# ADVANCES IN THE SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF BULK POROUS MATERIALS

*This special issue of the Journal of Materials Research contains articles that were accepted in response to an invitation for manuscripts.*


## Porous materials: Less is more


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The presence of porosity in a material was first shown by Robert Hooke (1635–1703) who, in his investigations of the natural world using the newly available microscope, observed that the structure of cork was based on regular hollow units which he termed "cells", because they reminded him of the cells of a monastery.[1] Indeed, the fact that most natural structures are porous is a clear indication that porosity plays a determining role in establishing a well-defined and suitable set of properties under constrained optimization conditions, compatible with bottom-up growth.[2] A similar observation can also be made for natural and processed foods, in which the presence of porosity is instrumental in tailoring important characteristics such as the geometric surface area (and therefore the dissolution rate and the intensity of flavors), the elastic modulus and toughness (with directly affects the chewing experience), the permeability (adding the possibility of homogeneously mixing fluid and solid components), and even the ratio between profit and direct cost (most of the food products comprise a high volume fraction of quite inexpensive air. . .).[3,4]

When looking at applications in virtually every field of technology, from energy to the environment or from health and safety to transportation and electronics (e.g., porous low k dielectrics and heat sinks), we can recognize that many components in simple or complex devices contain some degree of designed porosity, which specifically equips them to deliver a set of required (and sometime contradictory) performances. It is, indeed, the unique combination of features that porous materials possess that significantly extend their properties.[5] While unintentional porosity in a material or a part remains detrimental and great efforts are still invested to prevent uncontrolled pores, engineered and tailored porosity is becoming more and more prevalent in advanced materials. Many benefits are derived from the deliberate introduction into a material of voids, pores or cells with controlled geometrical parameters.[6] The processing procedures affect their morphology and architecture at every length scale, besides characteristics such as surface finish, flaw population, residual porosity in the cell walls and compositional purity, which also strongly influence properties as well as the cost of the component. Therefore, development and innovations in manufacturing are a key factor toward enabling the fabrication of components possessing the desired porosity features (such as average pore size, fraction, shape, orientation and connectivity, as well as their distribution and gradients). In this respect, scaling-up manufacturing methods from laboratory-size to industrial scale is of particular importance, as it enables the production of porous materials with reproducible properties at costs low enough for one or more mass markets (e.g., Styrofoam used for containers, packaging and insulation).

The three-dimensional assemblage of a large number of pores can occur in a variety of ways, leading to materials (in the form of a monolith or as a coating or part of a composite) possessing widely different architectures, from foams to honeycombs, from fiber networks to scaffolds, from connected hollow bodies to syntactic foams and sandwich panels, from bio-inspired structures to micro- and meso-porous materials and parts possessing hierarchical and/or graded porosity. Porous materials provide a great degree of design flexibility in their use, in relation to their architecture, composition and surface functionalization. Such widely different morphologies, structures and architectures result in a wide range of properties, so that the implementation of novel testing procedures and the development of precise ways for quantifying all the diverse features of a porous structure are required. This also points to the increasingly crucial role played by modeling in enabling the description and prediction of the effect of porosity on selected properties, aided by quantitative morphological characterization tools such as tomography, now available with a sub-micron resolution.

Tailored porosity is therefore the defining characteristic that allows us to use the well-known materials science

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paradigm connecting processing, microstructure, properties and performance, opening up a new dimension in designing materials, where microstructure (addressing the base material and mostly affected by composition and processing) is expanded to the level of pore or cell wall micro-architecture.

This Focus Issue contains a large number of papers reporting on advances in highly porous (i.e., with porosity $> \sim 30$ vol%) materials demonstrating the wide range of functional and mechanical properties achievable with a wide variety of pore morphology and architecture, which span many size scales, and which complement the more traditional material microstructure (e.g., degree of crystallization, grain size, precipitates, surface finish) and composition. These articles illustrate the wide-ranging interest in porous materials that can be currently found in academia and industry and offer a snapshot of the current state of the art, highlighting ongoing research in one particularly active part of the larger field of heterogeneous materials.

Often, special journal issues devoted to porous materials have focused on a single class of materials, i.e. polymers, metals or ceramics. We strongly believe there is a need for a more integrated approach to the topic, and we hope this Issue, in the spirit of the original book by Gibson and Ashby,[5] will inspire researchers to look at fields different from their own, learning from the experiences gained in other areas and stimulating interaction with colleagues in different fields. Common areas of interest include, of course, processing, properties, structure and modeling. It is interesting to note that several of the applications pursued are very similar, with the intrinsic differences between the features of each class of materials being the key discriminating factor in the choice of the material composition.

While some of the research focus and development are specific to the type of material class considered, we can also observe that some common trends exist. For instance, in all materials areas, there have been developments in the past decade or so at the micrometer length scale and recent and continuing developments at the nanometer scale, combined with rapid advances in modeling enabled by an exponentially increasing computational capability, which have opened up new vistas to bring the science and technology of porous materials in service to society in innovative new ways.

In porous polymers, the length scale for the cells has traditionally been of the order of millimeters, and the foam materials are typically of very low density, consisting of ~95% or more voids and only a few percent of solid material. Advances at the micrometer scale have opened the possibility to replace solid polymers with microcellular polymers in many applications where the full properties of solid polymers are not needed. Thin polymer sheets, of 1–2 mm thickness that could not be foamed by traditional processes can now be made microcellular. These developments have opened the way to save up to 50% of polymers used in many applications, providing economic benefits as well as favorable environmental impact by conservation of resources. As an example, a current area of investigation is cost-effective manufacture of lightweight and energy efficient advanced panel systems, made from microcellular polymers, for future housing construction.

In porous ceramics, macrocellular components have been around for decades in the form of foams for molten metal filtration or honeycombs for eliminating exhaust pollutants such as NOx and soot particles. A great effort is currently underway to improve the properties of these widespread components to fulfill the ever increasing demands in terms of performance of cast parts and environmental control. At the same time, it has been observed that the reduction in cell size leads to an increase in strength of the ceramic parts, and that the ability to introduce pores in different size scales (from the nanometer to the millimeter) in the same component improves critical filter features such as the specific surface area, while maintaining low pressure drop values. Components possessing hierarchical porosity have indeed been demonstrated to possess improved properties over single-mode porous components, with the macroporous framework ensuring the chemical and mechanical stability and good mass transport properties (i.e., lower pressure drop, a higher rate of external transfer of mass, greater turbulence and increasing convective heat transfer), while the smaller pores provide the functionality for a given application (e.g., enhanced catalytic properties or selectively binding an analyte).

In porous and cellular metals, the trend toward finer cell size is also underway. The early research was focused on aluminum foams with millimeter- and sub-millimeter-size cells, usually created in the liquid state at relatively low cost for large-scale structural parts. There is currently much research directed toward micro-cellular metals based on alloy systems different from aluminum, in particular higher-melting iron-, copper- and nickel-based alloys, for which powder metallurgy is often used, allowing for the creation of smaller pores in the range of 10–100 μm. Porous titanium has been under particularly vigorous study because its biocompatibility makes it an ideal permanent bone implant: in this case, pores with at least ~100 μm interconnecting windows are necessary to allow long-range bone in-growth, and research is more focused on pore architecture, e.g. their connectivity, size and surface roughness which can affect cell growth. Interest has recently been strongly focused on nanoporous metals, in particular nanoporous gold which is produced by very simple dealloying methods. At the other end of the scale, with pores in the millimeter range arranged in fully regular structures, metallic scaffolds and 3D lattices are architectured porous materials which can be created by additive manufacturing, assembly of wires or electrodeposition upon regular polymer scaffolds, with structural, biological and functional applications. The same is true for architectured, regular polymer scaffolds (e.g., produced by two-photon polymerization or by self assembly of hollow or full spheres) and ceramic scaffolds and sandwiches (e.g., produced by extrusion or solid free form processes). With the capability for net-shape forming via additive manufacturing, the difference between architectured cellular materials (e.g., scaffolds) and architectured cellular structures (fully formed objects and parts) becomes somewhat undefined.

For all classes of porous materials, significant advances are envisioned in the realm of biology and medicine at the micrometer length scale. Live cells in body fluids are in the 20–40 μm range. When a material has a microporous structure with a high degree of interconnectivity with cell windows of the correct size, then the live cells can flow thru these pathways and colonize the implant. Such components have a good healing response because they mimic the structure of bone. Another major application at this length scale is in tissue engineering where cellular scaffolds made from biodegradable polymers, ceramics or dissolvable alloys, are envisioned to provide support until natural tissue can grow and take over. Moreover, the combination of ceramic and polymers in a same component (e.g., bioglass foams infiltrated with a biopolymer, or ceramic scaffolds on which a nanosized polymeric fiber mat has been electrospun) or cell-seeded titanium foams have also been recently proposed.

At the nanoscale, the cellular polymers field can be said to be in a truly emerging state. There are many potential advances and applications of open and closed-cell nanofoams being investigated. For example, in microelectronic devices, as the chip making technology advances from the current 0.18 μm layers to 0.13 μm and to 0.10 μm, there is an urgent need for new materials with much lower dielectric constants, and polymers with nano-scale bubbles on the order of 100 nm are envisioned as solutions. Also, nanopores may provide a more efficient pathway for gas transport within a polymer. Such structures could help with identification of particles at the pore sites or surfaces, and could help assess the dispersion of particles in the polymer. Furthermore, nanoporous polymers are expected to provide low-cost materials for many filtration applications, such as water purification and battery separators.

Nanosized pores in ceramics are also an exciting field of research, especially for highly specialized applications such as hydrogen generation, where the ability to have a high selectivity among different gases based on their molecular diameter is a key enabling factor for the industrial implementation of innovative energy sources. Moreover, nano-porous ceramics (micro-porous, with a pore size $< 2$ nm, or meso-porous, with a pore size $< 50$ nm) have long been employed in various applications, such as low k dielectrics and catalyst supports, adsorbents or sensors, the latter taking advantage of their extremely large specific surface area, that can be higher than 2000 $m^2/g$. For nanoscale metals, as mentioned earlier, research has focused on gold, because of the extreme ease of fabrication and the high functionality of gold. There is however rapid branching toward other nanoporous metals, e.g., noble metals such as platinum and palladium, and transition metals such as titanium, copper and iron, where the very high specific surface area coupled with high electrical conductivity permit functional (non-structural) applications such as electrodes for solar cells or batteries and substrates for catalysts.

To conclude, we would like to provide a short list of recent or important overview references for readers interested to learn more about porous ceramics,[7–11] polymers[12–16] and metals.[17–21]

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