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ScienceDirect
Applied Catalysis B: Environmental 79 (2008) 89–99
APPLIED CATALYSIS B: ENVIRONMENTAL
www.elsevier.com/locate/apcatb

Review

Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell

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Received 14 March 2007; received in revised form 21 September 2007; accepted 28 September 2007
Available online 12 October 2007

Abstract

The research and development of catalysts with high activity and high durability is a significant issue for proton exchange membrane fuel cell (PEMFC). Nitrogen-doped carbon nanostructures and their composites demonstrate promising potential for PEMFC catalysts application. The nitrogen doping strategies of carbon nanostructures and the electrocatalytic aspects of nitrogen-containing carbon with and without catalytic metals on it are reviewed. Pt-based catalysts with nitrogen-doped carbon as support exhibit enhanced catalytic activity and durability toward oxygen reduction and methanol oxidation, which can be attributed to the high dispersion of Pt nanoparticles and the modified interaction between Pt nanoparticles and the support. For most of the non-Pt metal catalysts (Fe, Co, etc.) presently investigated for potential application in PEMFC, nitrogen is the indispensable element, and even though there are still controversies, the pyridinic type nitrogen is generally considered to be responsible for the catalytic sites. But the catalytic activity is still low and the stability issue is another challenging problem for non-Pt metal catalysts. Nitrogen-doped carbon, without catalytic metals on it, also shows enhanced catalytic activity. But many issues still need further investigation in order to get catalysts with targeted activity and durability.

Keywords: Proton exchange membrane fuel cell; Nitrogen doping; Carbon nanostructures; Non-Pt catalysts; Oxygen reduction; Durability

Contents

1. Introduction

Due to the attractive system efficiencies and environmental benefits, fuel cells have been attracting much attention as an alternative power generation in 21st century. Among all the various kinds of fuel cells [1], proton exchange membrane fuel cell (PEMFC) is believed to be the main candidate power source for next-generation light-duty vehicles because of its fast startup and immediate response to changes in the demand for power. It has also shown great promise for mobile applications such as portable electronics. However, the commercialization of PEMFC has been proved to be difficult to achieve [2]. One of the main problems encountered in its commercialization is the prohibitive cost of component materials (the membrane, the bipolar plate, the catalyst

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doi:10.1016/j.apcatb.2007.09.047

(presently carbon supported Pt and its alloys), etc.) [3–6]. The production cost of certain component materials, such as membranes and bipolar plates, is expected to be greatly decreased by the economies of scale (i.e., the mass production) [7], but it might be not true for catalysts in light of the probable upward pressure on Pt price, a limited natural resource of Pt [8], as volume increases [9]. So it is a prerequisite to decrease the usage of Pt, which requires to increase the mass specific activity of the catalyst, or to find an alternative non-noble metal catalyst that can give an acceptable catalytic performance [10], in order to achieve a competitive low cost of fuel cell. Other problems of present PEMFC include low material durability [11–13] and system reliability [14].

It is generally believed [15,16] that metal catalysts should be deposited on porous nanostructure materials in order to increase the specific surface area, which is the prerequisite to obtain an acceptable catalytic performance (gauged in the activity per gram metal). The surface chemistry and the structure of the support materials can greatly influence the activity of the resultant catalysts. This is because the interaction between the support and metal catalyst can modify the electric structure of catalytic metals which in turn changes the catalytic activity [4,17–19], and the durability of the resultant catalysts depends on the metal-support interaction and the durability of the support materials [11,12,20].

Carbon is an ideal support for electrocatalysts for PEM fuel cell [21]. In fact, no other material except carbon has the essential properties of high electronic conductivity, corrosion resistance, surface properties, easy reclaim of precious catalytic metals and the low cost. In general, the conventional support carbon black (Vulcan XC-72) is used for the dispersion of Pt nanoparticles. The appearance of novel carbon support materials, such as graphite nanofibers (GNFs) [22,23], carbon nanotubes (CNTs) [4,11,17,24–29], carbon nanohorns [30] and carbon nanocoils [31–34], provides new opportunities of carbon supports for PEM fuel cell applications. They have shown promising results towards fuel cell electrode reactions: oxygen reduction reaction (ORR) and the electrochemical oxidation of small organic molecules (methanol, alcohol, dimethyl ether) [17,28]. But, in terms of activity, cost and durability, current catalysts can still not satisfy the requirements of target PEMFC [2,3,7,35]. So people are striving to find novel catalyst materials (both the catalytic metals and support materials). These efforts include: (i) to increase the specific activity of Pt-based materials by alloying Pt with other metals, developing novel structure of Pt (porous Pt, Pt-skin structure [36,37], core–shell structure [38]) and so on; (ii) to find out non-Pt metal catalysts [39,40]; (iii) to find out novel support materials through modern advance in nanoscience and nanotechnology. Usually the (iii) strategy is employed together with the first two strategies.

One approach to find a novel support is to dope porous carbon nanostructure materials with nitrogen. As is known, carbon nanostructure materials (e.g., CNT, CNF) have shown already promising potential applications in many fields [41,42]: electronics, sensors, polymer composites, hydrogen storage, catalysis and electrodes, due to their unique structures at the molecular and nanoscale levels [41]. Doping carbon nanostructures adds another dimension to these structures' properties [43–47]. Doping of carbon can affect such properties as pH, catalytic activity, conductivity and nanostructure. Nitrogen-doped carbon nanotubes/nanofibers (N-CNT/N-CNF) with metal catalysts or without metals on them show enhanced catalytic activity toward oxygen reduction reaction (ORR) [48–50], which is the Holy Grail in the fuel cell community, because the over-potential loss due to the slow reaction kinetics of ORR is more than quarter of the total ideal electrode potential, which greatly decreases the energy efficiency, the specific power and energy density of a fuel cell. Nitrogen-doped carbon as the catalyst support is also expected to improve the durability of the resultant catalysts, because of the enhanced π bonding [11,51,52] and the basic property [53], due to the strong electron donor behavior of nitrogen [43,54,46,55].

The research and development of nitrogen-doped nanostructured carbon and their composite as potential catalytic materials for PEM fuel cell in recent past years are reviewed based on selected research reports from peer-reviewed journal publications. This review article consists of the following sections: (i) the nitrogen-doping method of carbon nanostructure materials, (ii) Pt-based catalysts with N-carbon as the support, (iii) the alternative non-noble metal catalysts based on N-carbon, (iv) the inherent catalytic activity of N-carbon (without metals on it).

2. Nitrogen doping methods

Nitrogen doping of carbon nanostructure materials can be categorized into two categories [42]: (i) doping directly during the synthesis of porous carbon nanostructure materials, which can be called as ''in situ'' doping; (ii) post-treatment of pre-synthesized carbon nanostructure materials with nitrogen-containing precursor (N_2, NH_3, etc.), i.e., post-doping.

The ''in situ'' doping method is often used in nitrogen-doped carbon nanotubes (N-CNT) and nitrogen-doped carbon nanofibers (N-CNF). Several reviews have been recently published on nitrogen-doped carbon, especially on nitrogen-doped carbon nanotubes [42,56]. Several methods can be employed to synthesize nitrogen-doped carbon nanotubes [42], which are similar to those used to synthesize pure carbon nanotubes [57–61]: (i) high-temperature synthesis methods such as arc-discharge [62,63] and laser ablation [64,65]; (ii) low-temperature synthesis methods such as chemical vapor deposition (CVD) [66,67]. CVD and other modified CVD methods (aerosol assisted CVD [68,69], floating catalyst CVD [70], microwave plasma enhanced CVD [71], pyrolysis-type CVD [46,66,72–74]) might be the most popular and economically competitive to produce nitrogen-doped carbon nanotubes; (iii) solvothermal synthesis method, which seems to produce stable large diameter nanotubes with very high nitrogen contents [75,76].

Post-treatment of carbon materials in nitrogen-containing atmosphere can also form N-doped carbon. Most of the post-dopings are carried out in NH_3 at high temperatures (600–900 °C) [48,77–79]. Jiang and Gao's research [77] showed that