



Review

Ordered mesoporous materials for lithium-ion batteries

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ABSTRACT

This article reviews the synthesis and applications of ordered mesoporous materials (excluding carbon or carbon-based nanocomposites) for lithium-ion batteries. Mesoporosity of electroactive materials is usually seen as an opportunity for increasing the specific surface area, but it can have a stronger impact on the electrochemical behavior of inorganic materials because the lattice networks are significantly altered. This alteration is, of course, more severe for microporous materials, but micropores are not electrochemically accessible. In the case of mesoporous materials, the electrochemical accessibility is strongly dependent on the pore physical and chemical structure. In other words, mesoporosity should be specifically designed for specific electrochemical systems. Here, the syntheses of mesoporous electroactive materials (mostly metal oxides) are reviewed by inspecting their electrochemical performance in lithium-ion batteries. The purpose is not just to have an ordered arrangement of mesopores, but also uniform pore walls with a thickness in the meso-size range. The applicability of mesoporous electroactive materials has been somehow overshadowed by the popularity of mesoporous carbon, but there are significant differences. While the wall thickness in the latter mainly controls the specific surface area, this defines the ratio or pathway of the solid-state diffusion in the former, which is the rate-determining step in lithium-ion batteries. The ultimate goal is to highlight the potential for designing the lattice network to make more edge units ready to participate in the electrochemical reactions. It is believed that the mechanism of Li intercalation into the side lattice units is different from the conventional solid-state diffusion throughout the compact lattice network of a bulk material. It is clarified that the role of uniform thin pore walls is more important than that of pore size, though, the latter is usually the point of attention in the literature.

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1. Introduction

The porosity of electrode materials in lithium-ion batteries is of utmost importance since the rate-determining step is the solid-state diffusion. Hence, nanostructured materials have recently attracted considerable attention as potential candidates to improve the rate capability by minimizing the solid-state diffusion lengths. Macroporous materials provide a 3D architecture for facile diffusion of the electroactive species within the electrode [1], but this comes at the cost of low tapping density. On the other hand, micropores are too small for an efficient electrochemical accessibility. Mesoporosity seems to be the right size for the diffusion of electroactive species while the electrolytes can fill the mesopores.

Roughly speaking, most of the nanomaterials synthesized by common methods such as hydrothermal have mesoporosity. However, this mesoporosity does not serve the performance as expected, since the mesopores are not ordered, and thus, the diffusion pathway is not straightforward. In fact, many of these pores are not electrochemically accessible regardless of their sizes as might be blocked in the random arrangement. A breakthrough was the introduction of ordered mesoporous materials. The discovery of the M41S family of mesoporous silicates based on supramolecular templates paved the path for the preparation of various mesoporous materials [2,3]. In the seminal works of the Mobil Co. scientists, MCM-41 (2D-hexagonal, *p6m*), MCM-48 (bicontinuous cubic, *la3d*), and MCM-50 (lamellar) were prepared by silica condensation in the presence of alkyl trimethylammonium surfactants as the supramolecular templates [2,3]. Soon this approach was extended by changing various controllable

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parameters such as temperature, pH, cationic and anionic nature of the surfactants, etc. [4–8].

These ordered mesoporous silicas were employed as hard templates for the synthesis of a wide variety of materials, but the flagship was ordered mesoporous carbon (OMC), which has been widely employed in various electrochemical systems for energy storage and conversion [9]. The OMCs have been used as high surface area carbon (with good electrochemical accessibility due to its ordered structure) or as a scaffold to accommodate the electroactive materials. There is a growing interest in energy storage materials, which work based on conversion mechanisms such as anode materials in lithium-ion batteries [10] or cathode materials of new generations of lithium batteries like lithium-sulfur [11] and lithium-selenium batteries [12]. In these cases, the primary duty of the OMC is to hold the electroactive materials in the course of charging/discharging while providing space for the essential volume expansion as a result of lithiation.

In addition to the OMC, the mesoporous silica templates have also been utilized for the preparation of mesoporous electrodes. The early attempts aimed to prepare nanocomposites of mesoporous silica and the electroactive material [13], and in the same line of research, the mesopores were utilized as the host for the second component of an electroactive nanocomposite. In this system, the high surface area is not the target, as the solid-state diffusion is still the dominant form of ion transport throughout the electroactive material; but the uniform distribution of the nanocomposite components can cause a more facile solid-state diffusion, and contributes to the matrix structural stability [14]. In addition, since most of the high capacity electroactive materials undergo volume changes in the course of charging/discharging, because the size of the extracting Li ions is comparable with the overall size of the lattice, the mesoporous architecture provides an opportunity for the material to alleviate the volume changes through the neighboring mesopores [15].

The next step, which is the main themes of the present manuscript, was to synthesize various intercalation materials with ordered mesoporous architectures. Although these materials can provide new insight for fundamentally understanding the intercalation process at the atomic scale in addition to the practical potentials, they have been somehow overshadowed by two sister classes of materials: OMC and mesoporous electroactive materials having random porosity. In the first case, the diffusion is within the mesopores, but the diffusion of interest in the ordered mesoporous electroactive materials is within the pore walls. This indicates that the desirable architecture of the ordered mesoporous electroactive material might be completely different from that of OMC, though the latter has built the common perception of the ordered mesoporous materials in the realm of electrochemistry. In the second case, the solid-state diffusion and the diffusion within the mesopores cannot be designed in a nanostructured particle with random mesoporosity.

Although the synthesis of mesoporous silica is straightforward, the preliminary reports on the synthesis of metal oxides were controversial as the metal oxide lattice can easily collapse during the structural changes induced in the course of calcination because of the facile crystallization [16,17]. This emphasizes that the mesoporous electroactive materials can undergo severe structural changes during the electrochemical cycling too.

Bruce and his co-workers studied the influence of pore size and wall thickness on the battery performance of mesoporous β - MnO_2 [18]. Although there was no straightforward and linear dependency, the rate capability was better for smaller pores and thinner walls. Considering the fact that β - MnO_2 is electrochemically inactive in its bulk form, the latter report clearly indicates the importance of thin walls of mesoporous materials in building a new

architecture in which the edge lattice are somehow dominant in the mechanism of the electrochemical reaction. The present manuscript reviews the impact of mesoporosity on the battery performance of common electrode materials for lithium-ion batteries. In this direction, the first aim is to collect the available reports on ordered mesoporous battery materials as they are somehow lost in the popularity of mesoporous materials. The present manuscript focus is on the importance of the ordered structure throughout the mesoporosity.

2. Terminology

There are standard definitions for microporous, mesoporous, and macroporous materials based on the pore size, but it is sometimes difficult to apply this categorization to porous materials with random pores. This is of critical importance for the electroactive material, as one may expect a straightforward electrochemical process through similar pores by a given label. For instance, many electrode materials are labeled as mesoporous, but they are just nanomaterials with some mesoporosity. Thus, there is no guarantee that there are actual mesopores for guided diffusion of electroactive species. This class of materials (whether rightly or wrongfully labeled as mesoporous materials) do not fall within the scope of this manuscript, which aims to inspect the special role of mesoporous architecture on the electrochemical behavior of electrode materials.

One may prefer the term *ordered mesoporous* for the materials having aligned similar mesopores like those originally prepared for the ordered mesoporous silica. However, this terminology is also ambiguous at least for two reasons. First, many authors simply use the term mesoporous for the material prepared by the silica templates. Second, these materials may seem ordered in TEM observations, but there is no guarantee that they have uniformity within the mesopores. From a materials science perspective, ordered alignment of the mesopores can be sufficient for the *ordered* label, but for electrochemical applications, chemical and irregularities on the pore walls are much more important than a uniform distribution of the pores along each other.

Fig. 1 displays a mesoporous material, which seems quite ordered. However, the ordered structure means that the nanoparticles have been uniformly attached to form a uniform microparticle as illustrated in the schematic model [19]. As the elemental mapping shows the material is chemically uniform (Fig. 1d). However, this does not guarantee the uniform interconnection of the mesopores for the diffusing counterions. In electrochemical systems, mesoporosity can provide a new mechanism for the fast diffusion if all mesopores are electrochemically accessible throughout the material.

The vague point is that mesoporous materials with non-uniform pores and walls are actually nanostructured materials. In many works, it is attempted to prove the superiority of the battery performance of a mesoporous material by comparing it with the corresponding nanostructured material. The latter is somehow referred to non-uniformity of pores in the meso size range in the corresponding nanomaterial. However, since the non-uniformity of the pores is relative in both non-uniform mesoporous and nanostructured material, this labeling is somewhat ambiguous. On the contrary to the ordered mesoporosity in which mesopores are composed of uniform walls, the non-uniform mesoporous materials are actually a random assembly of nanoparticles.

Hence, it should be emphasized that there are numerous papers in the literature studied materials labeled as mesoporous, but only a fraction of them can be subject to the special properties reviewed here. This is of utmost importance, as this misleading has limited the potential development of mesoporous materials under

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