Pulse-reverse treatment of carbon nanomaterials for the electrochemical storage of energy

V V Zhylinski¹, V B Drozdovich¹, A V Krauklis², S A Zhdanok² and I M Zharski¹

¹Belarusian State Technological University, Minsk, Sverdlov Str., 13a, 220006, Belarus
²A V Lyekov Heat and Mass Transfer Institute of NAS Belarus, Minsk, P. Browki Str., 15, 220072, Belarus

E-mail: zhilinski@yandex.ru, elchemdvb@mail.ru

Abstract. The paper dwells upon the investigation of carbon nanomaterials synthesized by an electric arc-method from methane-air mixture under atmospheric pressure in presence of Ni catalyst. These materials may be used for the electrochemical storage of energy. According to the data of transmission electron microscopy the carbon nanomaterials are generally represented by carbon nanotubes with the diameter of 20-80 nm. The pulse-reverse treatment of carbon nanomaterials in concentrated sulphuric electrolytes with addition of fluoride and lithium ions is carried out to increase their discharge capacity in 1 M H₂SO₄ and 1 M KOH. The properties of carbon nanomaterials are studied using the Brunauer-Emmett-Teller method, chemical energy-dispersive X-ray analysis, potentiostatic charge method of electrochemical saturation of hydrogen and potentiodynamic discharge method. The maximum discharge capacity of 940 C g⁻¹ in 1 M H₂SO₄ is revealed for CNMs subjected to pulse-reverse treatment in concentrated sulphuric electrolyte containing fluoride and lithium ions.

1. Introduction

Carbon nanomaterials (CNM), their production, purification and certification are intensively investigated [1–6] to be used for electrochemical storage of energy. Their unique electrical, thermal, and chemical properties of these materials are due to the carbon nanotubes that usually constitute big part of CNMs. Individual carbon tubes have properties of both microparticle and single nanosize molecule and belong to the class of quasi-one-dimensional nanoscale objects [1]. Especially, the carbon nanotubes have large specific surface, high electrical conductivity and relative chemical inertness. These materials are potential additives to the electrodes of lithium-ionic and lithium-polymeric accumulators and as electrode materials of electrochemical supercapacitors and hydrogen electric accumulators. However they may be used only as nanostructured bulk CNMs in which carbon nanotubes can potentially outperform other forms of carbon (amorphous carbon, parts of graphite etc.) [2-6].

The traditional synthesis of CNMs such as electric arc discharge, laser ablation, thermal and plasma-enhanced chemical deposition generally give carbon powders with significant amount of amorphous carbon and metal-catalyst impurity [2–4]. The carbon nanotubes can be purified by high-temperature annealing, plasma treatment and chemical methods. In most cases purification of carbon nanotubes lead to an uncontrolled destruction of carbon nanotubes and assisted oxidation. Moreover, the oxidation is accompanied by the formation of a large number of carboxylic, hydroxyl, ketone groups [1–7] that can substantially change the change chemical properties of CNMs.
An alternative method of purification is electrochemical treatment of CNMs which makes it possible to control over oxidation-reduction processes of carbon nanotubes [2-5, 7]. Moreover, many investigations are aimed at improving these treatments by injecting intercalation ions (Li⁺, Na⁺ etc.) and activators of electrode oxidation processes [3–7].

One of these methods is the potentiostatic treatment of CNMs under potential exceeding thermodynamic potential of oxygen evolution in the concentrated sulphuric acid electrolytes [7]. This treatment of CNMs can significantly increase the index of electrochemical hydrogen sorption in 1 M H₂SO₄ and 1 M KOH. This effect is attained by the oxidation of layered structures of CNMs under the potentiostatic polarization in concentrated sulphuric-acid electrolyte. It has been established [7] that the electrochemical hydrogen sorption in CNMs increases due to pulse-reverse treatment of CNMs using potentiostatic pulse-reverse modes with a long anodic pulse and shot cathodic pulse at potentials which exceed thermodynamic potential of oxygen and hydrogen evolution respectively. This article focuses on investigation of pulse-reverse CNMs treatment in concentrated sulphuric-acid electrolyte containing fluoride and lithium ions.

2. Materials and Methods

We investigate the CNMs synthesized from methane-air mixture by the electric-arc method at atmospheric pressure in the presence of the Ni catalyst. The aqueous suspension (0.1 wt.%) of synthesized carbon masses undergoes ultrasonic treatment to separate them [8]. The fraction of CNMs is observed on the surface of the suspension after ultrasonic treatment at specific power of 7 kJ ml⁻¹ and frequency of 20 kilohertz. It can be seen (figure 1) that this fraction of CNMs consists of carbon nanotubes 20-60 nm in diameter and small fibrils whereas the initial carbon material mainly contains large particles of amorphous carbon and graphite (figure 1).

According to the data of the TEM investigation, the CNMs obtained by the ultrasonic treatment are black powder with bulk density of 0.45 g cm⁻³ consisting of amorphous carbon (less than 30 %), carbon fibrils 100-1000 nm in diameter and 1-15 µm in length and carbon nanotubes 20-80 nm in diameter and 1-10 µm in length [8].

![Figure 1. TEM images of the initial carbon material (a) synthesized from methane-air mixture by electric-arc method and the CNMs (b) obtained by ultrasonic treatment.](image)

The electrochemical treatment of CNMs in the concentrated sulphuric acid (96 wt.%) containing lithium and fluorine ions is carried out at the temperature of 298 K. The concentration of Li⁺ and F⁻ ions is varied from 2 to 20 g l⁻¹. The electrochemical treatment is carried out in potentiostatic and pulse-reverse modes [8]. Table 1 displays other parameters of electrochemical treatment of CNMs. After electrochemical treatment the CNMs are washed by distilled water.
Table 1. Parameters of electrochemical treatment of CNMs.

| Current mode | Anode potential (V) | Anode pause (s) | Cathode potential (V) | Anode pause (s) | Time (h) |
|--------------|---------------------|-----------------|-----------------------|-----------------|----------|
| Potentiostatic | +3.5a               | –               | –                     | –               | 1        |
| Pulse-reverse | +3.5a               | 20              | –1.3a                 | 10              | 1        |

*a Potentials are referenced by the normal hydrogen electrode at temperature of 298 K.

Charge-discharge characteristics of initial and electrochemically treated CNMs were investigated in 1 M H₂SO₄ and 1 M KOH. The charge was carried out in potentiostatic mode under −0.2 V and −1.0 V in 1 M H₂SO₄ and 1 M KOH, respectively. The discharge was carried out in potentiodynamic mode, the potential rate being 0.01 V s⁻¹ using the voltammetric system IPC Pro. The absorbance infrared spectra of solid CNMs and KBr mixture are detected by NexusTM ESP (Thermo Nicolet). The mass ratio of CNMs and KBr is 1:500. The specific surface of CNMs was determined by the nitrogen BET method using NOVA 2200. The chemical energy-dispersion X-ray analysis of CNMs was carried out by the system EDX JED-2201 JEOL.

3. Results and Discussion

The electrochemical properties and discharge capacity of CNMs were estimated by discharge characteristics (figure 2). It was established that the discharge currents of the initial CNMs reach 1.2 A g⁻¹ and 1.0 A g⁻¹ in 1 M H₂SO₄ and 1 M KOH, respectively. The discharge capacity was automatically calculated by the voltammetric system IPC Pro is 150 C g⁻¹. This capacity of CNMs can be accumulated by the formation of double electric layer and sorption of hydrogen on a large specific surface which was 140 m² g⁻¹ according to the nitrogen BET method.

Figure 2. (a, b) Discharge potentiodynamic curves of (1) initial CNMs, (2) CNMs after potentiostatic treatment in concentrated H₂SO₄, (3–6) CNMs after pulse-reverse treatment (3) in concentrated H₂SO₄, containing (4) fluoride ions, (5) lithium ions, and containing (6) lithium and fluoride ions.

The pulse-reverse treatment of CNMs in concentrated sulphuric acid resulted in some oxidation of carbon materials [7]. According to the energy-dispersion X-ray analysis (table 2), the mass fraction of carbon decreased from 87 to 78.5 wt.% while the fraction of oxygen increased from 6 to 20.4 wt.% after pulse-reverse treatment in concentrated sulphuric acid. In addition, the presence of the sulfur fraction...
indicated active intercalation of CNMs in the solution of H\textsubscript{2}SO\textsubscript{4}. This effect and increasing oxygen fraction may lead to increase in electrochemical activity of treated CNMs in 1 M H\textsubscript{2}SO\textsubscript{4} and 1 M KOH (figure 2).

| Element   | Energy (keV) | W (wt.%) |
|-----------|--------------|----------|
| C         | 0.294        | 78.5±0.3 |
| O         | 0.582        | 20.4±4.0 |
| S         | 2.307        | 0.6±0.3  |
| **Other elements (K, Na)** | – | 0.3 |

Types of oxygen-containing groups can be qualitatively analyzed using absorbance infrared spectra of CNMs. Marked peaks are observed at 2923 cm\textsuperscript{-1} and 2850 cm\textsuperscript{-1} that corresponds to the fluctuations of C-C and C-OH bonds (figure 3).

The peak at 1716 cm\textsuperscript{-1} corresponds to C=O bond which is characteristic of ketonic, carboxylic and lacton groups. They can catalyze processes of electrochemical sorption and reduction of hydrogen [9]. Marked peaks at 1578 cm\textsuperscript{-1} and 890 cm\textsuperscript{-1} are caused by the deformations of aromatic structure. The maximal peak at 1200 cm\textsuperscript{-1} corresponds to oxygen of phenol type. The initial CNMs in contrast to the treated ones are characterized by the peak at 1630 cm\textsuperscript{-1} due to the presence of significant amount of C=C bond. Thus treated CNMs demonstrate more clearly marked peaks of C=O and C-OH bonds what indicates an increased number of oxygen-containing groups after pulse-reverse treatment in concentrated sulphuric acid.

The additive of 8 g l\textsuperscript{-1} Li\textsuperscript{+} in concentrated sulphuric electrolyte of electrochemical treatment corresponds to higher discharge capacity of treated CNMs which achieved 640 and 530 C g\textsuperscript{-1} in 1 M H\textsubscript{2}SO\textsubscript{4} and 1 M KOH, respectively (table 3).
In this case the discharge currents reached 6.5 A g\(^{-1}\) and 3.0 A g\(^{-1}\) in 1 M H\(_2\)SO\(_4\) and 1 M KOH respectively (figure 2). This influence of the Li\(^+\) additive was obviously caused by active diffusion and electromigration of Li\(^+\) in CNMs structures during the cathode polarization. The lithium ions are known\([10]\) to promote intercalation of interlaminar spaces of CNMs and increase of amount of CNMs defects. This order-disorder transformation can lead to the formation of turbo-stratified carbon nets of AB or ABC types\([10]\).

The additive of 13.5 g l\(^{-1}\) F\(^-\) in concentrated sulphuric acid resulted in better efficiency of electrochemical treatment that corresponded to a higher value of discharge capacity of CNMs activated by this method in comparison with other values of discharge capacity of CNMs activated at other concentrations of F\(^-\) (table 3). This influence of the fluoride anions could be caused by their specific adsorption on the anode. They partially block the oxygen evolution that can cause some processes such as ozone evolution, synthesis of peroxysulphate acids and peroxide carbon groups\([11]\).

The maximum discharge currents in 1 M H\(_2\)SO\(_4\) and 1 M KOH are reached for the CNMs after pulse-reverse treatment in concentrated sulphuric electrolyte wich contains 8 g l\(^{-1}\) Li\(^+\) and 13.5 g l\(^{-1}\)

**Table 3. Influence of ion additions in concentrated sulphuric acid on specific capacity of treated CNMs.**

| Type of addition | Concentration of ion (g l\(^{-1}\)) | Specific capacity of CNMs (C g\(^{-1}\)) |
|------------------|-----------------------------------|----------------------------------------|
|                  |                                   | in 1 M H\(_2\)SO\(_4\) | in 1 M KOH |
| Li\(^+\)         | 2.0                               | 510                      | 385         |
|                  | 4.0                               | 580                      | 415         |
|                  | 6.0                               | 590                      | 460         |
|                  | 8.0                               | 640                      | 530         |
|                  | 10.0                              | 580                      | 480         |
| F\(^-\)          | 4.5                               | 530                      | 280         |
|                  | 9.0                               | 580                      | 290         |
|                  | 13.5                              | 600                      | 305         |
|                  | 18.0                              | 590                      | 300         |
|                  | 22.5                              | 585                      | 300         |

In this case the discharge currents reached 6.5 A g\(^{-1}\) and 3.0 A g\(^{-1}\) in 1 M H\(_2\)SO\(_4\) and 1 M KOH respectively (figure 2). This influence of the Li\(^+\) additive was obviously caused by active diffusion and electromigration of Li\(^+\) in CNMs structures during the cathode polarization. The lithium ions are known\([10]\) to promote intercalation of interlaminar spaces of CNMs and increase of amount of CNMs defects. This order-disorder transformation can lead to the formation of turbo-stratified carbon nets of AB or ABC types\([10]\).

The additive of 13.5 g l\(^{-1}\) F\(^-\) in concentrated sulphuric acid resulted in better efficiency of electrochemical treatment that corresponded to a higher value of discharge capacity of CNMs activated by this method in comparison with other values of discharge capacity of CNMs activated at other concentrations of F\(^-\) (table 3). This influence of the fluoride anions could be caused by their specific adsorption on the anode. They partially block the oxygen evolution that can cause some processes such as ozone evolution, synthesis of peroxysulphate acids and peroxide carbon groups\([11]\).

The maximum discharge currents in 1 M H\(_2\)SO\(_4\) and 1 M KOH are reached for the CNMs after pulse-reverse treatment in concentrated sulphuric electrolyte wich contains 8 g l\(^{-1}\) Li\(^+\) and 13.5 g l\(^{-1}\)
fluoride ions (figure 2). The discharge current of these CNMs under the potential of oxygen electrode is more than 3 times higher than that of the initial CNMs in 1 M H₂SO₄ and 1 M KOH. The maximum capacity of activated CNMs reaches 940 C g⁻¹ in 1 M H₂SO₄ and 600 C g⁻¹ in 1 M KOH (figure 4). This effect may be caused by the complex influence of fluoride and lithium ions on the efficiency of pulse-reverse treatment of CNMs in concentrated sulphuric acid. The fluoride ions activate oxidation and dispersion of CNMs under anode polarization. The lithium ions may lead to increasing number of CNMs defects by the processes of intercalation and de-intercalation of interlaminar spaces. As a result we can observe increased discharge capacity of CNMs subjected to pulse-reverse treatment in concentrated sulphuric electrolyte containing fluoride and lithium ions.

4. Conclusions

The electrochemical treatment of CNMs in the pulse-reverse mode results in intercalation of carbon materials by H₂SO₄ and oxidation that is indicated by increase of oxygen and sulfur contents in the treated CNMs. This oxidation is accompanied with the formation of phenol, ketonic, carboxylic and lacton groups. Moreover, the discharge capacity of the treated CNMs increases in 4 times as higher as discharge capacity of initial CNMs. The introduction of lithium or fluoride ions in concentrated sulphuric acid increases the discharge capacity of the treated CNMs. However, the maximum capacity of 940 C g⁻¹ in 1 M H₂SO₄ is achieved in the CNMs subjected to pulse-reverse treatment when concentrated sulphuric electrolyte contains 8 g l⁻¹ Li⁺ and 13.5 g l⁻¹ F⁻ ions. This effect is caused by the complex influence of fluoride and lithium ions. It may lead to morphologic changes of CNMs and increase of defects. These changes are made by Li⁺ intercalation of layered structures of CNMs and formation of oxygen-containing groups in the presence of F⁻ ions.

Thus the CNMs treated by this method are potential materials for the electrochemical storage of energy. They may be used for electrochemical supercapacitor, hydrogen electric accumulator.

References

[1] Yun Y-H, Dong Zh, Shanov V, Heineman W R, Brian Halsall H, Bhattacharya A, Conforti L, Narayan R K, Ball W S and Schulz M J 2007 Nanotoday 2 30.
[2] Dai K, Zhang D-S, Yu B-K, Fang J-H and Shi L-Y 2006 J. Shanghai Univ. 2 557.
[3] Liua Ch G, Fangb H T, Lia F, Liua M and Chenga H M 2006 J. Power Sources 160 758.
[4] Lin Ch-Ch and Hsien-Chieh H 2009 J. Power Sources 188 332.
[5] Wang Q, Li Ch, Yuan G and Gu Ch-Zh 2009 Chinese Phys. Lett. 26 86.
[6] Kalb M, Kavan L and Dunsch L 2009 J. Am. Chem. Soc. 131 4529.
[7] Zhylnski V V, Drozdovich V B, Zhdanok S A and Krauklis A V 2010 Possibility of using activated CNM in electrochemical energy accumulation devices Electrochemical Technologies and Materials for XXI Century: Abstracts of 9th Int. Frumkin Symp. (Moscow, Russia, 25–29 October 2010) (Institut of Phisical Chemistry and Electrochemistry) ed A Yu Tsivadze (Moscow: IPCE) p 145.
[8] Buyakov I F, Volzhankin V M, Krauklis A V, Samtsov P P and Soltsev A P 2005 Formation of Carbon Nanomaterials Under the Conditions Formed by Atmospheric Pressure High-Voltage Plasma Int. Colloquium on Physics of Shock Waves, Combustion, Detonation and Non-Equilibrium Processes (Minsk, Belarus, 14–19 November 2005) (A V Lykov Heat and Mass Transfer Institute) ed S A Zhdanok (Minsk: MIC) pp 54-56.
[9] Bandosza T J and Aniaa C O 2006 Interface Science and Technology 7 159.
[10] Yang Zh-H and Wu H-Q 2001 Solid State Ionics 143 173.
[11] Stein A, Wang Zh and Fierke M A 2009 Adv. Mater. 21 265.