Features in Energy Accumulation in Double Layer on the surface of Graphene Material.

Mikhail Evgenievich Kompan, Vladislav Gennadievich Malyshkin and Alexander Yurievich Maslov

Ioffe Institute, Politekhnicheskaya 26, St Petersburg, 194021, Russia

Viktor Petrovich Kuznetsov

"NII GIRICOND" JS Co, 10 Kurchatova str., St.Petersburg, 194223, Russia

Viktor Aleksandrovich Krivchenko

Chemistry Department, Moscow State University, 119991 Moscow Russia

(Dated: November 3, 2015)

$Id: quantlim.tex,v 1.16 2015/12/27 23:09:27 mal Exp$

An application of quantum size carbon structures–graphenes as electrodes of supercapacitors is studied. A fundamental limit of energy and power density arising from quantum nature of objects due to singularity in graphene density of states near Dirac point is determined and technical solutions to partially offset the negative factors are considered. The maximum possible specific capacitance of nanostructured electrode materials is determined.
I. INTRODUCTION

Devices and materials for energy storage are of paramount importance to modern technology. Requirements and the corresponding technical conditions are so different that practically used technical solutions vary greatly. Common approaches to a wide range of technical solutions and examples can be found in the monographs [1, 2].

Storage of electrical charge in double layer (EDCL) is a fundamental principle of electrochemical capacitors, or supercapacitors. Energy storage mechanism in these devices is different from the mechanism in conventional capacitor; However, since the total energy in both cases is proportional to electrode area, the search of effective material for electrodes is an important problem in both cases. Recent development led to numerous supercapacitor devices with electrodes made of graphene-based materials [3–7]. Nevertheless, none of these studies have reached the specific capacitance, corresponding to known graphenes specific area 2630 m²/g geometric limit. We use the term ”graphene–based materials” (GBM) as a collective term for the materials studied in publications on graphene application (for example [9]), as their properties are quite different [10] from ideal graphene, but at the same time exhibit the main features of these objects. In addition to possible technological factors, there is exist capacity reduction [11–13] due to fundamental features of graphene. Consequently, the effective specific capacity of the graphene material is a function of accumulated charge and under certain conditions can be substantially, more than an order of magnitude, lower than that expected from specific surface estimation. An effect of extra charge carriers, coming either from doping the material or from charging the supercapacitor, on specific capacity is exhibited.

II. CAPACITANCE

In this paper we study the influence of the same factors on energy characteristics of the graphene material. Electrical energy accumulated on GBM electrodes is equivalent [14] the energy of to serially connected regular (geometric, determined by electrodes surface) capacitance and so called quantum capacitance. The differential capacitance $c(U)$ of graphene sheet charged from an external source $U$ can be expressed as

$$\frac{1}{c_T(U)} = \frac{dU}{dQ} = \frac{dU_g}{dQ} + \frac{dE}{dQ}$$ (1)
where $U_g$ is the electrostatic potential and $E$ is the energy of electron (hole) in the conduction (valence) band (here and below, it is assumed that the second electrode of the capacitor has infinite capacitance). The first term in Eq. (1) represents the typical geometric capacitance ($\frac{dU_g}{dQ} = 1/C_g$) and the second term reflects the influence of quantum effects. The total capacitance can only be smaller than the "classical" $C_g$ one, and the accumulated specific energy can be only lower. The equivalence of GBM capacitance to serially connected double layer capacitance and quantum capacitance should have as a consequence not only the reduction in capacitance, but also potential redistribution, as they are serially connected.

External voltage applied to the GBM capacitor (measured at its electrodes) is a sum of $U_g$ (regular capacitor) and $E$ (quantum capacitor). The microscopic nature of these potentials is different. $U_g$ voltage is related to geometric capacitance, applied to a double charged layer at electrode surface- electrolyte boundary. $E$ - voltage "applied" to the quantum capacitance. The origin $E$ is charge redistribution within conduction band, what lead to Fermi level shift and is equivalent to additional $E$ potential applied. Given the density of states in the conduction band this $E$ can be calculated from the charge on the capacitor, as following.

Consider the quantum portion of differential capacity

\[
\frac{dQ}{dE} = c(E)
\]

(2)

In typical capacitors, the potential (energy per unit charge) arises due to the electrostatic interaction of accumulated electric charges. In the case of graphene, the relationship between introduced charges and required energy involves additional coupling that is related to the finite electron density of states (DOS) in graphene. The energy band structure of graphene has a singularity at six equivalent points on the boundary of the Brillouin zone. At these points, the boundary states of the conduction band and valence band appear as two cones sharing a common vertex\[15\]. The DOS of conduction electrons ($n$) and holes is zero at the singular point and linearly increases with energy as

\[
n(E) = \alpha E
\]

(3)

Under not very high $E$ and Graphene quantum linear dispersion relation $c(E) = k |E|$ for undoped graphene, and in homogeneously doped graphene

\[
c(E) = k |E - E_d|
\]

(4)
FIG. 1. Graphene $c(E)$ for different $E_d$ (left) and $c(E)$ for a system with two $E_d$ (right).

where the $E_d$ is doping level – the difference between Fermi level and singular point. In case of inhomogeneously doped graphene the (1) should be averaged over $E_d$ and the result for two $E_d$ is presented in Fig. 1. For practical applications the total charge and energy accumulated is of most interest. Integrating (2) from 0 to $E$ obtain

$$Q(E) = \int_0^E c(U)dU$$  \hfill (5)

$$W(E) = \int_0^E Uc(U)dU$$ \hfill (6)

The formulas (5) and (6) allows total charge $Q$ and energy $W$ to be calculated. Consider the case when charging (or discharging) current is a constant $I$. Then $Q = It$ and total potential on supercapacitor is a sum of regular double layer potential $U_g = Q/C_{dl}$ and Fermi level shift $E$, that (5) on upper limit.

$$Q = It$$ \hfill (7)

$$Q = U_g/C_{dl}$$ \hfill (8)

$$U = E + U_g$$ \hfill (9)

The easiest way to calculate charging curve $U(t)$ is to calculate it in parametric form, using $E$ as a parameter, calculating $U(E)$ and $t(E)$ from (5), (8) and (7). The $U(Q)$, Fig. 2, because of an additional $E(Q)$ contribution to $U_g(Q)$, means capacity reduction due to quantum effects. However, this quantum contribution $E(Q)$ depend on density of states at $U = 0$ and can be greatly reduced by doping supercapacitor electrodes as shown in Fig 2 (bottom). Now additional charge would lead to a small Fermi level shift, thus reducing $E(Q)$ contribution, responsible for capacity reduction. There is one more factor that limits accumulation of charge and energy on EDLC - the "Stability window" of the electrolyte. The
FIG. 2. Left: $U_g(Q)$, $E(Q)$ and $U(Q)$ for supercapacitors with GBM electrodes. Right: $U(Q)$ for differently doped electrodes.

FIG. 3. Potential redistribution on the supercapacitor.

Voltage applied to double layer is limited by electrolyte decomposition potential. The limit is the maximal voltage not yet causing electrolyte (liquid or solid) decomposition. For solid electrolyte RbAg4I5 this value is about 0.55V; for water-based electrolyte of about 1V, and for electrolytes based on organic solvents limiting voltage typically is 2.5-3 V. Important, that this limitation is applicable only to double layer potential $U_g$. There is no similar limitation mechanism applied to $E$. Thus, the above discussion shows that the total voltage that can be applied to the EDLC type under discussion, is higher than the one determined from the "stability window" on classical surfaces.

The calculations in Fig. 3 were made under the same conditions as in our paper[14].
where we took into account graphene density of states, what lead to dependence of the capacitance on the capacitor charge. In Fig 3 the $x$ is total voltage, and $y$ is the fraction, applied to double layer (applied to electrolyte). Fixing $y$ value at electrolyte decomposing potential then projecting to $x$ one can obtain maximal potential, which can be applied to the capacitor without electrolyte decomposition. The graph shows that the total voltage can be up to 1.5–3 times greater than electrolyte decomposition potential. The calculations show, that in spite of the reduction in the effective capacity, the effect can be partially compensated by the maximal potential increase.

A family of curves in Figure 3 reflects the redistribution of potential applied to the GBM (the lower axis, the potential between the solution in volume and GBM) between the voltage an the double layer (EDCL) (right axis) and the rise of the Fermi energy in the GBM (left axis). Two pairs of curves (a pair in each case) on the figure correspond to the two types GBM doping.

### III. POWER

Another extremely important parameter of energy storage device is the maximal output power. The parameter (besides voltage) determining the power is internal resistance. The internal resistance is often limited by the conductivity of electrodes material and device technology. Electrolyte conductivity, while important, is more difficult to optimize. A distinctive feature of EDLC on GBM should be the dependence of material conductivity on accumulated charge. The reason for this dependence should be the same density of state dependence on accumulated charge. In the simplest case the potential drop on internal resistance would be:

\[
U_R = I / \sigma(E) \tag{10}
\]

\[
U = E + U_g + U_R \tag{11}
\]

where the conductivity $\sigma(E)$ depend on carrier density through the $E$ potential, same as used for capacity calculations. In the Eq. (11) the internal resistance term is added to total potential. In the simplest case the $\sigma(E)$ dependency can be estimated from simple considerations. Standard graphene dispersion near band edge $E = \hbar V_F |k|$ have zero effective mass and almost infinite mobility. However, this is the case only near the band edge. In
the band is partially occupied, to the level of $E$, then the effective mass $m^*$, affecting the
mobility, can be estimated as

$$m^* = \frac{eE}{V_F}$$  \hspace{1cm} (12)

$$\mu = \frac{1}{\beta E}$$  \hspace{1cm} (13)

and growth with filling the band. Thus the dependence of conductivity on $E$ has two factors:
growing with $E$ the concentration of carriers \[3\] as $|E|$ and declining as $1/|E|$ mobility due to
effective mass \[12\] increase. For power measurement then the $\sigma(E)$ take a constant value.
In the case of graphene $\sigma(E)$ exhibit no singularity near $E = 0$, because of singularities
cancellation in numerator and denominator. This effect is different from typically studied
in graphene Dirac point conductivity, that consider small current experiments. Here on
large current, most interesting setup for supercapacitors, the effective mass expression\[12\]
is different and give as a result finite conductivity.

\section{IV. DISCUSSION}

In this work limit capacitance, maximal potential and power of supercapacitors with
electrodes made from GBM are estimated. It was shown that quantum capacity limit total
capacity, but the effect can be partially offset by 1) Doping graphene electrodes to increase
carriers concentration and 2) Due to potential redistribution between double layer and band
shift total voltage, that can be applied to the device become higher than in classical case,
thus allows partial offset of capacity reduction.

\[1\] Igor V Barsukov, Christopher S Johnson, Joseph E Doninger, and Vyacheslav Z Barsukov,
New Carbon Based Materials for Electrochemical Energy Storage Systems: Batteries, Supercapacitors and Fuel Cells, Vol. 229 (Springer Science & Business Media, 2006).

\[2\] Aiping Yu, Victor Chabot, and Jiujun Zhang, Electrochemical supercapacitors for energy
storage and delivery: fundamentals and applications (CRC Press, 2013).

\[3\] SRC Vivekchand, Chandra Sekhar Rout, KS Subrahmanyam, Achutharao Govindaraj, and CNR Rao, “Graphene-based electrochemical supercapacitors,”
Journal of Chemical Sciences 120, 9–13 (2008)
[4] Nasir Mahmood, Chenzhen Zhang, Han Yin, and Yanglong Hou, “Graphene-based nanocomposites for energy storage and conversion in lithium batteries, supercapacitors and fuel cells,” Journal of Materials Chemistry A 2, 15–32 (2014).

[5] Chenguang Liu, Zhenning Yu, David Neff, Aruna Zhamu, and Bor Z Jang, “Graphene-based supercapacitor with an ultrahigh energy density,” Nano letters 10, 4863–4868 (2010).

[6] Santhakumar Kannappan, Karthikeyan Kaliyappan, Rajesh Kumar Manian, Amaresh Samuthira Pandian, Hao Yang, Yun Sung Lee, Jae-Hyung Jang, and Wu Lu, “Graphene based supercapacitors with improved specific capacitance and fast charging time at high current density,” arXiv preprint arXiv:1311.1548 (2013).

[7] Yan Wang, Zhiqiang Shi, Yi Huang, Yanfeng Ma, Chengyang Wang, Pingming Chen, and Yongsheng Chen, “Supercapacitor devices based on graphene materials,” The Journal of Physical Chemistry C 113, 13103–13107 (2009).

[8] Prithu Mukhopadhyay and Rakesh K Gupta, Graphite, Graphene, and their polymer nanocomposites (CRC Press, 2012).

[9] Virendra Singh, Daeha Joung, Lei Zhai, Soumen Das, Saiful I Khondaker, and Sudipta Seal, “Graphene based materials: past, present and future,” Progress in Materials Science 56, 1178–1271 (2011).

[10] Yi Huang, Jiajie Liang, and Yongsheng Chen, “An overview of the applications of graphene-based materials in supercapacitors,” Small 8, 1805–1834 (2012).

[11] Serge Luryi, “Quantum capacitance devices,” Applied Physics Letters 52, 501–503 (1988).

[12] S Dröscher, P Roulleau, F Molitor, P Studerus, C Stampfer, K Ensslin, and T Ihn, “Quantum capacitance and density of states of graphene,” Applied Physics Letters 96, 152104 (2010).

[13] K Nagashio, T Nishimura, and A Toriumi, “Estimation of residual carrier density near the dirac point in graphene through quantum capacitance measurement,” Applied Physics Letters 102, 173507 (2013).

[14] ME Kompan and VG Malyshkin, “Ultimate capacitance characteristics of graphene electrodes for supercapacitors: Quantum restrictions,” Technical Physics Letters 41, 359–361 (2015).

[15] AH Castro Neto, F Guinea, NMR Peres, Kostya S Novoselov, and Andre K Geim, “The electronic properties of graphene,” Reviews of modern physics 81, 109 (2009).