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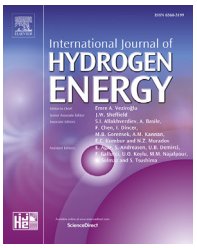

Electrochemical hydrogen storage performance of carbon nanosheets synthesized from bituminous coal

Hooman Seifi, Saeed Masoum *

Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran

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ABSTRACT

In this study, we successfully prepare porous carbon (PC) nanostructure derived from bituminous coal that shows it as a hopeful hydrogen storage adsorbent. The PC is characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscope (FT-IR), N_2 adsorption/desorption (BET), scanning electron microscope (SEM) and transmission electron microscope (TEM). The PC shows high ultramicroporosity and high total pore volume. This prepared PC achieves an excellent discharge capacity equal to 3485 mAh/g (corresponding to a hydrogen storage capacity of 11.6 wt%) at room temperature. Moreover, our results suggest that this PC can store H_2 in the range of 10.1–11.6 wt% which meets the U. S. Department of Energy (DOE) purpose of 2020. Due to its exceptional characteristics, this PC provides reversible higher hydrogen storage capacities than the previously reported porous carbons.

Introduction

Hydrogen, the most abundant element on Earth, is a carrier of high energy density (hydrogen has an energy content approximately three times larger than gasoline as the most widely used fuel in the US) and clean energy (released without harmful emissions and non-polluting nature), therefore, it is regarded as an ideal and environmentally friendly fuel energy carrier fuel for many energy applications, including portable fuel cell, transportation and stationary fuel cell applications [1,2].

Many chemical, electrochemical and physical methods have been useful to hydrogen storage. Among them, electrochemical storage methods are developed as one of the most favorable hydrogen storage approaches, which work at room temperature and ambient pressure and can be easily transmitted (because it includes electronic coulomb interaction) and direct hydrogen adsorption occurs in electrode material operation of electrochemical cells [3,4]. Jurewicz et al. showed that the hydrogen storage capacities of the identical porous material by a conventional approach (i.e., at 273 K and hydrogen pressure of 70 bar) and an electrochemical method, were improved from 0.4 wt% to 2 wt% that verifying the electrochemical hydrogen storage to be a more efficient and elegant storage method at ambient temperature and pressure [5].

According to the power of interaction between hydrogen and storage material, which significantly affects the thermodynamics and kinetics of the hydrogen adsorption/desorption, these materials are divided into three groups:

* *Corresponding author.*
E-mail address: masoum@kashanu.ac.ir (S. Masoum).

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i) physisorption, ii) on-board hydrides (reversible) and iii) off-board hydrides (regenerable). In materials as porous carbons, clathrates, metal-organic frameworks and zeolites, the mechanism of hydrogen storage is physisorption which hydrogen atoms are adsorbed on the surface of the pores which involved forces are van der Waals forces (intermolecular forces). These processes are reversible because the interaction energy is very low and is free of activation energy. However, the main drawback of using of these hydrogen storage materials is the weak intermolecular interaction (van der Waals forces) between hydrogen and surface of the adsorbents. Thus, the materials with physisorption mechanisms provide high capacities in high pressures and liquid nitrogen temperature, but their storage capacities become too low at ambient pressure and temperature. Research on the synthesized of highly porous materials, which enhanced interaction with hydrogen, is being attractive field. Nowadays, development of a simple, cost-effective and safe storage technique is an important field for the wide utilize of hydrogen as an attractive alternative to fuel oils (gasoline, kerosene, diesel, etc.), particularly for electric vehicles [6].

Recently, preparing novel effective electrochemical hydrogen storage material, as the most challenging barriers in the implementation of a "hydrogen economy" society, has attracted an excessive deal of consideration in the energy storage research field [7–9]. Numerous storage media such as metal alloys [10], metal hydride compounds [11], graphene oxide [12] and doped carbon nanotube [13] have been developed to uptake hydrogen. Among the several possibilities, the carbon-based adsorbents are promising as strong candidates, due to low-cost, high SSA, low density, good electrical conductivity, mechanical stability and mass productivity [14]. Many synthetic approaches, including physical, catalytic activation, and chemical processes have been advanced to create highly porous carbon materials [15]. One of the most important factors that has a vital effect on the construction mechanism, total surface area as well as electrochemical performances is the initial carbon precursor. Pitch, coal, wood and petroleum coke are most popular used as precursors of commercial PC productions [16,17]. In the past few years, reduction of fossil fuels availability and abundance of biomass lead to attract tremendous attention to biomass-derived PC. They were produced from raw natural material, such as starch, neat, acacia gum, banana fiber, woods, rice husk, fungi, bamboo, etc. [18–21]. Due to its cheapness and availability, coal is the most popular precursor of PC production [22]. Products of bituminous are in more demand, because they have higher abrasion resistance adhesiveness, hardness and carbon content, therefore, they are more robust than other coal-based carbons [23]. Over the past years, depending on the used carbon precursors and the activation process, numerous PC with diverse physicochemical properties have been synthesized and utilized as supercapacitor electrodes. Since mechanism of storage in the carbon materials is the electrical double-layer, more electrolyte ions, large surface areas, can be assembled at the interface between electrolyte and electrode. Thus, numerous techniques have been applied to enhance the surface areas of carbon materials, physical or chemical activation, including alkaline treatment, heat treatment, and plasma surface treatment [24,25]. In this study, an Iranian bituminous coal was selected as a precursor of PC.

Fierro et al. produced PC with high surface areas, and characterized that it had hydrogen storage capacities equal to 6.6 wt% at high pressure and very low temperature (−196 °C) [26]. The main drawback of sorption on PC is the requirement of using very low temperatures, since the typical adsorption heat (ΔH_{ads}) of hydrogen on carbon is roughly 6 kJ mol^{-1} [27]. To increase hydrogen density (more interaction between hydrogen and adsorbent), the temperature declined below the critical temperature (T_c of hydrogen is 33 K), hence the temperature lower than T_c of hydrogen gas is responsible for strong hydrogen/adsorbent interaction. Because of this disadvantage, the storage of liquid form of hydrogen can only be done in open systems, as regards, there is not existent any liquid phase above the T_c. However, to increase hydrogen/adsorbent interaction, the pressure of hydrogen in a closed system can be increased to ~10^4 bar at room temperature.

Major efforts have been concerned to develop suitable approaches for improving the carbon/hydrogen molecules interactions, thereby increasing hydrogen storage. In this report, we tried to use cheaper, raw natural and novel material with high capacity for hydrogen storage. Hence, the PC that is produced from Iranian bituminous coal is not harmful to human health and is low cost. In present work, a simple, fast and environmental friendly method has introduced for synthesizing of the bituminous-based PC and has used for hydrogen storage at atmospheric conditions and room temperature that is useful for the environment.

Experimental

Materials and measurements

The bituminous coal was collected from GilanGharb, Kermanshah, Iran. All chemical reagents were commercially available.

Fourier transform infrared spectra (FT-IR) were carried out by the KBr pellet method with a Shimadzu Varian 4300 spectrophotometer. Scanning electron microscope (SEM) images were recorded on Philips XL-30ESEM. X-ray diffraction (XRD) pattern was performed by Ni-filtered Cu Kα radiation on a Rigaku D-max C III. Analyses of N_2 adsorption/desorption were measured by Tristar 3000, Micromeritics (at −196 °C). Images of a transmission electron microscope (TEM) were recorded on a Philips EM208 operating at 200 kV.

Synthesis of porous carbon

The bituminous coal was washed with HCl (23%) to remove dust like impurities. After drying, concentrated sulfuric acid was added to it and mixed for 30 min. Then, the mixed solution was heated at 120 °C for 2 h. The precipitated black liquor was washed with distilled water until reaching neutral pH and removing the un-reacted excess acid. Then, products were centrifuged and dried at 150 °C for 1 h. Then obtained solid was mixed by HCl (23%) and HNO_3 (23%) at 80 °C and it was further activated thermally by an electric furnace at 500 °C for

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