

12 Annual Conference of the Materials Research Society of Serbia, Herceg Novi, Montenegro, September 6–10, 2010

# Electrode Nanostructures for Advanced Supercapacitors

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The ultimate physical limit approach is applied to the case of electrode nanostructures of double electric layer (DEL) supercapacitors (SCs) on the basis of advanced superionic conductors (AdSIC) required for the development of many high-tech directions. New nanoionic fundamentals (notion, criteria and estimations) are introduced and the ways for the creation of advanced carbon-based nanostructures suited for different types of SCs are proposed.

PACS: 81.05.ue, 88.85.jp, 82.47.Uv

## 1. Introduction

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. A measure for qualifying high-tech object as "advanced" one is determined by the distance from the "upper physical limit" to the "already attained" value of a characteristic. True "advanced nanostructures" should have direct relation to some would-be advanced devices [1], which in turn can be related to a promising science direction or technology, say the molecular [2] or carbon nanoelectronics [3]. The problem [4] of integrated-on-chip high-capacity capacitors becomes aggravated in deep-sub-voltage nanoelectronics [5]. Similar problem [6] exists in the area of portable electronics based on surface mount devices. Nanoionic devices [5, 7], e.g. supercapacitors (SCs), are necessary to the development of nanoelectronics, self-powered nanosystems [8], etc. In this work the ultimate physical limit approach is applied to double electric layer (DEL) SCs. The work gives an affirmative answer on the question: "Is there a reserve for significant rise of key characteristics of carbon based SCs [9]?"

## 2. Voltage of electrochemical decomposition of capacitive heterojunctions

The surface charge density  $\delta_Q$  on atomically smooth plane electrodes is limited by  $\delta_{Q\max} \approx 1.5 \times 10^{-4} \text{ C/cm}^2$  which corresponds to a unipolar ion charge on crystallographic densely packed planes with small indices. The breakdown field  $F_{\max} = \delta_{Q\max}/\varepsilon_0 \approx 1.7 \times 10^9 \text{ V cm}^{-1}$  in a plane capacitor has the energy  $\rho_E = (\varepsilon_0 k F_{\max}^2)/2 \approx 128 \text{ kJ/cm}^3$  (dielectric susceptibility  $k = 1$ ,  $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ ) which is significantly larger than the standard enthalpy of chemical compound formation (e.g.  $\Delta H_{\text{NaCl}} = 411 \text{ kJ/mol}$ ). It yields [5]

$$kF < \delta_{Q\max}/\varepsilon_0, \quad (1)$$

that shows the incompatibility of high field strength ( $F$ ) [10] with "colossal" [11]  $k$ . The relation (1) applied to a DEL with the thickness ( $l_{\text{DEL}}$ ) and effective susceptibility  $k$  yields:

$$(F_{\max} l_{\text{DEL}})(\varepsilon_0 k/l_{\text{DEL}}) < \delta_{Q\max}. \quad (2)$$

For ionic liquid/electronic conductor (EC) heterojunctions with the concentrations [12] of mobile charges of an order of  $10^{22} \text{ cm}^{-3}$ ,  $l_{\text{DEL}}$  is about 0.3–0.4 nm.

A new class of "advanced superionic conductors" (AdSICs) was marked out among solid ionic conductors [1, 5]. The crystalline structure of AdSICs is close to optimal one for fast ion transport (FIT). It determines a record-high level of ionic conductivity:  $\sigma_i \approx 0.3 \Omega^{-1} \text{ cm}^{-1}$ , and the activation energy of ion movement ( $\eta$ ) is about  $4k_B T(300 \text{ K}) \approx 0.1 \text{ eV}$ . The  $\alpha\text{-RbAg}_4\text{I}_5$  is a member of silver (copper) ion conductors of this new class [13, 14]. In AdSICs the concentration of mobile ions in the states of transition from one minimum of the potential relief (vacant crystallographic position) to another minimum is  $n_{ts} \sim N_i \exp(-\eta/k_B T)$ , where  $N_i \approx 10^{22} \text{ cm}^{-3}$  is the total concentration of mobile ions. The relation (2) can be applied to AdSIC/EC heterojunctions [11]. Whereas the  $\varepsilon_0 k/l_{\text{DEL}}$  is the density of surface capacitance ( $\delta_C$ ), then the  $F_{\max} l_{\text{DEL}}$  product can be defined as a new notion — the voltage of electrochemical decomposition of the AdSIC/EC heterojunction ( $V_{\text{dec}}$ ). Thus,

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

where  $\delta_{Q\max} \approx 1.5 \times 10^{-4} \text{ C/cm}^2 = 150 \text{ V}\mu\text{F/cm}^2$ . If a high value of  $\delta_C$  is attained, say  $\delta_C \gg 150 \mu\text{F/cm}^2$ ,  $V_{\text{dec}}$  will be small,  $\approx 0.1 \text{ V}$ , i.e. lower than the voltage of electrochemical decomposition of the bulk AdSICs ( $\approx 0.5 \text{ V}$  for ionic conductors on the basis of Ag-, Cu-halides). For structure-disordered AdSIC/EC without FIT ( $\delta_C \gg 150 \mu\text{F/cm}^2$ ,  $\eta \sim 0.5 \text{ eV}$ )  $V_{\text{dec}}$  is about the voltage of decomposition of the AdSIC bulk. If the voltage on the structure-ordered heterojunction (with FIT) exceeds  $V_{\text{dec}}$ , the degradation of atomic structure on the heterojunction and the decrease of  $\delta_C$  should take place.

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### 3. Relation between $k$ and $\eta$ for AdSIC/EC heterojunctions

For ionic crystals the  $k$  value is proportional to the shift of ions inside potential wells under the action of an external electric field of the unit value ( $1/\gamma$ ) [5, 11]. In linear approximation, the recovery force acting on a mobile ion in the minimum of the potential well is  $\partial\varphi/\partial r = -\gamma r$  ( $\gamma$  is the "rigidity of a chemical bond", and  $r$  is the shift of ion). The potential  $\varphi$  is proportional to the depth of the potential relief ( $\eta$ ) which is about 0.1 eV in the bulk of AdSICs. New key nanoionic relation can be introduced:

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

where  $\eta$  depends on the heterojunction atomic structure, and  $\delta_C$  is also proportional to the concentration of dipoles ( $n_{\text{dip}}$ ) induced at heterojunction. The relations (3) and (4) give

$$V_{\text{dec}} < \delta_{Q_{\text{max}}}/\delta_C \propto \eta/n_{\text{dip}}, \quad (5)$$

where  $\delta_{Q_{\text{max}}} \approx 150 \text{ V}\mu\text{F}/\text{cm}^2$ . The maximum hopping frequency of mobile ions between the minima of the potential relief (without considering the thermo-field effect) is given by

$$\nu_{\text{max}} = \nu_0 \exp(-\eta/k_{\text{B}}T). \quad (6)$$

The frequency of jump attempts ( $\nu_0$ ) is  $\sim 10^{12}$  Hz and  $k_{\text{B}}T \approx 0.026$  eV (300 K). The value  $\nu_{\text{max}}$  defines the upper limit of heterojunction operation frequency  $f_{\text{max}}$  via the logarithm:

$$\eta = k_{\text{B}}T(\ln \nu_0 - \ln \nu_{\text{max}}), \quad (7)$$

$\eta$  is about 0.36–0.3 eV for  $f_{\text{max}} \approx \nu_{\text{max}} \sim 10^6 \div 10^7$  Hz.

### 4. Interface design methods

The structure-disordered AdSIC/EC heterojunctions provide  $\delta_C \approx 10^2 \mu\text{F}/\text{cm}^2$  only at low operation frequencies ( $f \sim 10^{-2} \div 10^3$  Hz) [15] though the jump frequencies of mobile ions in the crystal relief of AdSICs are  $\sim 10^{10}$  Hz (300 K). It is the result of the FIT violation in the DEL at AdSIC/EC. The chemical composition and atomic structure of interface should be regarded as the additional "fields" determining the effective  $k$  and ion-transport characteristics of functional heterostructures. Interface engineering methods and control of self-organization effects in the AdSIC-nanosystems [1, 5, 16] are a basis for the creation of SCs with high energy-power characteristics. The consideration (3)–(8) does not mean that advanced devices with operation frequencies  $f_{\text{max}} \sim 10^8 \div 10^9$  Hz ( $\eta$  is about 0.24–0.18 eV) will be out of practice due to small  $V_{\text{dec}}$ . If the  $n_{\text{dip}}$  will be reduced below  $\approx 10^{14} \text{ cm}^{-2}$ , the AdSIC/ECs with  $\eta < 0.2$  eV and  $\delta_C \sim 100 \mu\text{F}/\text{cm}^2$  may have  $V_{\text{dec}}$  close to the voltage of electrochemical decomposition of the AdSIC bulk ( $\approx 0.5$  V). A great challenge is the development of interface design methods [17] for the creation of nano-sized AdSIC with  $\eta \approx k_{\text{B}}T$  (300 K) [5]. The nanostructures with record high ion-transport characteristics may be used in the future semiconductor-nanoionic deep-sub-voltage nanoelectronics and related technologies [5] and

will be suited for the realization of the "nano-morphic cell" concept [18], i.e. for the creation of nano- and microsystems integrated on an atomic level.

### 5. Large current on the non-Faraday imperfect AdSIC/EC heterojunctions

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 are scantily presented in the literature. The calculation of  $\delta_I$  (the internal surface of electrode  $\approx 10^3 \text{ m}^2/\text{g}$ ) [19] gives low values of  $\delta_I$  ( $10^{-5} \div 10^{-7} \text{ A}/\text{cm}^2$ ) for carbon-based electrodes of DEL-SCs. These values are significantly lower than the desired "possible" non-faradaic  $\delta_I$ . Even for Faraday reactions  $\text{M}^+ + \text{e} \leftrightarrow \text{M}$  (300 K) in liquid electrolyte/M-metal electrode systems, the exchange-current densities [20] may be higher than  $\delta_I$ . For AdSIC/EC the ultimate limit of  $\delta_I$  can be estimated as follows. If  $\delta_Q$  is about of  $10^{-4} \text{ C}/\text{cm}^2$  and recharge time is in the range  $10^{-8} \div 10^{-9}$  s (300 K), then maximum of  $\delta_I$  may be estimated as  $10^4 \div 10^5 \text{ A}/\text{cm}^2$ . However, for the carbon-AdSIC composite electrodes at 460 K [19],  $\delta_I$  is  $\sim 10^{11}$  times smaller.

In previous sections the nonlinear processes caused by the influence of external forces (the source of voltage or the generator of current) are not considered. Quasi-equilibrium regime of the SC-operation corresponds to the model, where the rate of the generation of mobile ions is rather large and the relaxation time ( $\tau_r$ ) is rather small in any spatial area of AdSIC/EC, so the kinetic restrictions are absent. In the regime of weak external forces the rate of generation of mobile ions is rather large and the deviation from heat equilibrium arises due to the spectrum of the relaxation times  $\tau_r$ . It leads to the linear models of system behavior, in which the parameters of processes are independent on time ( $t$ ) and external forces. A linear model can be described by the equivalent circuit with a set of  $RC$ -chains. The capacitor  $C$  corresponds to the spatial area, where the rate of generation of mobile ions is great enough, and the resistor  $R$  fits the area, where ion transport is defined by diffusion.

"Slow diffusion processes" on AdSIC/EC [15, 21] associated with the diffusion of non-basic charge carriers (defects of crystalline structure) were studied in detail by means of impedance spectroscopy ( $10^{-4} \div 10^6$  Hz). However, the works of this direction did not lead to the formulation of the following conceptual tasks: (i) a study of causes of FIT suppression, (ii) an identification of the boundary types of non-Faraday heterojunctions with FIT, (iii) a search for the methods of creation of AdSIC/EC with FIT. These tasks were first formulated in [22, 23], where the idea of the structurally-ordered (coherent) non-Faraday AdSIC/EC heterojunctions (with FIT) was introduced. The criterion of the non-Faraday AdSIC/EC perfect heterojunctions is  $\delta_C \sim 100 \mu\text{F}/\text{cm}^2$  (300 K),  $f_{\text{max}} \sim 10^9$  Hz.

Real non-Faraday AdSIC/EC interfaces have imperfect crystalline structure with non lowest-energy and without

FIT. Nonlinear behavior of such AdSIC/EC under the action of large external forces is caused by the limited generation rate of basic charge carriers and by the existence of relaxation processes. In this case there are required: (i) the definition of the regime of the AdSIC/EC- operation, (ii) the physical quantities determining external influence, relaxation processes and SC-characteristics. The Arrhenius type formula gives the evaluation of the relaxation time ( $\tau_r$ ):

$$1/\tau_r \propto \exp(-\eta/k_B T). \quad (8)$$

The universal method for the description of AdSIC/EC in a wide range of external conditions does not exist. The impedance method is limited by weak external forces (linear current-voltage dependence). Nonlinear behavior of AdSIC/EC was found [9]. In the regime of external strong influences high power density ( $\rho_W$ ) is provided by appropriate high  $\delta_I$  on the electrodes. Imperfect AdSIC/EC has a transient area, where “surface degradation” [24] (“structure distortion” [25] of AdSIC (high values of  $\eta$ ) exists. Let us assume that thermo-field effect [26] and structural relaxation on the charged interfaces [27] are small, i.e.  $\Delta t \ll RC$  and  $V \ll \eta/e$ , where  $V$  is the voltage on AdSIC/EC. Let  $x$  axis is directed perpendicularly to AdSIC/EC interface. If  $x = 0$  and  $x > 0$  correspond to EC at heteroboundary and ion conductor, respectively, then with increasing  $x$  the functions  $\eta(x)$  and  $\tau_r(x)$  decrease to the AdSIC bulk values ( $\approx 0.1$  eV and  $\sim 10^{-10}$  s). In quasi-equilibrium regime (generator of  $I$ ) in every moment of the time  $t$  the voltage  $V$  at AdSIC/EC has minimal value ( $V_{\min}$ ). It corresponds to the system energy minimum and the charge  $\delta_Q$  is accumulated in the layer  $x \approx 0$ , where low frequency DEL-capacitance  $\delta_C$  is maximum ( $\delta_{C \max} = \delta_Q/V_{\min}$ ). The increase of  $I$  (generator of  $I$ ) creates the conditions, when the rate of generation of basic charge carriers in the  $x \approx 0$  layer can be not sufficient for the given  $\delta_I$ , then non-equilibrium  $\delta_C$  appears ( $\delta_C = \partial\delta_Q/\partial V$ ). In AdSICs, a near-electrode layer of 1 nm thick and of 1 cm<sup>2</sup> area has the charge of mobile ions  $\approx 10^{-4}$  C. The leaving frequencies  $\nu_{\max}$  of these ions from potential wells (6) are  $\sim 10^9$  Hz (300 K) for  $\eta \approx 0.2$  eV. If EC provides electro-neutrality, then all mobile ions can be removed from the considered layer within  $\sim 10^{-9}$  s at the mean current density  $\sim \delta_{Q \max} \nu_{\max}$ , i.e.  $\delta_I \sim 10^5$  A/cm<sup>2</sup>. At  $\eta = 0.5$  eV the value  $\nu_{\max}$  is only  $\sim 4$  kHz (300 K) that fits  $\delta_I \sim 10^{-1}$  A/cm<sup>2</sup>. As the function  $\eta(x)$  decreases in the transition area, the layer  $x \approx x^*$  providing the preset  $\delta_I$  (determined by  $I$ -generator) exists and the charge accumulates in the vicinity of  $x^*$ . The increase of effective length of charge separation from  $x \approx 0$  (quasi-equilibrium regime) to  $x \approx x^*$  (regime of strong  $I$ ) implies that the DEL-capacitance  $\delta_C$  is the decreasing function of  $\delta_I$ . Above estimations give the  $\delta_I$  overrated values, since the majority of thermally excited ions return into initial potential wells. In addition, when  $\delta_{Q \max}$  is  $\sim 10^{-4}$  C/cm<sup>2</sup> the effects of structural relaxation in charged interfaces [27] are possible. For more real estimations the mean values of  $\delta_I$  ought to be  $\sim 10^2$  times

decreased. Thus, for atomically smooth EC-electrodes the quasi-equilibrium values of non-Faraday  $\delta_I$  and maximum  $\delta_C$  at AdSIC/EC are defined by:

$$\begin{aligned} \delta_I &< \sim 0.01 \delta_{Q \max} \nu_{\max} \\ &= 0.01 \delta_{Q \max} \nu_0 \exp(-\eta/k_B T). \end{aligned} \quad (9)$$

Inequalities (9) and  $\tau_r \ll \Delta t$  determine the quasi-equilibrium regime, and reverse relation

$$\delta_I \gtrsim 0.01 \delta_{Q \max} \nu_0 \exp(-\eta/k_B T) \quad (10)$$

is the criterion of large values of  $\delta_I$  and regime of external strong influences.

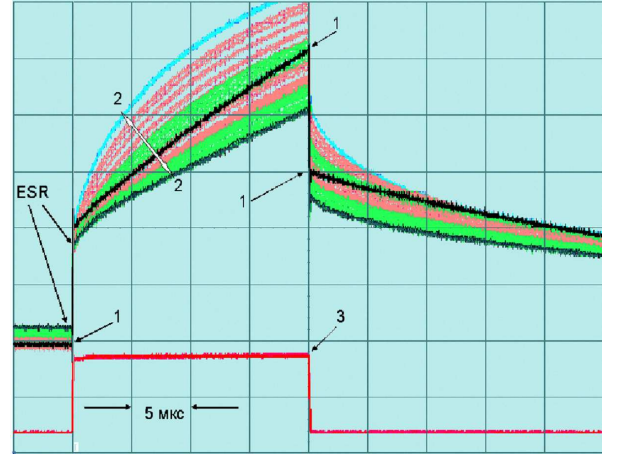


Fig. 1. Time dependence (horizontal scale 5  $\mu$ s/div) of voltages on experimental SC (2) and standard capacitor (1) at the recharging through ballast resistor  $R_b = 100 \Omega$  [11]. The capacitor 0.2  $\mu$ F (vertical scale 50 mV/div) connected in series with the resistor  $r = 20 \Omega$  and experimental SC (the footprint area is 200  $\times$  800 mm<sup>2</sup>) on silicon support in the temperature range 27  $^{\circ}$ C (upper line 2)–86  $^{\circ}$ C (lower line 2). The voltage (3) from the external generator (vertical scale 500 mV/div) for the cases 1) and 2).

The charge-discharge oscillograms [11] qualitatively confirming the correctness of the above estimations are presented in Fig. 1 (experimental SC with AdSIC/EC,  $\delta_C > 100 \mu$ F/cm<sup>2</sup>, the spectrum of oscillograms 2). In the temperature range 27  $\div$  86  $^{\circ}$ C the value  $\delta_C$  increases but  $\tau_r$  and equivalent series resistance (ESR) decrease. If the change of voltage  $\Delta V$  at heterojunction is considerably smaller than the external  $\Pi$ -impulse of voltage (applied to a cell through a large ballast resistor  $R_b$ ), then the regime of current generator take place. For the  $\delta_I$ -impulse satisfying to (10) and inequality  $\Delta t < \tau_r$  the thermodynamics equilibrium is absent in near-electrode layers with  $x < x^*$  but at  $x > x^*$ , where the values of  $\eta$  are close to 0.2 eV, the processes are quasi-static. Thus, the non-equilibrium distribution of the charge (potential) appears in the boundary area with the structurally disordered AdSIC with the  $\eta(x)$  coordinate dependence. The excited systems lose part of energy in the non-equilibrium processes [28], i.e. on condition that  $\Delta t > \tau_r$  the redistribution of charge ( $\delta_Q = \text{const}$ ) inside the  $x < x^*$  layer re-

duces  $V$  and provides the growth of the DEL-capacitance  $\delta_C(t) = \partial\delta_Q/\partial V(t)$  up to a quasi-static value. A minimum  $\delta_C$  is at  $t \rightarrow 0$ . The relaxation of  $V$  appears as the decrease of slope in the  $V(t)$  spectrum oscillograms 2. When the values of  $\delta_I$  are small and satisfy (9) the relaxation is weakly visible (the lower line in the spectrum 2, 86 °C). At small  $\delta_I$  (for instance, elevated  $T$ ) even the layers with large  $\eta(x \approx 0)$  provide the required  $\delta_I$ . Thus, in the regime of strong  $I$  the non-equilibrium  $\delta_C$  of AdSIC/EC is the function of  $\delta_I$ ,  $\eta(x)$ ,  $T$  and  $t$ .

## 6. 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 3D porous electrode of SC increases,  $\rho_E$  and  $\rho_C$  also increase (SCs with large capacitance per-area of footprint) [29], but  $\rho_W$  simultaneously decreases [30]. The relation  $\rho_E \times \rho_W \approx \text{const}$  take place for the given technology. So, it may be used for a qualitative evaluation of technology level of SCs. The developments (2008–2010) [31–33] show  $\rho_E \times \rho_W \sim 10^9 \text{ J}^2/\text{s kg}^2$  for the liquid electrolyte/nanostructured carbon electrodes. If  $\rho_E$  is about  $10^2 \text{ kJ/cm}^3$  at  $\delta_{Qmax} \approx 1.5 \times 10^{-4} \text{ C/cm}^2$ , then  $(\rho_E)_{\text{max}}$  per unit mass is  $< \sim 10^7 \text{ J/kg}$  (for inorganic materials with the density  $5 \times 10^{-3} \text{ kg/cm}^3$ ). The upper limit of  $\rho_W$  is defined by the ratio of  $(\rho_E)_{\text{max}}$  to the discharge time ( $\tau$ ). For SCs the discharge time of short circuit ( $\tau_{sc}$ ) is

$$\tau_{sc} \sim RC = (\delta_C l)/\sigma_i, \quad (11)$$

where  $R$  is the internal resistance of SC,  $C$  is the capacitance,  $\sigma_i$  is the ionic conductivity and  $l$  is the inter-electrode distance. The minimum  $l$  can be estimated by  $5 \times l_{\text{DEL}} \approx 2 \text{ nm}$  for the structures integrated on atomic level, and  $\sigma_i$  is about  $0.3 \text{ } \Omega^{-1}\text{cm}^{-1}$  (300 K). The  $\tau_{sc}$  time is  $\sim 10^{-10} \text{ s}$  for  $\delta_C$  about  $100 \text{ } \mu\text{F/cm}^2$ . The maximum of output power on an external resistor is attained at the total load about  $4R$  ( $\tau = 4\tau_{sc}$ ). Then the ultimate limits for  $\rho_E \times \rho_W$  and  $f_{\text{max}} \times \delta_C$  are much less than  $\sim 10^{24} \text{ J}^2/\text{s kg}^2$  and  $\sim 10^{12} \text{ Hz } \mu\text{F/cm}^2$ , respectively.

## 7. Quantum capacitance of advanced carbon electrode nanostructures

The capacitance in the range 135–205 F/g was reported for aqueous electrolyte/graphene-like electrode systems [31–33]. The values of  $\delta_C$  calculated per unit area of internal surface of electrode materials are about  $20 \text{ } \mu\text{F/cm}^2$  (internal surface  $\approx 700 \text{ m}^2/\text{g}$ ) [31, 33] and  $65 \text{ } \mu\text{F/cm}^2$  ( $\approx 320 \text{ m}^2/\text{g}$ ) [32]. For the AdSIC/nanoporous carbon systems [34], it yields  $\delta_C \approx 15 \mu\text{F/cm}^2$  ( $\approx 660 \text{ m}^2/\text{g}$ ). The explanation of discrepancy ( $15 \text{ } \mu\text{F/cm}^2$  vs.  $65 \text{ } \mu\text{F/cm}^2$ ) due to "the high accessibility by electrolyte ions" [32] should be rejected because the optimization of pore diameter distribution versus ion sizes gives  $\delta_C < 20 \text{ } \mu\text{F/cm}^2$  [35]. The influence of quantum capacitance ( $\delta_{qC}$ ) on the results of measuring  $\delta_C$  is usually not considered for SCs with carbon electrodes [36]. Recently, the "puzzling aspects of the interfacial capacitance" of carbon electrodes were attributed

to the existence of  $\delta_{qC}$  [37], which may be the dominant source of capacitance (in series with DEL-capacitance). It is valid for low-dimensional carbon, where the density of electronic states (DOS) at the Fermi level is small ( $\delta_{qC} \propto \text{DOS}$ ). The penetration of electric field into a conductor and lifting of the Fermi level (at the adding of a charge to the electrode) takes place in case of small  $\delta_{qC}$  (for graphene on the  $\text{SiO}_2$  substrate  $\delta_{qC} \propto n^{1/2}$ ,  $n$  is the value DOS) [37]. For  $n$  about  $9 \times 10^{12} \text{ cm}^{-2}$   $\delta_{qC}$  is  $7\text{--}10 \text{ } \mu\text{F/cm}^2$ . A bilayer graphene is a gapless semiconductor, in which the electrical field generates a bandgap [38]. An increase of  $\delta_{qC}$  with rising  $n$  was established [39].

Further optimization of porosity in the nanostructured carbon will not allow one to increase  $\rho_C$  significantly above 200 F/g (specific surface area of graphene is  $\approx 2600 \text{ m}^2/\text{g}$ ). The dopants [37] and the extended defects ("self-doping") [40] can increase the values  $n$ , electronic conductivity ( $\sigma_e$ ), and  $\delta_{qC}$  in the carbon materials. The nanotube fibers with  $\sigma_e$  about  $50 \text{ } \Omega^{-1} \text{ cm}^{-1}$  was attained [41]. This is 10 times higher than  $\sigma_e$  of graphene-like materials [31, 32] but much lower than  $\sigma_e$  ( $\approx 10^5 \text{ } \Omega^{-1}\text{cm}^{-1}$ ) of the 20-nm copper wires. As the  $\sigma_e$  of metallic carbon nanotubes ( $\approx 5 \times 10^5 \text{ } \Omega^{-1}\text{cm}^{-1}$ ) exceeds  $\sigma_e$  of copper nanowires, there is a reserve for decreasing of the equivalent series resistor (ESR) with increasing  $\sigma_e$  in carbon electrode materials.

The bottom limit of the single wall carbon nanotube (SWCNT) resistance in low voltage bias regime is defined [42] by

$$R_{\text{SWCNT}} = 1/4(h/e^2)(L/\lambda + 1), \quad (12)$$

where  $h = 6.6 \times 10^{-34} \text{ J s}$  is the Planck's constant,  $e = 1.6 \times 10^{-19} \text{ C}$  is the charge of an electron,  $L$  is the SWCNT length,  $\lambda$  is the temperature dependent mean free path length of electrons (for the metallic SWCNTs it is about  $1 \text{ } \mu\text{m}$  at 300 K). The factor 1/4 in (12) appears due to spin and sublattice degeneracy of electrons. So, the minimum fundamental resistance  $h/4e^2 \approx 6.5 \text{ k}\Omega$  is defined only by two electron-transparent contacts at  $\lambda \gg L$ .

The quantum capacitance per unit length of SWCNT ( $C_q$ ) with spin and sublattice degeneracy of electrons is [43]

$$C_q = 4(2e^2/h\nu_F), \quad (13)$$

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

$$\delta_{qC} = N\delta_C, \quad (14)$$

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

The important question is: 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 lin-

early with the cross-section area of a conductor [44], then  $C_q \propto N_{qc}$  under some assumptions [45],  $C_q \propto d^2$  for high aspect ratio conductors ( $d$  is the characteristic diametrical size) and  $\delta_{qC}$  for cylinder-like nano-conductors is

$$\delta_{qC} \propto d. \quad (15)$$

So, unique possibility for significant increase of  $\delta_{qC}$  in carbon electrodes is the application of nanostructures with extended dimensionality, e.g. bundles of metallic SWCNTs instead of 1D nanowires. There is an optimal  $d$  for ranking carbon nanostructures of SCs with high  $\rho_C$  to a class "advanced", that is defined by (14), (15) and, simultaneously, by preservation of high internal surface of electrode (that provides the minimization of  $d$ ).

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. According (4), the  $\delta_C$  can be increased by using AdSIC/EC with low potential barriers for mobile ions (large effective  $k$  of DEL). The capacity-frequency and energy-power properties of perfect AdSIC/EC depend on the atomic structure of interface. The application of interface design methods to the capacitive heterojunctions should take into account such factors as the large interfacial  $\delta_C$  attained by selection of commensurate structures [1, 16] of AdSIC/carbon and the choice of electrode porosity for the optimization of volume utilization. To obtain high  $\delta_{qC}$  with simultaneous preservation of high internal surface of electrode, it is necessary to use bundles of SWCNTs, uniform metal-covered carbon nanotubes (high DOS at the Fermi level, high conductivity [46]) or graphene sheets with dopants, extended defects [40], and metallic decoration. The prospects of graphene-based materials with high  $\delta_{qC}$  did not mentioned in the prognostic work [47] but relevant area is in a rapid progress (the major chip-makers are active in the research [3], other members of the grapheme-family have just been discovered [48, 49]) and so carbon-based nanostructures with high  $\delta_{qC}$  may be soon synthesized.

Advanced carbon nanostructures are considered [43–45, 50] as a future of nanoelectronics beyond 22-nm technology node (2016). Micron-sized carbon-based integrated on chip nanoionic SCs [1, 5] as well as the surface mount high-capacity SCs [6, 51] for portable electronics may be well compatible with future nanoelectronics technologies. Nanoionic devices first proposed by IMT RAS (“*The results obtained show that it is possible to form arrays of electrochemical devices with single elements  $\sim 10 \text{ nm}$  in size in the films*” [52] are now in the scope of interest of ITRS [53]. Future deep-sub-voltage nanoelectronics [11] will use nanoionic SCs [1] which are in scope of Samsung’s interest [54] now.

## 8. Summary

For the revealing of new possibilities in the area of creation of advanced carbon-based supercapacitors (SCs), the ultimate physical limit approach was applied to such a set of characteristics as the surface densities of charge

( $\delta_Q$ ), current ( $\delta_I$ ), electrostatic ( $\delta_C$ ) and quantum capacitance ( $\delta_{qC}$ ), volume densities of energy ( $\rho_E$ ) and power ( $\rho_W$ ), maximum operating frequency of capacitive nanostructure ( $f_{\max}$ ) and voltage of electrochemical decomposition ( $V_{\text{dec}}$ ) of advanced superionic conductor (AdSIC)/electronic conductor (EC) heterojunction, which were expressed through the crystal potential relief depth ( $\eta$ ) for mobile ions at the AdSIC/EC interface. In this work: (1) new notion, “the voltage of electrochemical decomposition of the ionic conductor/EC heterojunction“ ( $V_{\text{dec}}$ ) was introduced, and the ultimate limit criterion  $V_{\text{dec}}\delta_C < 150 \text{ V}\mu\text{F}/\text{cm}^2$  was revealed, (2) new nanoionic relation  $\delta_C \propto 1/\eta$  for AdSIC/EC 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  $\delta_C \sim 100 \mu\text{F}/\text{cm}^2$  and  $f_{\max} \sim 10^8 \div 10^9 \text{ Hz}$  was emphasized, (4) low non-faradaic  $\delta_I$  in DEL-SCs as compared with typical exchange-current densities for  $\text{M}^+ + \text{e} \leftrightarrow \text{M}$  (300 K) Faraday reactions in liquid electrolyte/M-metal systems was pointed out as a large reserve to increase of  $\rho_E$  and  $\rho_W$  in DEL-SCs. The criterion of transition into regime of external strong influences  $\delta_I \gtrsim 0.01\delta_{Q\max}\nu_0 \exp(-\eta/k_B T)$  is introduced for AdSIC/EC. It has been shown that a non-equilibrium DEL-capacitance  $\delta_C(t)$  of AdSIC/EC with the structurally-disordered interface depends on the  $\delta_I$ ,  $\eta(x)$ , temperature  $T$ , and time  $t$ , (5) criterion  $\approx 10^9 \text{ J}^2/\text{s kg}^2 < \rho_E \times \rho_W \gtrsim 10^{24} \text{ J}^2/\text{s kg}^2$  suited for ranking SCs to an advanced class 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 the creation of advanced carbon electrode nanostructures and SCs with  $\delta_{qC} \approx 5\delta_C \sim 500 \mu\text{F}/\text{cm}^2$  and  $\rho_E \times \rho_W \gtrsim 10^9 \text{ J}^2/\text{s kg}^2$ .

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

## Acknowledgments

This work on the hetero-integration of carbon nanoelectronics and nanoionics was supported by the “Nanomaterials and Nanostructures Program” (#21) of the Presidium of the Russian Academy of Sciences.

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