submitting a brief peer reviewed proposal. Major users (rarely solid state chemists) may bypass this system by contributing money to consortia (CATs or PRTs) that build and operate instruments. The number of users and important scientific problems that come to the national facilities could be enhanced by a thoughtful reassessment of the current proposal process. A mechanism by which rapid access for common and short duration experiments such as EXAFS, powder diffraction, single crystal diffraction, small angle scattering etc. can be achieved is strongly needed. This would allow scientists to take the results from their national facility experiments and feed them back into their efforts to make improved materials. This feedback loop does not work well if there is a >six month time delay between making a sample and obtaining the much-needed characterization. Rapid access for short duration experiments could be facilitated by remote experimentation, where possible.

Rapid turnaround between sample preparation and characterization is already available to scientists working at major facilities, as well as consortia members, and it should also be available to all university investigators. Managers of major facilities should consider adopting a short proposal cycle (perhaps 2 months) and implementing proposals that cover many short experiments over an extended period of time (perhaps 12 months) to minimize the amount of time spent waiting for access. Blocks of time for rapid access need to be programmed into instrument schedules so that users never have to wait more than a few weeks to get data if they have an approved proposal.

Dedicated instrumentation: the ease with which a piece of equipment can be used is often intimately tied to its flexibility. General purpose, very flexible, instruments that are rebuilt for every new experiment enable cutting edge experiments, but their use requires experience and considerable skill on the part of the experimenter. It is very important that dedicated instrumentation is available at national facilities so that relatively simple, but none the less important types of experiment, such as small angle diffraction, powder diffraction, single crystal diffraction, EXAFS etc. can be performed without wasting large amounts of time rebuilding an instrument prior to the collection of any useful data. Dedicated instruments reduce staffing costs and maximize scientific output. The benefits of dedicated instrumentation are very well illustrated by the protein crystallographic communities efforts. Their beam lines do one thing very well, rather than many things in an inefficient fashion. Many types of experiment that are of interest to the materials chemistry community are best performed using dedicated instrumentation and the funding agencies should consider supporting the construction of more dedicated high throughput instruments at synchrotron sources, in particular APS, so that the needs of the solid state chemistry and other communities are well supported.

Training and user support: technical support and user education play an extremely important role in maximizing the scientific return from our national facilities. Potential and existing users with exciting problems that could benefit greatly from our facilities need to be provided with an opportunity to learn about the tools that the national facilities offer and to learn how to use these tools in an effective manner. The education and training of users can only be achieved by working on several fronts.

Currently, there is a considerable activation barrier facing potential new users of a technique. The prospective experimenter often faces the following questions: What kind of measurement should I be doing and which facility is best? Will I learn what I need to know? Who can I contact at a major facility to talk about my experiment? Once I have done my experiment, how do I analyze the data? Once I have analyzed the data, can I be truly confident in the results? Many of these issues could be addressed by the construction of an online resource for the materials chemistry community. This resource might include information on the facilities that are available and the instrumentation that can be found at the facilities. Examples of different experiments that have been performed using these facilities could be given. These examples should be educational not PR material. A list of contact points is vital. A list of software for data analysis and experiment design could be provided. Tutorials providing guidance on both the fundamentals of a technique and help with the use of experiment design and data analysis software would also aid the effort. The construction and maintenance of this online resource is a major undertaking, and would need the attention of a scientist or scientists who is/are funded to maintain it. However, it would be very valuable to the community. It is important that such a resource includes all major facilities and provides a well-rounded view of capabilities.

Online educational material must be complemented by short courses that focus on specific techniques and the analysis of data from these techniques. Only face-to-face contact and hands-on experience can fully communicate the nuances of a technique. There are already some opportunities to attend courses that focus on experiments at major facilities. For example, Argonne National Laboratory offers a two-week summer school on X-ray and neutron methods that includes hands-on experience for students. Additionally, NIST offer courses covering small angle scattering and inelastic neutron scattering in alternating years. However, they are heavily oversubscribed, provide few opportunities for faculty development and there is a need for focused courses in other areas. For instance, access to good quality instruction in the use of techniques such as EXAFS would be very valuable as there is considerable judgment involved in the analysis of the data. Some of these short courses, particularly those focusing on data analysis could be offered at regional universities to minimize travel costs. These short courses should be funded directly by NSF, DOE or some other agency so that PIs do not have to find grant funds to start a new line of national facility work.

In addition to the provision of educational resources covering the theory behind a technique, there must be adequate support from facility staff for the planning and execution of experiments. At every stage of the experiment, it is desirable for new users to have a contact person at the facility. Traditionally, this contact would be the instrument scientist. However, instrument scientists are most commonly promoted for their scientific research rather than attending to the needs of the outside users. There should be a mechanism for the reward of staff who provide high quality support to outside users. There may also be a need for technical staff who are paid to guide new users through the process of planning an experiment, preparing a beam time proposal, executing the experiment and analyzing the data.

Every instrument at a major facility is unique and for an outside experimenter to make good use of them, there must be good instrument-specific training and support to address equipment problems. Careful attention needs to be given to the way in which CATs and PRTs provide support to outside users, as there may be insufficient motivation for them to provide a high level of support to investigators who are not consortium members.

8.5. The future development of national facilities

In addition to improving the efficiency with which existing equipment is utilized, we need to ensure that ongoing and future investments in the construction of new facilities and instruments have the greatest possible scientific impact. A major facility should not be a static entity, the instrumentation at the facility and the facility itself should be continually developed so that new technological advances can be harnessed to maintain and improve scientific productivity. It is extremely important that adequate funds for instrument construction and development are made available, as the world's best X-ray or neutron source will do little productive science in the absence of good instrumentation.

Careful consideration should be given to the needs of the entire scientific community when providing funds for the development of new instrumentation at existing facilities or new ones, such as the Spallation Neutron Source (SNS). The instrument suite of a facility should meet the needs of users who view neutrons or X-rays as a useful tool as well as those who view neutrons/X-rays as their primary research area. There is a tendency to build instruments that best serve scientific studies on the cutting edge of instrumental capabilities rather than serving the needs of the materials community at large. The NSF can serve as an honest broker in promoting the needs of the broader research community.

At synchrotron sources, such as the Advanced Photon Source, either dedicated instrumentation or blocks of time where instruments are set up for routine measurements need to be made available with the idea of serving a large pool of users rather than a select group of CAT members. One area where the materials community needs this is for powder or single crystal diffraction. While these experiments can be performed on the very flexible instruments that are commonly built at facilities such as APS, setting up these instruments can be very difficult. These measurements can be performed optimally and much more efficiently on dedicated instruments. The value of dedicated optimized instrumentation is well illustrated by the impressive output of dedicated protein crystallography beam lines.

From the perspective of the solid state chemistry community, there are some very interesting possibilities for new instruments at the SNS. Our community would benefit from many instruments that are currently being discussed: a high data rate high-resolution powder diffractometer, an ultrahigh resolution powder diffractometer, a wide Q range, medium resolution instrument for local order studies in crystalline materials, a wide Q range, low resolution instrument for glassy materials as well as a single crystal diffractometer. At the present time, only the high data rate high-resolution instrument is funded and is intended to be available as the SNS opens. An ultrahigh resolution powder diffractometer was proposed for the Long Wavelength Target Station at SNS. Unfortunately, this target station is not likely to be built in the near term, but a similar machine could be built on the high power target station, though it would have higher background levels and would make less efficient use of the source. This instrument would still offer best-in-world performance; resolution comparable to that of a synchrotron along with the advantages of neutrons: light element sensitivity, good quality high Q data and sensitivity to magnetism. The SNS also offers an opportunity to revolutionize single crystal neutron diffraction. This technique is not heavily utilized at the moment because it typically requires large crystals and it takes weeks to collect data on one sample. At the SNS it should be possible to build an instrument that will enable the collection of data on submillimeter crystals in less than a day. This would revolutionize the way in which the technique is employed and enable much new science, particularly in solid state chemistry. If the scientific community truly desires a machine with these characteristics, a mechanism for funding it must be found. The high performance nature of the SNS diffractometers makes them difficult to fund through traditional consortia: the cost of an instrument can exceed $10 million, and there are very few potential users who would want more than a week's instrument time per year. It should be noted that these instruments would serve a very large user base.

8.6. Summary of recommendations

The nation's major facilities support a large and diverse body of high quality work. However, the long-term return on our existing investment in these facilities could be further enhanced by careful attention to their operation, user support/education and long term development. In particular, the following issues are thought to be important:

- Travel costs are a significant impediment to attracting new users to major facilities. The NSF should consider the provision of a travel supplement to existing grants for unanticipated major facility experiments and offer summer/sabbatical support to a faculty wishing to expand their knowledge of these facilities.
- Security clearance procedures for access to major facilities should be kept as simple as possible. A common security clearance and ID requirement for all major facilities would be valuable.
- The proposal mechanisms adopted by major facilities should allow for a very rapid turn around on simple experiments such as SAXS, powder diffraction, EXAFS etc. A response in a few weeks rather than a few months would enable close coupling between in-house work on a material and major facility experiments.
- The geographical diversity of the nation's synchrotron and neutron facilities should be maintained. Short travel distances facilitate closer coupling between the work performed at major facilities and experiments at the home institution.
- The part time operation of some instruments in a service mode or the development of dedicated service instruments should be carefully considered. Samples could be mailed in and data taken quickly by on site staff. This would lead to reduced travel costs and greater scientific productivity. Single crystal diffraction, powder diffraction, and EXAFS measurements may be amenable to this approach.

- Remote control capabilities should be further developed so that some experiments can be performed without the need for security clearance and travel.
- The construction and operation of instruments that are dedicated to one type of experiment should be supported. Simple experiments such as powder or single crystal diffraction cannot be efficiently done on the very flexible instrumentation that is often constructed at synchrotron beam lines.
- An on-line resource providing guidance on the availability of instrumentation/facilities, the design of experiments, data analysis software, the fundamentals of techniques that are useful to the community, and the effective analysis of data should be constructed and maintained.
- The operation of short courses on the design and execution of experiments and the analysis of the resulting data should be financially supported. Expert hands-on guidance is of great value to people who are learning a new technique. The cost of offering such a course is small compared to the real cost of the beam time that might be poorly used in the absence of such training.
- The nation's major facilities will only realize their full potential if there is an ongoing investment in new instrumentation. Without good instrumentation, the world's best X-ray and neutron sources are of little value.
- In selecting funding priorities for new instruments, the needs of the user community at large must be carefully considered. This community includes those who employ national facilities as an occasional tool as well as those who are major users.

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