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Mesoscopic behaviour of multi-layered graphene: the meaning of supercapacitance revisited

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The electronic density of states and its contribution to the capacitance of graphene compounds (oxidized and reduced) were investigated using an electrochemical impedance-derived capacitance spectroscopic approach. It is clearly demonstrated that graphene oxide, which is known to exhibit semiconductor electronic characteristics, has little influence on the magnitude of the measured capacitance. Moreover, when graphene oxide is electrochemically reduced to graphene, the capacitance increases dramatically by about three orders of magnitude (from microfaradays to millifaradays). This increased capacitive effect has been interpreted as being directly associated with the electrochemical non-faradaic (super- or ultracapacitive) characteristics of the interface (i.e. associated with its electroactive area, for instance). The results obtained and interpretation made in this work demonstrate that the magnitude of the measured capacitance is a consequence of an electrochemical capacitive phenomenon (mesoscopic in essence; thus, the associated capacitance is equivalently termed mesoscopic capacitance) that energetically contains, in series, both electrostatic (geometrical) and quantum effects, thus being essentially different from those exclusively related to the amount of existing interfacial sites for ions (i.e. beyond those associated with pure double-layer capacitive effects). Conceptually, it is proposed that the mesoscopic capacitance of reduced graphene can be explained mainly through quantum chemical effects, ultimately following first-principles quantum mechanics supported on density functional theory, wherein the density of states is central.

Introduction

Graphene is one of the most intriguing molecular compounds, with its electron mobility being well known for its importance in electronic applications.1–15 The electron mobility of graphene is largely dependent on the electron scattering associated with charge impurities and other chemical inhomogeneities.1–6 Accordingly, graphene and its derivative compounds have been the subject of enormous research growth in the past few years.11–12 Control of the electron transport properties of graphene is critical for many applications; however, this is not the only important electrical characteristic exploited in recent research, albeit the most investigated.1–15 Another relevant electrical and also molecular-related property of graphene is associated with its energy storage capability,15–17 clearly allied to its molecular capacitive nature, which allows its application as, for instance, a low-cost supercapacitor.18 Indeed, by virtue of these intriguing properties, graphene holds great promise in many fields, such as analytical chemistry, electrochemical energy storage devices,19–22 chemical sensors,23 biosensors24, 25 and, generally, in medicine26, 27 and engineering.28, 29 For example, graphene has been widely used in recent years for the design and development of electrochemical sensors30, 31 and biosensors32–35 because of other (morphological) intrinsic properties such as a large surface-to-volume ratio. This, combined with the high conductivity and electron mobility at room temperature, allows graphene to exhibit excellent chemical tunability and biocompatibility. In combination with the higher density of edge plane sites, the large surface-to-volume ratio confers properties to graphene that turns this carbonaceous material into an excellent candidate for use as an electroactive material and working electrochemical electrode in the fabrication of sensitive electrochemical biosensors.36–39

Three-dimensional graphene-based architectures, such as hydrogels, aerogels, foams, and sponges, have attracted much attention owing to the combination of the structural interconnectivities and the outstanding electrical properties of graphene. The morphological characteristics of 3D graphene—low mass density, high porosity, and large surface area—are widely used in electronic industrial applications. These stable mechanical properties, once associated with fast ion and electron transport properties,
make graphene largely applicable industrially at low fabrication cost.

Amongst microelectronic applications, graphene has also been applied in the fabrication of transistors, which are now being considered an important alternative for post-silicon electronics,\(^\text{48}\) wherein tunnel field effect transistors (FETs) and bilayer pseudo-spin FETs are necessary. The tunnel-FET approach has already been explored in silicon and carbon-nanotube metal-oxide semiconductor FETs (MOSFETs)\(^\text{41, 42}\) and investigated on nanoribbons and bilayer graphene nanoscale structures.\(^\text{43}\) These devices have gained considerable attention in electron-device research. The bilayer pseudo-spin FET consists of a vertical stack of two graphene layers separated by a thin dielectric; under certain bias conditions, the tunnelling resistance of the bilayer pseudo-spin FET might be able to deliver fast and ultralow-power logic operation.

Notwithstanding the countless possibilities for electronics applications of this material, many details about the potential performance of graphene as a component of transistors in real-world applications remain unclear.\(^\text{44}\) Owing to its unique and extraordinary electronic properties, it has been speculated that graphene can carry a super-current,\(^\text{45}\) and it is clear that its rates are superior to those of graphite and carbon nanotubes. One ignored or neglected fact is that the outstanding electron transport properties of graphene are intrinsically associated with a large capacitance, which, from a classical mechanics point of view, is antagonistic with electron transport. Accordingly, although there are many reviews on the properties and applications of graphene,\(^\text{33, 36, 46, 47}\) only a few connect its intrinsic characteristics with its outstanding capability for energy storage.\(^\text{22, 60}\)

An exception to commonly studied subjects is the work recently conducted by Tao et al.\(^\text{48}\), who reported that graphene has a quantum capacitance magnitude that had not previously been generally considered. This study reports a direct measurement of the quantum capacitance of graphene (single and bilayer samples) as a function of the gate potential. The study findings emphasize the importance of charged impurities for both mobility and quantum capacitance, and indicate that quantum capacitance is the origin of the puzzling interfacial capacitance behaviour observed in carbon-based electrodes.

The focus of the present work is to evaluate the origin of molecular supercapacitance of electrochemically modified graphene and its correlations with quantum capacitance (thus, revisiting the origin of supercapacitance in multilayered graphene) using an electrochemical impedance-derived spectroscopic approach (i.e. a time-dependent technique). A theoretical background is provided in the following section.

![Figure 1](image)

**Figure 1.** A clear separation of faradaic and non-faradaic capacitive responses in electroactive monolayers (or mesoscopic systems) can be observed using electrochemical capacitance spectroscopy. (a, b) Body and Nyquist capacitive diagrams. Non-faradaic contributions (black) are obtained outside of faradaic windows (where only non-faradaic phenomena operate); when the electrochemical potential is poised at faradaic windows (precisely at the formal potential of the system) both faradaic and non-faradaic contributions exist (red). By using non-faradaic contributions as the background signal of this methodology, it is possible to subtract the red
Theoretical background

Time-dependent electrical measurements

Dielectric spectroscopy is derived from impedance spectroscopy, \( C^*(\omega) = (\omega C_0)^{-1} \) is the complex capacitance. Note that \( j = \sqrt{-1} \) is the imaginary unit. Dielectric spectroscopy is mainly applicable in solid-state systems so that dielectric spectroscopy is based on the conversion of this complex capacitance \( C^*(\omega) \) into a dielectric complex function, such as \( \varepsilon^*(\omega) = C^*(\omega)/C_0 \). \( C_0 \) is a constant geometric factor \( (e_0 A/L) \), referred to as the capacitance of the empty cell, where \( e_0 = 8.85 \times 10^{-12} \text{ F m}^{-1} \) is the dielectric permittivity of the empty space, \( L \) is the length separating the electrodes, and \( A \) is the area of the electrode.

Therefore, \( C_0 \) only depends on geometric factors applied during the measurements and follows the experimental setup that delineates the adopted cell's geometry. In general, the impedance and capacitance complex functions are just one form of a more general terminology known as immitance (complex functions). Accordingly, all of these functions are associated with particular classes of immitance spectroscopy (impedance, capacitance, modulus, etc.). Historically, because the complex impedance function is the most used, all other imittance spectroscopies are said to be impedance-based methods.

When the studied system is electrochemical in essence, there is an electrochemical potentiostatic control of the external potential; thus, when it is used specifically for electrochemical systems, impedance spectroscopy is termed electrochemical impedance spectroscopy. Nonetheless, in electrochemistry, the cell's geometry is difficult to determine, especially in those cases in which the electroactive material, assembled over the working electrode, is mesoscopic in essence, i.e., in which a geometric factor cannot be established or determined precisely. Given this situation, our research group has proposed that the complex capacitance function is a useful approach in studying electrochemical systems, and we have referred to this approach as electrochemical capacitance spectroscopy (ECS). Note that ECS is comparable to dielectric spectroscopy, but applied to electrochemical mesoscopic systems, where the geometrical factor of the working electrode or electroactive material cannot be established.

For instance, when ECS is applied to investigate monolayers of electroactive proteins assembled over gold electrodes, precise establishment of the geometric factor is challenging. (What would be the electroactive area of a redox protein?)

In this situation, the applicability of the method is illustrated in Figure 1, which clearly shows the ability of the approach to separate both concomitant existing phenomena, electrochemical and non-electrochemical relaxations, spectroscopically. The electrochemical relaxation (associated with the transfer of an entire number of electrons; known as the faradaic phenomenon) is completely separable from the non-electrochemical relaxation (referred to as the non-faradaic phenomenon). This separation is obviously important in studying supercapacitance and pseudo-capacitive phenomena, as will be demonstrated herein.

Associated with the faradaic relaxation (spectroscopically resolved, as shown in Figure 1) there is an associated intrinsic capacitance, termed the electrochemical (or redox) capacitance. The mesoscopic characteristic and physical meaning of this capacitance are supported by first-principle quantum mechanics analysis through conceptual density functional theory. Accordingly, ECS has been suitably used to determine the electrochemical capacitance of electrochemically active molecular layers directly associated with addressable quantum molecular states. Therefore, ECS is an impedance-derived spectroscopic (time- or frequency-dependent) method that allows measurement of the capacitance associated with molecular quantum states and mesoscopic electrochemical systems in general. Note that electrochemical systems are mesoscopic in essence. The mesoscopic term refers to those systems where the size scale is sufficiently low that quantum mechanical properties dominate over those properties predicted by the laws of classical mechanics, but where both operate concomitantly. For instance, ECS capacitance measurements have also been applied in the development of electroanalytical applications and biosensors, as well as in revealing and understanding the mesoscopic properties of molecular junctions, including the measurement of quantum conductance of double-stranded DNA nanowires.

Thus, ECS enables the investigation of widely known pseudo-capacitive phenomena occurring at electrochemical interfaces or molecular junctions that are composed of an electrode (serving as electron reservoir) and a given chemical compound (generally molecular) containing redox accessible states. The term pseudo-capacitance is generally identified within redox reactions (for instance occurring in lithium-ion batteries) and organic redox couples, such as those existing in redox capacitive biosensors and conducting organic polymers (also known as electroactive compounds). Although this term is well known in electrochemistry as an experimentially quantifiable capacitance (by ECS or transient electrochemical methods), it has no physical meaning supported in modern physics theories, that is, such as those based on first-principles quantum mechanics.
these contributions comes from an external electric potential (or gate potential) imposed on the system (for instance, the work done to charge the system electronically in the presence of fixed positively charged nuclei) and the other contribution comes from the energy associated with the electronic structure of the system, such as kinetic energy, and electron-electron interactions. The electrochemical capacitance is thus a capacitance that contains the contributions of the electrostatic potential and the energy involved with the charging of chemical structures (beyond electron gas-like structures, i.e. metallic structures). Consequently, it encompasses the electronic structure of the system, including the statistics of occupation of the energetic levels and sites for indistinguishable particles. In itself, the theory of electrochemical capacitance covers the theoretical background\textsuperscript{51, 52} for those terms largely referred as to pseudo-capacitance and supercapacitance. Therefore, the magnitude of the electrochemical capacitance depends on the characteristics of the density of states function and on the electroactive material to be charged and is directly associated with its electronic structure in the presence of an external electrostatic energy.

Therefore, we suggested that the pseudo-capacitance terminology be replaced by the more suitable term ‘electrochemical capacitance’ (wherein a fundamental physical mesoscopic theory exists).\textsuperscript{51, 52} To summarize, electrochemical capacitance is an equivalent capacitance that encompasses the classical energy associated with electrostatic forces (the electrostatic potential energy) and chemical forces (associated with thermodynamic potentials). These energies are associated, for instance, with the chemical potential of the system; involving all energies contained in the chemical system, i.e. beyond pure electrostatic charge separation. In summary, the term electrochemical capacitance applies to capacitive phenomena wherein both electrostatic and quantum contributions are present, energetically in an inseparable way, each contributing in series to this equivalent electrochemical capacitance [see Figure 4(c)].\textsuperscript{51, 55, 63}

**Charging electrochemical states**

The phenomenon of charging electrochemical states is intrinsically a time-dependent phenomenon because electrochemical currents are inherently dynamic, i.e. there are thermal time-dependent fluctuations of the electrochemical currents. Additionally, the currents can be time-dependent perturbed by an external applied voltage and, as such, this can be understood as electrical fields, induced through oscillating voltages at the electrode contact. The current response to the oscillating voltage perturbation is measured after a certain time of the perturbation. If quantum effects are present in the transport associated with the charging of quantum states, this time will be an RC characteristic time.
However, far from the classical point of view, the RC time contains corrections owing to the electron motion in the quantum states. We have recently demonstrated in two situations, for transport in DNA nanowires and for electroactive molecular layers, the latter comprising protein, ferrocenyl, and peptide molecular layers that this RC time characteristic of charging quantum states exists. In particular, as quantum effects are contained, the RC time dispersion depends on how the energetic states spread with the external electrostatic potential and the thermal bath wherein it is embedded (see Figure 2).\textsuperscript{54, 56} Obviously, the RC time dispersion controls the kinetics and dynamics of electron transfer and transport within this ensemble of mesoscopic RC time states (see Figure 2).

As an example, in Figure 2, we illustrate the effect of RC time dispersion caused by the variation of the external potential energy of the electronic structure associated with the molecular electroactive layers comprising ferrocenyl-hexanethiol monolayers self-assembled on gold electrodes. This external potential energy is defined as

$$U_N = \int \rho(\vec{r})V_N(\vec{r})d^2\vec{r}$$

where $V_N(\vec{r}) = -Ze/r$ is the potential of an electron at the spatial position $\vec{r}$, that is, the potential due to the electric field of the nucleus for the case of a nucleus centred at $\vec{r} = 0$ with $Ze$ charge, where $Z$ is a positive integer (the valence number), $e$ is the elementary charge, and $\Omega$ is the volume of the system.

It is clear that the energy $U_N$ can be altered by changing the dielectric constant of the solvent used to make the measurements. In Figure 2, these solvents are aqueous solvents with $\varepsilon_\text{aq} \approx 80$, acetonitrile with $\varepsilon_\text{an} \approx 40$, and dichloromethane with $\varepsilon_\text{dc} \approx 10$. It is important to note that the total density of electrochemical states is kept constant within experimental error (about $1.4 \times 10^{14}$ states cm$^{-2}$). This means that there is no variation of the number of electrochemistry states (or the number of ferrocene centres). In other words, the number of electrochemical states is constant during measurements and remains constant even after different measurements of the same molecularly modified electrode in the stated solvents.

The number of the states are calculated through integration of the Gaussian density of states shape $[N_N = 1/\varepsilon \int \varepsilon G_N(\Omega)dV]$, where $V$ is the potential of the electrode. Note that the Gaussian shapes are reversible, i.e. by swinging the electrode at different electrolyte environments, the density of states shape recovers the pattern formerly obtained (after a time for equilibration with the environment). This means that there is absolutely no influence of geometric factors on this observed phenomenon (since we are referring to the same physical-chemically modified electrode with the same surface and a total reversible behaviour in terms of the chemical electronic structure of these ensembles of ferrocene centres).

Moreover, because the total number of states is kept constant, the effect of the external potential energy (how electrons redistribute spatially around the nucleus of the atoms in the molecular layer), as stated in Equation (1), is only to redistribute the electronic cloud in this electroactive monolayer. As a result, $s$ different chemical potential $[\mu_i = (dE_i/d\rho_i)]$ for each solvent $i$ exists for the same molecular layer embedded into the $i$th solvent. According to density functional theory $E$ is the total energy, but at finite fixed temperature and pressure this accounts for the Gibbs free energy.

From the established classical point of view, the constant-phase-element-like behaviour (see legend of Figure 2) is purely associated with non-ideal capacitive characteristics. This is noted particularly by considering the Nyquist impedance diagram of Figure 2b, and is interpreted as changes to the geometric factor (when the double layer dominates) or changes due to a leak capacitive effect (when pseudo-capacitance is identified as the dominant phenomenon in the electroactive compounds). None of these phenomenological arguments is able to describe the experimental behaviour observed in Figure 2 so that sources of non-ideal electrochemical relaxations are not exclusively associated with a double-layer capacitance of the interface (or with the dielectric constant of the environment).

Accordingly, it should be noted, in Figure 2, that if only one particular energy level of the electrode, $eV$, is taken into account, for instance, the formal potential, i.e. $E_\text{F} = eV$, corresponding, in Figure 2(c), to the capacitance value associated with the peak, it would be noted that the capacitance is different there. This means that, for the same molecular compound, there are different capacitive values when the electrode is immersed in a different external potential energy. In terms of differential capacitance, this would correspond to a different numbers of states, but as we demonstrated, the number of states is constant. These observations are fully acceptable from a quantum mechanics point of view and are associated with changes in the density of states function and not with changes in, for instance, the electroactive area or assessable electrochemical states. The variational principle density functional theory, for example, states that there is a different $\mu_i$ for different external potential energy, but a unique value of $\mu_i$ exists under a fixed external potential energy.\textsuperscript{51, 52}

Furthermore, at the formal potential of the electrode (the centre of the density of states Gaussian curve), the capacitance values are the same at different external potentials, consequently the associated electrochemical currents $i = C_F(dV/dt) = C_F s$ (where $s$ is the scan rate) are different for the same molecular layer. Directly related to the fact that the ratio between electrical current and potential scan rate ($C_F = 1/s$) is the electrochemical capacitance, so that it governs the cyclic voltammetry shape

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[such as box- or slanted-shaped way] as shown, specifically for graphene, in Figure 3. Associated with the fact that the charging conductance \( G \) is dependent on the capacitance as \( G = k_e C_g \), where \( k_e \) is the electron transfer rate \( k_e = 1/R_s C_g \). We previously demonstrated that \( k_e \) is the inverse of the RC time constant of the process, where \( R_s \) is the charge relaxation resistance of the electrochemical process. Curiously, Figure 2 demonstrates that the kinetic dispersion arises as a result of the quantum mechanics characteristics of the RC time, associated with both the electron transport and storage. This reinforces the notion that non-ideal behaviour does not reside only in the capacitance, as normally treated in dielectric relaxation phenomenology, but in both resistance and capacitance. Physically speaking, on the one hand, in this quantum mechanical RC time relaxation approach, the electron is treated through the perception of wave-particle duality (group velocity) and the uncertainty principle is embedded in this concept. On the other hand, taking the electrochemical classical approach, the electron is pictured as a classical particle that is spatially located in specific geometric sites in the interface or on the bulk of the electroactive materials. In the wave picture (or quantum particle analysis), the electrons are delocalized between the electrode and quantum states in the molecular layer.

Therefore, in quantum approaches of RC time, the RC time distribution associated with the molecular ensemble of quantum states is the source of the non-ideal characteristics. This RC time constant is dependent on how the energy is lost (associated with \( R_s \) or stored (associated with \( C_g \)). Furthermore, the dynamic behaviour of the ensemble depends on how it disperses with the external static potential energy. These obviously affect the electron transfer rate (and \( k_e \) values, as shown in Figure 2(d)), first, because electron transfer rate is dependent on \( C_g \) and, second, because \( k_e \) also depends exponentially on the reorganization energy, which in turn depends on the dielectric characteristics of the environment, that is, at the formal potential, \( G = 1/R_s \propto C_g \exp[\lambda/k_BT] \), where \( \lambda \) is the reorganization energy.

The reorganization energy is largely known to be a function of the dielectricity of the solvent. In summary, the kinetic dispersion in a quantum mechanics perspective must be carefully studied on a systematic and case-by-case basis. We are not here interested in the kinetic dispersion that will obviously be present in graphene; rather, we are focused on the meaning of the capacitive effect and its dependence on chemistry, doping, etc.

**Electrochemical capacitance of carbonaceous materials**

The purpose of this work is to revisit supercapacitance phenomena in graphene (we are not, in this work, interested in exploring all the mesoscopic implications behind carbonaceous compounds, only the capacitive phenomena) from a mesoscopic perspective. According to electrochemical literature, a supercapacitor is a particular category of electrochemical double-layer capacitor, in which capacitive and surface faradaic charges coexist in such a way that resolving the two contributions (faradaic and non-faradaic) is not experimentally trivial. In the absence of diffusion phenomena, though, the ECS approach, as exemplified in Figure 1, is useful, on account of its inherent spectroscopic features. Therefore, in this work, we demonstrate that the capacitance of graphene is mainly an electrochemical capacitance (in its oxidized and reduced forms), wherein its molecular (or mesoscopic) scale (energetic feature), in essence, contributes predominantly to charge quantum and ionic states, in its reduced and oxidized forms, respectively.

In summary, the electrochemical capacitance of multi-layered graphene is here measured using an ECS methodology (comparable to cyclic voltammetric methods – see supplementary information). The obtained capacitance, the electrochemical capacitance, \( C_g = e^2 g(\mu) \), is used to quantify the electronic density of states of electrochemical reduced graphene, \( g(\mu) = dN/d\mu \), where \( N \) is the electron number density, \( \mu \) is the electrochemical potential energy level, and \( e \) is the elementary charge. The meaning of the electronic density of states is interpreted through the conceptual quantum mechanical ab-initio approach and associated with the observed capacitive phenomenon of the reduced state of graphene, as compared with its oxidized state, demonstrating that the origin of the supercapacitance can be mainly attributed to the density of electronic (or electrochemical) states, rather than to the similar double-layer capacitance phenomenon.

**Experimental procedures**

**Instrumentation**

Cyclic voltammetry and impedance measurement were carried out using an Autolab potentiostat PGSTAT30 (Ecochemie NL) equipped with an ADC750 and a frequency response analyser hardware module and software. Alternating current (AC) frequencies for impedance experiments (electrochemical impedance spectroscopy) ranged from 1 MHz down to 10 mHz, with an amplitude of 10 mV (peak to peak) acquired at a stationary potential of 0.0 V (with respect to a Ag/AgCl electrochemical reference electrode). All obtained impedance data were checked regarding compliance with the constraints of the Kramers–Kronig linear systems theory, using an appropriate routine of the Autolab frequency response analysis software. The complex impedance function, \( Z'(\omega) \), was converted into complex capacitance, \( C'(\omega) \), through the definition \( Z'(\omega) = 1/[\mu_0 C'(\omega)] \), in which \( \omega \) is the angular frequency and \( \mu = \sqrt{-1} \). From this operation, note that \( C'' = \varphi Z'' \) (the imaginary component of the complex capacitance) and \( C' = \varphi Z' \) (the real component of the complex capacitance), where \( \varphi = (\omega|Z'|)^{-1} \) and \( |Z'| \) is the modulus of \( Z' \). Electroactive areas were calculated by chronoamperometry using 2.0 \( \times \) 10\(^{-3}\) M hydroquinone, by applying 0.4 V for 5 s. Cyclic voltammetry and electrochemical
impedance spectroscopy scans were conducted in a 5 mL, one-compartment cell containing the glassy carbon electrode (GCE), an Ag|AgCl, KCl (3 M) reference electrode and a platinum counter electrode. Phosphate-buffered saline (PBS; 50 mM; pH, 7.4) was applied as supporting electrolyte.

**Electrochemically controllable synthesis of graphene-based compounds**

Graphene oxide (GO) was obtained by Sigma Aldrich. A certain amount of GO was dispersed in water to prepare 0.50 mg mL⁻¹ mixture. Prior to modification, the GCE electrode was mechanically polished with 1.0 μm, 0.3 μm, and 0.05 μm alumina slurries, sequentially, and then tested by cyclic voltammetry to confirm its availability. After being sonicated in re-distilled water and ethanol successively for 5 s, the GCE was prepared by casting 20 μL of as-prepared GO suspension onto the surface of the cleaned GCE with a pipette and then allowed to air dry to form a GO film for further use. Electrochemically reduced GO (RGO) film was prepared by a surface electrochemical reduction method. The GCE/RGO was fabricated by immersing the GO film/GCE into an aqueous electrolyte of 0.05 M PBS, and then scanning for 20 consecutive cycles at a rate of 100 mVs⁻¹ from 0 to −2.0 V (versus the Ag|AgCl electrode).

**Results & discussions**

**Chemical characteristics of electrochemically prepared RGO**

A number of different routes for synthesizing graphene have been demonstrated over recent years and are suitable for exploring the different potential applications that graphene has to offer. These routes can be divided into (a) mechanical and (b) chemical methods. A mechanical method, the 'Scotch tape technique', was used in 2005, to fabricate pristine graphene, which comprises sheets of sp² hybridized carbon that are defect-free, and is mainly useful for investigating the intrinsically physical properties of graphene; however, this route is limited and cannot be used to produce large-scale bulk material. Moreover, the chemical method consists of oxidative processes, where graphene is usually produced from graphite by the Staudenmaier, Brodie, and Hummers methods, from which chemically modified graphenes are obtained.

An interesting method of obtaining chemically modified graphene is the reduction of GO comprising the RGO by chemical methods, using compounds such as hydrazine in ammonia. The chemical treatment causes the reduction of epoxide groups, which are mainly located in the basal plane; electrochemical reduction causes the reduction of epoxy, aldehyde, and peroxide groups, while the reduction of hydroxyl, carbonyl, and carboxyl groups is caused by thermal treatment during the reduction process. As in experimental methods, electrochemical reduction was the methodology adopted to synthesize graphene in this work.

After the reduction of GO, RGO contains a lower amount of oxygen functional groups. These oxygen-containing groups affect the electrochemical performance of RGOs in terms of electron transfer rate or adsorption or desorption of molecules, and provide anchoring sites for biomolecules or other specific species for sensing applications.

The electrochemistry of sp² carbons is heterogeneous, since the electron transfer rate is very fast at the edges and defect sites of the sheets are very slow at the basal plane. It is known that the electrochemistry of a large variety of compounds is sensitive to surface defects and surface functional groups. Therefore, one can expect dramatically different electrochemical behaviours from the various chemically modified graphenes as they contain different amounts of defects and oxygen functionalities. In practice, it is the method by which graphene is synthesized that defines its properties and, consequently, its applications.

We carefully controlled the synthesis of electrochemically RGO compounds by reducing GO directly over the GCE, forming an electrochemically controllable GCE/RGO junction that can be characterized by ECS.

**Electrochemical properties of GCE/ERGO junctions**

Cyclic voltammetry was used to reduce GO directly on the surface of GCE. Figure 3(a) shows that the graphene oxide-modified GCE exhibited strong voltammetric reduction peaks between −0.9 and −1.8 V, which is in agreement with recent studies. This large reduction current is associated with the reduction of oxygen functional groups present on the surface of GO, which contains a wide variety of oxygen groups, such as epoxy, hydroxyl, carbonyl, carboxyl, aldehyde, and peroxide. Some of these groups, namely epoxy, aldehyde, and peroxide, are electrochemically reducible.

In the second cycle, the reductive peak decreased considerably and disappeared after several potential scans, demonstrating that the GO is reduced electrochemically at negative potentials and that the reduction of surfacet oxygenated species at GO occurred irreversibly and quickly, at least in the range of the used working potential. The following mechanism for the electrochemical reduction of GO has been proposed by Raj and John:

$$\text{GO} + \text{al}^+ + \text{be}^- \rightarrow \text{graphene} + \text{H}_2\text{O}$$
Figure 3(a) shows cyclic voltammograms obtained at 0.1 V s⁻¹ for GCE (dotted red), GCE/GO (blue), and GCE/RGO (black) in PBS. Compared with GCE/GO, the current-potential profiles obtained at GCE/RGO show higher capacitance currents; this is because the graphene oxide contains a large amount of oxygen.⁶ The long-range sp² structure is typically absent and the material is a mixture of sp³ and sp² hybridized carbon with very low conductivity.⁶ While in electrochemically reduced graphenes, the oxygen-containing groups are partially removed and the sp² order in graphene structure is restored.⁸⁷ Therefore, by assuming the well-known RGO¹⁻⁹ efficient electron transport properties combined with its charge capability, as will be further demonstrated here by ECS, we hypothesize that both properties observed for RGO are somehow related through the Debye length. In other words, the Debye length is the inverse of the wavelength associated with the electric field screening in the graphene layers or in molecular junctions or structures.

Superconductance interpretation of graphene based on conceptual density functional theory

By using ECS combined with conceptual density functional theory it was possible to reveal the true physical nature involved in the supercapacitance phenomena.⁴⁶ Density functional theory is a first-principle quantum mechanical theory that enables the electronic structure of compounds and the chemical system to be successfully computed through a precise and less expensive computational effort.⁵¹ By using density functional theory as a first-principle fundamental quantum mechanics method, Bueno et al.⁵¹ have demonstrated that the pseudo-capacitance phenomena (those capacitive effects associated with faradaic charging) are indeed conceptually understood and thus renamed them electrochemical capacitance phenomena (Cₑ).⁵¹, ⁵² to include electrostatic and quantum states effects, both contributions occurring (concurrently and concomitantly) in series,⁵¹, ⁵² leading to an equivalent electrochemical capacitance. Therefore, conceptually, the electrochemical capacitance, as theoretically formulated, contains and explains pseudo-capacitance phenomena. For instance, in the specific case in which the quantum states are directly associated with charging faradaic states, the electrochemical capacitance (or pseudo-capacitance) is named redox capacitance. In other words, the pseudo-capacitance phenomenon is then only a different manifestation of electrochemical capacitance, in which both electrostatic and quantum capacitance⁵¹, ⁵², ⁵⁶ (sometimes
referred as chemical capacitance) are energetically (note that the inverse of capacitance is proportional to the energy of the capacitor) connected in series (see also Figure 4(c)) as\textsuperscript{51, 52}

\[
\beta / C_2 = \gamma / C_1 + \gamma' / C_q
\]

where \(\beta\), \(\gamma\), and \(\gamma'\) are constant values associated with the number of electrons \(N\) exchanged during the charging or discharging of the molecular system and with the elementary charge, \(e\), \(C_e\) is the electrostatic or geometrical capacitance (the classical term of the capacitance or energy) and \(C_q\) is the quantum capacitance ultimately given by

\[
1 / C_q(\bar{\mu}) = q / e^2 \left[ 1 / g_l(\bar{\mu}) + 1 / g_r(\bar{\mu}) \right]
\]

where \(q = eN\) is the amount of charge exchanged between two different \(N\)-electron systems possessing two different density of states functions, that is, \(g_l(\bar{\mu}) = dN_l / d\bar{\mu}\) (left) and \(g_r(\bar{\mu}) = dN_r / d\bar{\mu}\) (right), as pictured in Figure 4(b). Note that \(\bar{\mu}\) refers to the energy state or levels associated with the electrochemical potential of the electrons in the electrode, working as an electronic probe to access the states at a given molecular junction of interest (see Figure 4(a)).

Assuming the exchange of a single electron between an electrochemically active compound with a density of states such as \(g_l(\bar{\mu})\) and an electron reservoir (electrode) with a density of states such as \(g_l(\bar{\mu})\), it can be demonstrated that the quantum capacitance is directly obtained by \(C_q = e^2 / dN_i / d\bar{\mu}\), where it was clearly assumed that \(g_l(\bar{\mu}) \gg g_r(\bar{\mu})\) in Equation (3) (see also Figure 4(b)).

Note that \(C_q\) is directly proportional to the electronic (or electrochemical) density of states, \(dN_i / d\bar{\mu}\), which is associated with states assessable on the molecular compound\textsuperscript{51, 52, 56, 89} because of the electrode perturbation in a time- or frequency-dependent mode.

From density functional theory analysis\textsuperscript{51, 52, 55} it has been demonstrated that the energy associated with the charging or discharging (through single-electron transfer) the level of energy in the molecular system is \(e^2 / C_q = \sum e_i^{KS} = d\bar{\mu} / dN_i\), where \(e_i^{KS}\) are the \(i\)th Kohn-Sham orbital states, and \(\eta = d\bar{\mu} / dN_i\). The latter \(\eta\) function is well known (in conceptual density functional theory) as the chemical hardness. It is associated with the charging or discharging of the chemical system itself (by adding or removing a single electron).\textsuperscript{52} Note that \(\eta\) increases with the difficulty of changing the electrochemical energy of the system, that is, the energy associated in occupying or vacating an electronic state under a fixed ionic strength and electrode potential.\textsuperscript{52}

In this work, we demonstrate that it is possible to use ECS to access \(g_l(\bar{\mu}) = dN_l / d\bar{\mu}\) (the density of electronic state) associated with electrochemically modified graphene compounds.

It is important to note that the electrostatic contribution in Equation (2) associated with the geometrical capacitance, \(C_e\), is inseparable of the quantum effects, stated in \(C_q\). \(C_e\) is a general phenomenon, as will be demonstrated in the following sections. The quantum contribution can dominate and varies sensitively with the variation of the energy of the electrode. Nonetheless, in moving a charge from one state to another in space, the Coulombic (or electrostatic) contribution will always operate independently of the density of states function that determines the quantum capacitance. This contribution, associated with the geometrical capacitance, is independent of electronic or ionic states; it exists in both limits. Thus, the geometrical capacitance is a constant that only depends on the geometric factor involved with the spatial displacement of the charge. Note that if both \(g_l(\bar{\mu})\) and \(g_r(\bar{\mu})\) in Equation (3) are large (as is the case of a gas of electrons or electrodes) the quantum capacitance is null and the electrochemical capacitance is equal to the geometric capacitance. Nonetheless, this situation is not applicable in electrochemistry, where the interfacial junctions are metallic and non-metallic (semiconductors, molecular, etc., and embedded in an electrolyte that is indeed responsible for screening the electrical field of the electrode). For instance, the constant geometrical characteristic of an electrostatic capacitance is illustrated by the capacitance of a plate capacitor such as \(C_p = \varepsilon_0 \varepsilon_r A / L\), where the \(A\) is the area and \(L\) is the distance between the plates; for an isolated sphere, this capacitance is \(C_s = \varepsilon_0 \varepsilon_r R\), where \(R\) is the radius of the sphere, and so on. Nonetheless, confusion must be avoided with the double-layer phenomenon, which depends on the ionic concentration in the solution phase.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) Schematic representation of graphene sheets over an electrode. Blue lines correspond to sheets containing accessible quantum states (or accessible density of electronic states) separated by a given chemical barrier or coupling referred as quantum channels (where electrons have a tunnelling barrier between the graphene sp\textsuperscript{2} electron transport plane). (b) Magnification of (a), emphasizing electron coupling between electrode and graphene electronic density of states, \(g_l(\bar{\mu})\). The electron chemical, which is the quantum capacitance plus the influence...}
\end{figure}
of the external potential, is directly measured by ECS as \( C_\text{ECS} = \frac{e^2}{dN_e/dq} \), where \( dN_e/dq \) is the accessible electronic density of states function of graphene sheets at the interval of energy \( d\varepsilon = -e dV \), where \( V \) is the potential of the electrode. Since \( C_\text{ECS} \) depends on \( dN_e/dq \), it is neither constant nor ideal. In terms of frequency dispersion, non-idealities arise depending on the density of states \( dN_e/dq \) shape; thus, frequency dispersion will follow this requirement. Note also in (b) that \( V_\text{e} \) refers to an external electrostatic (and stationary) potential bias. (c) Quantum electronic states of graphene are accessible through \( C_p \); the associated electron transfer rate is given by \( k = 1/(\hbar^2 C_p) \). These are both directly accessible by the ECS method, as discussed in the text. Note that in the specific case of this work we are interested in a junction formed by a GCE and electrochemically reduced graphene oxide (ERGO) as an electrochemically active compound possessing a measurable \( C_p \).

It can consequently be inferred that in measuring the capacitance associated with the assessment of the density of electronic states of graphene at a given electrolyte environment and stationary external potential, the measured capacitance is directly associated with the quantum capacitance under a fixed external ionic (strength) and electrostatic potential.\(^{51,52}\)

In particular, note that, depending on the chemical system being investigated, the electrochemical capacitance cannot be precisely evaluated by using traditional current measurements, i.e., by means of transient techniques, because transient techniques are not spectroscopic. As demonstrated in Figure 1, a superposition of effects is observed, wherein ionic (associated with non-faradaic effects only) and electronic (electrochemical) relaxations exist (note also that the geometric capacitive contribution contained in the electrochemical capacitance is different from those associated with ionic relaxation).\(^{52}\) Primarily, as exemplified in Figure 1, the electrochemical and non-faradaic relaxations can be similar in magnitude and thus hardly separable unless time-dependent spectroscopic approaches are used.\(^{53,54}\) In other words, the charging or discharging characteristics associated with the capacitance of a mesoscopic electrochemical system cannot be easily separated by means of traditional DC-based techniques, but are possible if AC-based approaches, such as ECS, are applied. Although DC-transient electrochemical methods enable the value of the capacitance of graphene to be obtained, as demonstrated in the supplementary information (Table S1-1), they do not enable the source of the capacitive contribution to be assigned, i.e., if they arise from pseudo-capacitive or non-faradaic effects. Nonetheless, by ECS, this task can be achieved, for instance, by identifying the magnitude and timescale over which the relaxations associated with charging events occur (see Figure S1-2). In particular, for the current experimental graphene data, the capacitive values obtained by DC and AC-based techniques are comparable (see electronic supplementary information, Table S1-1). This is because, at lower frequencies, the capacitance of the graphene system is associated with a pseudo-capacitive event that dominates over non-faradaic effects. If the scan rate, in cyclic voltammetry, is sufficiently low, the capacitance obtained by cyclic voltammetry and ECS methods coincides. Nonetheless, the existence of different charging timescales (see Figure S1-2) is only confirmed using ECS spectroscopic approach (and cannot be confirmed by DC methods). This is because, as demonstrated in Figure 1, ECS is able to separate spectroscopically different capacitive events.\(^{53-56}\)

Here, we use the ECS technique to understand the nature of the large magnitude (low frequency) capacitance of multilayered reduced graphene.

In summary, ECS enables direct determination of \( C_p(\mathbf{q}) \) in a simple and single spectroscopic measurement, where \( C_p(\mathbf{q}) \) is the electrochemical capacitance (meaning a capacitance containing both electrostatic and quantum state contributions) of the system. Furthermore, \( C_p(\mathbf{q}) \) has a clear meaning in conceptual (first-principle) density functional theory.\(^{51,52}\) It takes into account the contribution (ignored in the common electrostatic sense) of the electronic structure as evaluated through the Kohn–Sham (quantum) orbital states or by the relationship between the capacitance and the chemical hardness or softness of the electrochemical system.\(^{50,51}\)

**ECS measurements**

Electrochemical capacitance spectroscopy is based on impedimetric measurements, where the complex impedance, \( Z^*(\omega) \), is converted into a complex capacitance, \( C^*(\omega) \) (Figure 1). Thus, the ECS approach provides an electroanalytical signal (at low frequency) that is purely capacitive, owing to the assessment of the electronic states of graphene. These are resistively coupled with electrode states. The capacitive and resistive coupled effects generate a relaxation process (with a characteristic timescale given by the product of the resistance and capacitance terms, that is, RC). This RC process is responsible for the peaks observed in Figure 1 from which capacitance can be obtained (independently of the kinetic dispersion, as discussed in the introduction section)\(^{51,56,64}\) as demonstrated in Figure 1.

As observed in Figure 3(b), for a graphene system, there are no redox peaks on the current versus potential pattern of the voltammogram. Nonetheless, the relaxation process and its associated electrochemical capacitive process can be observed in a Nyquist capacitive plot obtained by ECS, as shown in Figure 5(b). The electrochemical capacitance, \( C_p \), defined in the introduction section, is directly obtained from the diameter of the semicircle of the Nyquist capacitive plot, as indicated in Figure 5(b) and insets (more details on the methodology associated with ECS approach can be found in the literature).\(^{55,57,58,60}\) The obtained \( C_p \) value is of the order of magnitude of \( \mu \text{F cm}^{-2} \) (normalized by the electroactive area of the electrode) for bare GCE (~9.8 \( \mu \text{F cm}^{-2} \)) and GCE/GO (~3.8 \( \mu \text{F cm}^{-2} \)) junction, as summarized in Table 1. As expected, following the reasoning of the discussion of Figure 2, the RC time constant
is not ideally dispersed, which can be observed by noting the existence of a flattened semicircle in Figure 5(b). In other words, a circular arc with the centre located below the abscissa exists; meaning that, according to the discussion in the introduction section, there is a distribution of RC times. We are not interested here in analysing the cause of this dispersion (whose sources were briefly discussed in the introduction section, see Figure 2) in graphene or carbonaceous materials.

These measurements (Table 1) are the expected capacitive values within typical non-faradaic double-layer capacitance phenomenology. It is well known that the double-layer capacitance is highly dependent on the specific surface area of the material accessible to ions. The non-faradaic phenomenon is largely associated with the ionic screening of the electronic charge of electrodes or with the electron activity associated with the area of the electrode that has no charge transfer contribution or electrochemical (faradaic) activity. Table 1 also shows the calculated electroactive areas (following the procedure described in the experimental section) for the three surfaces. As can be noted in Table 1 and Figure 5(b), the value of capacitance obtained for GCE-RGO junctions is very high, undeniably within mF cm⁻² (~5.3 mF cm⁻²), which is about 1000-fold higher than that obtained for GCE-GO junctions (typically 2-10 μF cm⁻²). Note also that the associated increase in the electroactive area is approximately 25-fold (much less than the increase observed for the capacitance). Accordingly, this increase of the capacitance cannot solely be attributed to an increase in the specific surface area. It should be stressed that the only difference between the GCE-GO and GCE-RGO junctions is the electrochemistry reduction of GO, as demonstrated in Figure 3.

Furthermore, the increase in the electronic or electrochemical current observed in Figure 3(b) after the electrochemical reduction of the GO does not only occur because of non-faradaic double-layer effects, although this would be the common sense interpretation by a classical electrochemist. The common sense interpretation treats double-layer capacitive effects close to those of geometrical effects (as discussed previously). Nonetheless, electric double-layer capacitance (following Gouy–Chapman modelling, which is considered to be very precise for an electronic conductor in contact with an electrolyte) is based on an interfacial capacitance (per unit of specific area) that depends on the thermodynamic of ions adsorbed in the surface. This interfacial capacitance follows

\[ C_{dl} = \varepsilon_r \varepsilon_0 \kappa \]  

(4)

where \( \varepsilon_r \) is the relative permittivity (generally referred to as the dielectric constant) of the material, \( \varepsilon_0 \) \( (\approx 8.85 \times 10^{-12} \text{ F m}^{-1}) \) is the dielectric constant or dielectric permittivity of the vacuum (or free space). Finally, \( \kappa \) is the inverse of the Debye length \( (\kappa_D = 1/\kappa) \), which is given by \( \kappa = (2e^2N/(\varepsilon_0 \varepsilon_r k_B T)) \), where \( N \) denotes the density of ionic charge (positive or negative) in the bulk of the electrolyte, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. \( C_{dl} = \varepsilon_r \varepsilon_0 \kappa \) can also be applied for plate, cylindrical, and spherical (or isolated conductive spherical) porous geometries and, because of this particular geometric configuration, it is largely confused with the capacitance previously referred to as geometrical capacitance. Nonetheless, \( C_{dl} \) is a particular approximation of \( C_P \), as shall be demonstrated next. Indeed, in the phenomenology involving \( C_{dl} \), although the ionic contribution is taken into account, the electronic structure contribution of the molecular system, such as those here associated with oxidized and reduced graphene (the same reasoning can be applied generally for any other carbonaceous material) is not considered.

### Table 1. Resistive and capacitive characteristics of different carbonaceous-electrolyte junctions as obtained by ECS measurements, compared with electroactive areas.

<table>
<thead>
<tr>
<th></th>
<th>( C_P ) (mF cm⁻²)</th>
<th>Electroactive area</th>
</tr>
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<tbody>
<tr>
<td>Bare GCE</td>
<td>((10.1 \pm 0.2) \times 10^3)</td>
<td>0.073 ± 0.007</td>
</tr>
<tr>
<td>GO</td>
<td>((3.8 \pm 0.01) \times 10^3)</td>
<td>0.0084 ± 0.001</td>
</tr>
<tr>
<td>RGO</td>
<td>5.3 ± 0.3</td>
<td>0.219 ± 0.009</td>
</tr>
</tbody>
</table>

Now, by assuming that \( C_P \) is general and by considering the electric field screening of the interface, it can be demonstrated that the screening is modelled by taking into account the particular case of the Lindhard formula, \(^{26}\) which is its approximation to the Thomas–Fermi screening, where \( \kappa \) is directly related with \( C_P \) as \( \kappa = (C_P/\varepsilon_0 \varepsilon_r)^{2/3} \); thus

\[ C_P = \varepsilon_r \varepsilon_0 \kappa^2 \]  

(5)

Assuming that the quantum states dominate when charging the electrochemical capacitors, it can be demonstrated that \( \kappa^2 = (e^2N)/(\varepsilon_0 \varepsilon_r) \). The meaning of quantum dominance on the charging of the states is that the charging sites behave as quantum and not classical states during the occupancy, that is, they are indistinguishable and Fermi statistics applies to the occupational statistics of these states.

Conversely, in the case where charging states are treated as classical distinguishable particles, \( \kappa^2 \) can be approximated to \( \kappa^2 = [(e^2N/(k_B T))/\varepsilon_0 \varepsilon_r] \) (the Boltzmann approximation), from where the Debye length as defined in the Gouy–Chapman model is then restated, clearly demonstrating that the double-layer phenomenon is only a particular case of the more general electrochemical capacitive phenomenon. Nonetheless, the Boltzmann approximation, in which the ionic concentration in the interface controls the electrical field screening, cannot be applied if the screening is controlled by the electronic occupation of the states in the interface of graphene junctions. In this case, wave (or quantum particle) behaviour dominates and controls the charging properties of the interface. In other words, Equation (5) is general in the sense that it considers not
only the classical distribution of ionic charge, but also the charge distribution that follows the electronic occupation of the states (clearly, the effect described here can be extended to other electrochemical-like capacitive effects). In summary, the Gouy–Chapman theory of the double layer is only a particular case of a more general theory, where the electrochemical capacitance, $C_P$, is central. As $C_P$ was previously defined from first-principles density functional theory, it is largely general within a quantum mechanical first-principles approach.

Figure 5. Typical (a) impedimetric and (b) capacitive Nyquist diagrams obtained for GCE (△), GO (●), and RGO (◆) in aqueous electrolyte of 0.05 M PBS. Note that (b) was constructed by converting impedance into capacitance, as explained in the experimental section. The impedance spectra (electrochemical impedance spectroscopy) were obtained for frequencies ranging from 1 MHz down to 10 mHz with an amplitude of 10 mV (peak to peak), all acquired at a stationary potential of 0.0 V (versus Ag/AgCl) electrochemical reference electrode) where molecular (quantum) capacitance of graphene is expected to be maximal (Figure 4). Inset shows GCE (△), GO (●), and RGO (◆) at high frequencies. Nyquist diagrams of the interfaces demonstrate minor changes in average impedance values, while differences in the systems are clearer in the capacitive representation. (c) and (d) are Bode capacitive diagrams. These diagrams show the RC-time constant associated with charging of capacitive states in the different junctions.

**Revisiting the supercapacitance of graphene**

The measurement of the (super or ultra) capacitance of the GCE-RGO junction has already been reported in the literature in different situations. Indeed this capacitance is very high, even when compared with self-assembled monolayers of ferrocene ethiol on gold, 51, 53-56, 63 for example, which has an expected magnitude of approximately 0.36–0.4 mF cm$^{-2}$ (approximately 14 times less than for the RGO measured herein) in non-aqueous electrolyte (for instance, dichloromethane). In self-assembled monolayers composed of thiolated ferrocene (redox-active self-assembled monolayers), the capacitance was shown to be related to the electronic occupation of specific orbitals in the metallic ferrocene centres, 53, 55 and the phenomenon is more clearly related with the faradaic characteristics where the entire number of electrons is transferred from the electrode to the molecular redox centres. This is easily associated with the occupation of the
molecular orbital states as energetically defined by
\[ e^2/N = \sum e_i^2 = d\rho / dN. \]
In other words, this phenomenon is related to the charging or discharging (redox couple states) of ferrocene quantum energetic centres.\(^{50}\)

As observed in Figure 3(b), GCE–RGO junctions do not present any evidence for the existence of redox activity (or faradaic processes), which would be noted by the presence of peaks in the current–potential pattern; as shown in the cyclic voltammograms, they are absent. Accordingly, in GCE–RGO junctions, as discussed previously, the observed value of the capacitance cannot be explained by non-faradaic effects (associated with a specific surface area) or by purely faradaic (associated with peak current) processes (owing to the absence of faradaic activity).

By following the physical explanations and phenomenology expressed in Equations (1) to (3), the supercapacitance of GCE–RGO junctions is explained from a chemical and electronic structure point of view by assuming the existence of charging or discharging processes on graphene, which are associated with delocalized electronic states in the conjugated π-orbital of the molecular structure.

Therefore, our premise is based on the existence of an electron flow across the π conjugated orbitals of the RGO (forming an electron cloud or two-dimensional electron gas). Thus, this indicates that a faradaic current is distributed along the volume of the graphene material (not localized in particular energetic regions, as in the case of redox monolayers). This delocalization does not enable the electrochemical current to be defined (as the peak in a given potential region), but enables charging of the electronic states of the graphene without a predominant change in its chemical potential. Figure 6 demonstrates the variation of the capacitance, \( C_\rho \), measured as a function of different electrochemical potentials \( \rho \) of the electrode, that is, from −0.2 V to +0.6 V versus the Ag/AgCl reference electrode. All values of the variation of \( C_\rho \) for GCE–RGO junctions refer to the difference between RGO and GCE (\( C_\rho^{\text{RGO}} - C_\rho^{\text{GCE}} \)), wherein they are confined between 1.8 and 5.1 mF cm\(^{-2}\) (see the red bars in Figure 6). Conversely, calculation of the difference between GCE and GO (\( C_\rho^{\text{GCE}} - C_\rho^{\text{GO}} \)) leads to values ranging from \( 4.79 \times 10^{-3} \) to \( 7.16 \times 10^{-3} \) mF cm\(^{-2}\). Note that the capacitance is less without the presence of RGO, as expected, and in this case the charging or discharging process is directly associated with (or screened by) the ionic strength of the electrolyte.

Nonetheless, in RGO, the electronic density of states function of graphene is energetically accessible along a wide range of potentials, which is different from what is observed in redox systems, wherein energy states are distributed in a Gaussian shape, thus comprising a Gaussian density of states\(^{53-56}\) centred in the Fermi level of the redox junction. Indeed, in RGO, as shown in Figure 7(a), the electronic density of states has a different shape (with a high density of states value observed at a wide range of potentials) possessing only small peak prominence at null potential versus the Ag/AgCl reference energetic level. As expected, the electronic density of states constructed for GCE and GO are minima, comparatively (see inset). In Figure 7(b), the electron density (N) varies as a function of electrode potential or energy from −0.2 V to 0.6 V. This is obtained by integration (step by step) of the curves given in Figure 7(a). Again, it is confirmed that the electron density of RGO is much higher than those of GO and bare GCE, confirming that RGO contains an electronic density that contributes to the supercapacitance phenomena of reduced graphene compounds.

![Figure 6. Difference in capacitance (ΔC) representing the modulus (absolute value) of the difference between GO minus (with respect to) GCE (black bars, inset) and ERGO minus (with respect to) GCE (red cross-hatched bars) as a function of the electrode potential. Capacitance values for this difference were obtained by the diameter of the semicircle of the capacitive Nyquist diagrams (C' versus C'), as shown in Figure 4, acquired as a function of the potential. It must be noted that the capacitive response of the bare GCE response is a minimum in a way that is almost the absolute response of RGO.](image)

**Conclusions**

Capacitance versus voltage (Figure 7(a)) profiles of the graphene compounds constructed using the ECS methodology have demonstrated that the electronic density of graphene is crucial in understanding its supercapacitance phenomena, which cannot definitively be explained by double-layer phenomenology alone. However, the phenomenon is explained by electrochemical capacitance, which is general and contains double-layer phenomena as a particular approximation. Nonetheless, for electrochemically modified graphene, the capacitance associated with charging its electronic density of states massively dominates the screening (according to Equation 4). The electrochemically reduced graphene has a higher electronic density of states and thus a higher electrochemical capacitance. The quantum (or chemical)
capacitance is an important concept that additionally has a prominent contribution to the electrochemical capacitance and is directly associated with the higher accessible electronic density of states function observed within modified graphene compounds (thus, the reduced graphene is dominated by quantum capacitive effects). Therefore, the supercapacitance phenomenon of graphene is not explained by double-layer capacitance or by faradaic interfacial charging effects. Nonetheless, these two phenomena are particular situations of the electrochemical capacitance phenomenon, which contains and explains both. The capacitance of graphene (oxidized and reduced) is associated with charging localized and non-localized electronic states and thus with particular circumstances of electrochemical capacitance.

Essentially, the capacitance of reduced graphene junctions comprises the contact of an infinite density of states with graphene compounds, allowing direct access to the electronic density of states of reduced graphene. This is a junction situation in which the total potential change on the molecular junction of graphene, caused by external electrode perturbation, has a variation that is divisible into an electrostatic term, which is driven by $dV = q/C_e$, and a quantum (chemical) term, which is driven by $d\tilde{V} = d\tilde{q}/e = q/[e^2\tilde{\varepsilon}\rho(q)]$, where $q = Ne$ is the total charge of the graphene states. These two invisibly coupled contributions are crucial to the understanding of molecular supercapacitance (and pseudo-capacitance) in general.

The supercapacitive effect and the associated physical phenomenology described here are summarized as being contained in the phenomenon of electrochemical capacitance and associated charge screening; these can be easily understood in terms of wavenumber (the reciprocal of the length-scale of interest) through the expression $C_\kappa = \varepsilon_\kappa\kappa^2$. From this expression it can be demonstrated that, when quantum capacitance is negligible (charging of the electronic states is negligible and ionic charge characteristic predominates on the screening of the electronic charge), $\kappa$ can be approximated to the classical double-layer phenomenon (Gouy–Chapman modelling of non-faradaic interfaces) where $\kappa$ is then expressed as the reciprocal of the Debye length. For all other cases, the shape of $C_\kappa$, which is proportional to the electronic density of states of the interface, must be known or determined, for instance, by using electrochemical impedance spectroscopy or ECS measurements.

**Figure 7.** Density of states: capacitance as a function of potential, obtained for GCE (▲), GO (●), and ERGO (●) in aqueous electrolyte of 0.05 M PBS, with sampling frequency (GCE: 14 Hz, GO: 83 Hz, and ERGO: 0.03 Hz) and potential range: −0.200 to 0.600 V. Inset: GCE (▲) and GO (●). (b) The same measurement as (a); however, ordinate values are the integration of the real capacitance ($C'$) as a function of electrode potential that thus accounts for electron density.

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**Notes and references**


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