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Viewpoint Article

The lure of ice-templating: Recent trends and opportunities for porous materials

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ABSTRACT

Ice-templating is a simple materials processing and shaping route where the growth of crystals from a solvent template the porosity. Although the principles of ice-templating were established a long time ago, it has lured considerable attention over the past 5 years to become a well-established processing route for porous materials of all kinds. In this viewpoint, I summarize the current status and recent trends of ice-templating studies. I then review the unique assets of ice-templating and propose a roadmap of the most promising or pressing questions and opportunities in this domain.

1. Introduction

When a suspension of particles is frozen, the growing crystals can repel and concentrate the particles in the space between them, until the ice eventually invades the inter-particle space [1]. After elimination of the crystals, the arrangement of concentrated particles in the frozen structure is maintained and the pores are a replica of the crystals. The process is simple and versatile. It has thus been tested with all kinds of materials, from ceramics to metals, polymers, carbon materials such as graphene or nanotubes, and composites thereof. During the past 10 years, the status of ice-templating has evolved from a new processing route to an established one. With hundreds of ice-templating papers published, we have now a good overview of what can be achieved and what makes ice-templating unique, in terms of both process and materials. This viewpoint thus aims to discuss the future of ice-templating and highlight areas that probably deserve a particular attention in the future.

2. Where do we stand today?

The interest for ice-templating was mostly driven by the anisotropy of the structure and sometimes of the properties. The templating mechanisms by the ice crystals are versatile and have been demonstrated for all classes of materials. Matter, whereas found as particles, monomers, or more generally objects, is segregated by the growing crystals. All ice-templated materials have thus a similar morphology, independently of their nature.

The objective of ice-templating has been, for a long time, to develop macroporosity. The templated pores are usually macropores, with a variety of morphologies. With the usual cooling rates reported (1 to 10 K/min), macropores in the 5–50 μm range are obtained [2]. However, many studies also demonstrated how to obtain micro- and mesoporosity [3]. Such techniques can be combined with the usual ice-templating routes to obtain hierarchical porosity.

The porosity content can be anywhere in the 0–100% range. On the extreme porosity content side, the main limitation is the strength of the material that we can handle. Such extreme porosity can be a limitation for ceramics or metals, but has been an advantage for polymeric and carbon-based materials, with the possibility discussed below of ice-templating aerogels with extreme porosity content. In the low porosity content range, the development of macroporosity is limited by the ability of ice crystals to repel particles in a highly-concentrated suspension. Above a solid loading threshold around 55–60 vol%, the crystals grow directly in the interparticle space, no macroporosity is thus obtained.

Many solvents have been successfully tested, including camphene, tertbutyl-alcohol (TBA), dioxane, naphtalene, cyclohexane, DMSO, and a few others [1]. Many of these solvents were used for polymers which are not water-soluble. However, the pore morphology that is sought can also dictate the choice of solvents.

We also have now a good idea of the typical processing time and size limitations. Because of practical and physical constraints, we do not have a total freedom in terms of sample dimensions/pore size

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combinations. With freeze-front velocity typically in the 5–50 μm/s range, the time required to freeze samples can vary from a few seconds (for thin films or microparticles) to several hours (for thick samples). Besides patience, the control of the freeze front velocity and morphology over long periods (hours) can be problematic. In most situations, one can freeze 1 cm samples within 10 min or so.

Ice-templating is mostly material-agnostic, all kinds of materials have thus been ice-templated. If the structural properties were the main interest for a long time, the last few years have seen many studies focused on other physical and functional properties (Table 1). The range of properties and applications that can be targeted is extremely broad.

Finally, we have a fair understanding of the fundamentals of the process, albeit mostly experimental. For the most part, we know which levers of the process should be pulled to control the microstructure, architecture, and properties of ice-templated materials. However, it is still difficult to predict the precise behavior of the system. A first screening of parameters (solid loading, cooling rate, etc.) must first be done on any new system (material, powder).

3. Recent trends

Three important trends have been observed in the last 2–3 years: (1) ice-templated metals, (2) ice-templated aerogels, and (3) the use of ice-templating to trigger self-organization or self-assembly.

3.1. Ice-templated metals

Metals are the latest class of ice-templated materials. This delay is related to a few specificities of metals that make ice-templating more difficult:

- The density of metals is usually higher than that of polymers and ceramics. Settling issues must be fixed [4,5].
- The availability of metal powders of suitable particle size (submicronic), which at the same time exhibit a limited reactivity for the solvent. The almost instantaneous oxidation of metals particles in water makes their use difficile. Metal oxide powders, reduced before or during sintering, can thus be used [6]. Alternatively, metal precursors (such as TiH_2) have also been ice-templated [7], followed by a reducing treatment.

Many metals have now been ice-templated (Fig. 1): Cu [8], Au [9], Fe [10], Mo [11], Ni [12], Sn [13], Ag [14], Ti [15], W [16], or stainless steel [4]. Ice-templating is a great alternative to the current routes available to obtain porous metals with unidirectional porosity. Now that the initial issues associated to metals have been fixed, we can expect more systematic assessments of their properties and potential.

3.2. Ice-templated aerogels

Because the solubility limit of pretty much anything in ice is extremely low, it is possible to start with an extremely dilute suspension and yet concentrate matter between the growing crystals. This unique feature has been used to ice-template a variety of aerogels (Fig. 2): carbon nanotubes [17–19], nanocellulose [20], carbon nanotubes/chitosan composites [21], or manganese dioxide [22]. Most of the work was nevertheless concentrated on graphene [23] and graphene oxide [24,25], when it was realized that ice-templating could be used to obtain bulk macroporous graphene with dimensions (centimeter) of practical sizes. Aerogels with a density as low as 0.14 mg/cm^3 [26] and 0.16 mg/cm^3 [27] have been reported, and there is no reason why we could not obtain even lower densities, starting with even more dilute suspensions. These aerogels have been considered for a variety of applications such as sensors, catalysis, anodes for fuel cells, battery, or super capacitors, adsorption, or even tissue engineering. Centimeter-size, macroporous graphene with a wall thickness as small as 1.2 nm can be obtained [25].

3.3. Self-organization, self-assembly

The systems investigated for a long time were powders with a broad particle size distribution and no specific morphology. It was recently realized that the concentration increase induced by the freeze-front could be used to trigger self-organization or self-assembly. The objective is thus not to just template the porosity, but also to create particular organizations of objects (particles, micelles) in the frozen structure. Two main ideas have been developed. The first idea is to use anisotropic objects such as platelets or fibers. If properly controlled, the freeze front can align and orient the anisotropic objects, and thus induce preferential orientations in the structure [28,29], but also create lightweight, percolating fiber scaffolds (SiC, cellulose) [30,31]. The alignment of objects can be used later to obtain specific morphologies and thus microstructures [32] and improves structural or functional properties. The increase of concentration between the ice crystals can also trigger self-assembly. This was reported with block copolymers, which can self-assemble into a variety of organized structures such as micelles when their concentration increases [33,34]. These micelles can then self-assemble into more complex configurations. Such self-assembly has been heavily investigated with evaporation, and its application to freezing is recent. This self-assembly has been used to elaborate porous materials with a hierarchical porosity: an organized mesoporosity templated by the micelles, combined with the usual ice-templated macroporosity.

4. The lure of ice-templating: what makes it unique?

The first and maybe most unique feature of ice-templating is the extreme increase of concentration induced by the growth of ice crystals, which means that extremely high porosity content can be achieved [25]. If this is not of particular interest for metals and ceramic-materials cannot be handled anymore when the porosity is too high, this is extremely valuable for the development of aerogels, as discussed above. The second asset of ice-templating is that self-organization takes place locally, but everywhere in the bulk at the same time. Compared to most of the self-assembly processes, the average processing time for large samples (centimeters) is much lower. In addition, because the growing crystals segregate the particles locally, large defects are unlikely to develop. A direct consequence is the possibility to obtain a high reliability of the materials processed [35]. The combination of directionality and range of macropore size put ice-templated materials in a sweet spot with little competition. If many alternatives exist to make directional macropores, few of them present the same versatility and even fewer can hit a similar pore size. Another possibly unique asset is the availability of many processing parameters to adjust the architecture and microstructure of ice-templated materials and thus decouple, to some extent, structure and properties. However, because many processing parameters are interdependent, such adjustments require careful, exhaustive studies and a good understanding and control of the process [36,37]. Ice-templating is also mostly material-agnostic. The main requirement is a low solubility limit of the material to be templated in the crystal, to make sure that the growing crystals expel the material and that the particles are small enough to be repelled and concentrated. The entry barrier is low, little equipment is required. In the most extreme case of a solvent that sublimates at room temperature and atmospheric pressure–such as camphene–and a material that does not need a high temperature treatment–a polymer–no equipment at all is required. It is possible to quickly master the basics of ice-templating and rapidly get started. Finally,

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