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Review article

Boron-enriched advanced energy materials

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ABSTRACT

Fossil fuels have been used as one of the essential energy sources for centuries. Considering the rapid depletion of fossil fuels and increase in environmental pollution, caused by vast fossil-fuel consumption, it is essential to minimize the use of energy wisely and efficiently and, therefore, rapid exploration of green and sustainable energy sources is warranted. In this context, the element boron plays an important role in the area of sustainable energy due to its unique physical and chemical properties. Thus, the boron-enriched composites have proved to be unique materials for a number of applications. This mini-review summarizes the most advanced progress in the area of boron-based nanostructured and macromolecular compounds for energy applications, particularly for its conversions, and as carriers and storage materials.

Contents

1. Introduction

To date, fossil fuels make main contribution to the ever-increasing global energy demand. With the worldwide rapid development of the economy and population explosion, the consumption of fossil fuels accelerates significantly, and thus the energy sources deplete rapidly. In addition, fossil fuels produce carbon dioxide upon combustion, which is called a green-house gas and contributes to global warming, as well recognized. Therefore, intensive effort has been devoted to the development of green, renewable energy, highly efficient methods of energy conversion and energy storage technologies. Concerning these goals, advanced devices with high efficiency, such as supercapacitors and fuel cells, are especially important in energy storage and conversion. High-performance materials play key roles in the area of sustainable energy [1–3]. Among the materials exploited, carbon nanostructures are vital for the advanced devices as main electrode composites and for hydrogen storage. Boronated carbon nanostructures have been well investigated to show promising properties as functional materials for these devices due to electron-deficient nature

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of the atomic boron. This mini-review surveys advanced progress in boraneous materials for use in energy and hydrogen storage, and thus it should provide the fundamental insight offering important guidelines for the future design of nanostructured materials in energy applications.

2. Boraneous materials for supercapacitors

Supercapacitor is potentially promising electrochemical energy storage and power output device due to its high power and energy density as well as its reasonable reusability [4]. They are of great interest as portable electronics, electric vehicles, and renewable energy systems operated on intermittent sources such as solar and wind mills. In general, there are two types of supercapacitors, namely pseudo-capacitor and electric double layer capacitor. Supercapacitors work on different mechanism from commonly used battery. They store and release energy through the interaction of the electrode interface and an electrolyte, while the batteries store and release energy *via* a chemical redox reaction [5,6]. Nanostructured carbons have been widely investigated as the excellent electrode composites due to their diversity of structures that generally provide extremely high surface areas and high electrical conductivity, along with their low-cost in production. Therefore, it is the material of great interest in the development of supercapacitors. Energy storage in carbon-based supercapacitors depends on charge uptake in the carbon/electrolyte interfacial surface region. It has been repeatedly demonstrated that the boron doping may improve the specific capacitance per surface area for the nanostructured carbons [7].

Boron is an electron deficient element that has been studied for decades as substitution in nanostructural carbons to promote the performances of Li-ion insertion, oxidation resistance and so on [8]. Boron enters the carbon lattice by substituting for carbon at the trigonal sites [9] and acts as electron acceptor because of its three valence electrons, causing a shift in the Fermi level to the conducting band and hence modifying the electronic structure of boron-doped carbon [10,11]. The change in electronic structure of carbon electrode materials can affect the electrical double layer capacitance. Most importantly, low-level boron doping shows catalytic effect on oxygen chemisorption on carbon surface, rendering the introduction of redox reactions related to oxygen functional groups on carbon surface [12,13]. Therefore, boron doping is able to modify the electrochemical capacitance of carbon materials, involving electrical double layer capacitance and pseudocapacitance [14].

Chen et al. prepared the mesoporous carbon with homogeneous boron dopant by co-impregnation and carbonization of sucrose and boric acid confined in mesopores of SBA-15 silica template [14]. Low-level boron doping shows catalytic effect on oxygen chemisorption at edge planes and alters the electronic structure of space charge layer of doped mesoporous carbon. These characteristics are responsible for substantial improvement of interfacial capacitance by 1.5–1.6 times higher in boron-doped carbon than that in boron-free carbon with alkaline electrolyte (6 M KOH) and/or acid electrolyte (1 M H_2SO_4). Such boron-doped mesoporous carbon can be expected to show maximum capacitance if further optimization of the local boron doping environment is done. This finding should be very useful for developing new doped carbon electrode materials for supercapacitors. Guo et al. prepared the boron and nitrogen co-doped porous carbons through a facile procedure using citric acid, boric acid and nitrogen as C, B and N precursors, respectively [15]. The resulting boron and nitrogen enriched carbon materials showed prominent capacitances. The nitrogen, boron and oxygen incorporated into the carbon matrix enhanced the wettability between the electrolyte and electrode materials, and the introduction of heteroatoms may result in the pseudocapacitive effect. Two samples of the boron and nitrogen enriched carbons (BNC), BNC-9 and BNC-15 were prepared with high specific surface areas of 894 and 726 m^2/g and showed the large specific capacitance up to 268 and 173 F/g, respectively, with the current of 0.1 A/g. When the current was set as 1 A/g, the energy densities were 3.8 and 3.0 Wh/kg and the power densities were 165 and 201 W/kg for BNC-9 and BNC-15, respectively. Thus, BNC-15 is more suitable to apply in high-power-demanded occasion, while BNC-9 tends to store more energy.

Wu et al. have demonstrated a simplified prototype device of high-performance all-solid-state supercapacitors, based on three-dimensional nitrogen and boron co-doped monolithic graphene aerogels [16], and this device possesses an electrode-separator-electrolyte integrated structure, in which the graphenes acted as additive/binder-free electrodes and a polyvinyl alcohol (PVA)/H_2SO_4 gel as a solid-state electrolyte and thinner separator. The graphene composites show 3D interconnected frameworks with a macroporous architecture, which are favorable for ion diffusion and electron transport in bulk electrode. In addition, the monolithic boron and/or nitrogen-doped graphenes can be easily processed into thin electrode plates with a desirable size upon physical pressing. Consequently, the resulting composites exhibited not only minimized device thickness, but also showed high specific capacitance (~62 F/g) and enhanced energy density (~8.65 Wh/kg) or power density (~1600 W/kg) with respect to undoped graphenes, or a layer-structured graphene paper [17].

Ling et al. prepared B/N co-doped carbon nanosheets by assembling the gelatin molecule in long-range order on 2D crystals of boric acid, followed by annealing [18]. The resulting B/N co-doped carbon nanosheets are very thin with ultrahigh aspect ratio, and excellent flexibility. The doped carbon nanosheets demonstrated excellent performance as supercapacitor electrodes, with an excellent high-rate capability of up to 100 A/g, and long lifetime of over 10,000–15,000 cycles with 105%–113% capacitance retention [18]. In addition, the synthetic approaches are feasible, economical and scalable. Synthesis and applications of an ultrafine amorphous nickel–boron alloy have been reported very recently [19]. The alloy has a high specific capacitance of 2230 F/g at 1 A/g in a three-electrode system, and the capacitance remained at 986 F/g when the current density is increased up to 20 A/g. Interestingly, the alloy was used to make an asymmetric supercapacitor with activated carbon, in which the amorphous Ni–B alloy was assembled as the cathode and activated carbon as the anode. The resulting device exhibited a high specific capacitance of 135.5 F/g at 1 A/g. It was claimed to deliver a maximum energy density of 59.3 Wh/kg at a power density of 1004 W/kg [19]. This device could be reused more than 5000 times with 88.2% specific capacitance retention.

3. Boraneous materials for lithium (Li)-ion batteries

Lithium-ion (Li-ion) batteries (LIBs), due to their reduced weight, high energy storage capability, and low self-discharge, have been widely used in many portable devices such as smart phones, laptops, digital cameras, electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs) and so on [20,21]. The secondary lithium-ion batteries are currently the best portable energy storage device for the consumer electronics market. A high energy density in batteries can be achieved by increasing the discharge capacity of the electrodes or by increasing the working potential of the cathode materials.

Among the three key components (cathode, anode and electrolyte) of LIB, cathode material is usually the most expensive one with highest weight in the battery, which justifies the intense