



Review article

Porous carbon modified with sulfur in energy related applications

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ARTICLE INFO

Article history:

Received 27 February 2017

Received in revised form

30 March 2017

Accepted 31 March 2017

Available online 2 April 2017

ABSTRACT

Depletion of fossil fuels, and associated with their usage global warming, needs for energy storage and harvesting, as well as high costs and detrimental environmental effects of metal-based catalyst directed the attention of scientists to carbon materials. So far, for these applications, an emphasis has been mainly on graphene and on modifications of its chemical and electronic properties with heteroatoms such as N, P, or S. That graphene, to enhance its surface properties, often needs to be modified not only chemically but also to increase its surface area and porosity. Taking it into account, and to promote simple and inexpensive materials, the focus of this review is on recent applications of porous carbons modified with sulfur in energy related applications. The obvious assets of these materials compared to graphene are their porosity and costs. We focus on sulfur doping and impregnation since this approach is relatively new, and promising results on applications of such materials as cathodes and anodes for lithium and sodium ion batteries, supercapacitors, ORR catalysts, photocatalysts, photosensitizers, and CO₂ reduction media have been reported. Our intention is to briefly summarize recent findings and to stimulate further research on the properties and cutting edge applications of porous carbons that should still be considered as exciting materials of promising future.

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1. Introduction

Nowadays environmental problems associated with consumption of fossil fuels directed the attention of scientists and engineers to a renewable energy production and storage. The development of these technologies, besides building wind turbines or solar panel

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farms, also involves an extensive research on new materials being able to harvest and store energy as well as to contribute to its production. This includes the development of efficient capacitors, batteries, solar cell panels and catalysts, which are active either in water splitting or in CO₂ conversion into ad-value products and fuels. Still in many of these applications, metals, especially those classified as noble, or metal oxides play a paramount role.

Since metal-based catalysts suffer from high costs, susceptibility to active sites poisoning, and they might have a detrimental environmental impact, carbon -based materials have been explored to develop highly efficient metal-free catalysts for applications in various industrial fields with an emphasis on clean energy production, harvesting and storage. The diversity of their physical and chemical properties, such as chemical and thermal stability, electrical conductivity, and a wide range of morphologies make them highly attractive candidates for applications in these strategically important fields.

For most of these uses, even though some of them go beyond adsorption, a high surface area and porosity are desirable properties [1]. To improve the features of carbon materials towards energy related applications, hybridization/modification with different non-metal elements has been widely explored. Those heteroatoms widen a band gap and improve electronic and catalytic activities of carbon hosts [2,3]. The introduction of N, P, B [4,5] atoms into sp²-hybridized carbon frameworks is considered as generally effective in modifying carbon's electrical properties and chemical activities. In recent years, sulfur-doped porous carbons have attracted much attention due to their specific surface features especially beneficial in the field of energy storage, harvesting and production [6–9].

Based on the recent development in carbon science, the objective of this review is to provide a concise summary on the importance of carbon pores with incorporated sulfur (either impregnated or doped) in their energy related applications. Here we do not pretend to provide a deep digest focusing on the best performing materials but we would like to emphasize the effects of sulfur incorporated to the carbon pores on the tested performance. Even though numerous studies have been published on sulfur modified graphene [10–12] or other nanocarbons [13–15], our intent is to exclusively target porous carbons. In our perspective these materials are very unique and porosity is their significant asset, which markedly distinguishes them from graphene or carbon nanotubes. This is also an asset which makes porous carbon science much more complex than that of graphene. On the other hand, recent developments in a high resolution microscopy confirmed that pore walls of nanoporous carbon are built of thin units resembling distorted graphene layers [16,17]. Thus, even with all their complexity and imperfection, these materials can be considered as “poor-person graphene”. That “poor-person graphene” provides pores without costly modifications such as a KOH treatment [18]. A confined nanospace of pores affects physical/chemical processes and often directs them to take other, unforeseen paths enhancing the target applications. These paths become even more diverse when electronic properties of carbon matrices are altered by an introduction of heteroatoms such as sulfur or nitrogen (Fig. 1) [19].

2. Approaches to introduce sulfur to the carbon surface/pore system

Even though the chemistry of sulfur-containing carbons had been addressed more than half a century ago [20,21], recent years have brought new advances owing to a shift in the needs towards more high-end applications than separations, and owing to the development in instrumental methods. The detailed review of the methods which lead to the introduction of sulfur to the carbon surface have been recently published by Kicinski and coworkers [8].

In this work we briefly summarize the approaches and divide the methods of the sulfur introduction to the carbon surface into three categories, following a physical nature of the approach used and a final goal of the modification applied (Fig. 2). The first and the oldest group of modifications can be considered as a “dry” approach. Here sulfur is introduced to the carbon surface by reducing its oxygen groups with H₂S at elevated temperatures. It has been reported that the treatment at temperatures lower than 200 °C leads to sulfur in mercaptans, bisulfides, sulfones, while a heat at temperatures higher than 400 °C results in stable sulfur in thiophenic configurations [22,23]. The amount of sulfur depends on the content and type of oxygen groups on the surface. Another group of methods, which we refer to as a “wet” approach, involves impregnation of carbon with sulfur-containing organic compounds. In this approach such species as P₄S₁₀ [24], CS₂ [25], benzyl disulfide [26], p-toluene sulfonic acid [27], thiophene methanol [28], and variety of other thiophene-based compounds are used to impregnate carbons [8]. Then the heat treatment is applied, and as in the “dry” approach, the decomposition of organic compounds and their reactions with the carbon matrix/its oxygen groups lead to the introduction of up to 10% sulfur to the surface. Sometimes polymerization of sulfur containing compounds in the pore space takes place. The third group of methods is a direct synthesis of carbons from sulfur-containing polymers by their either hydrothermal or direct carbonization at various temperatures. Examples of polymers include thienyl-based polymer network (poly(1,3,5-tris(thienyl)benzene) (PTTB) [11], 2-thiophenemethanol [29,30], sulfonated polyvinylbenzene [31], or polystyrene sulfonates [32]. In the direct carbonization approach the sulfur content can reach even up to 20 wt %. Sometimes pore formers or activation agents are needed to deliver porous carbon as a final product [33]. In all these addressed above methods sulfur species exist in the carbon matrix in a broad variety of configuration including C–S–C, S–O and S–H bonds. As mentioned above, a detailed list of sulfur-containing compounds used to modify carbons or served as their precursors is included in the review by Kicinski and coauthors [8].

The last approach to introduce sulfur to the carbon surface, which is addressed here, cannot be considered as a chemical modification in a strict meaning of this word. In this methodology, carbon works as a host to elemental sulfur deposited as a separate phase in the pore system. As a result, physical mixtures/composites are formed rather than uniform materials. To produce such hybrid materials, porous carbon is exposed to sulfur vapors at temperatures higher than 400 °C and sulfur is either condensed in the pores or intercalated between graphitic carbon layers. When this process is done at about 155 °C elemental sulfur is deposited in the pore system as a thin film that does not block the pores and thus provides a full accessibility of sulfur to reagents [34]. The melting temperature of monoclinic sulfur is 118.7 °C and the boiling temperature of sulfur is 444.6 °C [35]. Liquid sulfur is predominantly S₈ at the melting point, where cyclo-S₈ and catena-S₈ co-exist. S₈ is predominant at 444.6 °C, but it dissociates into short chain sulfur at higher temperatures (Fig. 3) [36]. A solution-based processing technique with dimethyl sulfoxide can reduce the particle size of sulfur and generate its homogeneous distribution in the carbon pores [37]. Sulfur impregnation can lead to 70 wt % S deposited on the surface.

3. Sulfur modified porous carbons as battery electrodes

3.1. Cathodes of Li–S batteries

Owing to the urgent needs of the efficient energy storage, increasing the energy density of lithium batteries has become an important focus of materials research (Fig. 3). Lithium-sulfur

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