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Synthesis and electrochemical properties of carbon nanotubes obtained by pyrolysis of acetylene using AB_5 alloy

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Abstract The paper discusses the efficiency of catalytic synthesis and structure of multi-wall carbon nanotubes obtained by acetylene decomposition over Mm (mischmetal)-based multi-component alloy of AB_5 type. Different parameters of catalytic chemical vapor deposition process have an influence on the efficiency. Some of them were changed to obtain the highest amount of carbon material. The samples were purified by acid and were characterized by BET surface area measurements, scanning electron microscopy, and transmission electron microscopy analysis. However, both catalyst and parameters of process (such as the flow rate of acetylene) need further examination to make it cost effective. The capacitance properties of carbon nanotubes as electrode materials for electrochemical capacitors are discussed. It has been shown that carbon nanotubes show moderate values of capacitance. In the form of a network, the material provides good charge propagation and can be used as a support and additive for different composite electrode materials.

Keywords Multi-wall carbon nanotubes · Catalytic vapor deposition · AB_5 alloy · Electrochemical capacitor

Introduction

Since carbon nanotubes were discovered in 1991 [1] by Iijima, various methods have been proposed for the synthesis of pure material. The carbon nanotubes have been reported to be very promising candidates for various applications [2–8] because of their extraordinary physical and mechanical properties. They are excellent candidates for application in composite reinforcement, actuators, sensors, and biosensors in biological technologies and component of electrode materials or catalyst supports.

If carbon nanotubes are to be used as a structural material, there is a need to develop production techniques of nanotubes on a large scale and, of course, to make them cost effective. The catalytic chemical vapor deposition (CCVD) method is one way of obtaining carbon nanotubes on a large scale. Many parameters, such as the size of catalyst, temperature, and flow rate of the reaction gas, have an influence on the carbon nanotubes grown by CCVD. The possibility of controlling microscopic parameters, such as the tube diameter, will allow the control of the main material properties. The most effective catalysts for the CCVD growth of carbon nanotubes, as was investigated in [9], are nickel (Ni)>cobalt (Co)>iron (Fe). The AB_5 type alloy was chosen as a catalyst, because of its high content of nickel and cobalt.

We have studied electrochemical performances of carbon nanotubes as electrodes used in electrochemical capacitor due to the fact that such devices have generated great interest because of their possible use in high power applications such as lasers and for propulsion in electric vehicles.

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Experimental

The commercial AB_5-type alloy of formulas LaMm-$Ni_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$ (Treibacher Industrie AG) with the average diameter of 57.06 μm was used as a catalyst. The chemical composition of this alloy was: Mm=La-rich mischmetal: 33.1 wt.%, La: 53.3 wt.%; Ce: 33.7 wt.%; Nd: 9.8 wt.%; Pr: 3.2 wt.%; other rare earths: 66.9 wt.%,

Ni: 47.8 wt.%; Co: 10.12 wt.%; Mn: 5.10 wt.%; Al: 1.86 wt.%; Fe: 0.055 wt.%. About 250 mg of alloy was placed in a quartz boat and then placed in a flow furnace. First, argon gas was introduced. When the furnace temperature reached 700 °C, the argon was shut down and the gas mixture of hydrogen and argon was introduced into the furnace for 0.5 h or for 1 h. Next, acetylene was introduced. As comparison, the carbon nanotubes were obtained with a different ratio of acetylene to hydrogen 2:1 and 4:1. When the furnace cooled down to room temperature in the presence of argon flow, carbon nanotubes were purified in concentrated hydrochloric acid.

A scanning electron microscope and a transmission electron microscope (SEM, TEM; Jeol Ltd.) were used to investigate the structure of carbon nanostructures. Specific surface area measurements were performed using ASAP 2010M. The capacitor electrodes were formed as pellets (10–12 mg) consisting of 90% active material and 10% binder (PVDF, Kynar Flex 2801). The nanotubes were tested in 6 M KOH and 1 M H_2SO_4 aqueous electrolyte using two-electrode Swagelok® systems. The electrochemical measurements were carried out using cyclic voltammetry (1 mV/s–20 V/s) and impedance spectroscopy (100 kHz–1 mHz) using Autolab Ecochemie BV-PGSTAT 30/FRA2. The capacitance values were calculated per active mass of one electrode.

The formula $C = \frac{I}{V} \cdot \frac{2}{m}$ (F/g) for cyclic voltammetry method was used, where I is the average current (mA) and V the scan rate of potential (mV/s). For impedance spectroscopy measurements, $C = \frac{1}{2 \cdot \pi \cdot f \cdot Z''} \cdot \frac{2}{m}$ (F/g) was applied, where: f is the frequency (Hz) and Z'' is the imaginary part of resistance (Ω).

Results and discussion

Previous experiments have shown that temperature of 600 °C is not enough to decompose acetylene over AB_5 catalyst. The efficiency of such a synthesis is negligible. All samples were prepared by decomposing acetylene at 700 °C. The sample

designated as CNTs 1 (carbon nanotubes 1) was pretreated for 0.5 h in a mixture of hydrogen/argon. The remaining samples were treated in such a mixture for 1 h. The catalyst is reduced from possible oxides to metallic form by these gases. CNTs 1 have a large specific surface area (109 m²/g) and more of amorphous carbon is produced. For comparison, the carbon nanotubes were also prepared in such conditions that the ratio of acetylene and hydrogen was set to 2:1 for CNTs 1 and CNTs 2 (BET=50 m²/g) and 4:1 for CNTs 3 (BET=50 m²/g). Keeping the acetylene flow constant and decreasing the flow rate of the mixture of hydrogen and argon, one could see more of amorphous carbon to be deposited inside the quartz reactor.

The ratio of acetylene to hydrogen in mixture has an influence on impurity and defects. By increasing the content of hydrogen in the mixture of gases, the carbon nanostructures with less impurity content is obtained. As we can see from the SEM images (Fig. 1), the diameter of the carbon nanotubes synthesized is about 30–50 nm. It is worth noticing that alloy with a micro-size diameter can produce carbon nanostructures. The high-resolution TEM (HRTEM) images were obtained to estimate the central canal of carbon nanotubes and their crystallinity. Figure 2 shows the HRTEM images for the carbon nanotubes. Both the outer and inner graphitic sheets of CNTs have poor crystallinity. The carbon nanotubes are made of ca. 30–35 sheets. However, outer graphitic sheets are less crystalline compared to inner sheets. The graphitic sheets are separated by approximately 0.36 nm. The central canal is very narrow, about 2.0–2.5 nm.

For capacitor application of carbon nanotubes obtained, the electrochemical properties were carefully investigated. The electrochemical characterization was performed in two electrode cells using 6 M KOH and 1 M H_2SO_4 aqueous electrolytes. Specific capacities of CNTs obtained as a result of using cycling voltammetry and impedance spectroscopy are comparable.

The carbon nanotubes are characterized by moderate values of capacitance ca. 10 F/g (per electrode material) for

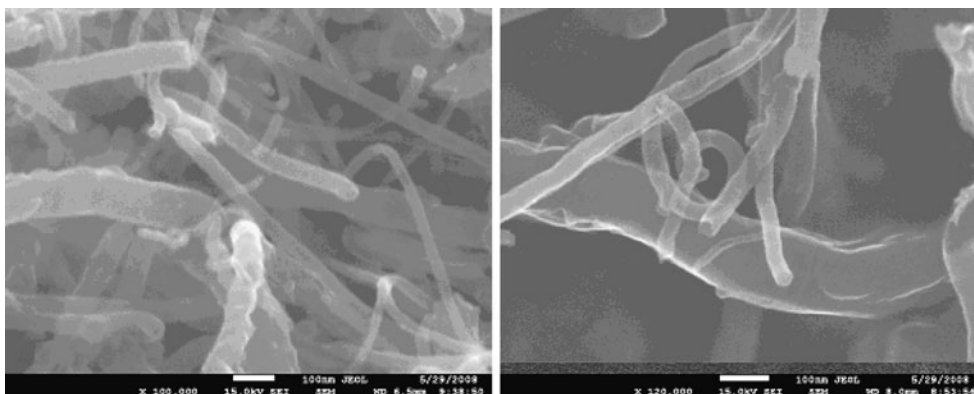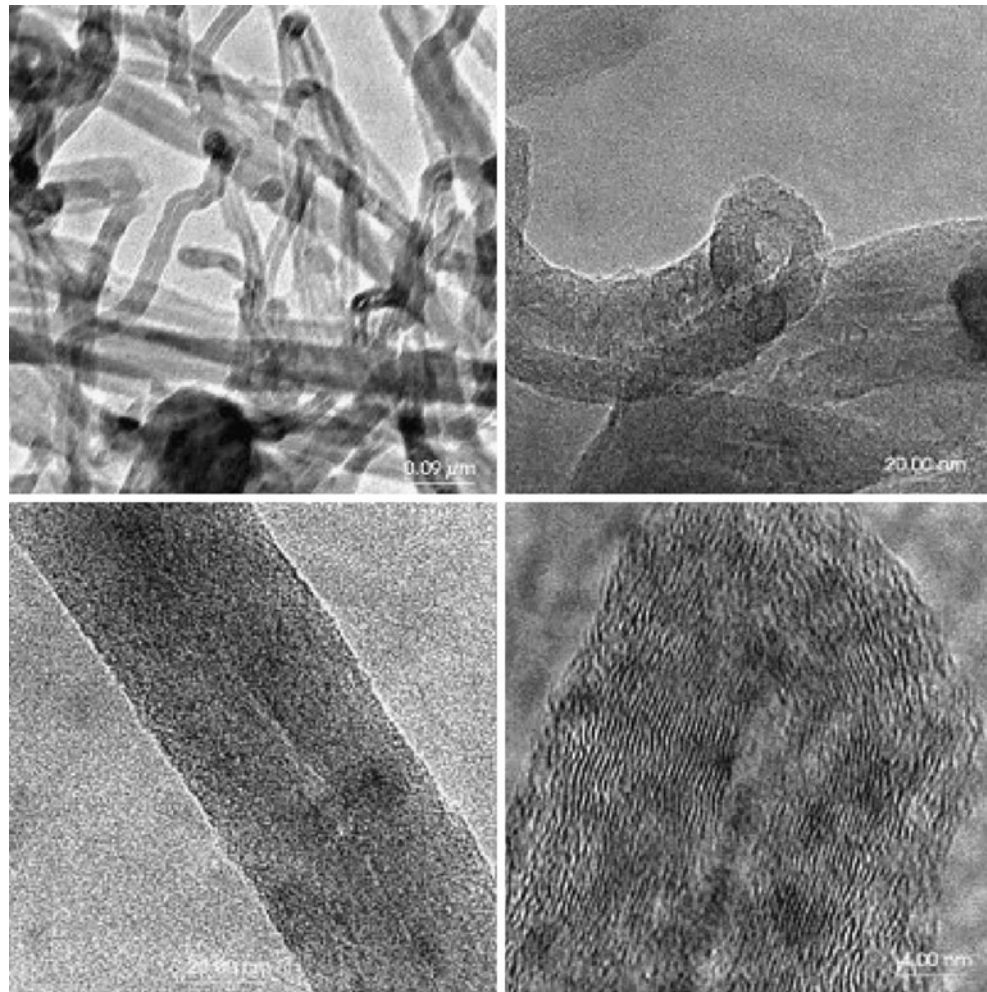**Fig. 1** Scanning electron micrographs of CNTs 3

Fig. 2 Transmission electron micrographs of the carbon nanotubes CNTs 2

moderate regimes. Such data are comparable to those reported by other investigators: 10–80 F/g (per electrode material) [10–11]. It is also noteworthy that voltammetry curves performed in alkaline medium (Fig. 3) have quite a good shape at an extremely high scan rate of 20 V/s.
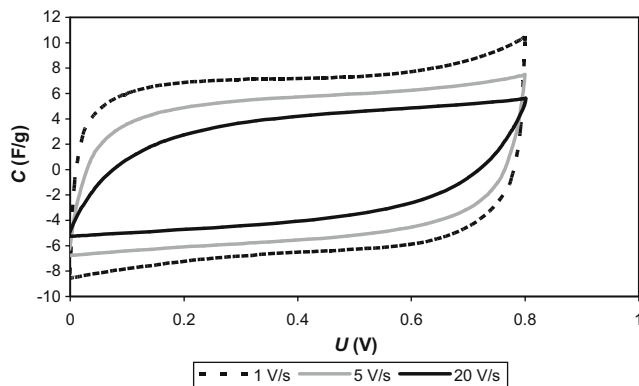
Good electrochemical properties have been confirmed by impedance spectroscopy measurements. Figure 4 shows dependence of capacitance versus frequency in acid and alkaline electrolytes. An insignificant (only 30%) drop in the value of capacitance at 10 Hz for CNTs 2 in alkaline medium is observed, which is extraordinary. This confirms
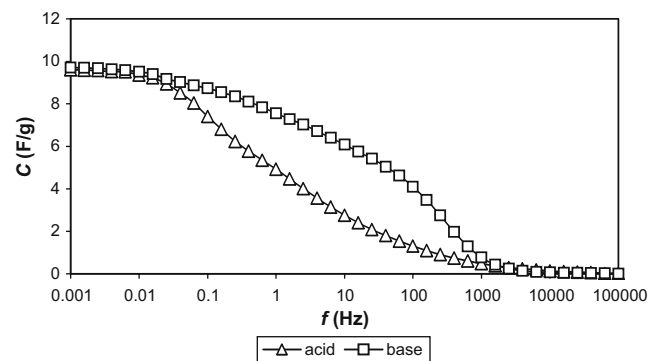

Fig. 3 Voltammetry characteristics of CNTs 2 at different scan rates in 6 M KOH (1 V/s–6.6 F/g, 5 V/s–5.0 F/g, 20 V/s–3.3 F/g)

Fig. 4 Dependence of capacitance versus frequency 1 M H_2SO_4 and 6 M KOH

that carbon nanotubes can play a role of excellent support or conducting additive for composite materials (e.g., conducting polymers, metal oxides, etc.) which are used as electrode material for electrochemical capacitors.

Conclusions

The paper presents the efficiency of catalytic synthesis of carbon nanotubes by acetylene decomposition over Mm-based multi-component alloy of AB_5 type. Different parameters of the CCVD process have an influence on the efficiency. Both catalyst and parameters of the process (such as the flow rate of acetylene) need further investigations. It is worth noticing that alloy with a micro-size diameter can produce carbon nanotubes (the diameter is about 30–50 nm). The capacitance properties of CNTs as electrode materials for electrochemical capacitors are discussed. In spite of the fact that carbon nanotubes show moderate values of capacitance (ca. 10 F/g), their networks allow for very good charge propagation and can be used as supports and/or conducting additives for different composite electrode materials. Although the carbon nanotubes have been proved to possess superior properties, their relatively high cost restricts their practical use at the present time. There is a need to continue research on development of a cost-effective way of carbon nanotube production.

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