



Faradaic and Capacitive Components of the CNT Electrochemical Responses

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The nature of the electrochemical responses from carbon nanotubes (CNTs), capacitive (physical), or Faradaic (chemical, also named p-doping or n-doping) remain controversial. In this chapter, the literature is reviewed and discussed trying to elucidate if some of the two processes prevails, how the presence of chemical reactions can be elucidated and which properties, specific from the chemical processes, can be exploited. Different electrochemical responses and theories trying to explain those responses are discussed. The separation and quantification methodologies of the capacitive and Faradaic components involved in some electrochemical responses from CNTs are presented.

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INTRODUCTION

When any material film based on carbon nanotubes (CNTs), as self-supported films or taking part of a device, are submitted in presence of liquid or solid electrolytes to potential steps, potential sweeps, or any other electrochemical methodology, an electrochemical response is obtained. The literature attributes the processes behind those responses to doping/de-doping processes, capacitive responses, oxidation and reduction processes, charge/discharge, and so on. So both, the name and the mechanism behind it are controversial (Li et al., 2002; Terrones, 2003; Rahman and Jeon, 2007; Zhai et al., 2011; Naoi et al., 2013; Ruiz et al., 2013; Simon and Gogotsi, 2013; Chopra et al., 2015; Ni et al., 2015). At the moment, it does not exist a widely accepted mechanism to explain the CNT electrochemical responses. It has been broadly accepted that they include mainly capacitive or physical effects, where balancing counter ions are oriented and disposed to compensate the excess of charges on their surface, but not changing the composition inside the CNTs bundles (Baughman et al., 1999; Riemenschneider et al., 2009a,b; Jiang et al., 2013). The almost square shape of the voltammetric responses in short potential ranges constitutes the main support of the claimed capacitive nature. At the same time, the authors accept that a uniform counter ions composition exists across the two films of CNTs acting as positive or negative pole of the capacitor. A uniform distribution of charges across the two constituent electrodes of a capacitor seems to contradict both, the Coulombic repulsion forces inside every capacitive electrode, and the attractive force from the second electrode translating most of the charges to the surface near the second electrode. A second issue offering technical difficulties is the long response time (seconds) required for the CNTs actuators to describe its maximum possible amplitude. The charge of the electrical double layer (EDL) of electrochemical capacitors in electrolyte concentrations higher than 10^{-3} M takes microseconds

(Bard and Faulkner, 1980). Those supporters of the capacitive nature argue that CNT electrodes in electrolytes contain some electrolyte. So, when the electrodes are submitted to a potential gradient step, the response time depends on both, the capacitance of the CNT electrodes and the resistance to the ionic movement of the CNT electrodes and of the electrolyte between those CNT electrodes. The charge of EDL depends on the effective surface of the bundle of CNTs in the electrode layer. From a microscopic viewpoint, CNT bundles and pores full of electrolyte compose the CNT electrodes.

On the other side, an increasing number of scientists attribute electrochemical responses to actual insertion/extraction of ions in the CNTs film through redox processes, changing the double bond distribution along each CNT, and therefore, originating a new material for every different number of charges extracted from the electronic structure of the CNTs (Che et al., 1998; Gao et al., 1999; Claye et al., 2000; Ghosh et al., 2005; Chen et al., 2008; Eom and Kwon, 2008; Majeed et al., 2013). Some of them claim that these redox processes occur at the edges or at defects on the CNTs (Li et al., 2002; Banks et al., 2005; Hoefler and Bandaru, 2013; Wang et al., 2014). Some of such defects may be due to the presence of some catalysts remaining from the CNTs synthesis (Lyon and Stevenson, 2007; Chng et al., 2013; Remy et al., 2015). The processes are also named doping and de-doping. Whatever the amount of the involved charges, it generates new ionic chemical compounds, $\text{CNT}^{n+}(\text{A}^-)_n$ for p-doping (oxidation) or $\text{CNT}^{n-}(\text{C}^+)_n$ for n-doping (reduction). According to the main characteristic of a chemical compound, it must not only have a uniform chemical potential, which guarantees the uniform ionic distribution across the anodic, oxidized (p-doped or n-dedoped) CNT film and a different, but also uniform composition, across the cathodic, reduced (p-dedoped or n-doped) CNT film. In order to lodge the counterions, free volume must be generated and the film swells during insertion of ions and shrinks during ion's ejection.

Clarifying the nature of the prevailing process taking place during electrochemical experiments from CNTs in electrolytic solutions, or its relative contribution, will provide valuable information to improve and optimize the design of new electrochemical devices based on CNTs. A prevalent capacitive process will allow the design of most efficient supercapacitors (Wildgoose et al., 2006; Endo et al., 2008; Liu et al., 2008; Zhang et al., 2009; Bondavalli et al., 2012; Kiamahalleh et al., 2012; Wang et al., 2012, 2015; Zheng et al., 2012; Li and Wei, 2013; Yan et al., 2014; Yiran et al., 2014; Abdalla et al., 2015); while a prevalent reactive, or faradic, process will allow the design of batteries for fast and ultrafast charge/discharge processes and multifunctional actuators having better control of the faradic movement (Dai et al., 2002; Landi et al., 2009; Du et al., 2011; Myung et al., 2015) acting, simultaneously, as sensor of the working and ambient conditions.

In this chapter, we will try to clarify the importance of faradic and capacitive processes in the electrochemical responses of CNTs, employing different electrochemical techniques and models.

ELECTROCHEMICAL RESPONSES FROM CNTs

Voltammetric Responses

Most of the literature considers that the voltammetric responses from CNTs not showing any specific maxima and minima, thus, not showing any redox peaks, are uncontroversial evidences for the exclusive presence of capacitive processes in the electrochemical responses (Barisci et al., 2000a,b; Madden et al., 2006; Ruch et al., 2009; Hekmat et al., 2014).

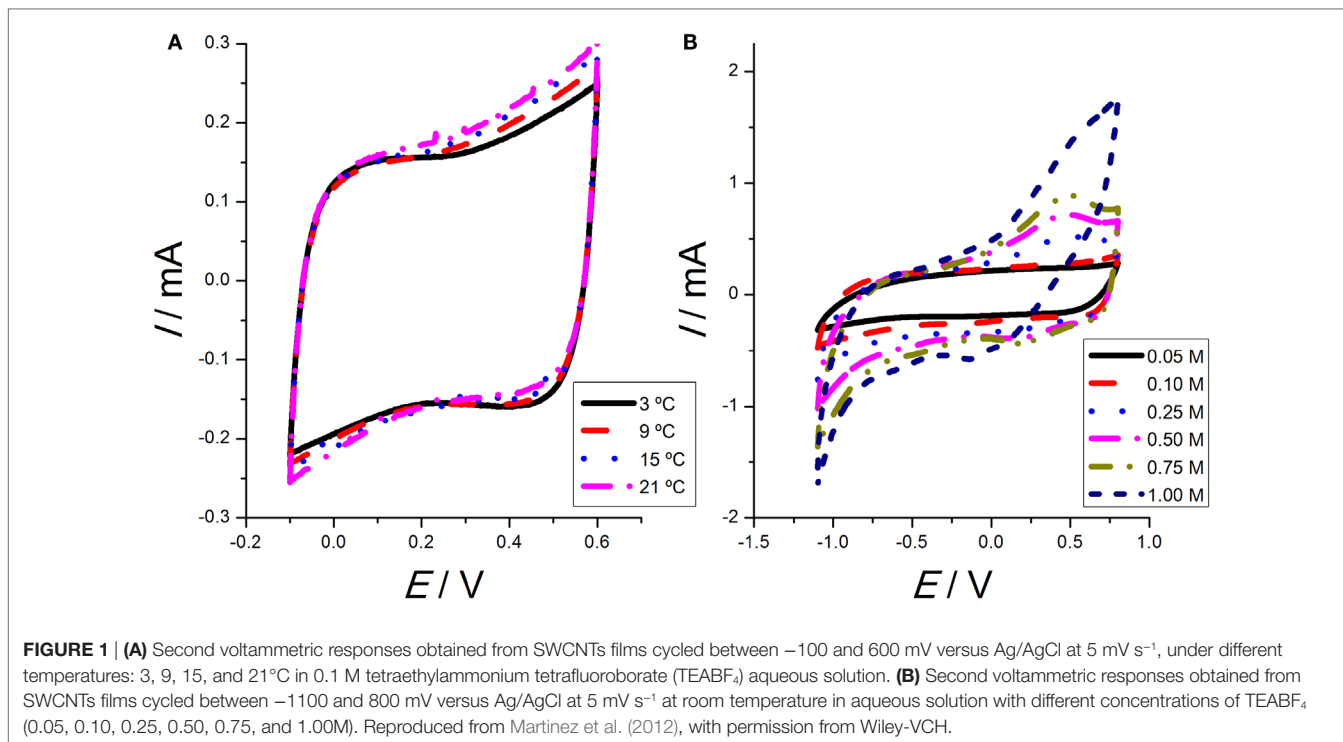
When the voltammetric results are obtained from single walled CNTs (SWCNTs) and an ionic liquid glued by a non-active polymer, PVDF-HFP/Ionic liquid/SWCNTs, see Martinez et al. (2012) for the details on the construction of the film with those three components, in a narrow potential window in tetraethylammonium tetrafluoroborate (TEABF_4) aqueous solution (between -100 and 600 mV versus Ag/AgCl), the voltammetric results show a capacitor-like response (**Figure 1A**). Repeating the experiments at different temperatures, the shape of the attained voltammograms does not change, but the involved charge, Q (obtained by integration of the voltammetric area below the anodic, or the cathodic current, $Q = \int I dt = 1/\nu \int I dE$, where I is the current flowing through the CNTs film, t is the flowing time, ν is the scan rate, and E is the potential) increases for rising temperatures (**Figure 1A**). This fact points to an increasing fraction of CNTs from the film participating in those electrochemical responses at rising temperatures.

On the other hand, some works claim for an important redox component (Barisci et al., 2000a,b). When the potential limits are extended (to -1100 mV versus Ag/AgCl), the voltammetric responses present some peaks and shoulders, which are attributed now to actual redox processes (**Figure 1B**). For increasing concentrations of TEABF_4 , a well-defined anodic maximum is observed at 450 mV versus Ag/AgCl. On the cathodic branch, a minimum is observed at 250 mV and a shoulder at -300 mV versus Ag/AgCl. The involved anodic or cathodic charges also increase for rising electrolyte concentrations.

Thus, we can conclude that most of the CNTs' voltammetric responses from the literature show a rectangular shape. Nevertheless, by changing the experimental conditions (the potential window, the working temperature, the electrolyte concentration, or the solvent) the voltammetric responses present well-defined peaks and shoulders. Those different results can support both, the capacitive nature of the involved processes (rectangular voltammograms) or their Faradaic nature (presence of peaks and shoulders on the voltammetric responses). So, the attained results and the prevailing model should result a function of the working conditions: further and complementary results from different electrochemical methodologies are required for a good clarification.

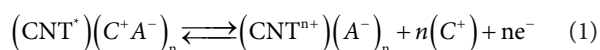
Chronoamperometric Responses

The presence of voltammetric maxima and the great influence of the electrolyte concentration suggest that the CNTs follow



oxidation/reduction reactions. In that case, the reaction rate must follow those relationships stated by the chemical kinetics.

Experimental analytical results from CNTs point to a prevalent exchange of cations during redox reactions (Gupta et al., 2004; Yun et al., 2005). The electrochemical reaction responsible of the p-doping process could be expressed as Eq. 1:



where $(\text{CNT}^*)(\text{C}^+\text{A}^-)$ represents the active centers on the neutral CNTs in the film, understood as those C atoms of the CNT that will store a positive charge after oxidation (extraction of one electron and restructuring of the double bonds) becoming $(\text{CNT}^{n+})(\text{A}^-)_n$; (C^+) represents the cation penetrating from the solution during reduction to compensate the charge of the A^- anions trapped inside the film during its preparation.

The equilibrium for the transfer of one electron can be expressed as Eq. 2:

$$K = \frac{k_{\text{red}}}{k_{\text{ox}}} = \frac{[(\text{CNT}^*)(\text{C}^+\text{A}^-)_n]^\alpha}{[(\text{CNT}^{n+})(\text{A}^-)_n]^\beta [\text{C}^+]^\delta} \quad (2)$$

where K is the equilibrium constant and k_{ox} and k_{red} are the oxidation and reduction, respectively, reaction kinetic constants or reaction coefficients, and α , β , and δ are the reaction orders for the concentration of the active centers in the CNTs film $[(\text{CNT}^*)(\text{C}^+\text{A}^-)]$, the oxidized CNTs, $[(\text{CNT}^{n+})(\text{A}^-)_n]$ in the film, and the concentration of cations in solution (or in a solid electrolyte), $[\text{C}^+]$, respectively.

Considering the empirical oxidation reaction (p-doping) rate from reaction 1 (a similar procedure can be developed for the reduction reaction (p-de-doping) rate), it can be expressed (Martinez et al., 2012) as Eq. 3:

$$r = A \exp\left(\frac{-E_a}{RT}\right) [(\text{CNT}^*)(\text{A}^- \text{C}^+)]^\alpha \quad (3)$$

where r represents the oxidation rate, $A \exp(-E_a/RT)$ is the rate coefficient (k), A is the pre-exponential factor, E_a is the activation energy, R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the experimental temperature (K).

Any electrochemical reaction, as Eq. 1, is a Faradaic process. The reaction rate (moles of electrons, counterions, and active centers exchanged or transformed per unit of time and unit of volume) also can be expressed as a function of the charge involved per unit of time: the density current, i , A cm^{-2} , flowing through the material, the film thickness, h , centimeters, and the Faraday constant, $F = 96485$ C mol^{-1} (Bard and Faulkner, 1980), Eq. 4:

$$r = \frac{i}{Fh} \quad (4)$$

By taking logarithms from Eq. 3, it is possible to get Eq. 5:

$$\ln r = \ln k + \alpha \ln [(\text{CNT}^*)(\text{A}^- \text{C}^+)] \quad (5)$$

The concentration of oxidized centers in the CNTs can be calculated from the charge consumed to oxidize the material, Q ;

the material weight, w ; its density, ρ , and the Faraday constant, F , using Eq. 6 (Otero and Garcia de Otazo, 2009):

$$[\text{CNT}^*] = \frac{Q/F}{w/\rho} \quad (6)$$

Thus, if the relative influence of Faradaic processes in the film oxidation is important, the reaction rate must be influenced by the physical and chemical variables acting on Eqs 3 and 4.

The possible presence of an oxidation reaction of the CNTs can be followed by submitting the material to potential steps from the same reduced state, got by polarization at the same reduction potential for the same reduction time, and stepping then the potential to the oxidation potential to get the same final concentration of active centers. Following Eq. 4, the oxidation rate is determined by the current flowing after the potential step: the chronoamperometric response. Equation 5 also indicates the experimental methodology required to check whether or not the process occurs under chemical kinetic control: by changing one variable, keeping the rest, every time. A semilogarithmic relationship between $1/T$ and r (when $[\text{CNT}^*]$ and $[C^+]$ are kept constant) and a double-logarithmic relationship between $[\text{CNT}^*]$ and r (when k and $[C^+]$ are kept constant) indicate that the electrochemical reaction is the process controlling the electrochemical response from CNTs.

Figure 2A shows the anodic chronoamperometric responses got from a CNT based film (Martinez et al., 2012). In order to check the effect of the $[\text{CNT}^*]$, different potential steps are needed from the same initial reduced state (got by reduction at the same cathodic potential for the same reduction time for each experiment) until different final oxidation states (got at different anodic potentials: so different charges are extracted from the CNTs film every time, Eq. 1, getting a different final concentration of CNT^*). The oxidation time must be enough to allow charging the EDL and the completion of the reaction. A very high-current flow through the system for long periods of time after the anodic potential step (>15 s). So, long time fact points to the presence of Faradaic processes: in a capacitive process the charge of the rigid EDL, when the ionic species is higher than 10^{-3}M , only takes microseconds (Bard and Faulkner, 1980).

By integration of the chronoamperometric responses the chronocoulograms (consumed charge versus time) can be obtained (**Figure 2B**). The slope of each chronocoulogram ($dQ/dt = i$) at the initial time ($t \rightarrow 0$) gives the initial oxidation rate, $r = (1/FV)(dQ/dt) = dc/dt$ being V the film volume and $c = Q/FV$ the concentration of active centers, required for testing Eq. 5. The slopes from **Figure 2B**, at the initial time, are the initial reaction rates. **Figure 2C** shows the empirical double-logarithmic relationships, Eq. 3, between $[\text{CNT}^*]$ and the initial reaction rate r for different electrolyte concentrations. **Figure 2D** presents the expected, Eq. 3; semilogarithmic Arrhenius relationships between r and $1/T$.

These empirical results fulfill the conditions stated by Eqs 2 and 3 and 5 for any chemical reaction. In conclusion, **Figure 2** corroborates that the electrochemical response of the CNTs takes

place under an electrochemical (Faradaic) kinetic control defined by Eqs 3 and 4 and 5.

The same methodology has been described and employed for the study of electrochemical kinetics in films of different conducting polymers: polythiophene (Otero and Santos, 2008), poly(3-methylthiophene) (Otero and Abadias, 2007, 2008), poly(3,4-ethylenedioxythiophene) (Otero and Caballero Romero, 2010), and polypyrrole (Otero and Garcia de Otazo, 2009; Otero and Martinez, 2011, 2013b).

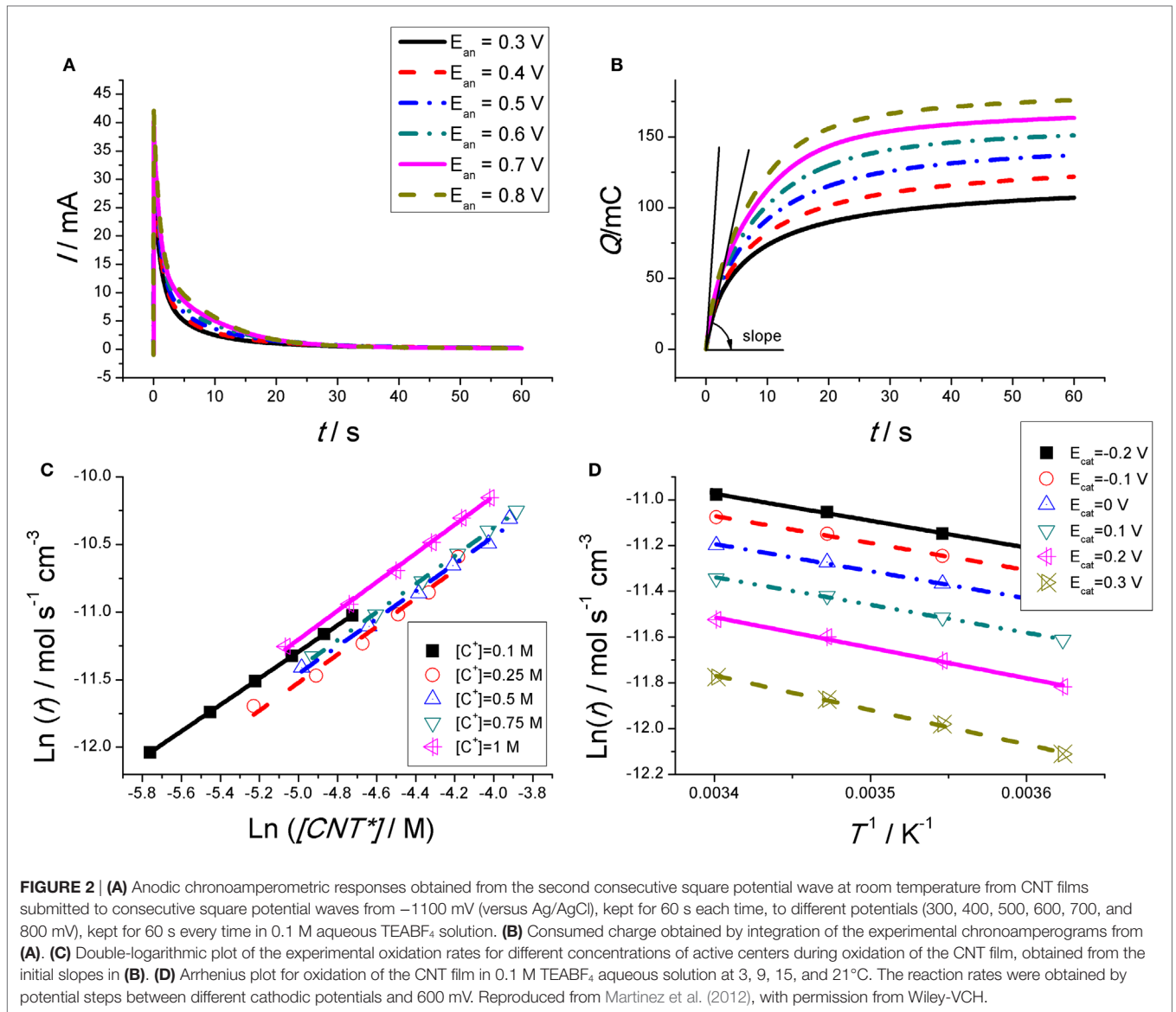
Relaxation Processes in CNTs

In conducting polymers, oxidation/reduction reactions induce structural movements at the molecular and macroscopic scale: conformational relaxation, swelling, shrinking, and conformational packing. Under these conditions, the local concentration of the counterions inside and around a conformational packed region of the film is low. For concentrations lower than 10^{-3}M , the charge required to charge the EDL during a potential step is a function of the ionic strength (Gouy-Chapman model) (Atkins and De Paula, 2002) and takes microseconds. Here, the oxidation of the CNTs and parallel charge of the EDL, of a packed structure of CNTs should take a long time (seconds) required for the reaction-driven structural relaxation.

Films of CNTs taking part of three-layer actuators give unexpected chronoamperometric responses, when submitted to potential steps, showing two maxima (**Figure 3A**) (Mukai et al., 2011; Gimenez et al., 2012). Similar responses during the oxidation–reduction of conducting polymers were theoretically described from physical–chemical principles by a simultaneous presence of capacitive and reactive processes. The second maximum indicate that the rate of the electrochemical oxidation is controlled by structural (nucleation–relaxation) processes (Otero et al., 1995, 1997a, 2010; Otero and Grande, 1996; Otero and Abadias, 2007, 2008; Otero and Santos, 2008; Otero and Garcia de Otazo, 2009; Arias-Pardilla et al., 2010a,b; Otero and Caballero Romero, 2010; Otero and Martinez, 2011, 2013b). Each of the processes is described by a stretched exponential function. The two stretched exponential functions (capacitive and reaction-driven structural nucleation–relaxation) can be deduced for conducting polymers and CNTs from basic polymeric and electrochemical principles, not including any adjustable parameter.

The stretched exponential functions have been used for long time in physical and biological science to adjust responses from systems having a distribution of relaxation times due to different local environments, local orders, or comprising different molecular or structural lengths or dimensions (Lee et al., 2001; Otero and Boyano, 2003; Otero et al., 2004a; Funston et al., 2007; Lin et al., 2008; Otero and Martinez, 2011).

The initial sharp peak of the chronoamperometric responses from CNTs can be attributed to the charge of the EDL. This response is modeled by a stretched exponential function (Holzle et al., 1994). For electrochemical responses, the general stretched exponential function can be expressed as Eq. 7 (Funston et al., 2007; West et al., 2009):



$$I = I_0 \exp\left(-\frac{t}{\tau}\right)^\delta; 0 < \delta < 1 \quad (7)$$

where I is the current, I_0 is the initial current, τ is the relaxation time, t is the elapsed time, and δ is the stretching coefficient.

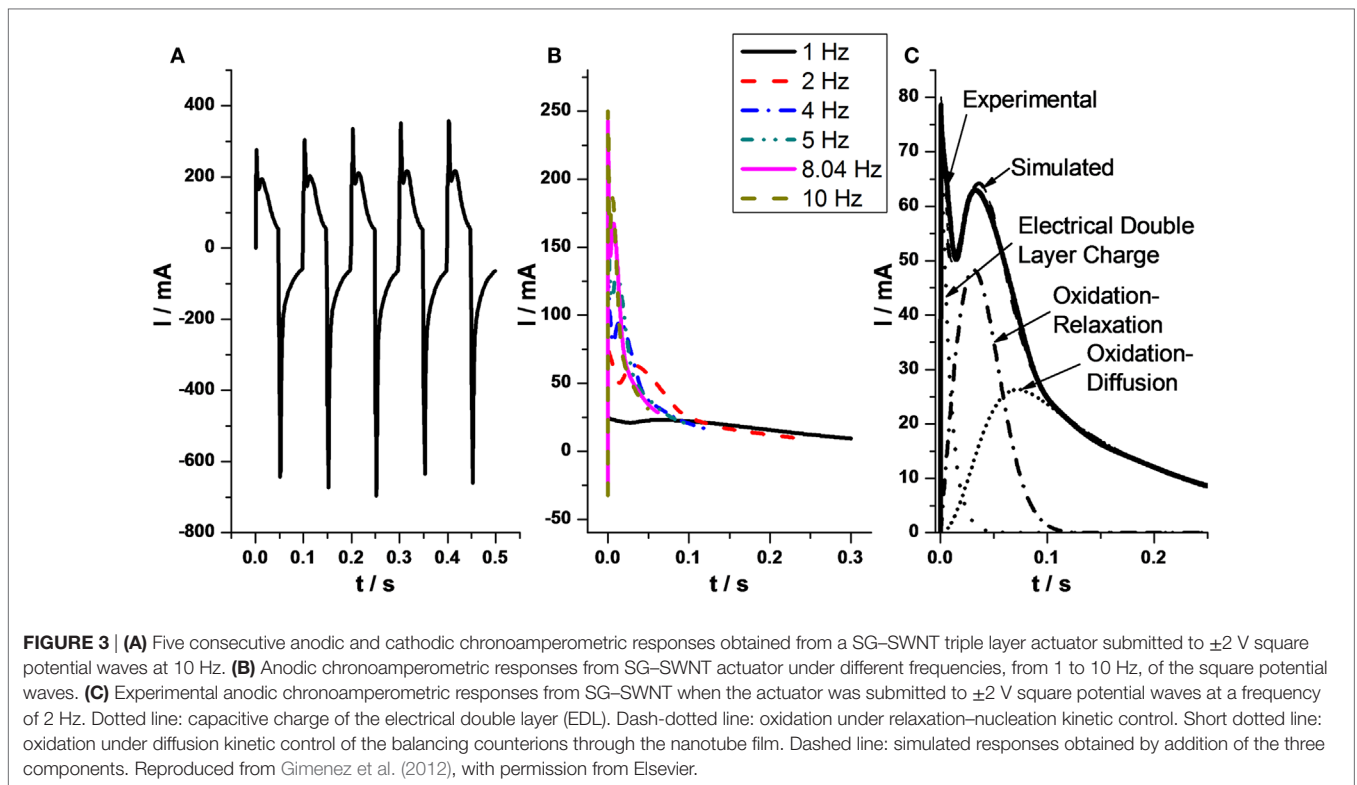
When $\delta = 1$, this equation corresponds to a Cottrell evolution of the current, occurring in absence of conformational relaxation control (Otero et al., 1997a). When the electrochemical response includes oxidation reactions, as Eq. 1, where the reaction rate is controlled by diffusion of the counterions through the CNTs film, the current passing through the electrode can be expressed as Eq. 8:

$$I_d(t) = bQ_d \exp(-bt) \quad (8)$$

where Q_d is the charge fraction consumed under reaction diffusion control. Compared with Eq. 7: $I_0 = bQ_d$ and $\tau = 1/b$. Under those conditions (diffusion kinetic control), the empirical charge consumed at any reaction time, t , $Q(t)$ after the potential step (obtained by integration of the chronoamperometric responses until that time) and the total charge of the electrochemical response are related by Eq. 9 (Otero et al., 1997a):

$$\ln\left[1 - \frac{Q(t)}{Q_d}\right] = -bt \quad (9)$$

The apparent diffusion coefficient, D , of the counterions from the solution through the partially oxidized material is



included by b through Eq. 10 (Otero et al., 2004b; Suarez et al., 2005):

$$b = \frac{2D}{h^2} \tag{10}$$

where h is the thickness of the CNTs film.

The chronoamperometric responses obtained from CNTs shows, moreover, the first peak related to the charge of the EDL and the beginning of the oxidation under possible diffusion control, a second maximum (Figure 3B) related to the initial oxidation under nucleation-relaxation control of a packed structure of the film, followed by its oxidation completion under diffusion kinetic control. From basic physical-chemical principles, the two processes are described by Eq. 11, including two stretched functions (Otero et al., 1997a,b):

$$I(t) = 2aQ_r t \exp(-at^2) + 2abQ_d \exp(-bt) \int_0^t t' \exp(bt' - at'^2) dt' \tag{11}$$

where Q_r is the charge consumed by the oxidation-relaxation process (when the material is compacted, some additional energy is needed to relax the packed structure generating the free volume required to lodge balancing counterions coming from the solution by diffusion through the material). The coefficient a can be expressed as Eq. 12 (Otero et al., 1995):

$$a = \frac{\pi N_0 \lambda^2}{\tau_0^2 A} \exp\left(\frac{-2\Delta H}{RT}\right) \tag{12}$$

where λ is the length of an elemental segment (average length of the CNTs here), N_0 is the number of nuclei where the oxidation-relaxation is initiated after the anodic potential step under each defined experimental condition, τ_0 is the pre-exponential factor of the relaxation time, A is the total film area, R is the universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature and ΔH is given by Eq. 13:

$$\Delta H = \Delta H^* + z_c \eta_c - z_r \eta \tag{13}$$

with ΔH^* is the conformational energy in the absence of any external electrical fields, z_c is the cathodic polarization coefficient (charge consumed to compact by electrochemical reduction 1 mol of CNT segments), η_c is the cathodic overpotential, z_r is the electrochemical relaxation coefficient (charge required to relax by electrochemical oxidation 1 mol of reduced and packed CNTs), and η is the anodic overpotential.

Equation 11 includes two different stretched exponential functions: the first term describes the oxidation under nucleation/relaxation kinetic control, $I_r(t) = 2aQ_r t \exp(-at^2)$; the second term describes the subsequent oxidation/swelling completion including counterion diffusion kinetic control. When the relaxation process is finished (the structure of the CNTs is swollen enough to allow the counterion's diffusion), t' becomes 0, and this second term can be expressed as Eq. 8.

Thus, the function describing all the full oxidation (chronoamperometric) response from the CNTs' film is constituted by three stretched functions, as expressed by Eq. 14:

$$I(t) = kQ_{EDL} \exp(-dt) + 2aQ_r t \exp(-at^2) + bQ_d \exp(-bt) \tag{14}$$

Each function quantifies (Figure 3C) a different process:

- Charge of the EDL: $kQ_{\text{EDL}} \exp(-kt)$.
- Oxidation under nucleation/relaxation control: $2aQ_i t \exp(-at^2)$.
- Oxidation-swelling completion under counterion's diffusion kinetic control through the film of CNTs: $2abQ_d \exp(-bt) \int_0^t t' \exp(bt' - at'^2) dt'$.

By addition of the three theoretical components the experimental response is overlapped.

At any oxidation time, each of the three components describes the fraction of current consumed to charge the EDL, by oxidation-relaxation of the compacted structure or for the oxidation of the relaxed material under diffusion kinetic control of the counterions, respectively. By integration of each of the functions the charge $\left(Q(t) = \int_0^t I(t) dt\right)$ consumed by each of the simultaneous processes is attained. The total experimental charge, obtained by integration of the chronoamperometric response must be the addition of the theoretical (by integration of the three different attained functions) charge consumed by each of the three components.

In conclusion, the charge consumed by the capacitive component (the charge of the EDL) and the charge consumed by the two Faradaic components (oxidation-relaxation and oxidation-diffusion) of the electrochemical response can be identified and quantitatively separated (Gimenez et al., 2012). The capacitive percentage ranges, for the studied experimental conditions, between 8.6 and 12.2% and the faradic component between 91.4 and 87.8%.

Chronopotentiometric Results: Dual Actuating-Sensing Properties of CNTs

A unique characteristic of the chemical equilibrium is that after any perturbation (change of any experimental variable) responds trying to compensate its effect. This is the Le Chatelier principle (Smith, 2004). This principle has been translated outside the chemical equilibrium (Martinez and Otero, 2012, 2014; Otero et al., 2012b; Otero and Martinez, 2015): for films of CNTs including chemical reactions driven by a constant current (under constant reaction rate, Eq. 4) any external perturbation acting on the reaction rate shifts the potential evolution (the potential senses the perturbation) in order to adjust the new energetic requirements. Thus, if the electrochemical response of the CNTs includes a chemical component (Faradaic) the evolution of the material potential from the same initial (reduced or oxidized) state to the same final (oxidized or reduced, respectively) state must give quantitative information about the variables affecting the oxidation/reduction Eq. 1 rates: electrolyte concentration, temperature, or mechanical variables. This principle was checked for CNTs applying square current waves (chronopotentiometric responses), changing every time only one experimental variable, keeping the rest constant, as in the case of the kinetics experiments presented in the previous section.

Carbon nanotubes were subjected to consecutive square current waves (± 0.5 mA) in aqueous solutions with different concentrations of TEABF₄: 0.05, 0.1, 0.25, 0.5, 0.75, and 1M. The attained chronopotentiograms (evolution of the CNTs potential with time) show a strong influence of electrolyte concentration (Figure 4A). As expected for any chemical reaction, for a higher concentration of one of the reactants (electrolyte), the reaction becomes easier occurring at a lower potential under flow of the same current, that is, for the same reaction rate.

The consumed electrical energy, U , is given by Eq. 15 (Beaty and Fink, 2013):

$$U = \int_0^t I(t)E(t)dt \quad (15)$$

where E is the potential.

For chronopotentiometric experiments, Eq. 15 can be expressed as Eq. 16, where the applied current is constant:

$$U = I \int_0^t E(t)dt \quad (16)$$

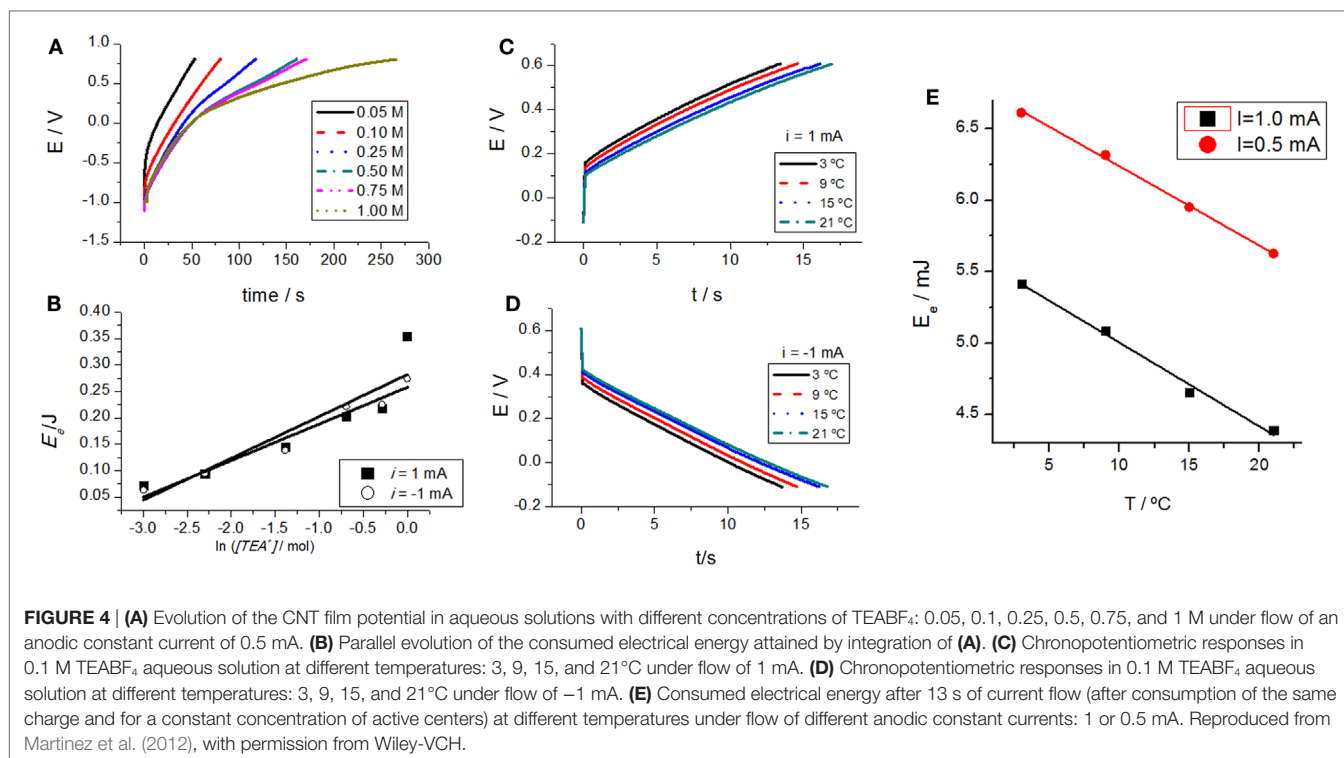
where $\int_0^t E(t)dt$ is the integral of each experimental chronopotentiometric response from the beginning of the current flow.

Thus, for the same oxidation state, after consumption of the same charge ($Q = it$), that is, after oxidation of the same number of active centers, the potential attained by the material, and the consumed electrical energy, follow a semilogarithmic dependence with the electrolyte concentration (Figure 4B). Figures 4A,B corroborate that the reactive material senses the electrolyte concentration while reacting.

The experimental procedure was repeated by changing the temperature for different experiments keeping the rest of experimental variables (consumed charges, applied currents, and electrolyte concentrations) constant. The material potential during oxidation and reduction changes with the experimental temperature, Figures 4C,D, respectively. The evolution of consumed electrical energy for a constant time (constant consumed charge) and different temperatures corroborates that the material, during reaction under flow of a constant current senses the working temperature (Figure 4E). The achieved potential or the consumed electrical energy, after a constant time of current flow, are the sensing magnitudes. The reacting material, and any device based on it, senses the working conditions. When CNTs take part, as active materials, of actuators, the actuator will sense working and surrounding conditions while working: this is a dual sensing-actuator system mimicking biological organs as haptic muscles. In summary, any electrochemical actuator based on CNTs and controlled by a constant current will sense through the device potential working temperature or electrolyte concentration variation: both sensing (potential or energy) and actuating (current) signals are present simultaneously in the two connecting wires while working.

OTHER CARBON-BASED MATERIALS

Similar electrochemical responses and subsequent conclusion to those here exposed were obtained from films of conducting



polymers (Conzuelo et al., 2010; Otero et al., 2012a; Otero and Martínez, 2013a,b, 2015) or graphene (Martínez et al., 2012). The presence of chemical reactions gives for the empirical reaction rates the expected semilogarithmic or double-logarithmic relationships for the studied experimental variables. In addition, the potential, or the consumed electrical energy under flow of a constant current, senses any working conditions or external perturbation during the reaction, as it corresponds to any chemical or electrochemical reaction.

CAPACITIVE, REACTIVE, AND STRUCTURAL COMPONENTS: FINAL REMARKS FOR IMPROVING ELECTROCHEMICAL DEVICES AND PRODUCTS

We can conclude that electrochemical responses from films including CNTs change when the electrolyte concentration or the working temperature change, as expected for any chemical reaction. When the capacitive and the reactive component of the electrochemical response can be separated, as it occurs for chronoamperometric responses showing two maxima, the reactive component consumes over 80% of the involved charge. The electrochemical reaction drives swelling, shrinking, conformational relaxation, and conformational compaction structural changes in films of CNTs, or including CNTs. When any of those structural changes constitute the rate limiting process of the electrochemical reaction they also control the rate of the concomitant

electrochemical application (actuator, supercapacitor, smart membrane, reactive conformational sensor, drug delivery, and so on).

On this way for the development of new devices based on the electrochemistry of CNTs, some preliminary optimization of the capacitive, Faradaic, and structural components of the electrochemical responses should be required. In particular, detecting which of the three components is the rate limiting process for each device will be useful for improving the response time, the energy efficiency, and the lifetime of the devices. Finally, the chemical nature of the electrochemical response should provide electrochemical devices based on CNTs with a unique biomimetic property: any of the devices will sense, while working, any physical or chemical property of the working or surrounding ambient variables acting on the reaction rate. This dual functionality is unique of the biological systems, as haptic muscles, without any parallel in present technological world.

AUTHOR CONTRIBUTIONS

All authors have contributed to write the paper and revise it.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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