Carbon nanostructures on capacitor electrodes

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Abstract. Carbon nanostructures, such as carbon nanowires, nanotubes, nanosheets, have found applications in many areas – from electronics to medicine. Recently, they attracted particular attention as materials for energy storage due to their large aspect ratios, specific surface areas, and electrical conductivity. An efficient method for their deposition on metallic surfaces at atmospheric pressure is microwave plasma-enhanced chemical vapor deposition (MPECVD). In this study, metallic surfaces with deposited carbon nanostructures were used for preparation of capacitor electrodes. The capacitance of an electrolytic capacitor with metal electrodes without and with deposited carbon nanostructures was measured by an electronic system. The resulting high value of the capacitance of a capacitor with electrodes with deposited carbon nanostructures is discussed on the basis of these structures morphology as studied by SEM.

1. Introduction
The energy needs of the modern world are constantly increasing, so that new alternative energy sources are being developed. The automotive industry is focused entirely on electric vehicles because of the depleted fossil fuels and the need to protect the environment by reducing the greenhouse gas pollution resulting from burning fossil fuels. This requires the development of new systems for accumulation, storage and conversion of electricity. Electrochemical supercapacitors are such an alternative, as they offer higher power densities, long life cycle, and quick charge and discharge time intervals [1]. Supercapacitors energy storage is based on the accumulation of charge on a large surface, intercalation of ions and reversible redox reactions. Supercapacitors are divided generally into three categories: electrostatic double-layer capacitors (EDLC), pseudo-capacitors and hybrid supercapacitors. The principle of storage of hybrid supercapacitors relies on a combination of the EDLC and pseudo-capacitor storage principles [2]. They have the properties of both electrolytic capacitors and rechargeable batteries, but differ in the following – they can accumulate significantly more energy per unit volume or mass than electrolytic capacitors, they accumulate and deliver charge much faster than batteries, and complete thousands of charging and discharging cycles before changing their properties. The capacitance of the supercapacitors depends mainly on the dielectric constant [3], the type of the electrolyte and the redox processes involved, the effective thickness of the double layer, and the material and surface available for charge accumulation. Aqueous electrolytes are a preferred choice because of their low cost and high availability and are most commonly used in the development stages of new electrochemical materials for supercapacitors [2]. The ion sources usually

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are potassium chloride, potassium hydroxide and sulfuric acid. Their main advantages are high ionic conductivity, mobility and low hazard levels. The organic electrolytes require conditions of low presence of water, while aqueous electrolytes can be used in open environments.

The materials for the electrodes can be divided into two categories, depending on the way of energy storage – materials for supercapacitors with double electric layer and with pseudo-capacity. The EDCL materials are carbon structures that provide large charge accumulation in the area between the electrode and the electrolyte. Activated carbon materials have become the industry standard for electrochemical supercapacitors. The relatively new carbon nanostructures, such as carbon nanotubes (CNT) [4], carbon nanowires, and vertical carbon nanosheets [5] offer a variety of improved parameters, namely, greatly increased surface and conductivity. They are very small in size resulting in a large electrode surface area and an improved power density achieved through the better accessibility of the electrolyte.

We present the design of an electrolyte supercapacitor with three types of carbon nanostructures deposited on nickel-foam electrodes. The capacitance with and without carbon nanowires on the electrodes is measured as a function of the electrolyte concentration and the results are discussed.

2. Deposition process and capacitor design

The microwave plasma-enhanced chemical vapor deposition (MPECVD) in gas mixtures Ar/CH₄ or Ar/H₂/CH₄ is an efficient method for fabrication of carbon nanostructures at atmospheric pressure [6, 7]. The synthesis is based on the decomposition of a carbon-containing precursor (CH₄) in the "hot" region (~3000 K) of the plasma flame into carbon atoms and molecules and hydrocarbon radicals, which are converted into solid carbon nuclei or form specific carbon nanostructures [8] on the substrate surface. In this respect, the importance has been confirmed of the CH₄ and C₂ radicals for the nucleation and coalescence of carbon nanosheets [9], especially in microwave systems.

The experiments on deposition of carbon nanostructures were carried out on a set-up described in detail in [7]. The microwave plasma source at a frequency \( f = 2.45 \, \text{GHz} \) produces a plasma flame with a diameter of 2 – 3 mm and a length of up to 15 mm in a deposition chamber. The plasma parameters and gas temperature are measured using optical diagnostic techniques [7].

The light from the plasma flame is collected by a collimator and fed through an optical fiber to the optical spectrometers (HORIBA i550, and Ocean Optics HR4000). Figure 1 presents part of the spectrum emitted by the plasma column in an Ar/H₂/CH₄ gas mixture registered by an HR4000 spectrometer under the deposition conditions.

The emission spectrum of the plasma flame indicated effective decomposition of methane and production of C₂ molecules, C atoms and their radicals. The gas temperature (2800 K – 3800 K) was obtained by fitting the experimental spectra with the simulated CN band. The substrate was nickel foam (NI003852 Nickel Foam, GoodFellow, UK) with porosity 95%. The substrate (5 mm×5 mm) was placed in the same quartz chamber close to the plasma tube and heated by a heater and by the plasma flame up to 750 °C. The substrate temperature was controlled and monitored by an electronic thermocouple system. A DC bias in the range (-50 V – -400 V) with respect to the plasma source was applied to the substrate.

![Figure 1. Emission spectrum of the CN band and Swan band of C₂ molecules. The enlarged spectrum in the figure is the 247.88-nm line of C atoms.](Image)

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By tailoring the plasma environment and monitoring the substrate temperature, a controlled synthesis of CNT, carbon nanowires and vertical sheets can be achieved at specific values of the microwave power density. Maintaining a specified substrate temperature is essential for the synthesis of various carbon structures, as nanowires, nanotubes (400 – 600 °C) or vertical nanosheets (600 – 700 °C) [8, 9]. In the experiments reported here, these three types of carbon nanostructures were deposited on the nickel-foam substrate at the above-mentioned temperature ranges with a DC bias applied to the substrate and increasing microwave power density in the plasma flame.

Carbon nanowires were obtained on a nickel-foam surface at substrate temperatures $T \sim 450 – 550$ °C and power densities $P \sim 400$ W/cm$^2$, while at 600 °C carbon nanotubes were formed. Figure 2 shows SEM images of carbon nanowires and nanotubes.

**Figure 2.** Carbon nanowires and nanotubes deposited on the surface of a nickel-foam substrate.

Vertical carbon nanosheets were deposited (figure 3) at substrate temperatures above 620 °C and a higher microwave power density. The three types of nanostructures have huge surface areas; it is thus of interest to test their properties as layers deposited on the electrodes of an electrolytic capacitor. The effect of the first type of nanostructures was studied by preparing two square electrodes with a size of 5 mm×5 mm and forming a layer of carbon nanowires on nickel-foam; it was not homogeneous, the main part of the structures being deposited on the upper surface of the electrode (figure 4).

**Figure 3.** Vertical carbon nanosheets on the substrate surface.

**Figure 4.** Capacitor design with nickel-foam electrodes with carbon nanowires deposited on the metal surface.
Electrolytic capacitor prototypes were then constructed with metal electrodes with a rectangular section with specific geometric dimensions of the glass cell. The electrodes were connected to metal terminals to allow measurement of the capacitance, placed in the cell and separated by a dielectric barrier (Celgard) to prevent the direct contact between them. A dilute potassium base (KOH) was used as electrolyte filling the cell to the level of the metal electrodes. The capacitance of this electrolytic capacitor with metal electrodes with deposited carbon nanostructures was measured and compared to that of the capacitor with the same electrodes without carbon nanostructures. The capacitance measured at three concentrations of KOH are presented in figure 5. As seen, the capacitor with deposited nanowires on the upper surface has a higher capacitance, but the increase of the surface due to the nanostructures is small in comparison to the full surface of the nickel-foam electrode. The capacity increases with the concentration of the electrolyte; this effect will be studied in future works.

3. Conclusions
Electrodes with three types of carbon nanostructures on their surface are prepared for potential application as supercapacitor electrodes. A prototype is designed of electrolytic capacitor with carbon nanowires deposited on its electrodes. Its capacitance is measured at different concentrations of the electrolyte; a higher capacitance is measured of the capacitor with carbon nanostructures deposited on the electrodes.

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