Modification of carbon textile Busofit T-040 by plasma treatment

A M Borisov¹, N L Bogdashkina², M V Gerasimov², V E Kasatkin², I A Kovalev¹, E V Korobeinikov¹, V V Sleptsov¹ and P A Schur¹

¹Moscow Aviation Institute (National Research University), Volokolamskoe sh. 4, 125993, Moscow, Russia
²Frumkin Institute of Physical Chemistry & Electrochemistry, Leninsky Ave. 31, 4, 125993, Moscow, Russia

E-mail: anatoly_borisov@mail.ru

Abstract. The ion-plasma modification of viscose based carbon fibers of carbon textile «Busofit T-040» have been studied by the methods of scanning electron microscopy and electrochemical impedance spectroscopy. The values of the integral and surface capacitance are close after plasma treatment and it should be assumed that the contribution of the porous Busofit to the resulting capacitance is minimal. Ion-plasma treatment allows to obtain a specific capacity up to 20 μF/cm² which is 30 times higher than that of untreated material.

The paper is devoted to the study of ion-plasma modification of viscose based carbon fibers of carbon textile «Busofit T-040» which is promising for use in the electrochemical supercapacitors (ESC) [1, 2]. To increase the specific capacitance of ESC various methods for modifying the surface of electrodes are used, in particular, the deposition of thin films of transition metals and their oxides, as well as conducting polymers (polyaniline, polypyrrole, polythiophenes) [2, 3].

The modification of the carbon fiber surface has been performed at the MAI magnetron sputtering unit using a titanium cathode. The discharge was carried out in argon at a pressure of 2–6 mTorr. Processing with duration from 5 to 20 minutes led to the formation of a titanium film from 0.5 to 1.7 microns. The samples were studied by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) and also by Electrochemical Impedance Spectroscopy (EIS). The EIS study was carried using the potentiostatic complex «IPC-FRA» developed at Frumkin Institute of Physical Chemistry & Electrochemistry (IPCE RAS), providing a potentiostatic polarization of the samples with superimposed harmonic signal of adjustable amplitude in the frequency range from 10 mHz to 100 kHz. Measurements of the impedance spectra were performed in 1M Na₂SO₄ solution at the immersion potentials values with the application of alternating polarization from 25 to 50 mV. The software «Dummy Circuit Solver» developed by IPCE RAS has been used to select the optimal dummy circuit structures and to calculate the nominal values of its elements from the experimental EIS data.

Typical SEM images of carbon fiber before and after ion-plasma processing are shown in figure 1. Fiber diameter is 5–8 microns. It can be seen that the deposited titanium film reduces the open porosity. The main elements in the modified layer are titanium and oxygen in a ratio close to the stoichiometry of TiO₂.
The presence of oxygen in the fiber is apparently due to the adsorption of water molecules from the residual vacuum.

Examples of EIS Nyquist plots of samples before and after processing are shown in figure 2. The samples show a more or less well-defined arc on Nyquist plot in the high-frequency region (1–100 kHz). At the low-frequencies the straight sections are observed.

The Nyquist plot for an ideal capacitor has the form of a vertical branch ($Z_{Re} = 0, Z_{Im} = j/\omega C$), and the plot for a real capacitor is an arc of a semicircle with large radius which is determined by the polarization resistance of the self-discharge reactions of the capacitor [4]. If the charges on the capacitor plates are not compact or the electrode surface is non-uniform, the Nyquist plot arc flattens and it is advisable to use for the model a Constant Phase Element (CPE) instead of a capacitor.
The impedance $Z$ of the CPE element depending on the cyclic frequency $\omega$ described by the equation $Z=1/(T\omega^{\phi})(\cos(\phi\pi)-j\sin(\phi\pi))$ where $T$ is the proportionality factor, $\phi$ – phase index, $j$ – imaginary unit. Depending on the value of $\phi$ the CPE element acquires the following physical nature. It is the resistance, the capacity, the inductance or Warburg diffusion element for $\phi = 0$, $\phi = 1$, $\phi = -1$ or $\phi = 0.5$, respectively. For the phase shift does not reach $\pi$, we can estimate the capacity of the equivalent capacitor $C$, which provides the same time constant for the circuit where it takes the place of the CPE $C = (T^{1-\phi})^{1/\text{cm}}$ [5], where $R$ is the parallel resistor.

To estimate the capacitive characteristics we used the simplest dummy circuit “1” as the resistor $R$ parallel-connected to CPE with a combination of resistor $R_0$ and inductance $L$ in series to take into account the electrolyte resistance and formal accounting of all inductive processes, figure 3. In this circuit the resistor $R$ simulates the processes leading to the self-discharge of the electrical double layer capacitance and the parameters of the CPE element allow us to estimate the capacitive properties of the samples.

![Figure 3. Simplest dummy circuit “1”.](image)

For a better description of the experimental results we considered a more complex equivalent circuit “2” taking into account the porosity of the samples, figure 4. In addition to the parallel circuit CPE/_1/R_1 which is the same as in circuit “1” and simulates the processes on the outer surface of the electrode, a parallel-connected combination of elements is added to simulate the processes in the thickness of the porous electrode. Here $R_0$ is responsible for the resistance of the electrolyte in the pores; the element CPE/_2 is used for estimation of capacitive characteristics and $W$ is Warburg element. The element $L$ in the circuit “2” scheme is not used given the almost complete absence of inductive disturbance in the measurement.

![Figure 4. Complex equivalent circuit “2”.](image)

This equivalent circuit adequately describes the experimental Nyquist plots in the entire frequency range from 0.1 Hz to 100 kHz, see figure 2. The circuit CPE/_2/R_1 relates to the characteristics of the outer layers of the porous specimens. For all samples the resistor values are in the range of 20–50 Ohm and differ by no more than 2.5 times. The phase factor of all samples is close to 1 which allows us to treat the parameter $T$, as well as the capacitance.

The low-frequency chain has a strong effect in the range of less than 100 Hz when the effect of bulk porosity is apparent. The averaged resistance of the electrolyte $R_e$ in the pores varies by an order of magnitude (from 3 to 30 Ohm-cm²). The modulus $T$ of the CPE element changes by more than 3 orders of magnitude while its phase factor for all samples is about 0.6–0.7. Thus, the contribution to the capacitive characteristics of internal pores is limited by diffusion processes in them and the practically significant capacitance in the frequency range of 100 Hz...100 kHz is mainly due to the external surface of the samples.

Modeling the frequency response with two types of dummy circuits allows us to estimate the contribution of bulk porosity to the capacitive characteristics of samples. If we compare the values of the integral equivalent capacitance of the samples for dummy circuit “1” and the values for circuit “2”, we can estimate its contribution to the capacitive properties from the difference. It turned out that for the sample before treatment, the internal porosity provides a noticeable (up to 60 %) increment to the surface capacity. After processing the values of the integral and surface capacitance are close, and it should be assumed that the contribution of the porous layer to the resulting capacitance is minimal.
The phase factor $\phi$ in this case turns out to be close to 1 which makes such materials as the capacitors. Ion-plasma treatment allows to obtain a specific capacity up to 20 $\mu$F/cm$^2$ which is 30 times higher than that of untreated material.

**Acknowledgement**
This work was supported by the Russian Ministry of Education and Science by an agreement to provide subsidies №14.577.21.0275 from 26.09.2017.

**References**
[1] Stakhanova S V, Astakhov M V, Klimont A A, Krechetov I S, Kalashnik A T, Galimzyanov R R and Semushin K A 2015 *Butlerov Communications* **41** 130–7
[2] Sleptsov V V, Kulikov S N, Kukushkin D Yu and Wu D H 2015 *Nanoengineering* **3** 7–14
[3] Zheng J P, Huang J and Jow T R 1997 *Journal of the electrochemical Society* **144** 2026–31
[4] Vinogradova S S, Iskhakova I O, Kaydrikov R A and Zhuravlev B L 2012 *The method of impedance spectroscopy in corrosion studies* (Kazan: KNRTU)
[5] Ma H, Cheng X, Li G, Chen S, Quan Z, Zhao S and Niu L 2000 *Corrosion Science* **42** 1669–83