Electrochimica Acta 228 (2017) 82–90

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Nanocomposite composed of multiwall carbon nanotubes covered by hematite nanoparticles as anode material for Li-ion batteries

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ARTICLE INFO

Article history:
Received 19 August 2016
Received in revised form 15 December 2016
Accepted 9 January 2017
Available online 11 January 2017

Keywords:
anode material
hematite
Li-ion battery
multiwall carbon nanotube
nanocomposite

ABSTRACT

This work describes the detailed studies performed on the nanocomposite composed of chemically-modified multiwall carbon nanotubes covered by hematite nanoparticles which diameters vary from 10 nm to 70 nm. This nanomaterial was fabricated in two-steps facile chemical synthesis and was characterized with the use of several experimental techniques, such as: thermogravimetric analysis, differential thermal analysis, Raman spectroscopy, X-ray diffraction, and transmission Mössbauer spectroscopy in order to determine its structure precisely. Moreover, the investigated nanocomposite was tested as an anode material of Li-ion batteries. Its cycling performance was stable during 40 cycles, while its capacity was retained at the level of 330 and 230 mAh/g at the discharge/charge rate of 25 and 200 mA/g, respectively.

1. Introduction

At present, a development of portable technologies is very fast and there is no sign of slowdown in this field. However, all sorts of mobile devices need to have an adequate source of energy to work properly. Therefore, an essential issue is the energy storage, usually in a form of electricity. This can be achieved by the electricity conversion into the chemical energy which is also easy to accumulate [1]. Thereby, such conversion process is commonly used in the case of different energy storage systems, including supercapacitors, fuel cells as well as Li-ion batteries. Nevertheless, so far the last mentioned energy storage device has only been successfully applied in many portable technologies, such as: laptops, smartphones, tablets, pacemakers for artificial hearts, etc., but can be also used as an electricity storage devices for electric vehicles (EVs) [2]. Among all of applications, the Li-ion batteries require high specific energy, high specific power, broad working temperature range, very low self-discharge and long life [3–5].

In general, Li-ions batteries are composed of the three main components: negative electrode (anode), positive electrode (cathode) and an electrolyte [2,6]. To improve the electrochemical performance of this type of batteries, the studies on each of these elements are important. However, up till now the most crucial issue in the case of Li-ion batteries improvement seems to be a search of new and high-performance anode materials which could replace the commercially applied graphite electrodes [4–7]. This is mainly caused by the fact that the graphitic anode cannot reach a capacity higher than 372 mAh/g and this capacity limit is almost achieved in some currently used commercial graphite electrodes [8]. However, it is not common phenomenon. Therefore, there is a vast amount of publications where the new potential anode materials are shown as the alternative anodes for Li-ion batteries. Usually, they are classified into three groups: the insertion-type materials (e.g. graphite and other carbon-based materials,

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http://dx.doi.org/10.1016/j.electacta.2017.01.051
0013-4686/

$Li_4Ti_5O_{12}$, TiO_2), the conversion-type materials (e.g. cobalt oxides, iron oxides, nickel oxides), and the alloying-type materials (e.g. Sn, Si, Ge, Al) [2,5,9,10]. Their simplified lithium storage mechanisms are presented below:

• Insertion-type material

$$MO_y + x\,Li^+ \rightleftarrows Li_xMO_y \quad (1)$$

where MO_y – TiO_2 or carbon nanotubes

• Conversion-type material

$$MO + 2\,Li^+ \rightleftarrows M + Li_2O \quad (2)$$

where MO – transition metal oxide

• Alloying-type material

$$M + Li^+ \rightleftarrows LiM \quad (3)$$

where LiM – alloy

As usual, each of anode materials has its own advantages and drawbacks. For instance, the lithium storage in the case of insertion-type materials is based on insertion (intercalation) of Li^+ ions into the electrode structure during the battery charging and their deinsertion during the battery discharging [2,5,6]. Hence, this type of materials exhibits a low expansion coefficient during the process of lithium storage. At the same time, the insertion-type materials usually display much lower values of specific capacities than other groups of anode materials. On the other hand, most of conversion- and alloying-types of materials suffer for a low electric conductivity and they reveal the high expansion coefficients due to formation of metals covered by lithium oxides or alloys (see presented mechanisms). This is a main reason of a physical crumbling of electrode which is often called pulverization [2,6]. This process aims to a progressive irreversible degradation of electrode even during the first few discharge/charge cycles [11,12]. Hence, an idea of nanocomposite materials preparation, which can merge the advantages of different anode materials, has been proposed by the research community.

Although in recent years plenty of publications have appeared showing different possible anode materials, the new carbon-based nanocomposites are still one of the most frequently studied in the case of Li-ion batteries [5–8]. Undoubtedly, this is related to several issues, including: the enhancement of electronic conductivity of anode, a better diffusion of Li^+ ions into electrode and the preservation of a morphological stability during battery cycling. Moreover, it is worth noting that the carbon-based nanocomposite materials usually combine the insertion mechanisms of lithium storage with conversion or alloying mechanisms [6]. All of these

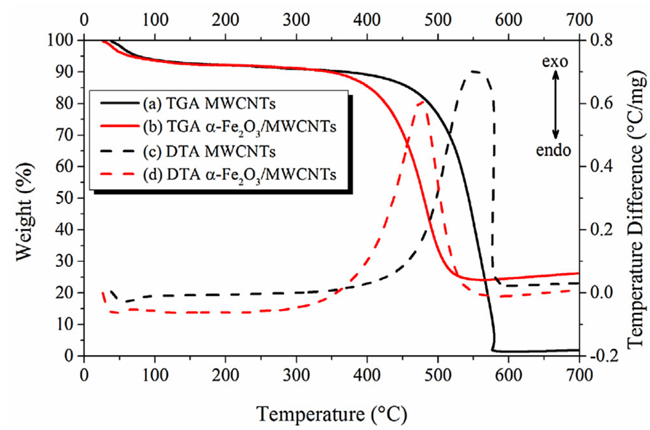

Fig. 2. TGA-DTA curves of MWCNTs-$COONH_4$ (MWCNTs) and MWCNTs-$COONH_4$ coated by iron oxide nanoparticles (Fe_xO_y-MWCNTs) collected in the artificial air.

features lead to the significant improvement of battery capacity as well as cycleability.

Among the carbon allotropes, which can be applied in Li-ion batteries as a nanocomposite anode material, carbon nanotubes (CNTs) seem to be one of the most suitable. They exhibit a high tensile strength (50 ÷ 200 GPa [13]) as well as a high electronic conductivity (102 ÷ 106 S/cm [5]), and at the same time they are relatively chemically inactive. These properties provide a good enough conductivity and cause that carbon nanotubes can act as a damper which reduce greatly the electrode expansion during the lithium storage in the form of metal or alloy [5,6]. Therefore, CNTs are the appropriate candidate for being the support matrixes in the case of nanocomposite anodes in Li-ion batteries.

It is known that the nanostructured transition metal oxides, in particular iron oxides, satisfy the conversion-type anode material criteria. Moreover, they can be used in order to form the carbon-based nanocomposites through various chemical procedures. Among all of them, hematite (α-Fe_2O_3) is the most thermodynamically stable one and at the same time this oxide is easily accessible, low-cost, and environmentally-friendly [8,26]. Another benefit of α-Fe_2O_3 is its high theoretical capacity which equals 1007 mAh/g [7,8,26]. These features allow identifying this iron oxide as a promising material for the application in Li-ion batteries.

Considering all of above discussed issues, in this work a preparation route and an application of nanocomposite is described, that is composed of chemically-modified multiwall carbon nanotubes (MWCNTs) covered by randomly-deposited nanoparticles of hematite (α-Fe_2O_3) which fulfils all requirements

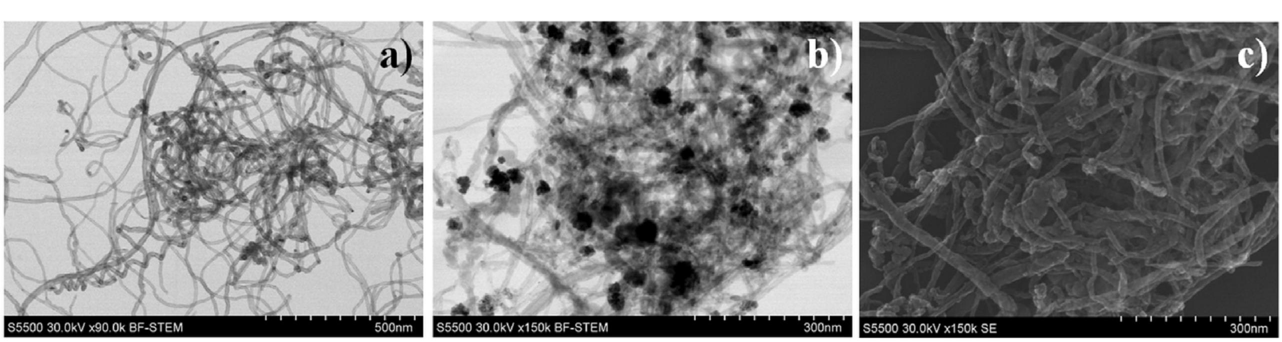

Fig. 1. STEM images of (a) MWCNTs-$COONH_4$, (b) TEM mode and corresponding (c) SEM mode of MWCNTs-$COONH_4$ coated by iron oxide nanoparticles.