Gravimetric and Dynamic Deconvolution of Global EQCM Response of Carbon Nanotube Based Electrodes by *Ac*-Electrogravimetry

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Abstract: The capacitive charge storage of carbon nanotube (CNT) based electrodes was investigated by *ac*-electrogravimetry which couples fast quartz crystal microbalance (QCM) and electrochemical impedance spectroscopy (EIS). In contact with an aqueous NaCl electrolyte, evidence was found that there are two types of cations ($Na^+.H_2O$ and H^+) electroadsorbed with different kinetics for cathodic potentials and the Cl^- ions for anodic potentials together with free water molecules. The reconstruction of the total mass response from independent *ac*-electrogravimetry measurements agrees perfectly well with the global EQCM response. Our findings reveal the unique sensitivity of the *ac*-electrogravimetry to provide a fair gravimetric and dynamic deconvolution of the global EQCM responses.

Keywords: Carbon nanotubes, supercapacitors, EQCM, *ac*-electrogravimetry, ion transfer dynamics, electroadsorption.

1. Introduction

The efficiency of energy storage devices depends largely on the physical properties of the materials that are constituted of, such as the specific surface area, porosity and/or morphology [1,2].

Nanostructured carbon materials have been extensively studied as electrodes for electrochemical double layer capacitors (EDLC) [3,4]. The pore size of the carbon and its relation to the size of the ions is an important factor and should be optimized to maximize the specific capacity. Answering the questions concerning the charging mechanisms is experimentally difficult because there are not any appropriate electrochemical or physico-chemical methods that allow a direct access to such information. Recent electrochemical quartz crystal microbalance (EQCM) based analyses started to address these questions [5-11]. It was successfully combined with electronic conductance studies or with nuclear magnetic resonance (NMR) to access to a full description of the electric double layer [6,9].

However, none of these methods alone provides the information on the exact identification of the electroadsorbed ionic species, their dynamics of transfer at the interfaces, as well as the role of the electrolyte composition and the effect of ions solvation on the charge storage efficiency. The dynamic aspects of ion electroadsorption inside carbon based electrodes remains a partially unsolved issue.

Here, an alternative characterization tool was proposed which couples fast quartz crystal microbalance (QCM) and electrochemical impedance spectroscopy (EIS) (also called *ac*-electrogravimetry) [12-15]. It was employed to characterize supercapacitive charge storage mechanism of single wall carbon nanotube (SWCNT) based electrodes revealing the unique sensitivity of the *ac*-electrogravimetry to provide gravimetric and dynamic deconvolution of a global EQCM response.

2. Experimental

SWCNTs were deposited by the "drop-casting" method on the gold electrode (0.20 cm^2) of quartz crystal resonators (9 MHz-AWS, Valencia, Spain). Typically, ~8 µl of a solution containing 90 wt. % SWCNT powder (length: 300-2300 nm and diameter: 0.7-1.1 nm, Sigma-Aldrich) and 10 wt. % PVDF-HFP polymer binder (poly(vinylidene fluoride-hexafluoropropylene), Sigma-Aldrich) in N-methyl-2-pyrrolidone (NMP) was deposited using a lab-made mask. The deposited mass was estimated by measuring, Δf_m, before and after the deposition and by converting it to the mass change (Δm), using the Sauerbrey equation ($\Delta m = -k_s.\Delta f_m$ where k_s is the calibration constant (16.3 × 10^7 Hz/g.cm^2)) [16].

EQCM measurements were performed in aqueous 0.5 M NaCl at pH=7 under nitrogen atmosphere. A platinum grid was used as counter electrode and Ag/AgCl as reference electrode. The gravimetric regime was assured by keeping film thickness acoustically thin (<500nm).

For *ac*−electrogravimetry, a four−channel frequency response analyzer (FRA, Solartron 1254) and a lab-made potentiostat (SOTELEM-PGSTAT) were used. The QCM was used under dynamic regime, the working electrode (WE) was polarized at a selected potential, and a sinusoidal small amplitude potential perturbation (60 mV rms) was superimposed. The microbalance frequency change, Δf_m, corresponding to the mass response, Δm, of the WE was measured simultaneously with the *ac* response, ΔI, of the electrochemical system. The frequency range was between 63 kHz and 10 mHz. The resulting signals were sent to the four−channel FRA, which allowed the electrogravimetric transfer function (TF), $\frac{\Delta m}{\Delta E}(\omega)$, and the electrochemical impedance, $\frac{\Delta E}{\Delta I}(\omega)$, to be simultaneously obtained at a given potential [12-15]. The measurements were performed in 0.5 M NaCl at pH=7 and at every 100 mV in the following potential range: -0.45 V-0.45 V *vs* Ag/AgCl.

3. Theoretical Background

For supercapacitive SWCNT thin films, the change of the concentration, ΔC_i, of each species (e.*x.* i = cation1 (c1) and cation 2 (c2), and free solvent (s)) over a potential ΔE step can be estimated using Eq. (1):

$$\left.\frac{\Delta C_{c_i}}{\Delta E}\right|_{th}(\omega) = -\frac{G_{c_i}}{(j\omega d_f) + K_{c_i}}$$

(1)

where $\omega=2\pi f$ is the pulsation, d_f is the film thickness and K_i and G_i are the partial derivatives of the flux, J_i, with respect to the concentration and the potential, respectively. K_i is related to the kinetics of the ionic or free solvent transfer. G_i is the inverse of the transfer resistance, $Rt_i = \frac{1}{FG_i}$, of the species at the film/electrolyte interface [12-15].

The charge/potential TF, $\left.\frac{\Delta q}{\Delta E}\right|_{th}(\omega)$, is calculated for the electroadsorption of the two cations (as an example), c1 and c2 by using the Faraday number, F, and the film thickness, d_f:

$$\left.\frac{\Delta q}{\Delta E}\right|_{th}(\omega) = Fd_f\left(\frac{G_{c1}}{j\omega d_f + K_{c1}} + \frac{G_{c2}}{j\omega d_f + K_{c2}}\right)$$

(2)

The electrogravimetric TF, $\left.\frac{\Delta m}{\Delta E}\right|_{th}(\omega)$, can be calculated theoretically, taking into account the charged and uncharged species contribution through the two parameters K_s and G_s:

$$\left.\frac{\Delta m}{\Delta E}\right|_{th}(\omega) = -d_f\left(m_{c1}\frac{G_{c1}}{\left(j\omega d_f\right) + K_{c1}} + m_{c2}\frac{G_{c2}}{\left(j\omega d_f\right) + K_{c2}} + m_s\frac{G_s}{\left(j\omega d_f\right) + K_s}\right)$$

(3)

where m_{c1}, m_{c2}, and m_s are the atomic weight of involved species.

4. Results and Discussion

Electrochemical performance of SWCNT based thin films was characterized in a classical manner *via* cyclic electrogravimetry in 0.5 M aqueous NaCl. Figure 1A shows quasi-rectangular shaped cyclic voltammetry (CV) responses indicating that the charge storage is mainly due to the reversible electroadsorption of the ions which is in good agreement with the results of the similar systems [11]. The corresponding mass variations is followed by simultaneous QCM measurements as a function of potential (Fig. 1B). Figure 1B presents a change in slope around 0.1V *vs* Ag/AgCl where $\frac{\Delta m}{\Delta E}\langle 0$ and $\frac{\Delta m}{\Delta E}\rangle 0$ for the transfer of cations and the anions, respectively. It indicates that the point of zero charge (PZC) is around this value. To obtain indications on the nature of the transferred species, the $F \times \frac{\Delta m}{\Delta q} = F \frac{\Delta m / \Delta t}{\Delta Q / \Delta t}$ function was calculated from the EQCM data (Fig. 1A,B) which corresponds to the molar mass of the species exchanged at the electrode/electrolyte interfaces at a given scan rate. Figure 1C shows that the estimated molar mass values are between 23 and 40 g.mol^{-1} in the potential range from 0.4 V to 0.05 V *vs* Ag/AgCl. The higher values suggest that the cations are hydrated and/or accompanied by free solvent molecules. The contribution of *(i)* counter ions solely, *(ii)* counter ions and solvent or *(iii)* both counter- and co-ions (without solvent) in carbon based electrodes were intensively investigated by Levi and Aurbach *et al.* [10], and similar cases were considered in doped conducting polymers and conventional redox systems by Bruckenstein and Hillman *et al.* [17-20].

Our findings and the literature results strongly suggest that the EQCM data envelops the subtleties of the supercapacitive charge storage. This global EQCM response, measured at a certain scan rate cannot give an easy access to the details related to the capacitive charge storage mechanism. Therefore, an *ac*-electrogravimetric study is conducted for the deconvolution of the global EQCM response into distinct contributions with a resolution at the temporal level.

Fig. 2A and 2B present $\frac{\Delta q}{\Delta E}(\omega)$ and $\frac{\Delta m}{\Delta E}(\omega)$ transfer functions (TFs) (at -0.4 V) where the experimental data are fitted using Eq. 2 and 3, respectively (details of the model in Ref. 12-15). For fitting the experimental data, several configurations were considered involving Na^+, H^+, their hydrated counterparts and free H_2O with the strict criteria that a good agreement between the experimental and the theoretical function in terms of shape and frequencies was achieved. Figure 2B depicts an example of a mass/potential TF where the three species participate to the

electroadsorption process, *i.e.* $Na^+.H_2O$, H^+ and free H_2O (no anion contribution is expected at -0.4 V). The partial mass/potential TFs were also analyzed to validate our hypothesis involving three different species; they are estimated, for example by removing the c2 contribution, calculating $\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c1s}$ or by removing the c1 contribution, calculating $\left.\frac{\Delta m}{\Delta E}\right|_{th}^{c2s}$ (not shown). The hydrated Na^+ appears at high frequency (fast process) whereas the protons participate at low frequency (slow process). The kinetics of the free solvent molecules is close to that of hydrated Na^+ species suggesting that polar water molecules are electrodragged together with hydrated Na^+.

As the measurements were performed over the potential, K_i (kinetics of transfer) and G_i (related to the ease of interfacial transfer) parameters were also estimated at different potential values (Fig. 2C and 2D). Two different cationic species and free water molecules were

detected in the potential range from -0.4 V to 0 V (no major anions contribution in that region). The hydrated Na^+ ions are persistently the fastest species, *i.e.* $K_i\left(Na^+.H_2O\right) \rangle K_i\left(H^+\right)$ (Fig. 2C). The G_i parameter permits the Rt_i (transfer resistance) to be calculated which can explain the ease or the difficulty in the transfer at the electrode/electrolyte interface. The Rt_i values present the following order: $Rt_i\left(H^+\right) \rangle Rt_i\left(Na^+.H_2O\right)$ (inverse of the K_i).

These findings strongly suggest that $Na^+.H_2O$, although formally larger than H^+, are faster and easier to be electroadsorbed at the SWCNT/electrolyte interfaces. This, a priori anomalous behavior can be discussed in terms of cation concentration or of the relationship between the dehydration energy and the ion size. For the former, the proton concentration is lower compared to the sodium and can affect the kinetics of transfer. For the latter, the smaller ions are more tightly bound to their water molecules such that it exists an inverse relationship between the dehydration energy and the ion size [21-23]. Additionally, the possibility that electroadsorption occurs in two different sites; directly on the surface (sites more accessible for the hydrated sodium) or inside the nanotubes (sites less accessible for the dehydrated protons) can be suggested.

The participation of the anions (Cl^-) to the electroadsorption process was also detected at around the PZC (Fig. 2C,D) probably due to the permselectivity failure of the SWCNT films around this value leading to the mixed adsorption [7]. Their transfer resistance is high around PZC which decreases at more anodic potentials *i.e.* 0.4 V vs Ag/AgCl.

A major advantage of *ac*-electrogravimetry is the estimation of the relative concentration change with respect to the individual species (after integration of $\left.\frac{\Delta C_i}{\Delta E}\right)_{\omega \to 0} = -\frac{G_i}{K_i}$, C_i - C_0 values can be determined) [12,13]. It is noteworthy that despite the slow kinetics and high transfer resistance of the protons, their contribution to the charge storage is not negligible

(Fig. 3A). For more anodic potentials (when the SWCNT surface is positively charged), the electroadsorption of anions occurs keeping the electroneutrality of the electrode/electrolyte interface.

The concentration variation of individual species (C_i - C_0) obtained from the *ac*-electrogravimerty are converted into their respective mass variations (Fig. 3B). Subsequently, the total mass response of the SWCNT electrode is reconstructed by addition of the individual contributions (Fig. 3C) which agrees perfectly well with the global EQCM results (Fig. 3D) (*i.e.* $\Delta m_{ac-electrogravimetry} = 0.65 \mu g.cm^{-1}$ and $\Delta m_{EQCM} = 0.62 \mu g.cm^{-1}$ for the cathodic potentials). It is further highlighted that *ac*-electrogravimetry results are obtained from individual measurements at stationary potentials and the reconstructed mass response is in good agreement with the EQCM data from cyclic voltammetry. This is highly significant since it evidences that the *ac*-electrogravimetry result in Fig. 3B is indeed a deconvolution of the global EQCM mass response into distinct contributions. Since *ac*-electrogravimtery provides additional information on the kinetics of the respective species, then it is legitimate to call it a gravimetric and dynamic deconvolution.

5. Conclusions

The contribution of two cations ($Na^+.H_2O$ and H^+) and an anion (Cl^-) were detected when the SWCNT electrode surface is negatively and positively charged, respectively. The deconvolution of the global EQCM response into distinct contributions (identification of ions, solvation numbers and free solvent contributions) and the kinetics of electroadsorption are the strong assets of the *ac*-electrogravimetry which cannot be attained *via* EQCM alone. The methodology can be extended to characterize other carbon based electrodes and pave the way toward more performant electrode/electrolyte systems in energy storage.

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Figure Captions

Fig. 1 The CV curves (A), the simultaneous mass responses (B) and the $F \times \frac{\Delta m}{\Delta q}$ function (C) of the SWCNT based thin films in 0.5 M NaCl at pH=7.

Fig. 2 $\frac{\Delta q}{\Delta E}(\omega)$ (A) and $\frac{\Delta m}{\Delta E}(\omega)$ (B) at -0.4V *vs* Ag/AgCl, kinetic parameters K_i ($cm.s^{-1}$) (C), and the transfer resistance values, R_{ti} ($\Omega.cm^2$) (D) of the SWCNT based thin films as a function of potential in 0.5 M NaCl at pH=7.

Fig. 3 Relative concentration variation, $C_i - C_0$ (A), relative mass variation (B) (calculated from A) of respective species in the SWCNT based electrode, measured in 0.5 M NaCl at pH=7. Total mass variation reconstructed from *ac*-electrogravimerty (C) is compared with the EQCM data (D).

Figures

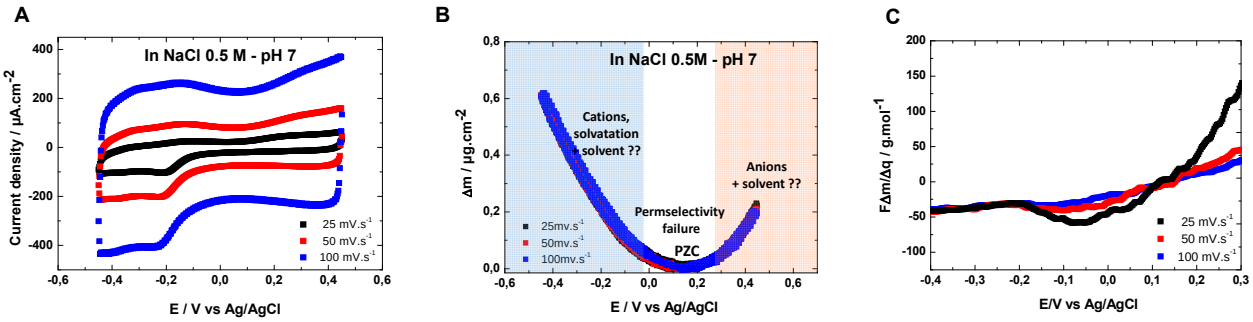


Fig. 1

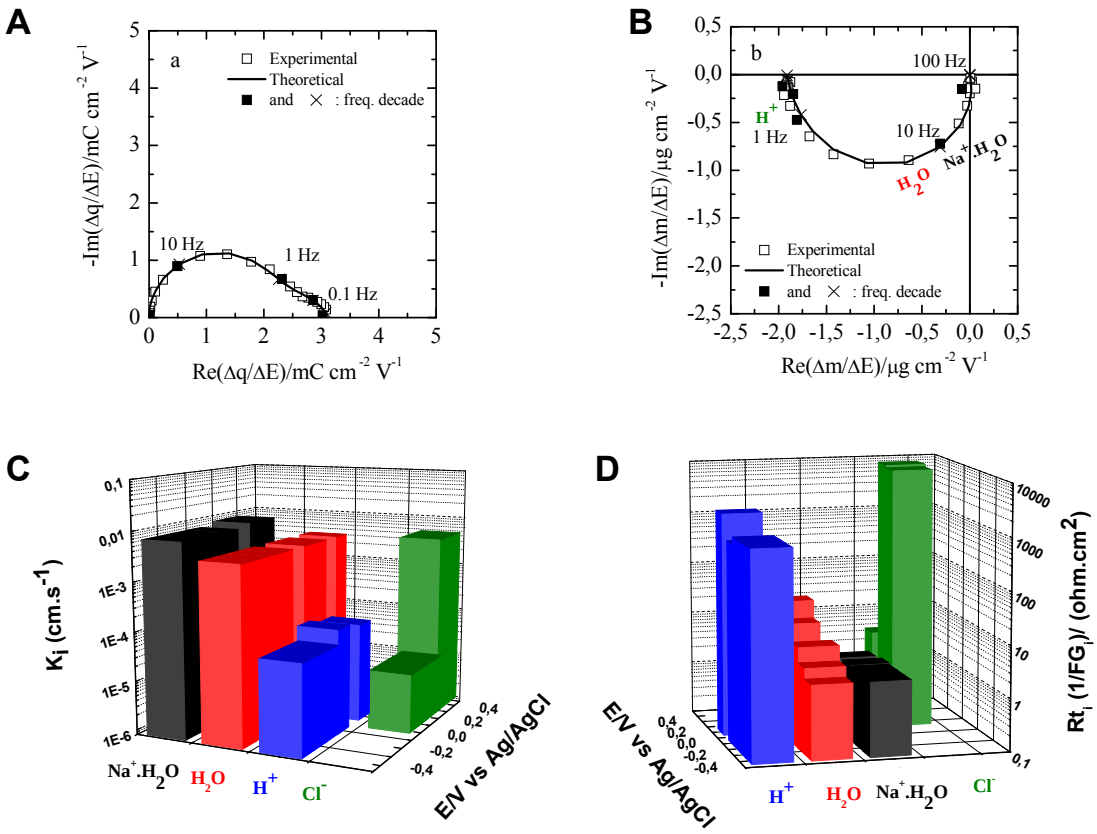

A
a
Experimental
Theoretical
and : freq. decade
10 Hz
1 Hz
0.1 Hz
-Im(Δq/ΔE)/mC cm-2 V-1
Re(Δq/ΔE)/mC cm-2 V-1
B
b
100 Hz
10 Hz
1 Hz
H+
Na+.H2O
H2O
Experimental
Theoretical
and : freq. decade
-Im(Δm/ΔE)/μg cm-2 V-1
Re(Δm/ΔE)/μg cm-2 V-1
C
Ki (cm.s-1)
Na+.H2O
H2O
H+
Cl-
E/V vs Ag/AgCl
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E/V vs Ag/AgCl
H+
H2O
Na+.H2O
Cl-

Fig. 2

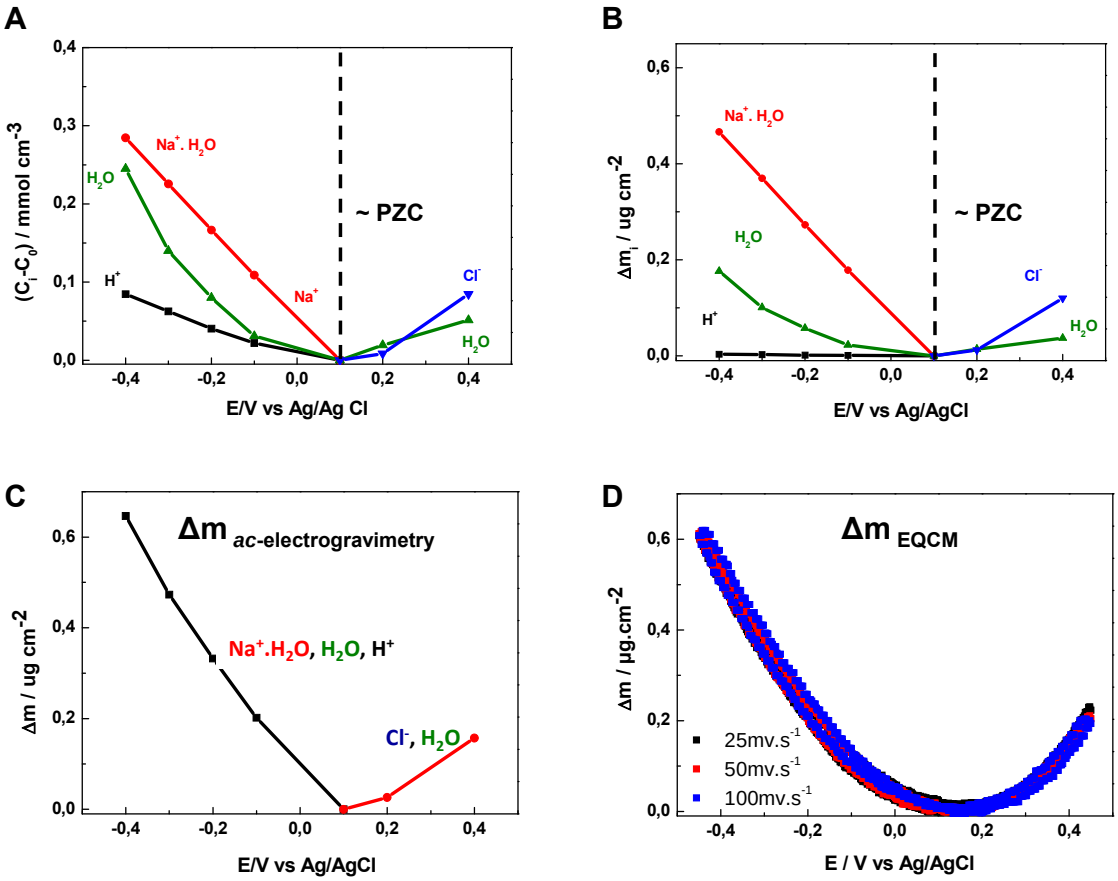

A
(C_i-C_0) / mmol cm^-3
Na+. H2O
H2O
H+
Na+
Cl-
H2O
~ PZC
E/V vs Ag/Ag Cl
B
Δm_i / ug cm^-2
Na+. H2O
H2O
H+
Cl-
H2O
~ PZC
E/V vs Ag/AgCl
C
Δm / ug cm^-2
Δm ac-electrogravimetry
Na+.H2O, H2O, H+
Cl-, H2O
E/V vs Ag/AgCl
D
Δm / µg.cm^-2
Δm EQCM
25mv.s^-1
50mv.s^-1
100mv.s^-1
E / V vs Ag/AgCl

Fig. 3