

ELECTRONIC SUPPLEMENTARY INFORMATION

The mesoscopic behaviour of multi-layered graphene: the meaning of supercapacitance revisited

Fabiana A. Gutierrez,^{a,b} Flavio C. Bedatty Fernandes^a, Gustavo A. Rivas^b and Paulo R. Bueno^{a†}

^a Instituto de Química, Univ. Estadual Paulista (UNESP), Departamento de Físico-Química, Nanobionics Research Group (www.nanobionics.pro.br), Araraquara, São Paulo, Brazil.

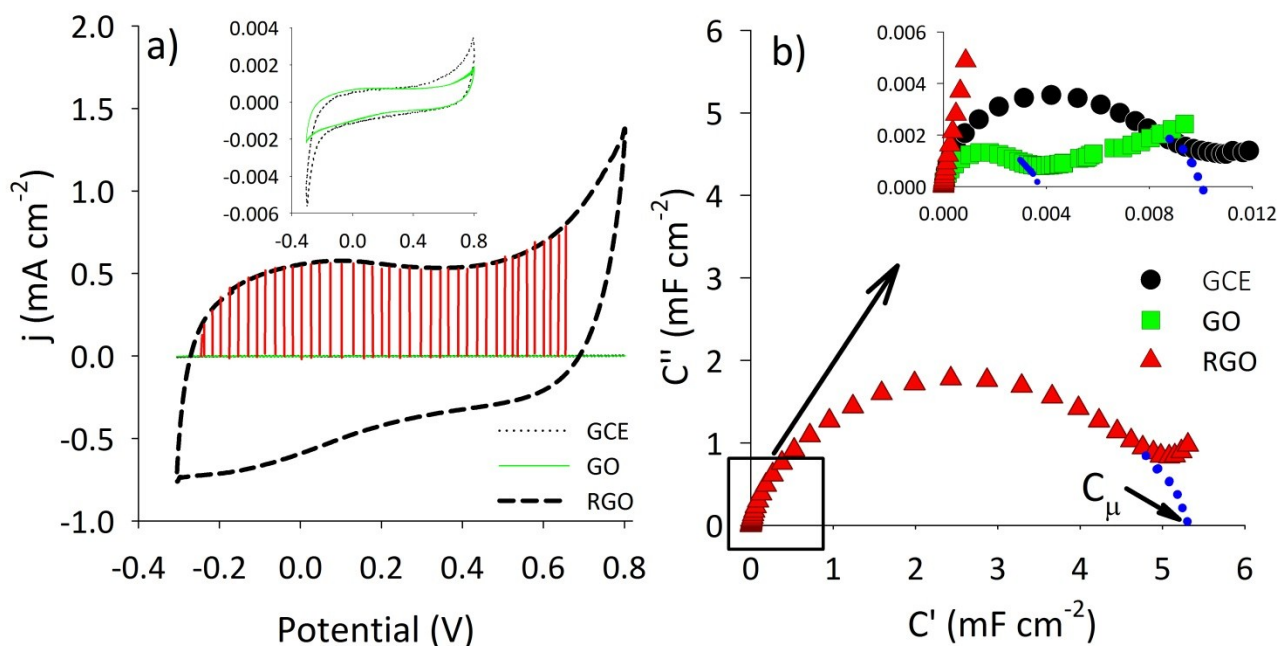
^b Instituto de Investigaciones en Físico-química de Córdoba, Universidad Nacional de Córdoba, Facultad de Ciencias Químicas, Córdoba, Argentina.

†Corresponding author, e-mail: prbueno@iq.unesp.br.

SUPPLEMENTARY INFORMATION

SI.1. Cyclic voltammetry (CV) and Electrochemical Capacitance Spectroscopy (ECS)

As can be observed in Figure SI-1 and Table 1 the experimental capacitance obtained from CV and ECS approaches are equivalent in magnitude within experimental errors. This confirms that contributions from non-faradaic effects (double-layer capacitance) are minima in RGO. Hence the obtained capacitance is mainly governed by charging electronic density-of-states existing in the reduced graphene compounds. This can be equivalently confirmed when we compare the charging relaxations of RGO and GO in Figure SI-2.



SI-1. (a) CV curves of the bare GCE (black dotted line), GCE/GO (green solid line) and GCE/RGO (black dashed line) in aqueous electrolyte of 50 mM PBS at a scan rate of 0.1 V s⁻¹. The inset shows the bare GCE (black) and GCE/GO junction (green) responses.

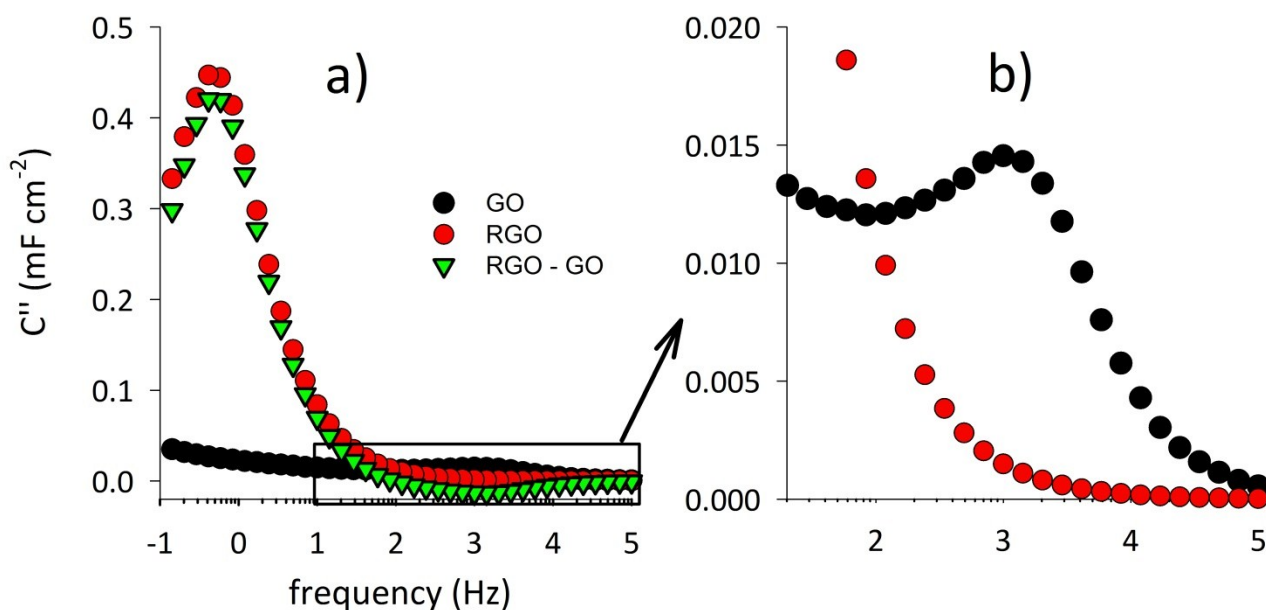
ELECTRONIC SUPPLEMENTARY INFORMATION

The values of capacitance were found as $10.2 \mu\text{F cm}^{-2}$ and $6.4 \mu\text{F cm}^{-2}$ for GCE and GO, respectively, and it increased to $5230 \mu\text{F cm}^{-2}$ after formation of RGO (640 fold-higher). All values as shown in Table SI-1 were calculated by the integration of the graphical area obtained by the current *versus* potential ($i \times V$) as illustrated by the red hachured area (defining the potential range used to calculate the capacitances). (b) Typical capacitive Nyquist diagrams obtained for GCE (●), GO (■), and RGO (▲) in aqueous electrolyte of 50 mM PBS. Note that (b) was constructed by converting impedance into capacitance as explained in the main text. The impedance spectra (EIS) were obtained in frequencies ranging from 1 MHz down to 1 mHz with an amplitude of 10 mV (peak to peak), all acquired at potential a stationary potential of 0 V (with respect to Ag|AgCl electrochemical reference electrode) where molecular (quantum) capacitance of graphene is expected to be maximal. Inset in (b) shows GCE, GO, and RGO behavior at higher frequencies. The value of capacitance was obtained as the diameter of the semicircle as illustrated by the blue dotted line. Please note that for GCE and GO, the value of capacitance refers only to the ordinary double layer capacitance phenomenology whereas the electrochemical capacitance (C_{μ}^{-}) concept is only pertinent to material with accessible electronic states as RGO, wherein quantum or mesoscopic effects exists. Thus, GCE, GO and RGO surfaces showed values of capacitance of $10.1 \mu\text{F cm}^{-2}$, $3.8 \mu\text{F cm}^{-2}$ and $5300 \mu\text{F cm}^{-2}$, respectively, the same value (within experimental errors) observed to those obtained by CV.

SI -Table 1. The capacitance values obtained by CV and ECS approach for bare GCE surface, GO and RGO. The GO and RGO were constructed from 0.5 mg mL^{-1} GO solution.

	Capacitance by CV (mF cm ⁻²)	Capacitance by ECS (mF cm ⁻²)
GCE	$(10.2 \pm 1.2) \times 10^{-3}$	$(10.1 \pm 0.2) \times 10^{-3}$
GO	$(6.4 \pm 0.8) \times 10^{-3}$	$(3.8 \pm 0.01) \times 10^{-3}$
RGO	5.2 ± 0.7	5.3 ± 0.3

SI.2. Analysis of charging relaxations in graphene compounds by ECS



SI-2. (a) Bode diagram comprising imaginary component of complex capacitance (C'') versus logarithm of frequency for GO (●), RGO (●) and the subtraction of RGO and RO (▼). The GO and RGO films were shown here were constructed from a GO solution at 0.01 mg mL^{-1} (diluted 50 times regarding to the solution used to construct the GO and RGO films showed in the main text even through

ELECTRONIC SUPPLEMENTARY INFORMATION

demonstrating the spectroscopic capability of the ECS approach). All measurements were taken in aqueous electrolyte of 50 mM PBS. (b) Inset of indicated part in (a), demonstrating that the relaxation of process of GO is much lower in magnitude than that observed by RGO. The impedance spectra (EIS) were obtained with frequency ranging from 1 MHz down to 1 mHz with an amplitude of 10 mV (peak to peak), all acquired at potential a stationary potential of 0.0 V (with respect to Ag|AgCl electrochemical reference electrode) where molecular (quantum) capacitance of graphene is expected to be maximal and then converted to capacitance. Inset in (a) and (b) shows GO, RGO and RGO-GO at high frequency.

Figure SI-2 similarly to Figure 1, as introduced in the main text, demonstrate that the relaxations associated with charging the electronic and non-faradaic surface states of graphene are different not only in magnitude, but also in timescale. For GO the charging relaxation occurs about 1 kHz meanwhile for RGO it occurs about 1 Hz. Furthermore, the capacitance related to GO relaxation process is of the same magnitude of that observed for GCE as shown in Table SI-1 and both are minimal compared to that observed for RGO. Because of that, when using GO as the background signal, and by subtracting the GO from RGO signal, the effect is minimal to the capacitance or relaxation [see Figure SI-2 (a)]. The RGO and GO signals are decoupled and the contribution of RGO electronic charging relaxation is dominant. In summary, the capacitive phenomenon occurring in RGO is electrochemical in essence (predominantly quantum) and explained by the physical meaning within electrochemical capacitance.

SI.3. Kramers-Kronig test of complex spectroscopic data

The Kronig-Kramers (KK) test can be used to check whether the measured system is stable in time and linear. Although we have not applied equivalent circuit analysis in the present manuscript, the stability and linearity are a prerequisite for fitting complex impedance data to equivalent circuits. If the system changes in time, the data points measured on the beginning of the experiment do not agree with those measured at the end of the experiment. Since stability problems are most likely to be observed in lower frequencies, the implementation of electrochemical impedance spectroscopy usually involves scanning from high to lower frequencies.

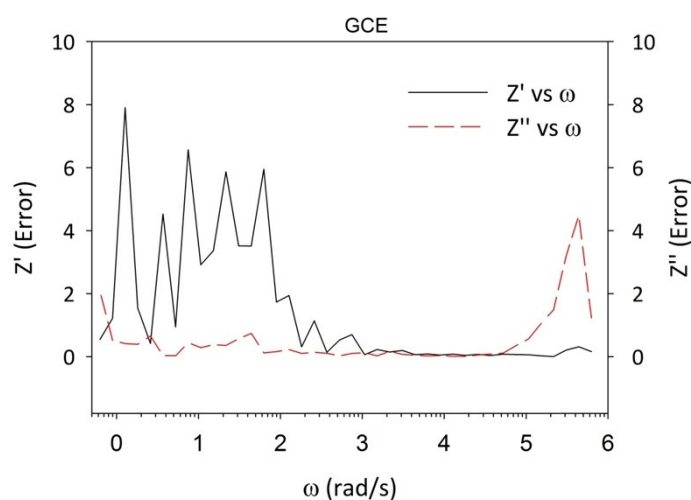
The result of the KK test is the value of pseudo, χ_{ps}^2 , the sum of squares of the relative residuals. In each case the χ^2 for the real and the imaginary part is reported (overall χ^2 is a sum of real and imaginary χ^2). Large χ^2 values indicate that the data quality is low. A small value, on the other hand, usually indicates a good fit.

$$\chi_{ps}^2 = \sum_{i=1}^N \frac{[Z_{re,i} - Z_{re}(\omega_i)]^2 + [Z_{im,i} - Z_{im}(\omega_i)]^2}{|Z(\omega_i)|}$$

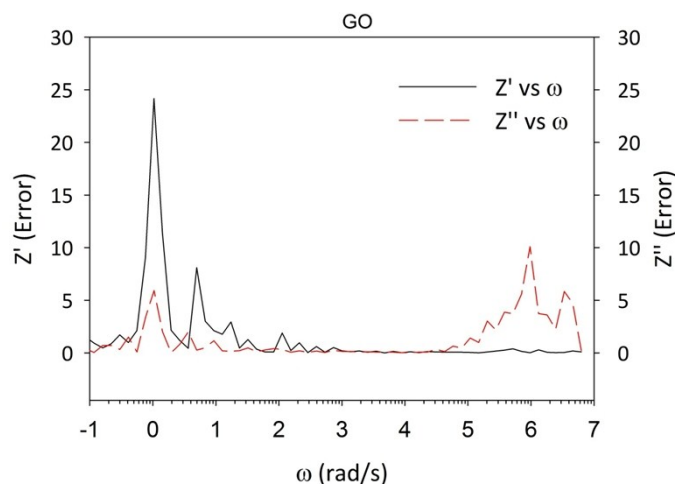
$$\chi_{re}^2 = \sum_{i=1}^N \frac{[Z_{re,i} - Z_{re}(\omega_i)]^2}{|Z(\omega_i)|} \quad \chi_{im}^2 = \sum_{i=1}^N \frac{[Z_{im,i} - Z_{im}(\omega_i)]^2}{|Z(\omega_i)|}$$

ELECTRONIC SUPPLEMENTARY INFORMATION

Nonetheless, what is actually large and small depends on the number and the value of data points. As a rule of thumb, values lower than 10^{-6} usually means an excellent fit, reasonable between 10^{-5} and 10^{-6} , marginal between 10^{-4} and 10^{-5} and bad for even higher values. Moreover, the residuals should be small and randomly distributed around zero. In the Figures SI-3, SI-4 and SI-5 we showed the KK tests obtained for GCE, GO and RGO, respectively, associated with EIS/ECS data presented in the main manuscript. The measurements on GCE showed residual values of χ^2 for $|Z|$, Z' and Z'' between 1.2 to 2.9×10^{-5} (reasonable fits) while values between 0.9 to 1.9×10^{-5} (also reasonable) were found to GO surface. Concerning RGO the KK tests were excellent with values for $|Z|$, Z' and Z'' between 4.0 to 8.8×10^{-6} .

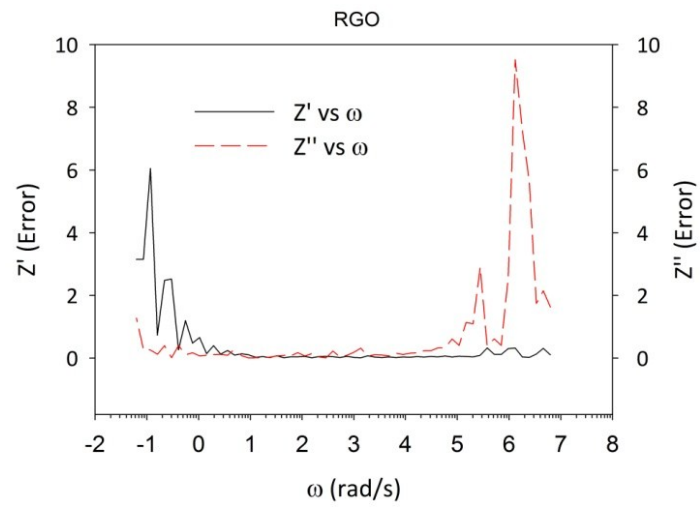


SI-3. KK test for GCE surface.



SI-4. KK test for GO surface.

ELECTRONIC SUPPLEMENTARY INFORMATION



SI-5. KK test for electrochemical (RGO) surface.