

# “Advanced Carbon Nanostructures” for “Advanced Supercapacitors:” what Does it Mean?

A. L. Despotuli\* and A. V. Andreeva

*Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences Chernogolovka,  
142432 Moscow Region, Russia*

For ranking a high-tech object to a class “advanced . . .,” both the object and scope of its potential application should be defined in terms of relevant characteristics and criteria. The elaboration of required criteria might speed up the technological progress. The ultimate physical limit approach is applied to the case of electrode nanostructures of double electric layer supercapacitors (SCs) required for the development of many high-tech directions. In the frame of new nanoionic fundamentals the ways for the creation of advanced carbon-based nanostructures suited for different types of SCs are proposed.

**Keywords:** Carbon Nanostructures, Supercapacitors, Nanoionics.

## 1. INTRODUCTION

The terminological word combinations such as “advanced technologies,” “advanced devices,” etc. have not been specified yet. No definitions of “advanced materials” are available in the Wikipedia and Encyclopaedia Britannica but the references to scientific journals with such titles can be found therein. There are hierarchies: true “advanced nanostructures” should have direct relation to some would-be advanced devices (“from advanced materials to advanced devices”<sup>1</sup>) which in turn can be related to an important and promising science direction or technology, say, carbon nanoelectronics. To avoid “slogans” or arbitrary interpretations, the definite criteria should be formulated that would permit qualifying the nanostructure or device as “advanced object.”

Many of modern nanotechnology developments will not find a wide application. Only some of them will be used in 5–10 years when the present-day high-tech mainstream will be replaced by novel one. To win an “all-round competition,” i.e., to meet the demands of high criteria in a multidimensional field of characteristics, the developments must have a great potential for a long-term progress. The distance from the “already reached” to the “upper limit” value of a property or a characteristic (desired “possible”) is a measure for qualifying high-tech object as “advanced” one. A significant shortening of the above distance will demand to use new technological principles.

Ion conducting nanostructures and devices will play an important role in nanoelectronics and nanosystems<sup>1–4</sup> which require hetero-integration of semiconductor devices, energy and power sources, sensors, actuators, etc. Nanoelectronics looks beyond the horizon of conventional integrated circuits (post-silicon electronics<sup>5</sup>), where the molecular<sup>6</sup> or carbon electronics (nanotubes,<sup>7</sup> graphene-based nanostructures<sup>8</sup>) may be predominant.

Capacitors are the essential elements of any electronics. The problem of integrated-on-chip high-capacity capacitors was recognized as fundamental one for microelectronics.<sup>9</sup> This problem becomes more and more sharpened in nanoelectronics and the market for integrated-on-chip supercapacitors (SCs) grows.<sup>4</sup> Moreover, capacitors are components of the largest size in portable electronics based on surface mount devices (micro SMD). The carbon-based impulse SMD-SCs compatible with the future carbon nanoelectronics may be used instead of the usual SMD-capacitors. Within the context of above problem, the question arises: is there a reserve for significant improvement of the frequency–capacity and energy–power characteristics of carbon-based SCs? This point was emphasized also by the authors<sup>10</sup> who developed the half-industrial and commercial SCs, e.g., all solid state SCs with the nanostructured carbon/advanced superionic conductor (AdSIC) heterojunctions.<sup>11, 12</sup>

The results of ultimate physical limit approach to nanostructures suitable for double electric layer (DEL) SCs are presented as an affirmative response on the above question. The consideration is performed in terms of the surface

\*Author to whom correspondence should be addressed.

densities of charge ( $\delta_Q$ ), current ( $\delta_I$ ), electrostatic DEL-capacitance ( $\delta_C$ ) and quantum capacitance ( $\delta_{QC}$ ), volume densities of energy ( $\rho_E$ ) and power ( $\rho_W$ ), maximal operational frequency of functional nanostructure ( $f_{\max}$ ), voltage of electrochemical decomposition ( $V_{\text{dec}}$ ) of ionic conductor/electronic conductor (EC) heterojunction, and crystal potential relief depth ( $\eta$ ) in an AdSIC.

### 1.1. Voltage of Electrochemical Decomposition of ADSIC/EC Heterojunction

The surface charge density  $\delta_Q$  on atomically smooth plane electrodes is limited by the charge  $\delta_{Q\max} \approx 1.5 \times 10^{-4} \text{ C/cm}^2$  which corresponds to an unipolar ion charge on densely packed crystallographic planes with small indices. The breakdown field strength  $F_{\max} = \delta_{Q\max}/\epsilon_0 \approx 1.7 \times 10^9 \text{ V/cm}$  in a plane capacitor corresponds to the energy  $\rho_E = (\epsilon_0 k F_{\max}^2)/2 \approx 128 \text{ kJ/cm}^3$  (dielectric susceptibility  $k = 1$ ,  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$  is the vacuum permittivity) which is significantly larger than the standard enthalpy of chemical compound formation (e.g.,  $\Delta H_{\text{NaCl}} = 411 \text{ kJ/mol}$ ). It yields the inequality:<sup>4</sup>

$$kF < \delta_{Q\max}/\epsilon_0 \quad (1)$$

which shows the fundamental incompatibility of a “colossal”  $k$  with a high field strength  $F$  ( $5 \times 10^6 \text{ V/cm}^{13}$ ). The DEL-thickness ( $l_{\text{DEL}}$ ) at the ionic liquid/EC heterojunction is about 0.3–0.4 nm for ionic liquids with a concentration of mobile charges as in a metal, i.e.,  $\approx 10^{22} \text{ cm}^{-3}$ .<sup>14</sup> The inequality (1) can be applied to the DEL

$$(F_{\max} l_{\text{DEL}})(\epsilon_0 k / l_{\text{DEL}}) < \delta_{Q\max} \quad (2)$$

where  $k$  is the effective dielectric susceptibility of  $l_{\text{DEL}}$ .

A new class of “advanced superionic conductors” (AdSICs) among all solid ionic conductors was marked out in Refs. [1, 4]. The crystalline structure of AdSICs is close to optimum for fast ion transport. It determines a record-high level of ion-transport characteristics (ionic unipolar conductivity  $\sigma_i \approx 0.3 \text{ Ohm}^{-1}\text{cm}^{-1}$  at 300 K, activation energy of ion movement  $\approx 4k_B T \approx 0.1 \text{ eV}$ ). The rubidium silver iodide  $\alpha\text{-RbAg}_4\text{I}_5$  is an archetypal member of silver (copper) ion conductors of this class. A “rigid” ionic sublattice of AdSIC (e.g.,  $\text{I}^-$ -sublattice in  $\alpha\text{-AgI}$ ) provides an empty crystal space of conduction channels<sup>15–17</sup> for  $\text{Ag}^+$ -mobile ions. These ions move through the crystal by successive jumps from one vacant crystallographic position to another with unusual rapid velocity, since the crystal potential relief depth  $\eta$  is only about 0.1 eV. The concentration of mobile ions in the states of transition from one minimum of the potential relief (vacant crystallographic position) to another can be estimated by  $n_{\text{ts}} \sim N_i \exp(-\eta/k_B T)$  where  $N_i \approx 10^{22} \text{ cm}^{-3}$  is the total concentration of ions of mobile kind. The concentration of ions in the transition states must be regarded as the  $N_i$  on the

time scale exceeding the mean lifetime of mobile ions in the oscillation states ( $\tau_{\text{osc}} \sim 10^{-10} \text{ s}$ , 300 K) in the minima of the potential relief.

The relation (2) can be applied to AdSIC/EC nano-heterojunctions.<sup>1, 18, 19</sup> The value  $\epsilon_0 k / l_{\text{DEL}}$  has the form of  $\delta_C$  for a plane capacitor with a nanometer-scale interelectrode distance  $l_{\text{DEL}}$  and atomic smooth electrodes. The product  $F_{\max} l_{\text{DEL}}$  can be defined as a new notion—the voltage of electrochemical decomposition of an AdSIC/EC heterojunction  $V_{\text{dec}}$ . The inequality (2) can be rewritten then as

$$V_{\text{dec}} \delta_C < \delta_{Q\max} \quad (3)$$

where  $\delta_{Q\max} \approx 1.5 \times 10^{-4} \text{ C/cm}^2 = 150 \text{ V } \mu\text{F/cm}^2$ . If the high value  $\delta_C \gg 150 \text{ } \mu\text{F/cm}^2$  is attained,  $V_{\text{dec}}$  will be small,  $\approx 0.1 \text{ V}$ , i.e., lower than the voltage of electrochemical decomposition of the bulk AdSICs (about 0.5 V for ionic conductors on the basis of Ag- and Cu-halides). The value  $V_{\text{dec}}$  should coincide with the voltage of electrochemical decomposition of bulk AdSIC for structure-disordered AdSIC/EC heterojunctions (without fast ion transport due to a large  $\eta$  value,  $\approx 0.5 \text{ eV}$ ) with  $\delta_C \ll 150 \text{ } \mu\text{F/cm}^2$ . If the voltage across the structure-ordered AdSIC/EC heterojunction (with fast ion transport<sup>1</sup>) exceeds of  $V_{\text{dec}}$  a degradation of the interface and a decrease of  $\delta_C$  will take place.

### 1.2. Relation Between $k$ and $\eta$ for ADSIC/EC Heterojunctions

The value  $k$  for ionic crystals is proportional to the displacement of ions in potential wells under the action of an external electric field of the unit value ( $1/\gamma$ ).<sup>4</sup> In linear approximation, the recovery force acting on a mobile ion in the minimum of a potential well is  $\partial\varphi/\partial r = -\gamma r$ , where  $\gamma$  is the “rigidity of a chemical bond,” and  $r$  is the displacement of ion. The potential  $\varphi$  is supposed to be proportional to the depth of a potential relief well ( $\eta \approx 0.1 \text{ eV}$  in the bulk of AdSICs). Thus, a new key nanoionic relation can be introduced:

$$\delta_C \propto k \propto 1/\eta \quad (4)$$

where the  $\eta$  value depends on the atomic structure of a heterojunction.

The value  $\delta_C$  is also proportional to the concentration of dipoles ( $n_{\text{dip}}$ ) induced at heterojunction. The concentration of  $n_{\text{dip}}$  for AdSICs is several times smaller than the concentration of vacant crystallographic positions ( $n_{\text{vcp}}$ ) available for mobile ions. So, the relations (3) and (4) give

$$V_{\text{dec}} < \delta_{Q\max}/\delta_C \approx \alpha_\eta \eta / n_{\text{dip}} \quad (5)$$

where  $\delta_{Q\max} \approx 150 \text{ V } \mu\text{F/cm}^2$  and a coefficient ( $\alpha_\eta$ ) needs for further numerical estimates. The maximum hopping frequency of mobile ions between the minima of the potential relief is given by the relation (without considering the thermo-field effect):

$$\nu_{\max} = \nu_0 \exp(-\eta/k_B T) \quad (6)$$

where the frequency of jump attempts ( $\nu_0$ ) is  $\sim 10^{12}$  Hz and  $k_B T \approx 0.026$  eV (300 K). The value  $\nu_{\max}$  defines the upper limit for the operation frequency  $f_{\max}$  of an AdSIC/EC heterojunction. Taking the logarithm of the Eq. (6) gives

$$\eta = k_B T (\ln \nu_0 - \ln \nu_{\max}) \quad (7)$$

where  $\eta$  is in the range 0.36–0.3 eV for  $f_{\max} \approx \nu_{\max} \sim 10^6$ – $10^7$  Hz. The relation (5) gives the value of  $\alpha_\eta$

$$\alpha_\eta > V_{\text{dec}} n_{\text{dip}} / \eta \quad (8)$$

If the experimental data are:  $V_{\text{dec}} \approx 0.25$  V,  $n_{\text{dip}} \approx 3 \times 10^{14}$  cm $^{-2}$  and  $f_{\max} \approx 10^7$  Hz ( $\eta \approx 0.3$  eV) at  $\delta_C \gg 150$   $\mu\text{F}/\text{cm}^2$ , then  $\alpha_\eta > 2.5 \times 10^{33}$  C $^{-1}$  cm $^{-2}$ .

### 1.3. Interface Design Methods

SCs based on AdSICs have been developed in the last decades.<sup>12</sup> However, the  $\delta_C$  values for AdSIC/EC structure-disordered heterojunctions are  $\approx 10^2$   $\mu\text{F}/\text{cm}^2$  only at low frequencies ( $f \sim 10^{-2}$ – $10^3$  Hz), which are small as compared to those of jumps of mobile ions in the AdSIC crystal lattice ( $\sim 10$  GHz at 300 K). Low operation frequencies of AdSIC/EC heterojunctions are the result of violation of fast ion transport in ultra-thin DEL at the interface. In typical cases, e.g., for structure-disordered RbAg $_4$ I $_5$ /Pt heterojunction,<sup>20</sup> the  $f_{\max} \times \delta_C$  product has low values, 1– $10^4$  Hz  $\mu\text{F}/\text{cm}^2$ .

The peculiar chemical composition and atomic structure of the AdSIC/EC heterojunction should be regarded as the additional “fields” determining the effective  $k$  and ion-transport characteristics of functional heterostructures. Interface crystal engineering methods and control of self-organization effects in the AdSIC nanosystems<sup>1,4,21</sup> are a basis for the creation of SCs with high frequency–capacity characteristics.

The consideration (3)–(8) does not mean that high-capacity heterostructures with operation frequencies in the range  $f_{\max} \sim 10^8$ – $10^9$  Hz ( $\eta$  is in the range 0.24–0.18 eV) will be out of practice due to small  $V_{\text{dec}}$ . In fact, if the concentration of induced dipoles  $n_{\text{dip}}$  is reduced below  $\approx 10^{14}$  cm $^{-2}$  by interface design, the AdSIC/EC heterojunction with  $\eta < 0.2$  eV and  $\delta_C \sim 100$   $\mu\text{F}/\text{cm}^2$  will have  $V_{\text{dec}}$  close to the voltage of electrochemical decomposition of the bulk AdSIC ( $\approx 0.5$  V).

A great challenge is the development of interface design methods for the creation of AdSIC-nanostructures with  $\eta \approx k_B T$  (300 K).<sup>4</sup> Such nanostructures with record high ion-transport characteristics may be used in the future semiconductor-nanoionic hybrid deep-sub-voltage nano-electronics and related technologies.<sup>4</sup> The application of interface design methods to various nanostructures may reveal new technological principles and give the realization of the concept of “nano-morphic cell,”<sup>3</sup> i.e., nano- and microsystems integrated on atomic level, in the long-term future.

### 1.4. Non-Faraday Current Density versus Exchange-Current Density

It is usually asserted that DEL-SCs provide the higher power as compared with galvanic batteries. The primary characteristic for power capability of SCs is the dependence of  $\rho_E$  versus  $\delta_I$ . Unfortunately, experimental data on the  $\delta_I$ -behavior of SCs in different conditions are presented in literature scantily. The calculation of surface current density (the internal surface of the electrode  $\approx 10^3$  m $^2/\text{g}$ )<sup>12</sup> gives low values of  $\delta_I \sim 10^{-5}$ – $10^{-7}$  A/cm $^2$  for carbon-based electrodes of DEL-SCs. These values are significantly lower than the desired “possible” non-Faraday  $\delta_I$ . Even if there are the Faraday reactions  $M^+ + e \leftrightarrow M$  (300 K) in liquid electrolyte/ $M$ -metal electrode systems the values of exchange-current densities may be higher than  $\delta_I$ .<sup>22</sup>

The ultimate limit of  $\delta_I$  for AdSIC/EC heterojunctions can be determined as follows. If  $\delta_Q$  is  $\approx 10^{-4}$  C/cm $^2$  and discharge time is in the range  $10^{-8}$ – $10^{-9}$  s (300 K) then maximum of  $\delta_I$  is  $\sim 10^4$ – $10^5$  A/cm $^2$ . It is  $\sim 10^{11}$  times higher than  $\delta_I$  for the carbon-AdSIC composite electrodes at 460 K (all solid state SCs of the K58-12 type manufactured by the “GIRIKOND” corporation, Russia<sup>12</sup>).

### 1.5. Magnitude of $\rho_e \times \rho_w$ as Indicator of Technology Level

Both  $\rho_E$  and  $\rho_C$  are figures of merit of SC performance. If the thickness of a 3D porous electrode of SC increases, the  $\rho_E$  and  $\rho_C$  also increase (SCs with large capacitance per-area of footprint<sup>23</sup>), but  $\rho_W$  decreases simultaneously.<sup>24</sup> Therefore, the relation  $\rho_E \times \rho_W \approx \text{const}$  holds in working regimes and may be used for evaluation of technology level of nanostructures and SCs. The SC-developments of 2008–2010,<sup>25–27</sup> demonstrate the achievement of the value  $\rho_E \times \rho_W \approx 10^9$  J $^2/\text{s kg}^2$  for the liquid electrolyte/nanostructured carbon electrode systems. The upper limit of the  $\rho_E \times \rho_W$  product may be estimated as follows. The  $\rho_E = (\epsilon_0 \text{ kF}_{\text{max}}^2)/2 \approx 128$  kJ/cm $^3$  at  $\delta_{Q\text{max}} = 1.5 \times 10^{-4}$  C/cm $^2$ . So, the maximum value  $(\rho_E)_{\text{max}}$  per unit mass will be less than  $\sim 10^7$  J/kg (for a typical density of inorganic materials  $5 \times 10^{-3}$  kg/cm $^3$ ). The upper limit of  $\rho_W$  is defined by the ratio of  $(\rho_E)_{\text{max}}$  to the recharge time of circuit ( $\tau$ ). The recharge time of short circuit ( $\tau_{\text{sc}}$ ) for SCs with plane atomic smooth electrodes is

$$\tau_{\text{sc}} \sim RxC = (\delta_C l)/\sigma_i \quad (9)$$

where  $R$  is the internal resistance of SC,  $C$  is the capacitance,  $l$  is the interelectrode distance, and  $\sigma_i$  is the specific ionic conductivity of electrolyte. The minimum value of  $l$  can be estimated by  $5 \times l_{\text{DEL}} \approx 2$  nm for the structures integrated on atomic level, and  $\sigma_i$  is about 0.3 Ohm $^{-1}$  cm $^{-1}$  (300 K). The time  $\tau_{\text{sc}}$  is  $\sim 10^{-10}$  s for  $\delta_C \approx 100$   $\mu\text{F}/\text{cm}^2$ . The maximum of output power on an external resistance

is attained at the total load  $\approx 4R$  ( $\tau = 4\tau_{sc}$ ). Then the ultimate limits for the  $\rho_E \times \rho_W$  and  $f_{max} \times \delta_C$  products are significantly less than  $\sim 10^{24}$  J<sup>2</sup>/s kg<sup>2</sup> and  $\sim 10^{12}$  Hz  $\mu$ F/cm<sup>2</sup>, respectively. These cumulative parameters indicate the potential for improvement of SCs.

### 1.6. Quantum Capacitance of Advanced Carbon Nanostructures

The specific capacitance in the range 135–205 F/g was reported for aqueous electrolyte/graphene-like electrode systems.<sup>25–27</sup> The values of  $\delta_C$  calculated per unit area of internal surface of electrode materials are about 20  $\mu$ F/cm<sup>2</sup> (internal surface  $\approx 700$  m<sup>2</sup>/g)<sup>25,27</sup> and 65  $\mu$ F/cm<sup>2</sup> ( $\approx 320$  m<sup>2</sup>/g).<sup>26</sup> Analogous calculations for the AdSIC/nanoporous carbon systems<sup>11</sup> yield  $\delta_C \approx 15$   $\mu$ F/cm<sup>2</sup> ( $\approx 660$  m<sup>2</sup>/g). The explanation of discrepancy (15  $\mu$ F/cm<sup>2</sup> versus 65  $\mu$ F/cm<sup>2</sup>) through the mechanism of “the high accessibility by electrolyte ions”<sup>26</sup> should be rejected because the optimization of pore diameter distribution versus ion sizes gives  $< 20$   $\mu$ F/cm<sup>2</sup>.<sup>28</sup>

The influence of quantum capacitance on the values of  $\delta_C$ -carbon electrode materials is usually not considered in the works devoted to SCs. In the basic work<sup>29</sup> “puzzling aspects of the interfacial capacitance” of carbon electrodes are attributed to the existence of the quantum capacitance ( $\delta_{qc}$ ) which may be the dominant source of capacitance (in series with DEL-capacitance) for the low dimension materials with low density of electronic states at the Fermi level. The penetration of electric field into a conductor and lifting of the Fermi level (at the adding a charge to the electrode) take place in this case. According to Ref. [29], the  $\delta_{qc}$  value is  $\propto n^{1/2}$  for graphene on the SiO<sub>2</sub> substrate, where  $n$  is the carrier concentration. The  $\delta_{qc}$  value is about 7–10  $\mu$ F/cm<sup>2</sup> for the impurity concentration  $\approx 8.6 \times 10^{12}$  cm<sup>-2</sup>. A bilayer graphene is a gapless semiconductor in which the penetration of electrical field generates a finite bandgap.<sup>30</sup> A significant increase of  $\delta_{qc}$  with increasing  $n$  for single walled carbon nanotubes (SWCNTs) was established.<sup>31</sup>

It can be assumed that further optimization of the volume usage of a nanostructured carbon electrode (regulation of porosity) does not allow an increase of the  $\rho_C$  value much above the 200 F/g level (one atom thick graphene has the specific surface area  $\approx 2600$  m<sup>2</sup>/g). The dopants<sup>29</sup> and the extended defects (‘self-doping’)<sup>32</sup> can increase the carrier concentration  $n$ , electronic conductivity ( $\sigma_e$ ), and  $\delta_{qc}$  of carbon electrode materials. The  $\sigma_e$  value of nanotube fibers  $\approx 50$  Ohm<sup>-1</sup> cm<sup>-1</sup> was attained.<sup>33</sup> This is 10 times higher than the analogous values  $\sigma_e$  obtained for graphene-like materials<sup>25,26</sup> but much lower than  $\sigma_e \approx 10^5$  Ohm<sup>-1</sup> cm<sup>-1</sup> of the 20-nm copper wires.<sup>33</sup> Because the value  $\sigma_e$  of metallic carbon nanotubes ( $\approx 5 \times 10^5$  Ohm<sup>-1</sup> cm<sup>-1</sup>) exceeds  $\sigma_e$  of copper nanowires, there is a reserve for decreasing the equivalent series resistance

(ESR) with simultaneous increasing  $\delta_C$  in carbon electrode materials.

The bottom limit of the SWCNT resistance in the low voltage bias regime is defined by the relation<sup>34</sup>

$$R_{swcnt} = 1/4 \times (h/e^2)(L/\lambda + 1) \quad (10)$$

where  $h = 6.6 \times 10^{-34}$  J s is Planck’s constant,  $e = 1.6 \times 10^{-19}$  C is the charge of an electron,  $L$  is the SWCNT length, and  $\lambda$  is the temperature dependent mean free path length of electrons (for metallic SWCNT  $\approx 1$   $\mu$ m at 300 K). The factor 1/4 in (10) appears due to spin and sublattice degeneracy of electrons (each nanotube has four quantum conducting channels in parallel). So, the minimum fundamental resistance  $h/4e^2 \approx 6.5$  kOhm is defined only by two transparent contacts at  $\lambda \gg L$ .

The quantum capacitance per unit length of SWCNT with spin and sublattice degeneracy of electrons is<sup>35</sup>

$$C_q = 4x(2e^2/hv_F) \quad (11)$$

where  $C_q$  is about  $4 \times 10^{-16}$  F/ $\mu$ m at the Fermi velocity  $v_F \approx 8x \times 10^5$  m/s and factor 4 in (11) appears due to spin and sublattice degeneracy of electrons. Recalculation of quantum capacitance ( $4 \times 10^{-16}$  F) per unit area of free-standing SWCNT with the smallest diameter  $d_{min} \approx 0.4$  nm ( $L = \lambda \approx 1$   $\mu$ m) yields  $\delta_{qc} < 30$   $\mu$ F/cm<sup>2</sup>. Advanced carbon electrode nanostructures should have

$$\delta_{qc} = N\delta_C \quad (12)$$

where  $\delta_C$  is a DEL-capacitance and  $N$  is a number in the range 3–5 due to  $\delta_{qc}$  in series with  $\delta_C$ .

### 1.7. Quantum Capacitance of Advanced Carbon Electrode Nanostructures and Heterojunctions

The main question of this work: whether there is an opportunity for significant increase of  $\rho_C$  in ion conductor/carbon nanostructures. As the total number of quantum conduction channels in parallel ( $N_{qc}$ ) increases linearly with the cross-section area of a conductor,<sup>36</sup> so  $C_q \propto N_{qc}$  under some assumptions<sup>37</sup> and  $C_q \propto d^2$  for high aspect ratio conductors ( $d$  is the characteristic diametrical size of a conductor). The quantum capacitance per unit area for cylinder-like nano-conductors is

$$\delta_{qc} \propto d \quad (13)$$

Therefore, a unique possibility for a significant increase of  $\delta_{qc}$  in carbon electrode materials is the application of nanostructures with extended dimensionality, e.g., bundles of metallic SWCNTs, instead of 1D nanowires. There is a critical optimal  $d$  for ranking carbon electrode nanostructures of SCs with high  $\rho_C$  to a class “advanced.” This  $d$  value is defined by relations (12), (13) and, simultaneously, by preservation of high internal surface of electrode (that provides the minimization of  $d$ ).

The  $\delta_C$  value depends on structure of DEL. Further minimization of  $l_{DEL}$  is impossible because the ionic screening length for interfaces with the limit high concentration of charge carriers ( $\approx 10^{22} \text{ cm}^{-3}$ ) is only 0.3–0.4 nm. The  $\delta_C$  value can be increased according to (4) by using AdSIC/EC heterojunctions with low potential barriers  $\eta$  for mobile ions at the interface (large effective  $k$  of DEL). The capacity–frequency and energy–power properties of perfect heterojunctions depend on the atomic-scale structure of interfaces. The application of interface design methods to the heterojunctions with ion conductor/carbon based electrode should take into account such factors as large interfacial value of  $\delta_C$  attained by selection of commensurate structures of solid electrolyte/electrode materials<sup>1,21</sup> and choice of electrode porosity for the optimization of volume utilization. To obtain a high value of  $\delta_{qC}$  with simultaneous preservation of high internal surface of an electrode, it is necessary to use bundles of SWCNTs, uniform metal-covered carbon nanotubes (high state density at the Fermi level, high conductivity<sup>38</sup>) or graphene sheets with dopants, extended defects,<sup>32</sup> and metallic decoration. The prospects of graphene-based materials with high  $\delta_{qC}$  values were not mentioned in the prognostic work<sup>8</sup> but appropriate materials and technology are in a rapid progress (the major chip-makers are active in the research,<sup>5</sup> other members of the family under review have just been discovered<sup>39,40</sup>). We think graphene-based nanostructures with high  $\delta_{qC}$  will be synthesized soon.

Advanced carbon nanostructures are considered as a feasible future of nanoelectronics beyond 22-nm technology node (2016),<sup>35–37,41</sup> therefore micron-sized integrated SCs<sup>4</sup> and the surface mount SCs for portable electronics<sup>42</sup> (including carbon-based micro-SCs<sup>43</sup>) may be well compatible with microelectronics technologies.

## 2. SUMMARY

For the revealing of new possibilities for the creation of advanced carbon-based supercapacitors (SCs), the ultimate physical limit approach was applied to such characteristics as the surface densities of charge ( $\delta_Q$ ), current ( $\delta_I$ ), electrostatic capacitance ( $\delta_C$ ) and quantum capacitance ( $\delta_{qC}$ ), volume densities of energy ( $\rho_E$ ) and power ( $\rho_W$ ), maximum operational frequency of functional nanostructure ( $f_{max}$ ), voltage of electrochemical decomposition ( $V_{dec}$ ) of ionic conductor/electronic conductor (EC) heterojunction, and crystal potential relief depth ( $\eta$ ) in an ionic conductor. In this work:

- (1) new notion, the voltage of electrochemical decomposition of the ionic conductor/electronic conductor heterojunction  $V_{dec}$  was introduced, and the ultimate limit criterion  $V_{dec} \delta_C < 150 \text{ V } \mu\text{F}/\text{cm}^2$  was revealed;
- (2) new nanoionic relation  $\delta_C \propto 1/\eta$  for the advanced superionic conductor/electronic conductor heterojunctions was defined;

- (3) inevitability of using of interface design methods and effects of self-organization for the creation of advanced heterojunctions with the double electric layer (DEL) capacitance  $\delta_C \sim 100 \text{ } \mu\text{F}/\text{cm}^2$  and  $f_{max} \sim 10^8\text{--}10^9 \text{ Hz}$  was emphasized;

- (4) low current density  $\delta_I$  of functional heterojunctions in non-Faraday DEL-SCs as compared with typical exchange-current densities for  $M^+ + e \leftrightarrow M$  (300 K) Faraday reactions in liquid electrolyte/ $M$ -metal electrode systems (300 K) was pointed out as a large reserve to increase the  $\rho_E$  and  $\rho_W$  densities in DEL-SCs;

- (5) criterion  $\approx 10^9 \text{ J}^2/\text{s kg}^2 < \rho_E \times \rho_W \ll \sim 10^{24} \text{ J}^2/\text{s kg}^2$  suited for ranking SCs as advanced devices was proposed;

- (6) small values  $\delta_{qC}$  (about 10–20  $\mu\text{F}/\text{cm}^2$ ) in the pristine graphene and 1D carbon nanomaterials were recognized as the main obstacle for improving DEL-SCs and the condition  $\delta_{qC} \approx 5 \delta_C$  was proposed as the criterion for ranking carbon nanostructures to an advanced class;

- (7) uniform metal-covered carbon nanotubes, bundles of metal SWCNTs and graphene sheets with high concentrations of dopants and extended defects were proposed for creation of advanced carbon electrode nanostructures and SCs with  $\delta_{qC} \approx 5 \delta_C \sim 500 \text{ } \mu\text{F}/\text{cm}^2$  and  $\rho_E \times \rho_W > \sim 10^9 \text{ J}^2/\text{s kg}^2$ .

The elaboration of conventional criteria that would permit qualifying the carbon-based nanostructures, materials and devices as “advanced” ones can speed up the technological progress in the field of SCs and adjacent directions.

**Acknowledgment:** This work on the hetero-intergration of carbon nanoelectronics and nanoionics is supported by the Nanomaterials and Nanostructures Program (No. 21) of the Presidium of the Russian Academy of Sciences.

## References and Notes

1. A. L. Despotuli, A. V. Andreeva, and B. Rambabu, *Ionic*s 11, 306 (2005).
2. V. V. Zhirnov and R. Cavin, *Nat. Nanotechnol.* 3, 377 (2008).
3. R. K. Cavin and V. V. Zhirnov, *Proc. of Mater. Res. Soc. Symp.: Materials and Devices for “Beyond CMOS” Scaling* 1067E, B01 (2008).
4. A. L. Despotuli and A. V. Andreeva, *Int. J. Nanosci.* 8, 389 (2009).
5. F. Schwierz, *Nat. Nanotechnol.* 5, 487 (2010).
6. G. F. Cerofolini and E. Romano, *Appl. Phys. A* 91, 181 (2008).
7. A. Javey and J. Kong (eds.), *Carbon Nanotube Electronics (Integrated Circuits and Systems)*, Springer US, New York (2009), p. 267.
8. A. K. Geim, *Science* 324, 1530 (2009).
9. G. E. Moore, *Electronics* 38, 114 (1965).
10. M. E. Kompan, V. P. Kuznetsov, and V. G. Malyshekin, *Zhurnal Tekhnicheskoi Fiziki/Russian Journal of Applied Physics* 80, 100 (2010).
11. V. P. Kuznetsov and M. E. Kompan, *Russ. J. Electrochem.* 45, 538 (2009).
12. V. P. Kuznetsov, J. V. Guzhov, and M. E. Kompan, *Russ. J. Electrochem.* 43, 576 (2007).
13. B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, F. Bauer, and Q. M. Zhang, *Science* 313, 334 (2006).
14. S. Baldelli, *Acc. Chem. Res.* 8, 389 (2008).
15. S. Geller, *Science* 157, 308 (1967).

16. K. Funke, R. D. Banhatti, D. Wilmer, R. Dinnebier, A. Fitch, and M. Jansen, *J. Phys. Chem. A* 110, 3010 (2006).
17. J.-H. Chang, A. Zurn, and H. G. von Schnering, *Z. Anorg. Allg. Chem.* 634, 2156 (2008).
18. A. L. Despotuli and V. I. Nikolaichik, *Solid State Ionics* 60, 275 (1993).
19. A. L. Despotuli and A. V. Andreeva, *Nanotechnologies in Russia* 5, 506 (2010).
20. F. A. Karamov, *Superionic Conductors: Heterostructures and Elements of Functional Electronics Based on Them*, Cambridge International Science Publish, Cambridge (2008), p. 250.
21. A. V. Andreeva and A. L. Despotuli, *Ionics* 11, 152 (2005).
22. J. O'M. Bockris, A. K. N. Reddy, and A. Camboa-Aldeco, *Modern Electrochemistry 2A, Fundamentals of Electroics*, Kluwer/Plenum, New York (2000), p. 806.
23. J. R. McDonough, J. W. Choi, Y. Yang, F. L. Mantia, Y. Zhang, and Y. Cui, *Appl. Phys. Lett.* 95, 243109 (2009).
24. R. Kotz and M. Carlen, *Electrochim. Acta* 45, 2483 (2000).
25. M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, *Nano Lett.* 8, 3498 (2008).
26. Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, and Y. Chen, *J. Phys. Chem. C* 113, 13103 (2009).
27. J. Yan, T. Wei, B. Shao, F. Ma, Z. Fan, M. Zhang, C. Zheng, Y. Shang, W. Qian, and F. Wei, *Carbon* 48, 1731 (2010).
28. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, *Science* 313, 1760 (2006).
29. J. Xia, F. Chen, J. Li, and N. Tao, *Nat. Nanotechnol.* 4, 505 (2009).
30. T.-T. Tang, Y. Zhang, C.-H. Park, B. Geng, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, S. G. Louie, Y. R. Shen, and F. Wang, *Nat. Nanotechnol.* 5, 32 (2009).
31. J. Dai, J. Li, H. Zeng, and X. Cui, *Appl. Phys. Lett.* 94, 093114 (2009).
32. J. Lahiri, Y. Lin, P. Bozkurt, I. I. Oleynik, and M. Batzill, *Nat. Nanotechnol.* 5, 326 (2010).
33. F. Gao, L. Viry, M. Maugey, P. Poulin, and N. Mano, *Nat. Commun.* 1, 2 (2010).
34. M. S. Purewal, B. H. Hong, A. Ravi, and B. Chandra, J. Hone, and P. Kim, *Phys. Rev. Lett.* 98, 186808 (2007).
35. C. Rutherglen and P. J. Burke, *Small* 5, 884 (2009).
36. J. Zhou, S. Sreekala, P. M. Ajayan, and S. K. Nayak, *J. Phys.: Condens. Matter* 20, 095209 (2008).
37. N. Srivastava, H. Li, F. Kreupl, and K. Banerjee, *IEEE Trans. Nanotechnol.* 8, 542 (2009).
38. S. Dag, E. Durgun, and S. Ciraci, *Phys. Rev. B* 69, 121407(R) (2004).
39. R. R. Nair, W. C. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H. M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, K. S. Novoselov, A. K. Geim, I. V. Grigorieva, and A. N. Grigorenko, <http://arxiv.org/ftp/arxiv/papers/1006/1006.3016.pdf>
40. J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Mullen, and R. Fasel, *Nature* 466, 470 (2010).
41. A. Naeemi, R. Sarvari, and J. D. Meindl, *IEEE Elect. Dev. Lett.* 26, 84 (2005).
42. A. L. Despotuli, A. V. Andreeva, V. V. Vedenev, V. V. Aristov, and P. P. Maltsev, *J. of Nano- and Microsystem Technique (in Rus.)* 3, 30 (2006).
43. J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, and Y. Gogotsi, *Science* 328, 480 (2010).

Received: 7 May 2010. Accepted: 6 August 2010.