Fractional circuit model for supercapacitors with polyaniline/carbon nanotube composite-based electrodes

I.O. Yavtushenko¹, R.T. Sibatov¹,², A.I. Somov¹, M.Yu. Makhmud-Akhunov¹
¹ Technological Research Institute, Ulyanovsk State University, Russia
² Institute of Nanotechnology of Microelectronics of the Russian Academy of Sciences (INME RAS), Russia
E-mail: yavigor@mail.ru, ren_sib@bk.ru

Abstract. Supercapacitors with polyaniline/multiwalled carbon nanotube (PANI/MWCNT) composite-based electrodes are fabricated and studied. The cases of electrodes with randomly distributed and vertically aligned MWCNTs are considered. The measured discharge curves demonstrate the presence of memory effect in studied devices. The fractional-order equivalent circuit model is proposed to describe the impedance spectra.

1. Introduction
Electrochemical supercapacitors (ESC) are high-capacity energy storage devices for applications requiring high power density, hybrid cars and electric vehicles, wind turbines, photovoltaic systems, biomedical sensors, etc [1, 2]. ESCs differ in charge storage mechanism, cell structure, electrolyte and electrode materials. By charge storage mechanism, there are distinguished [3]: 1) supercapacitors with an electric double-layer (EDL), where the capacitance arises due to the accumulation of charges on the electrode-electrolyte interface, 2) pseudo-capacitors with fast reversible Faraday redox reactions at the electrodes, 3) hybrid electrochemical supercapacitors that use EDL and Faraday capacitive mechanisms. To increase the area of the double electric layer in supercapacitors, electrodes with a highly developed surface are used. These electrodes can include porous materials based on activated carbon, carbon nanotubes, graphene oxide, foamed metals or conducting polymers, and other materials.

Polyaniline (PANI) was one of the first electroactive materials that opened the way to the fundamental and practical development of pseudo-capacitors [4]. In recent times, PANI has attracted additional attention due to its invaluable advantages in composition with other electroactive nanomaterials. Carbon nanotubes (CNTs) were among the first carbon nanomaterials used for improving the electrochemical performance of PANI-based supercapacitors [5]. Performance of PANI-CNT supercapacitor depends on the appropriate architecture of the corresponding nanocomposites.

One of the successful approaches in phenomenological modeling of supercapacitors is based on the use of fractional circuit models [4]. Usually, these models are formulated in terms of equivalent circuits containing a constant phase element (CPE) sometimes called a capacitor of...
fractional order or a fractal element. These models predict the presence of memory effect in the devices and are effective to estimate state-of-charge.

In this work, we fabricate and study supercapacitors with polyaniline/multiwalled carbon nanotube (PANI/MWCNT) composite-based electrodes. Nanocomposites with randomly distributed and vertically aligned MWCNTs are used. Using the impedance spectra, we fit the fractional-order equivalent circuit model for different types of nanocomposites.

2. Materials and experimental methods
We studied two types of supercapacitors denoted as PANI/VA-MWCNT and PANI/RD-MWCNT. The first type contains vertically aligned array of carbon nanotubes (VA-MWCNT) in electrodes, and the second type implies randomly distributed nanotubes (with random orientation and position). In the first case, organic compound was grown by the pyrolysis method, in the second case, it was deposited from the solution by dropping. The area of the plates is of 0.5 cm$^2$ in both cases. The CNT layer was covered with a thin layer of polyaniline (emeraldine form), obtained by the chemical method of oxidation of an aniline solution. The thickness of one formed PANI layer is about 150 nm. The second lining was made using the same technology. A solution of polyvinyl alcohol (PVA) and phosphoric acid was used as a layer between the plates. A schematic representation of the structure of the first type is presented in Figure 1,a.

The parameters of the studied system were estimated by cyclic voltammetry and impedance spectroscopy. The measurements were made with the potentiostat-galvanostat P-40X (Electrochemical Instruments). Voltammograms are measured in the range from $-0.5$ V to $0.5$ V at a potential sweep speed of 20 and 100 mV/s. Impedance spectra were taken in the frequency range from 0.1 Hz to 50 kHz with an amplitude of 50 mV. The corresponding equivalent circuit model is presented in Figure 1,d.

Figure 1. Schematic representation of the cell with polyaniline/vertically aligned carbon nanotube array electrodes (a). Voltammograms for two types of PANI/MWCNT supercapacitors using electrodes with vertically aligned nanotubes (b), or randomly distributed MWCNTs (c). Equivalent circuit model (d) used in this work for PANI/VA-MWCNT supercapacitors.
3. Phenomenological model

Typical voltammograms for the studied structures are demonstrated in Figure 1,b,c. The obtained sample PANI/RD-MWCNT is characterized by low capacity. Much better capacitive properties are observed for PANI/VA-MWCNT. The capacity determined from voltammogram is of $C_1 = 6.73 \cdot 10^{-2}$ F. Obviously, this fact is associated not only with an increase specific surface area of the electrode due to the ordered arrangement of CNTs on the substrate normal to the surface, but also by the presence of an ohmic contact between the titanium substrate and the CNTs. The application of CNTs coated with a PANI layer from the solution leads to difficulties in charge distribution due to the contact barrier of a thin PANI layer and a titanium substrate. It is characteristic that holding the system for four months leads to a decrease in capacity by 12%, which is possibly associated with processes of changing the structure of the polyvinyl interlayer during exposure to air, namely, the loss of mechanical strength due to locally arising mechanical stresses, which in turn can lead to the formation of microcracks. This suggests the need to vacuum the structure of the capacitor.

The determination of the parameters of multilayer structures, as well as the analysis of the influence of their developed structure on capacitive properties, was carried out by the method of electrochemical impedance spectroscopy (EIS) [8, 9]. A typical form of impedance spectra for the two analyzed types of structures, as well as their equivalent circuits, are presented in Figure 2. As noted above, the presence of an ohmic contact between an ordered layer of CNTs and a Ti substrate is confirmed by a significant decrease in the resulting resistance in comparison with a sample coated with a layer of randomly arranged CNTs.

The use of a polymer conductive layer (PANI) is promising from the point of view of the durability of the formed systems, as well as an increase in capacitive characteristics. To study the effect of this layer on the characteristics of the system, samples with different number of PANI layers were investigated. The corresponding impedance spectra and voltammograms are shown in Figures 2 and 3, respectively.

Figure 2. Impedance spectra of PANI/VA-MWCNT supercapacitors with one (a) and two (b) PANI layers. An equivalent circuit and fitting spectra are shown as well.

The equivalent circuit model used to describe impedance spectra is presented in Figure 1.d. The constant phase element is characterized by the impedance $Z_{\text{CPE}} = C_\alpha^{-1}(j\omega)^{-\alpha}$. The model contains two Warburg elements (short $W_s$ and open $W_o$). Element $W_s$ is characterized by the impedance of finite-length diffusion with transmissive boundary, element $W_o$ corresponds to the
impedance of finite-length diffusion with reflective boundary,

$$Z_{Ws} = \frac{W_s}{\sqrt{\omega}}(1 - j) \tanh \left( b_s \sqrt{j\omega} \right), \quad Z_{Wo} = \frac{W_o}{\sqrt{\omega}}(1 - j) \coth \left( b_o \sqrt{j\omega} \right).$$

In these formula, $W_s$ and $W_o$ are Warburg coefficients, and $b_{s,o} = d/\sqrt{D}$, where $d$ is a thickness of the Nernst diffusion layer, and $D$ is the ion diffusion coefficient. The fitted parameters are presented in Table 1. We used EIS Spectrum Analyser software to fit impedance spectra. The presented results are obtained by the Levenberg-Marquard algorithm with amplitude minimisation.

| Parameter | PANI/VA-MWCNT 1 | PANI/VA-MWCNT 2 |
|-----------|-----------------|-----------------|
| $R$, Ohm  | 4.124           | 1.623           |
| $r$, Ohm  | 0.704           | 1.360           |
| $C_\alpha$, $10^{-4}$ s$^{\alpha}$·Ohm$^{-1}$ | 5.558 | 1.270 |
| $\alpha$ | 0.8068          | 0.8654          |
| $W_s$     | 6.497           | 10.513          |
| $b_s$     | 2.408           | 2.272           |
| $W_o$     | 8.081           | 0.348           |
| $b_o$     | 0.238           | 0.0263          |

The influence of the PANI layer thickness on the capacitive properties of the system is determined by the arising barrier transition (space charge region) of the CNT-PANI contact, which can increase under the influence of an external electric field. An increase in the thickness of the PANI layer leads to the creation of a transition that more effectively restricts the motion of charges, which causes an increase in the capacitive parameters of the system.

**Figure 3.** Cyclic voltammograms of PANI/VA-MWCNT supercapacitors with one (a) and two (b) PANI layers. Sweep rates are 20 mV/s and 100 mV/s.

**4. Conclusion**

Supercapacitors with PANI/MWCNT composite-based electrodes are fabricated and studied. The cases of electrodes with randomly distributed and vertically aligned MWCNTs are
considered. The supercapacitor with randomly distributed MWCNTs demonstrated poor capacitive properties. Much higher capacity is observed for the PANI/MWCNT supercapacitor with vertically aligned array of tubes. The measured discharge curves demonstrate the presence of memory effect in studied devices. The fractional-order equivalent circuit model is proposed to describe the impedance spectra.

Acknowledgments
This work is supported by the Russian Science Foundation (project no. 19-71-10063). R.T.S. acknowledges the support from the Ministry of Science and Higher Education of the Russian Federation (state program 0004-2019-0001).

References
[1] Conway, B. E. (2013). Electrochemical supercapacitors: scientific fundamentals and technological applications. Springer Science & Business Media.
[2] Abbey, C., & Joos, G. (2007). Supercapacitor energy storage for wind energy applications. IEEE transactions on Industry applications, 43(3), 769-776.
[3] Yu, A., Chabot, V., & Zhang, J. (2017). Electrochemical supercapacitors for energy storage and delivery: fundamentals and applications. CRC press.
[4] Eftekhar, A., Li, L., & Yang, Y. (2017). Polyaniline supercapacitors. Journal of Power Sources, 347, 86-107.
[5] Gupta, V., & Miura, N. (2006). Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors. Electrochimica Acta, 52(4), 1721-1726.
[6] Freeborn, T. J., Maundy, B., & Elwakil, A. S. (2015). Fractional-order models of supercapacitors, batteries and fuel cells: a survey. Materials for Renewable and Sustainable Energy, 4(3), 9.
[7] Aoki, K. J., Chen, J., & He, R. (2020). Potential step for double-layer capacitances obeying the power law. ACS omega, 5(13), 7497-7502.
[8] Lasia, A. (2002). Electrochemical impedance spectroscopy and its applications. In: Modern Aspects of Electrochemistry (pp. 143–248). Springer, Boston, MA.
[9] Kitsyuk, E. P., Sibatov, R. T., & Svetukhin, V. V. (2020). Memory effect and fractional differential dynamics in planar microsupercapacitors based on multiwalled carbon nanotube arrays. Energies, 13(1), 213.
[10] Sibatov, R. T., & Uchaikin, V. V. (2019). Fractional kinetics of charge carriers in supercapacitors. Handbook of Fractional Calculus with Applications. Vol.8, Applications in Engineering, Life and Social Sciences, Part B, 8 87-118
[11] Uchaikin, V. V., Ambrozевич, A. S., Sibatov, R. T., Ambrozевич, S. A., & Morozova, E. V. (2016). Memory and nonlinear transport effects in charging-discharging of a supercapacitor. Technical Physics, 61(2), 250-259.