



Power law for frequency-dependence of double layer capacitance of graphene flakes



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ABSTRACT

The double layer capacitance per weight of graphene (GN) flakes in aqueous solution at the polarized potential increases with a decrease in the ac-frequency, obeying the inverse of the power law of the frequency. The power law is demonstrated to be equivalent to the constant phase element. The frequency-dependence increases with the thickness of the GN films. Thus, the lower the frequency and the thinner the film is, the larger is the capacitance density per weight. This is confirmed by cyclic voltammetry for several thickness of GN films and several scan rates. Resistance-like voltammograms at thick films are caused by frequency-dispersion. The overall capacitive properties of the GN films are as follows: the thickness of one GN flake is estimated to be 2 nm in average from the comparison of the thickness with the capacitances at the HOPG, which is consistent with values by the STM and AFM images.

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1. Introduction

Carbon powder has been used as stacked electrode materials, which include carbon nanotubes, carbon nano fibers, and graphene powder. These materials have been explored for candidates of supercapacitors. Thicker carbon films obviously enhance the capacitance. They also increase frequency-dependence of their capacitors [1,2], because the dependence is generally exhibited more strongly at electrodes with surface roughness of fractal dimension [3–10], with high porosity [11–13], heterogeneous distributions of current density [14–17], inhomogeneous adsorption [18], and inhomogeneous coating materials [19,20]. The common reason for the frequency dependence is heterogeneity of electrodes. Since the capacitance varies with both thickness and frequency complicatedly, it is not easy to predict capacitance values *a priori*. It is of interest to find a general rule of governing them in the context of thickness and frequency. First of all, we discuss the general behavior of the frequency dependence in the light of the impedance measurements.

The frequency dependence has been interpreted as distribution of various time constants of double layer capacitors [21]. A traditional equivalent circuit for the double layer impedance is an ideal capacitor, which is connected in series with the solution resistance [22]. The circuit in series should yield a vertical line in a Nyquist plot [23,24], whereas the Nyquist plots of real double layer capacitances have frequently provided lines with slopes less than 10 [25]. The

non-vertical line has been modeled by the so-called constant phase element (CPE) [26–30]. The impedance of the CPE, Z_{CPE} , is expressed by the power α , ranging from 0 to 1, of a complex impedance. i.e.

$$Z_{CPE} = 1/(Q(i\omega)^\alpha) = \{\cos(\pi\alpha/2) - i \sin(\pi\alpha/2)\}/(Q\omega^\alpha) \quad (1)$$

where ω is angular velocity of applied ac-voltage, and Q is a constant. The slope of the line in the Nyquist plot is $\tan(\pi\alpha/2)$. The CPE can reproduce experimental results well, but does not explain any origin of physicochemical phenomena such as frequency-dispersion and adsorption [31]. The data analysis by the CPE is close to the analysis with a frequency-independent phase angle different from 90° [28].

We have explained Eq. (1) as an inevitable result of the frequency-dispersion [25,32–34], as follows. The time-derivative of the double layer charge q , i.e. $I = dq/dt$, at the capacitance, C , for the applied voltage $V = V_0 \exp(i\omega t)$ is given by

$$I = \frac{d(C(\omega)V(t))}{dt} = C(\omega) \frac{dV(t)}{dt} + V(t) \frac{dC(t)}{dt} \quad (2)$$

Values of dC/dt are not conventionally available, but those of $dC/d\omega$ are readily available. Since $\omega = t^{-1}$, we have

$$\frac{dC(t)}{dt} = \frac{dC}{d(1/t)} \frac{d(1/t)}{dt} = -t^{-2} \frac{dC}{d\omega} \quad (3)$$

Consequently, Eq. (2) can be rewritten as

$$I = i\omega CV - t^{-2} V \frac{dC}{d\omega} = \left(i\omega C - \omega^2 \frac{dC}{d\omega} \right) V \quad (4)$$

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The admittance in Eq. (4), $i\omega CV - \omega^2(dC/d\omega)$, is the sum of the out-of-phase component and the in-phase component. Hence the equivalent circuit can be expressed in terms of a parallel combination of C (defined as C_p) and the resistance ($-\omega^{-2}/(dC/d\omega) = R_p$). The parallel combination of the double layer has been introduced by Bockris et al. [35] in order to explain dielectric relaxation. It has been verified experimentally by changing solution resistance [25] as well as fitting experimental results [19]. The parallel resistance R_p , depending on frequency, has been demonstrated to have surface properties in that it does not only vary with distance between two electrodes [32], with salt concentrations [33], or kinds of solvents [25], but also it is inversely proportional to the area of electrode surfaces [33]. The double layer capacitance, C_d , conventionally observed can be then expressed as

$$i\omega C_d = 1/R_p + i\omega C_p \quad (5)$$

This is nothing but the admittance ($1/Z$) of the conventionally observed double layer impedance, Z . The relations between Eqs. (1) and (5) are

$$|Q\omega^\alpha| = \sqrt{R_p^{-2} + \omega^2 C_p^2} = \omega \sqrt{(f(dC_p/df))^2 + C_p^2} \quad (6)$$

$$\tan(\pi\alpha/2) = \omega C_p R_p = -C_p / \{f(dC_p/df)\} \quad (7)$$

where R_p was replaced on the right-hand sides by $-\omega^{-2}/(dC/d\omega)$. Since C_p has a linear relation with $\log f$ [25,32,33], the term $(dC_p/df)f$ is almost constant. Then α can be determined unequivocally through Eq. (7). The correspondence of the CPE to the frequency-dependence in Eqs. (6) and (7) indicates that the CPE behavior should result quantitatively from the frequency-dispersion.

The above quantitative interpretation of the CPE does not elucidate a physical meaning of the frequency-dispersion. It is not easy to evaluate domain size of heterogeneity although few attempts have been reported on local electrochemical impedance spectroscopy [36–38]. Since the frequency-dependence at highly oriented pyrolytic graphite (HOPG) electrode is less than that at polycrystalline platinum electrodes [32,39], the domain size of heterogeneity may be of the order of magnitude of roughness or grain of polycrystalline surface.

When conducting powder-like materials are accumulated on an electrode as in supercapacitors, the heterogeneity may increase to enlarge the CPE effect, or to decrease α . Since the capacitance is given by $Q/\omega^{1-\alpha}$ from Eq. (1), the enlarged CPE effect decreases the capacitance values with an increase in the frequency. Consequently, values of the capacitances should be specified by not only values of α but also the frequency or the time to be used for measurements. This report aims at finding an empirical rule of dependence of the capacitances made of graphene (GN) flakes on frequency and GN thickness.

2. Experimental

Water was distilled and then was ion-exchanged by a ultrapure water system, CPW-100 (Advantec, Tokyo). All the chemicals were of analytical grade. Graphite powder (98%, 7 μm in average diameter) was purchased from Ito Koken (Mie, Japan), and was used as received. HOPG was purchased from Bruker Corp. Before each voltammetric run and coating processes for the electrodes, the HOPG surface was exfoliated with adhesive tape.

The suspension of graphite oxide (GO) was prepared according to the Hummers method [40]. Removal of salt from the suspension was made by centrifugation with a cooling centrifuge (Tomy, Tokyo) at the maximum, 10,600g and by dispersion in pure water. The centrifugation and the dispersion were iterated three times. An aliquot of the purified suspension was dried and weighed to determine the weight concentration. A GO suspension of 100 mm^3 with

a known concentration was dropped on the exfoliated HOPG plate ($12 \times 12 \text{ mm}^2$), and was dried in an oven at 60 $^\circ\text{C}$ for one hour. The dried GO film was reduced chemically with 0.2 M (=mol dm^{-3}) hydrazine monohydrate aqueous solution in a vessel kept at 90 $^\circ\text{C}$ for one hour [41] to yield the GN film. The reduced film was rinsed with water. Two GO- and two GN-coated HOPG plates were prepared simultaneously. They were faced each other with the space of ca 5 mm, supported with a rubber block. 0.5 M KCl solution was filled into the space, as shown in Fig. 1(A).

Density of the dried GN, ρ , was determined by means of pycnometry, which was used for evaluating the density of swollen polyacrylic latex particles [42]. The method was to obtain weights of a ca 50 cm^3 dried pycnometer (m_0) and that (m_w) of the pycnometer into which water was filled. The difference divided by the density of water, $\rho_w = 0.997 \text{ g cm}^{-3}$, is the volume of the pycnometer at 25 $^\circ\text{C}$. The suspension of GN, which was deionized by centrifugation, was filled in the pycnometer, and weighed (m_s). The pycnometer filled with the suspension was dried at 90 $^\circ\text{C}$ in an oven for one day, was cooled to the room temperature, and weighed (m_{sd}). Then the volume of the pycnometer can be represented by the two ways:

$$V = \frac{m_w - m_0}{\rho_w} = \frac{m_s - m_{sd}}{\rho_w} + \frac{m_{sd} - m_0}{\rho} \quad (8)$$

Then ρ is given by

$$\frac{\rho}{\rho_w} = \frac{m_{sd} - m_0}{m_w - m_0 - m_s + m_{sd}} \quad (9)$$

The four weights were obtained reproducibly with the digit of mg. Then we had $\rho = 1.29 \pm 0.01 \text{ g cm}^{-3}$. We applied the above method to the GO suspension to evaluate the density of dried GO. It was $1.26 \pm 0.03 \text{ g cm}^{-3}$. Both densities are almost the same within errors. According to the thermogravimetry previously made [43], the GN flakes contain graphite oxide inside.

A drop of 0.5 M KCl solution was inserted into two GO- or GN-coated plates. The contact area of the KCl drop was evaluated from photographs, on the basis of which Fig. 1(A) was drawn. The difference in the shape of the menisci for the GO and GN supports higher hydrophobicity of GN than GO. The thickness of the film was calculated from the added volume of the GO suspension with the known weight concentration, the area of the electrode in contact with the solution, and the densities.

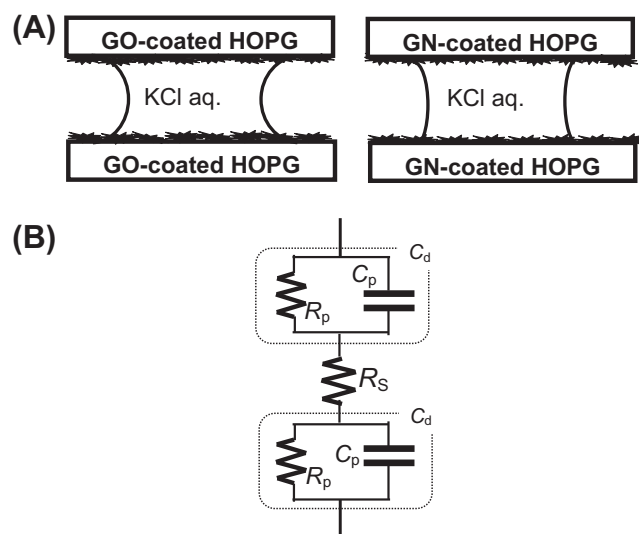


Fig. 1. Cell structure for ac-impedance measurements (A), and its equivalent circuit (B).

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