

Dirac cone filling dynamics due to field effect at graphene electrochemical interfaces

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Dynamics of charge accumulation at electrochemical graphene interfaces is important for capacitor, battery, and sensor applications. These dynamics depend on quantum capacitance and filling time (τ) of the Dirac cone in graphene when the field effect is present at these interfaces. By analyzing the impedance-spectroscopy literature data on the graphene electrochemical interfaces with water and sulfuric acid aqueous solution, we have revealed that in these cases τ is 0.4 and 0.022 s, respectively. These values are consistent with the hypothesis that at these interfaces τ is determined by the reconstruction time of molecules (polarized for water and charged for acidic solutions); hence, measurement of τ is promising for the molecular sensor fabrication.

Keywords: quantum capacitance, graphene, interface, molecular bonding, relaxation time.

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Graphene interfaces with solutions of various molecules are used in, e.g., advanced capacitor and battery devices [1–4], as well as in chemical and biological sensors [5–8]. Fig. 1 presents an equivalent circuit for determining capacitance of a graphene electrochemical interface [9–11].

Frequency-dependent capacitance of a double layer (C_{dl}) is determined by the ratio of the double layer charge accumulated over the applied voltage period (T) to this voltage. The double-layer electrostatic capacitance (C_{dl0}) is the C_{dl} limit as T tends to infinity, and is conventionally estimated as the capacitance of a parallel-plate capacitor with the inter-electrode distance equal to the molecular ion radius [9]; the capacitance dependence on voltage is neglected. Quantum capacitance (C_q) [12] plays an important role in low-dimensional systems with low density of charge carrier states, e.g. in graphene. In the case of graphene, C_q does depend on the applied voltage, and this dependence is determined by the Dirac cone filling or emptying [13] with varying voltage [9]. Despite the importance of parameter C_q for practical applications and great interest in studying it, frequency dynamics of the Dirac cone filling and emptying under the field effect has not yet been sufficiently studied for graphene electrochemical interfaces [1,11]. In our recent study [11], we revealed the existence of a time threshold of about 0.1–1 s for the voltage dependence of

the graphene-water interface capacitance (C_{int}). Since the C_{int} temporal dynamics plays a certain role for various graphene electrochemical interfaces, practical applications need understanding how general such a temporal dynamics is. Until now, similar dynamics for other electrochemical graphene interfaces has not yet been analyzed in detail. Thus, it is important to reveal and analyze similar dynamics of capacitance of other electrochemical graphene interfaces, and also to develop a model explaining it.

Initial data on the frequency dependence of capacitance at different voltages were taken from [1,11]. Figs. 2, *a* and *b* present the frequency dependences of capacitance C_{int} for interfaces between graphene and water [11] and between graphene nanoribbon and one-molar sulfuric acid solution [1], which were obtained after normalizing the initial C_{int} values to its values near the Dirac point (defined as capacitance minima depending on voltage) at different frequencies. This normalization provides clear visualization of the frequency dynamics of voltage-dependent C_{int} . Figs. 2, *a* and *b* show that dynamics in these experiments are qualitatively similar and that results of both studies exhibit a characteristic time limit (relaxation time) (τ): when T exceeds this limit, the C_{int} dependence on voltage becomes drastically stronger. In addition, Figs. 2, *a* and *b* demonstrate that τ for the capacitances of graphene interfaces with water and sulfuric acid solution are about 0.4 and 0.022 s, respectively. In [1,11], the C_{int} temporal dynamics was not clearly explained; therefore, in this paper we propose the following model.

The observed voltage dependence of $F \times \omega \times E$ is caused by voltage dependence of C_q showing that the measured capacitance minimum ([1] and [11]) is reached upon passing through the Dirac point (see, e.g. [9]). In the stationary case, the C_q dependence on voltage near the Dirac point is

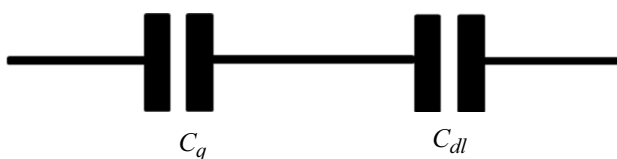


Figure 1. Equivalent circuit of the graphene electrochemical interface capacitance.

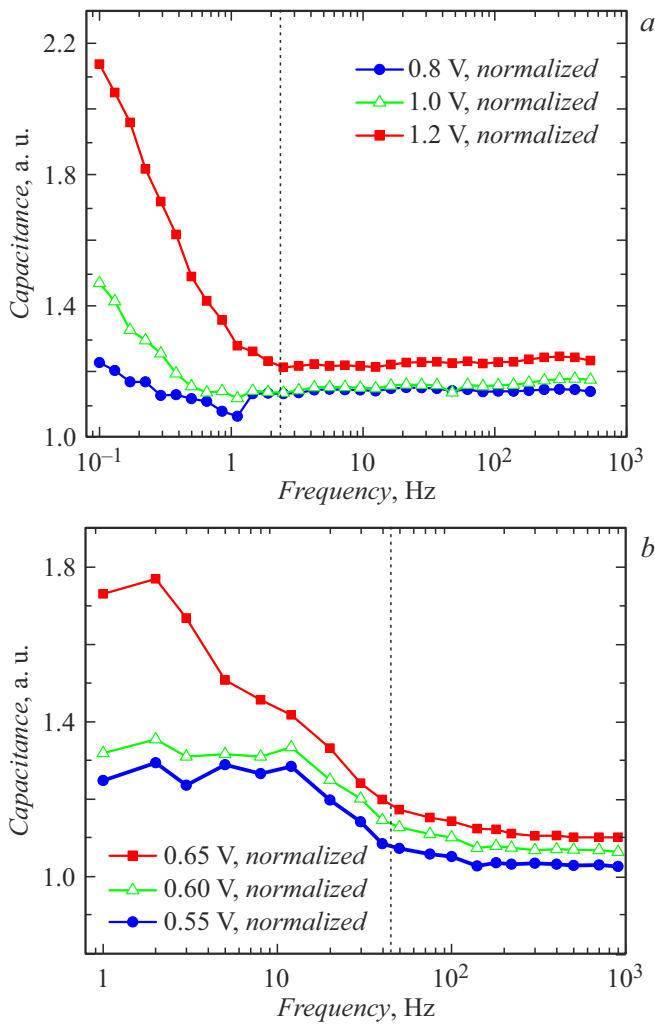


Figure 2. Experimental frequency dependences of capacitance at different voltages applied to the graphene interface with water [11] (a) and one-molar sulfuric acid solution [1] (b) after normalization to the capacitance measured in the mentioned studies near the Dirac point. Dotted lines indicate the capacitance relaxation times at these electrochemical interfaces.

defined as [9]:

$$C_q \approx (2e^3 V_{ch}) / (\pi \hbar^2 v_F^2),$$

where $\hbar$ is the Planck's constant, e is the electron charge, $v_F \approx c/300$ is the Fermi velocity of Dirac electrons, c is the speed of light, V_{ch} is the potential applied to graphene. Thereat, the τ values are determined by the times of Dirac cone filling or emptying which are necessary for the system to vary C_q with varying level of graphene electrochemical potential under the field effect. The model for field effect in semiconductor field-effect transistors [14,15] conventionally implies controlling the charge carrier density in semiconductors by varying the gate charge density so as to compensate for the semiconductor space charge. In this model for the graphene electrochemical interface, we consider a similar mechanism for controlling the graphene charge carrier

density by creating the interface molecular charged nanostructures that compensate for graphene charge carriers. This compensation makes the charge accumulated in graphene equal in magnitude to the molecular charge accumulated at the graphene electrochemical interface. Note that electron transfer between graphene and water molecules is typically almost fully impossible, since this interface forms with carbon a blocking contact [16]. Despite the authors of [1] assumed the substantiality of pseudocapacitive reactions at the electrochemical interface with graphene nanoribbons, the statement about the blocking contact is largely confirmed for this case as well. Their experiment exhibited in the low-frequency region a significant excess of capacitance over pseudocapacitance (up to 6 times at 1 Hz) (see Fig. 3E in [1]). Note also that the actual excess of electrostatic capacitance over pseudocapacitance is probably even greater due to the C_{dl0} underestimation caused by incomplete charging of C_{dl0} over the voltage period in the frequency range under study. Therefore, in our model we neglect, as a first approximation, the Faradaic processes and pseudocapacitance and use the equivalent circuit for C_{int} given in Fig. 1. Note also that in graphene under study the concentration of defects and impurities which could affect the capacitance [17] is quite low (about $5 \cdot 10^{10} \text{ cm}^{-2}$) [18]. Probably, additional charge carriers emerge under the field effect as a result of their transport from ohmic metal contacts on graphene in the process of charging the interface capacitance. Under the considered conditions, no significant hysteresis effects were observed; therefore, in this paper we consider the case of electrostatic interaction between charge carriers in graphene and molecular charges at its interface without taking into account any chemical or quasi-chemical bonds between them [18,19]. Thus, the model explains the voltage dependence of C_{int} by that of C_q . At the same time, due to the field effect, temporal dynamics of voltage-dependent C_{int} is defined by temporal dynamics of C_{dl} because of typically longer relaxation times of the processes of molecular charge accumulation (Figs. 1, 3, a and b), which are longer than relaxation times of electronic processes taking place in filling or emptying the Dirac cone in graphene in case compensation for the charge accumulated in the interface were arbitrarily rapid. The frequency dependence of C_{dl} has been extensively studied for non-graphene electrodes. Traditionally, they exhibited a C_{dl} increase with decreasing frequency (see, e.g., [20]), which corresponds to a more complete C_{dl0} charging over a longer voltage period.

In the case of interface between graphene and deionized water, the water pH is 7, hydrogen ion concentration is 10^{-7} mol/l , and ion content in the near-graphene water H^+ is insufficient to form a double layer with the interface molecular charge density of about $5.6 \cdot 10^{13} \text{ cm}^{-2}$ (this estimate was obtained for the typical value $C_{dl} \approx 9 \mu\text{F/cm}^2$ [3] and voltage of about 1 V). When the double layer is formed at the graphene/water electrochemical interface, the positively charged hydrogen part of the polarized water molecule is located closer to the negatively charged

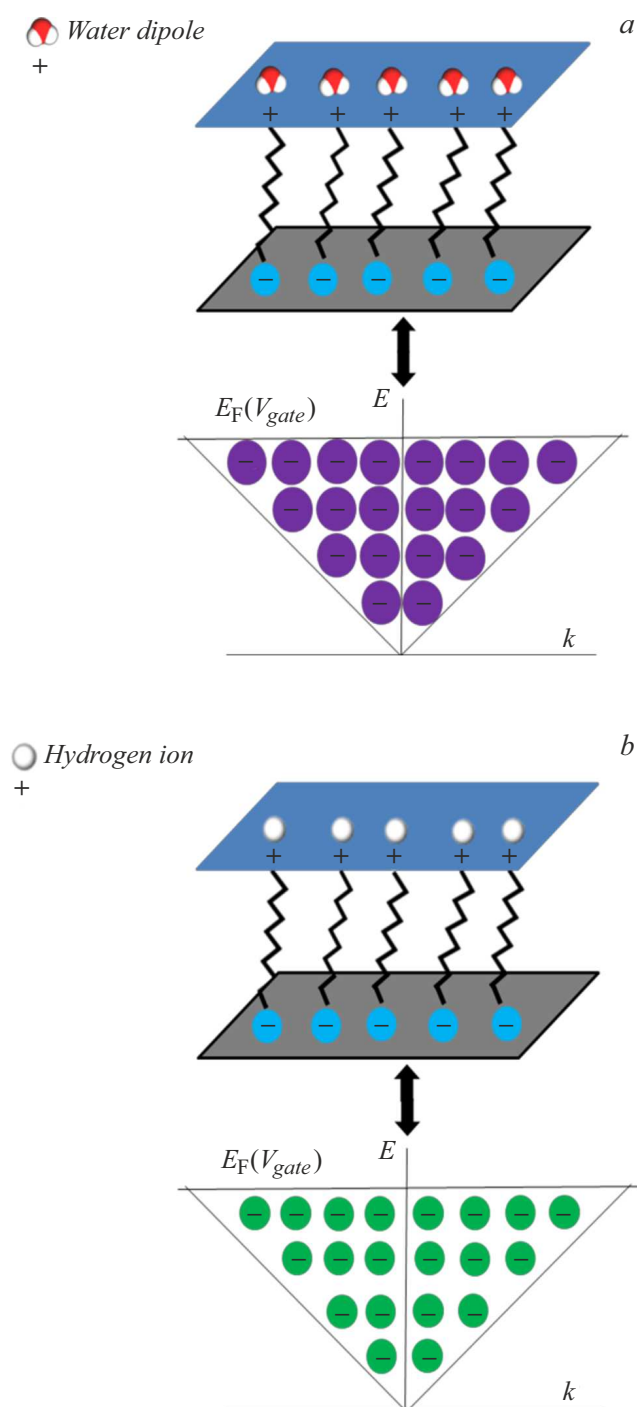


Figure 3. Schematic representation of the graphene electrochemical interface with water (a) and aqueous solution of sulfuric acid (b) under the field effect. Schematic images of relevant Dirac cones are also presented.

graphene electrode than the negatively charged part of the water molecule. Therefore, it seems natural that the graphene π -electrons are at least partially compensated by the positive part of such molecules; so, the field effect gets realized. In this case, the main type of molecules involved in creating the field effect are water molecule dipoles about

18 a.m.u. in mass (Fig. 3, a). At the same time, in the case of the graphene interface with one-molar aqueous solution of sulfuric acid, the H^+ ion concentration upon complete dissociation is approximately $2 \cdot 10^7$ times higher than in water. This makes possible realization of the field effect on the graphene electrode due to electrostatic compensation of the electron charge in graphene by hydrogen ions H^+ about 1 a.m.u. in mass (Fig. 3, b).

The time it takes for the interface molecular nanostructures to be restructured generally depends on the type of molecules they consist of, concentration of these molecules, and other solution parameters whose determination is often an important practical task. Therefore, measuring τ is a promising way of creating new graphene-based molecular sensors capable of detecting ions H^+ and other molecular ions involved in the double layer formation in electrolytes.

In the course of further studies by low-frequency impedance spectroscopy, it will be necessary to establish the area of applicability of the analyzed effects in view of both the possibility of using various types of graphene and related nanostructures, and sensory response for various chemical and biological solutions. The results of this study are important to be considered in designing next-generation capacitors, batteries, and chemical or biological sensors.

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Conflict of interests

The authors declare that they have no conflict of interests.

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