

Short communication

Carbon nanofibers as hydrogen adsorbing materials for power sources

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Abstract

Porous carbon nanofibers are synthesized by CVD method from acetylene with use of iron-containing catalysts. Activation of the nanofibers in melted potassium hydroxide results in increasing surface area from initial 300–400 m² g⁻¹ to 1700 m² g⁻¹. As follows from XRD data, activated nanofibers do not contain regular packages of graphene layers, but retain high electric conductivity. Deposition of copper improves electrochemical hydrogen storing characteristics of carbon nanofibers. Carbon nanomaterials obtained can be used as hydrogen storing materials in batteries instead of hydride forming metals.

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1. Introduction

Metal hydride batteries produced now are based on alloys of rare metals of AB₅ and AB₂ types. Electrical capacity of these alloys reaches 300–450 A h g⁻¹. However, these alloys are complex for production and have some disadvantages. So, search for new materials capable of electrochemical hydrogen storage is continued. Among them new nanocarbon materials such as nanotubes, nanofibers, fullerenes, carbine, attract attention as possible hydrogen adsorbing electrode materials in alkaline solutions [1–3]. Carbon nanofibers were reported to retain 10–15 wt% of hydrogen [4,5]. This considerably exceeds amount of hydrogen stored by LaNi₅. Theoretically, as it follows from calculation by Faraday law, 15 wt% of reversibly adsorbed hydrogen corresponds to nearly 4000 mA h per 1 g of carbon material. In known carbon nanofibers (CNF) materials adsorption of hydrogen is not completely reversible, and often high pressure is needed to achieve maximal capacity. Besides this, hydrogen adsorption capacity strongly depends on the CNF pre-treatment and hydrogen purity. Nevertheless, we think that there are no fundamental obstacles to solve these problems.

Today use of nanocarbon materials is limited by their high cost (thousands dollars for 1 kg of nanotubes). However, the raw materials for CNT and CNF production by CVD technology (methane, ethylene, acetylene, and propylene) are not expensive. Our calculation shows that in large-scale manufacture the cost of CNT and CNF can be lowered to about \$100 kg⁻¹ and even less. If the problems named above were solved, carbon nanostructures could be more efficient hydrogen storing materials than metal alloys due to high surface area and porosity, low density.

According to data published, carbon nanofibers with graphene layers oriented perpendicularly or angularly to fiber axis are most efficient for adsorption of hydrogen. It was assumed that hydrogen intercalates into nanodimensional cavities formed by graphene layers. Porous carbon nanofibers were obtained [6]. Principally, porosity could be favorable for electrochemical applications. In its order, structure of nanocarbon materials obtained by CVD method in great extent depends on catalyst used. It was also reported that modifying of carbon nanofibers with some metals (Ni) considerably increases ability of such materials to adsorb hydrogen [7]. It is known that introduction of copper into composition of hydrogen adsorbing alloys based on LaNi₅ and Ti–Zr–Ni improves their characteristics [8,9]. They believed that the Cu addition improves the electronic conductivity of the electrode, and facilitates electrochemical hydriding [9]. It was interesting to

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study the influence of copper on electrochemical characteristics of CNF.

The aim of our work is synthesis of carbon nanofibers and their modifying by different methods in order to obtain carbon nanomaterials capable to electrochemical absorbing and storing hydrogen.

2. Experimental

Carbon nanofibers were obtained by CVD method from acetylene at 620 °C. Catalysts were obtained by pyrolysis of iron stearate dispersed on alumoaerosil. It was found that catalysts were much more active when pyrolysis was carried out in oxygen-free atmosphere. It was assumed that carbon clusters formed from organics in these conditions, together with iron clusters, operate as a seed for growth of carbon nanostructures [10]. The CNF obtained were purified from metal oxides by treatment with solutions of alkali and acid. Surface area was measured by argon desorption method. Usually surface area was near 300–500 m² g⁻¹ depending on synthesis conditions. Diameter of CNF was 50–400 nm, specific electrical resistance 0.08–0.4 Ohm cm. Typical electron image of CNF is shown in Fig. 1. Probably the porous structure observed is composed of graphene layers non-coaxial to the nanofiber axes.

Activation of CNF was performed by treatment with melted KOH for 2 h at 750 °C in argon flow [11]. During activation vapor of metallic potassium evolved and condensed on cold top of stainless steel reactor. After treatment the substance was washed with water, treated with hydrochloric acid and again washed with water.

Surface area of activated CNF so obtained depended on nature of original CNF. In some experiments we obtained activated materials with effective surface area (by argon) up to 4000–6000 m² g⁻¹. In this work activated CNF with surface area 1700 m² g⁻¹ were studied.

Electrochemical testings of nanocarbon electrodes were performed with use of a model Ni-MH cell in galvanostatic mode. Large surface nickel oxide electrode was used as a counter-

electrode. Five molar KOH solution containing 1 M LiOH was used as electrolyte. The anode for testing was made in form of a disk 30 mm in diameter pressured with nickel net. As a binder PTFE suspension was used (5% to mass of CNF). Deposition of copper on CNF was performed by galvanic method from copper sulfate solution containing 200 g dm⁻³ of CuSO₄·5H₂O and 40 g dm⁻³ of H₂SO₄. Sample of CNF (0.2 g) was placed into a box made of nickel net. Current density was 200 mA per 1 cm² of the box geometric surface. Amount of copper deposited on CNF was determined by atom adsorption spectral analysis. Samples of CNF containing 2 wt% and 5 wt% of Cu were studied.

After preparation the nanocarbon electrode was kept in model cell during 1 h with open circuit. The testing cycle was started from charging. All charging cycles lasted for 3 h. Then circuit was opened for 5 min and discharging was carried to cell voltage of 0.5 V (all potentials are given compared to standard silver-chloride electrode). Charge and discharge currents were equal to 50 mA g⁻¹ for electrodes, containing non-modified CNF. For copper modified CNF electrodes the charge current was 200 mA g⁻¹, and discharge current 100 mA g⁻¹. At that the capacity of electrode achieved 400 mA h g⁻¹.

Self-discharge of the hydrogen adsorbing nanocarbon electrodes was studied as following. First, the cell was charged with current of 50 mA g⁻¹ up to capacity of 450 mA h g⁻¹. Then the cell was left to stay during day and night or week. After this potential was measured at open circuit, and discharge was made at current 20 mA g⁻¹. The discharge capacity so measured was compared with capacity of freshly charged cell.

Electron images were recorded with use of transmission electron microscope JEM-100 CXII. XRD patterns were recorded with use of DRON-3 diffractometer, radiation Cu K α .

3. Results and discussion

In Fig. 2 there are shown XRD patterns of original CNF and CNF, activated with melted KOH (surface area 1700 m² g⁻¹). After activation the peak corresponding to reflection 002 of

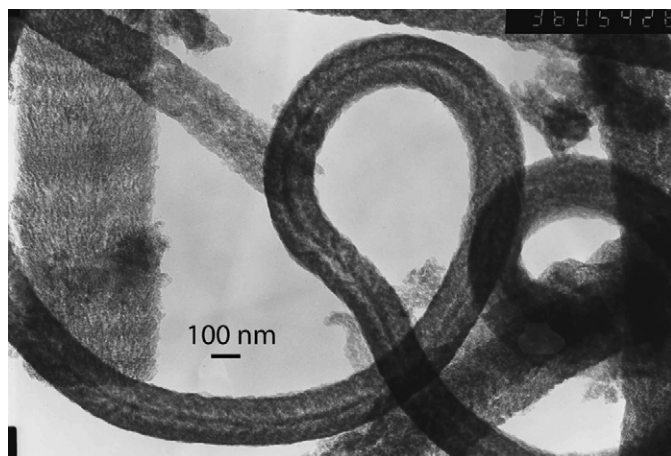


Fig. 1. Typical electron image of CNF obtained by CVD method from acetylene on Fe/C/SiO₂ catalyst.

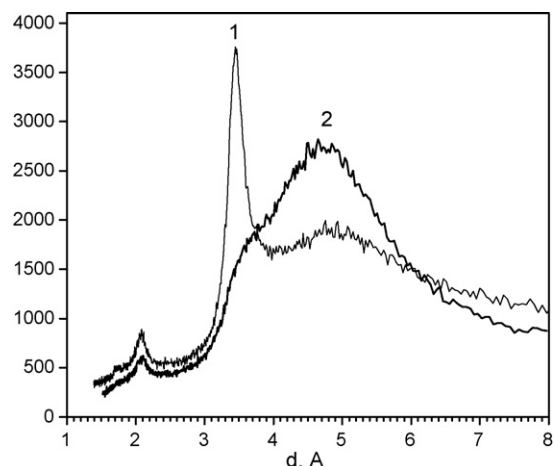


Fig. 2. XRD patterns of CNF (1) and CNF, activated with melted KOH (2).

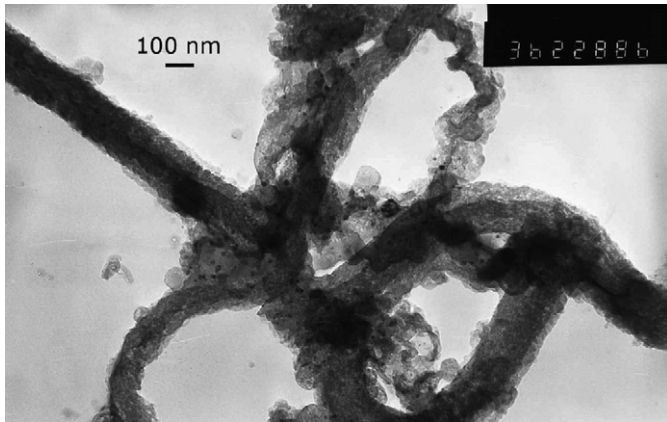


Fig. 3. Typical electron image of CNF activated melted KOH modified with 2 wt% of copper.

graphite ($d=3.44 \text{ \AA}$) disappeared, while wide halo near 5 \AA increased. The unchanged peak at 2.12 \AA probably can be assigned to reflection 001 of graphene layers. In spite of disordering of structure specific electrical resistance after activation decreased to 0.05 Ohm cm , compared to 0.4 Ohm cm for starting CNF. This proves that graphene layers remain undestroyed, and activation results (besides of burning some less ordered carbon) in violation of parallel packing of layers. Electron image of activated CNF modified with 2 wt% of copper (Fig. 3) visually shows much less regular structure than CNF before activation (Fig. 1).

To compare electrochemical characteristics of different hydrogen adsorbing materials, electrodes were prepared containing acetylene soot (AS), activated carbon felt (ACF, $1000 \text{ m}^2 \text{ g}^{-1}$), CNF ($330 \text{ m}^2 \text{ g}^{-1}$), and activated CNF (ACNF, $1700 \text{ m}^2 \text{ g}^{-1}$). In Fig. 4 there are shown discharge plots for cell with hydrogen adsorbing electrodes containing AS (plot 1), ACF (plot 2), CNF (plot 3), and ACNF (plot 4). As is seen, for usual carbon materials discharge capacity is very small— 3.2 mA h g^{-1} for AS and 9.2 mA h g^{-1} for ACF. For nanocarbon materials discharge capacity was

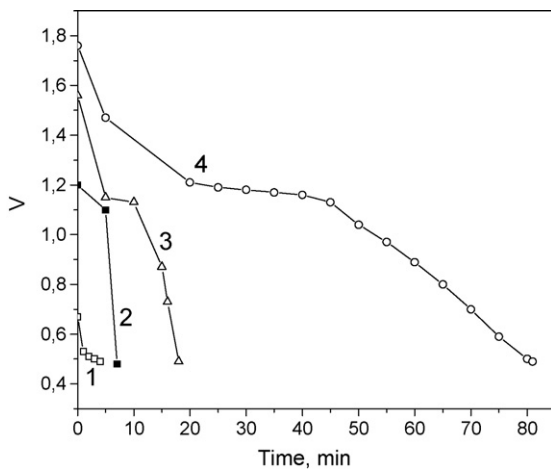


Fig. 4. Discharge plots for model cell with anode based on carbon materials: (1) acetylene soot, (2) activated carbon felt ($1000 \text{ m}^2 \text{ g}^{-1}$), (3) carbon nanofibers ($330 \text{ m}^2 \text{ g}^{-1}$), and (4) activated carbon nanofibers ($1700 \text{ m}^2 \text{ g}^{-1}$).

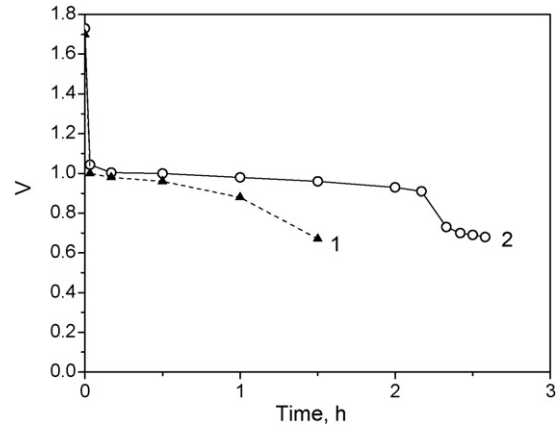


Fig. 5. Discharge plots for model cell with anode based on activated CNF modified with copper: 1–2 wt% Cu; 2–5 wt% Cu.

much higher— 16.7 mA h g^{-1} for CNF and 135 mA h g^{-1} for ACNF. Shapes of charge and discharge plots, containing plateau, as well as potential of the plateau, indicate that electrochemical reaction of hydrogen oxidation–reduction proceeds.

It is interesting that non-activated CNF has much more capacity compared to AS and ACF, in spite of lower surface area. Probably intercalation of hydrogen into nanocavities between non-coaxially oriented graphene layers occur. Great increase of capacity after activation of CNF may be caused by disordering of graphene layers packing which results in formation of nanocavities easily accessible for hydrogen.

Deposition of copper on ACNF results in great increase of discharge capacity (Fig. 5), to 150 mA h g^{-1} (2 wt% Cu, plot 1) and 250 mA h g^{-1} (5 wt% Cu, plot 2).

In Figs. 6 and 7 there are shown dependences of discharge capacity on number of charge–discharge cycles for electrodes containing ACNF and ACNF modified with 5 wt% Cu. As is seen, modifying of ACNF with copper not only increases electrical capacity ($Q, \text{ mA h g}^{-1}$), but also sharply increases stability of Q after charge–discharge cycles. After 100 cycles capacity of ACNF electrode without Cu decreased to 25% of initial, while

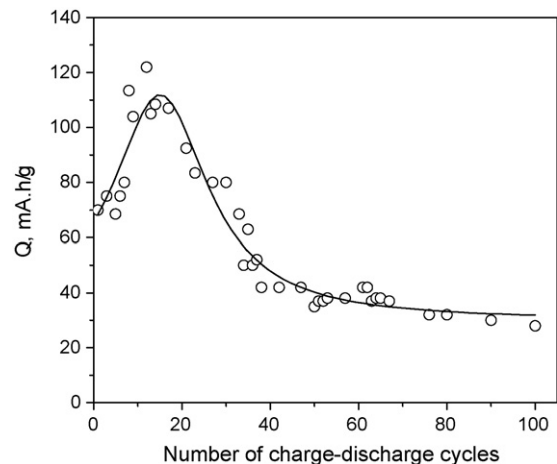


Fig. 6. Change of discharge capacity of model cell with anode made of activated CNF ($1700 \text{ m}^2 \text{ g}^{-1}$) with number of charge–discharge cycles.

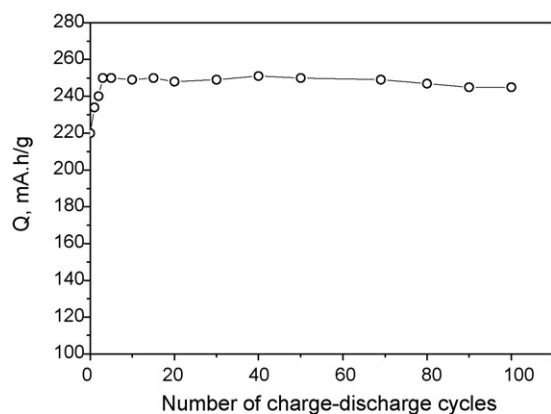


Fig. 7. Change of discharge capacity of model cell with anode made of activated CNF ($1700 \text{ m}^2 \text{ g}^{-1}$) modified with 5 wt% Cu with number of charge–discharge cycles.

electrode of ACNF modified with 5 wt% Cu after 100 cycles retained 98% of initial capacity.

For explaining this phenomenon let's consider the cell consisting of nickel oxide electrode and negative CNF electrode. While charging following processes occur:



Presumably, atomic hydrogen formed by reaction (2) incorporates into nanocavities of CNF. While storing partial desorption of hydrogen occurs. This results in self-discharge. For preventing the self-discharge and improving electrochemical parameters the best materials for negative electrode are those which, besides capability to bind atomic hydrogen, have high overpotential of molecular hydrogen evolution in alkaline media. The last feature is characteristic for copper.

For better understanding of the effect of copper on the electrode characteristics it is essential to know the mechanism of hydrogen adsorption in CNF. If hydrogen is retained on surface of CNF only as physically adsorbed molecular hydrogen, effect of minor additives hardly can be explained. On the other hand, relatively high hydrogen adsorption capacity (several wt%) reported in numerous publications also cannot be explained only by physical adsorption of molecular hydrogen by CNF. It was assumed that hydrogen incorporates between graphene layers of CNF. This resulted in formation of void like space and turning graphene planes curved and lengthened [5]. In ref. [12] increase of C-parameter by 40% after introduction of hydrogen at high pressure was observed.

The state of hydrogen incorporated into cavities or between graphene layers of CNF remains obscure. If we assume that hydrogen is intercalated into CNF with some transfer of electron density from hydrogen atoms or molecules to graphene, stability of such system can depend on electron energy levels of the host, which, in its order, depends on doping with metals.

Further, if hydrogen can be intercalated into CNF, this does not abolish that some part of hydrogen is adsorbed physically on CNF surface, with some equilibrium and exchange

kinetics between these forms of hydrogen. Physically adsorbed hydrogen can expire from electrode, and so the cell capacity decreases with time. Conversion of intercalated hydrogen into physically adsorbed can occur by different mechanisms. The possible one is diffusion of protons from nanocavities containing intercalated hydrogen to open surface simultaneously with electron transfer, with following formation of hydrogen atoms and their recombination to molecules. If so, it can be supposed that metals which are characterized by high overpotential of molecular hydrogen evolution in alkaline solution (particularly copper) should also decrease the rate of transformation of intercalated hydrogen into physically adsorbed hydrogen molecules. However, this is our assumption. For better understanding we need to know the physical state of hydrogen intercalated into CNF.

Improving of electrochemical characteristics due to modifying with copper was observed also for hydride forming metal alloys based on Ti–Zr–Ni [9]. This was explained by that the thin Cu layer on the surface improves the electronic conductivity of the electrode and facilitates electrochemical formation of hydride.

It was also interesting to compare extent of self-discharge for different carbon electrodes. Testing has shown that for electrodes based on AS and ACF self-discharge was 100% (0% capacity) in 24 h. For CNF ($330 \text{ m}^2 \text{ g}^{-1}$) residual capacity after 24 h was 3% from initial. For ACNF ($1700 \text{ m}^2 \text{ g}^{-1}$) residual capacity was 56% after 24 h and 24% after a week, and for ACNF, modified with 5% Cu—100% after 24 h and 90% after a month of storing. Thus, modifying with copper also considerably increases stability of capacity at storing of the cell. It should be noted, that the model cell used was not hermetic, and some expiration of hydrogen was possible.

4. Conclusions

1. Activation of CNF with melted potassium hydroxide results in considerable improving of electrochemical characteristics of hydrogen adsorbing electrode.
2. Modifying of activated CNF with copper improves discharge characteristics of negative electrode probably due to retarding of molecular hydrogen formation on CNF during charging and storing of the electrode.

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