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Anthraquinone modification of microporous carbide derived carbon films for on-chip micro-supercapacitors applications

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ABSTRACT

The modification of carbide derived carbon (CDC) thin film electrodes with anthraquinone (AQ) molecules was demonstrated by using pulsed chronoamperometry, in 0.1 M $\text{NEt}_4\text{BF}_4/\text{ACN}$ solution of AQ diazonium derivative. The functionalization of CDC electrodes was only possible when a critical pore size is reached: only 2 nm pore diameter CDC can be grafted with AQ moieties, smaller pore size leading to a poorly functionalized electrode. High AQ surface coverage of $0.88 \times 10^{-10} \text{ mol.cm}^{-2}$ was determined using 2 nm pore size CDC. Despite a decrease in double layer capacitance value of about 10%, the total capacitance of the AQ-modified on-chip CDC electrodes was twice larger than that of pristine CDC film, leading to high total capacitance value of 44 mF.cm^{-2} (338 F.cm^{-3}). The cyclability of the AQ-modified on-chip CDC electrode was also investigated. The faradic contribution of AQ grafted molecules progressively decreased during cycling and only 39% of the normalized capacity remained after 500 cycles; this decrease has been assigned to electrostatic repulsion of dianionic AQ confined in narrow micropores in the alkaline media.

Keywords:

micro-supercapacitors
carbide-derived carbon
anthraquinone
electrochemical grafting
diazonium chemistry

1. Introduction

Portable electronic devices require integrated energy storage devices providing high power and energy delivery [1]. However, while Electrochemical Double Layer Capacitors (EDLCs), that can handle fast charge and discharge for more than 1 000 000 times, are very promising to power numerous applications, they still deliver moderate energy densities, which remains a hinder for their implementation in electrical and electronic devices [2,3]. To tackle this limitation, innovative electrolytes with larger potential window or new electrode materials have been designed [4–8]. Both strategies impact the double layer capacitance which comes from the charge separation at the electrode/electrolyte interface, where electrolyte ions reversibly adsorb to balance the charges at the electrode [2]. Pseudocapacitive materials provide higher

capacitance values owing to fast redox reactions occurring at the surface or sub-surface of metal oxides [9].

An alternative to this strategy consists in modifying carbon materials with foreign heteroatoms [10] or electrochemically active molecules [11], where the grafted molecules offer faradic contribution originating from redox reactions in addition to the double layer capacitive current [12]. Therefore, many studies have focused on the functionalization of carbon with electroactive moieties. Diazonium chemistry is a convenient way to reach this goal. The reduction of the diazonium cation proceeds through a concerted mechanism in which an electron transfer and di-nitrogen loss lead to the formation of an aryl radical. The resulting radical species further react with the surface to form a covalent bond with active sites on the electrode [13–16]. Delamar and co-workers were the first to take advantage of the electrochemical reduction of diazonium cations to modify carbon electrodes [17,18]. Precursor solutions for such electrochemical grafting can be prepared either from dissolution of diazonium derivatives in acetonitrile [19], or by *in situ* generation of diazonium salts from the parent aniline [20,21]. Both methods have been used to graft

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various aryl radicals on a large variety of substrates such as high surface area carbons, metals or semi-conductors [22–25].

Electrochemical grafting can be achieved using a three electrode configuration [26,27]. For example, one-step electrochemical grafting of anthraquinone molecules on carbon surfaces using *in-situ* generated anthraquinone diazonium salts was successfully performed in both organic and aqueous media containing the amino precursor and tert-butyl nitrite or sodium nitrite, respectively [28]. While the surface concentration increased as the grafting potential becomes more cathodic, it was proposed that multilayers of aryl radical can be grown from diazonium reduction. Although the diazonium salts are not designed to polymerize, films significantly thicker than monolayers can be obtained due to radical species formed in the vicinity of the electrode that can react with the previously grafted molecules [11,15].

The grafting of quinones has been extensively studied in the literature as they allow a two electron transfer during reduction process [29,30]. Chemical grafting of quinones was performed on glassy carbon [31], carbon nanotubes (CNTs) [32], onion-like carbons (OLCs) [33], graphite [34], CVD grown graphene [35] and porous carbons [36–38] in order to improve the performance of these EDLCs electrodes. As an example, grafting of AQ on porous Black Pearls carbon (AQ-BP) led to a drastic improvement of the capacitance up to 195 F.g⁻¹ for an AQ loading of 14% wt, compared with 100 F.g⁻¹ for non-modified carbon [37]. Furthermore, the AQ-BP showed acceptable capacitance retention until 100 mV.s⁻¹ and good cyclability with only 17% faradic capacitance loss observed after 10 000 charge/discharge cycles [37]. Similarly, the capacitance delivered by 9,10-phenanthrenequinone grafted OLCs in 1 M H₂SO₄ was 3 to 9 times higher than for pristine OLC [33]. Galvanostatic charge/discharge experiments showed good cyclability of the modified OLC, with 97% of the initial capacitance retained after 10 000 cycles [33].

Grafted carbons have been successfully used in symmetrical or asymmetric hybrid supercapacitors [39,40]. For instance, AQ-grafted carbon fabrics were used as negative electrode in an asymmetric cell against a positive dihydroxybenzene modified carbon fabric electrode, providing an energy density that was found to be double the value obtained for a symmetric device with two unmodified carbon fabric electrodes [41]. Aside, asymmetric supercapacitor was built with AQ-grafted carbon fabrics at the negative electrode and pseudocapacitive ruthenium oxide as positive electrode, providing a gravimetric capacitance of 109 F.g⁻¹ over a slightly increased 1.3 V potential window [42]. However, to the best of our knowledge, the grafting of quinone moieties has never been reported on carbide derived carbons (CDC) despite the fact that such carbon based electrodes were depicted as highly desirable in various applications including bulk devices [43] and micro-supercapacitors [44].

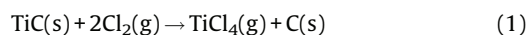
Recently, we reported the fabrication of on-chip carbide derived carbon films for micro-supercapacitors applications [44,45]. Carbide-derived carbons are produced from the selective extraction of metallic atoms from a metal carbide precursor through high temperature chlorination process, offering a fine control at nanometer scale of the carbon porosity [46]. This narrow pore size distribution (PSD) led to high volumetric capacitance values, and allowed the preparation of high performance CDC based

micro-supercapacitors embedded on silicon chips [44]. The present study aims at preparing CDC films grafted with anthraquinone moieties for on-chip micro-supercapacitor electrodes. Chemical and electrochemical grafting were performed on Si/SiO₂/TiC/CDC substrates in organic electrolyte containing the diazonium derivative, namely anthraquinone-1-diazonium. The influence of the electrochemical process used for the diazonium reduction is discussed, as well as the relation between the AQ coverage and the CDC porous structure.

2. Experimental

2.1. On-chip CDC films preparation

In order to get rid of the preparation of composite electrodes using active material, binder and conductive additive, the electrochemical tests were performed on on-chip porous carbide-derived carbon films such as described elsewhere [44,45]. Briefly, TiC films were deposited at 750 °C and 10⁻² mbar on Si/SiO₂ wafers using non-reactive direct current magnetron sputtering process (DC-MS) from a TiC target (99.5%, 10 cm diameter, 6 mm thick) under argon atmosphere. Deposition time has been tuned in order to deposit the requested thickness. The layered Si/SiO₂/TiC sample was then introduced in a furnace under argon purge and heated at the desired temperature. The titanium carbide film was then converted into porous CDC by reacting with chlorine gas following the reaction below (1):



The thickness of the CDC electrodes depends on the chlorination duration and partial chlorination led to strongly adherent on-chip CDC films [44] with a TiC adhesion layer in between the silicon substrate and the porous carbon layer, which will be denominated as CDC electrode in this study. Aside, full chlorination of the TiC layer was performed by increasing the chlorination time which in turn led to the separation of CDC film from the Si/SiO₂ substrate due to the lack of TiC intermediate adhesive layer [44]. Thus, the formation of self-supported CDC films of several square centimeters (footprint area) can be achieved. These self-supported CDC films were used to estimate the CDC weight per cm² for further AQ coverage calculation. Indeed, several self-supported CDC films were weighted with a SARTORIUS (Germany) analytical balance. Then the total area of CDC was established by analyzing with imageJ software optical pictures of the films taken with a suited camera. Thus, the weights of CDC chlorinated at 450 °C and 700 °C were calculated to be 1.4 × 10⁻⁴ and 1.2 × 10⁻⁴ g.cm⁻².μm⁻¹, respectively.

Annealing was performed for 1 h at 600 °C under H₂ atmosphere to remove chlorine residues trapped into the micropores [44]. Raman spectroscopy and energy dispersive X-ray analyses confirm that i) TiC is no longer present after full chlorination of the films, ii) Ti content in the CDC layer was less than 1 at.%. All on-chip CDC film thicknesses were measured between 1 and 5 μm to make the comparison of the electrochemical tests relevant. The main structural properties of the as-prepared CDC films are listed in Table 1, according to previous reports [47]. The use of such thin film electrode allows the investigation of the intrinsic properties of CDC without the drawbacks usually related to the fabrication of

Table 1
Structural properties of the as-prepared on-chip CDC films.

Chlorination temperature (T _{Cl} ^o)	S _{BET} (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mean pore size (nm)
450	977	0.47	0.59
700	1026	0.73	0.85

composite electrodes, i.e. the addition of electronically non-conductive polymeric binder and the need for conductive carbon to balance the moderate electronic conductivity of thick composite electrode ($<1 \text{ S cm}^{-1}$) [48].

2.2. Anthraquinone grafting

2.2.1. Reagents

Tetraethylammonium tetrafluoroborate (NEt_4BF_4 , Acros Organics) was dried at 120°C under vacuum for 24 h and dissolved in acetonitrile (ACN, 99.9% Extra-dry, Acros Organics). Then, Fast Red Al salt (anthraquinone-1-diazonium hemi(zinc chloride), Sigma-Aldrich) was added to the electrolyte.

2.2.2. Chemical grafting

The surface coverage of porous carbon by electrochemically active species strongly depends on the grafting conditions. While chemical routes have been extensively used for carbon modification [13], the electrochemical grafting is faster and provides higher grafting loadings [27]. Two methods were used to graft AQ molecules on microporous on-chip CDC film. A spontaneous modification (chemical route) [49] was achieved by immersing the CDC electrode for 3.5 h in acetonitrile solution containing AQ-1-diazonium concentrated at 20 mM and 0.1 M NEt_4BF_4 . The modified on-chip CDC film was then washed with aliquots of ethanol prior to electrochemical characterization.

2.2.3. Electrochemical grafting

The electrochemical modification of on-chip CDC electrodes was achieved using a Biologic VMP3 potentiostat in a three-electrode configuration. To perform the electrochemical grafting of anthraquinone molecules, AQ-1-diazonium was dissolved at 5 mM in 0.1 M $\text{NEt}_4\text{BF}_4/\text{ACN}$ electrolyte. On-chip CDC films were used as working electrodes, whereas counter and reference electrodes consisted of a Pt wire and Ag/AgCl electrode, respectively. Cyclic voltammetry experiments were first performed from E_{OCV} to negative potentials until the reduction peak of the AQ diazonium derivative was observed [50]. From these obtained CV curves, we define E_{red} and E_{end} which corresponds to the peak potential of the AQ-1-diazonium reduction, and the potential at which the reduction is complete, respectively. Then, pulsed chronoamperometry steps were adapted from the method previously described [38]: a rest period at E_{OCV} was kept for 90 ms, followed by a 10 ms pulse at E_{end} or E_{red} . Finally, the AQ-grafted CDC film was washed with aliquots of ethanol to remove the organic electrolyte.

2.2.4. Electrochemical characterizations of the modified CDC film

Electrochemical characterizations of the as-prepared AQ-grafted CDC films were performed in 1 M KOH using the on-chip CDC film as working electrode, a Pt wire as counter electrode and a saturated calomel electrode SCE as reference. Cyclic voltammetry was also performed on the pristine CDC film prior to the modification process. AQ molecules are known to contribute to

the charge storage mechanism by a 2-electron reduction of the quinone groups in acidic electrolytes to give hydroquinone, while the transfer of two electrons is supported by a charge compensation of cationic species (2 protons or any other cations from the supporting electrolyte) or water molecules in alkaline electrolyte [38] (Scheme 1).

The modification of carbon with chloroanthraquinone has demonstrated that the loading estimated from the charge passed is in good agreement with the quantification from chlorine detection [51]. The total charge Q_{tot} passed in the electrode is the sum of a double layer contribution Q_{EDLC} and the faradic contribution due to the AQ redox process Q_{AQ} (C). Q_{AQ} was determined from CV curves with EC-Lab software by calculating the charge corresponding to the oxidation wave of the AQ grafted sample [11,38]. The AQ capacity Q_{AQ} was normalized to the CDC film footprint area, as gravimetric capacity and capacitance are meaningless for micro-supercapacitors electrodes [52]. The coulombic charge could then be translated into equivalent electrode capacitance C_{AQ} (F.cm^{-2}) for comparison purpose by dividing by the potential window of the CDC electrode, i.e. 1.1 V. The double layer capacitance C_{EDLC} (F) was deduced from the subtraction of the faradic contribution to the integrated charge current following the equation (2):

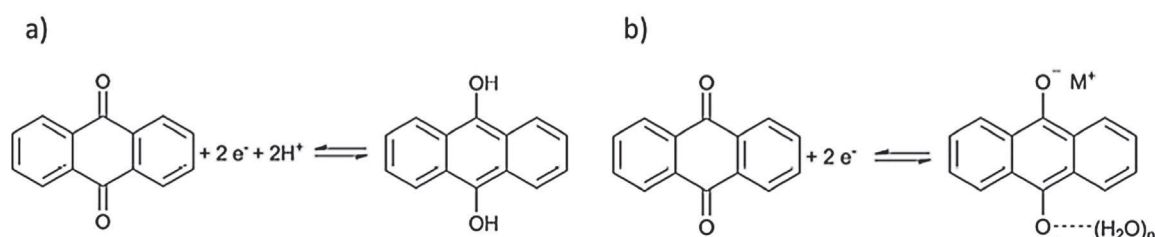
$$C_{\text{EDLC}} = \frac{\int I.dE}{\nu\Delta E} - \frac{Q_{\text{AQ}}}{\Delta E} \quad (2)$$

where I stands for the charge current (A), ν the scan rate (V.s^{-1}) and ΔE the potential window (V). The double layer capacitance C_{EDLC} was also normalized to the CDC film area (F.cm^{-2}). Since samples with different thicknesses have been grown, the areal capacitance may vary from one sample to another. However, pristine and functionalized electrodes are compared in the study whenever they have similar thicknesses. All the potentials refer to the normal hydrogen electrode (NHE).

3. Results and discussion

3.1. Chemical grafting of AQ

The voltammogram of a 450°C chlorinated CDC film tested in 1 M KOH before (dashed line) and after (solid triangles) chemical grafting with AQ molecules is presented in Fig. 1. The current was normalized to the CDC film footprint surface area and thickness. Both CV curves exhibit a quasi-rectangular shape within a 1.1 V potential window, typical from capacitive signature of carbon material in KOH electrolyte [21]. Furthermore, small oxidation and reduction waves are observed at -0.18 V vs NHE and -0.37 V vs NHE, respectively, after modification. Indeed, AQ-grafted molecules contribute to the total capacitance of the CDC film by adding a faradic current coming from redox mechanism. However, only a small coulombic contribution of 0.8 mC.cm^{-2} (equivalent to a mean areal capacitance of 0.7 mF.cm^{-2} over 1.1 V) is calculated from the anodic peak for the modified CDC film. This transforms



Scheme 1. Reduction of anthraquinone (AQ) in (a) acidic electrolyte and (b) basic electrolyte [38]. In the latter case, the negative charge on oxygen can be compensated either by a cation (M^+) and/or by hydrogen bonds with water molecules.

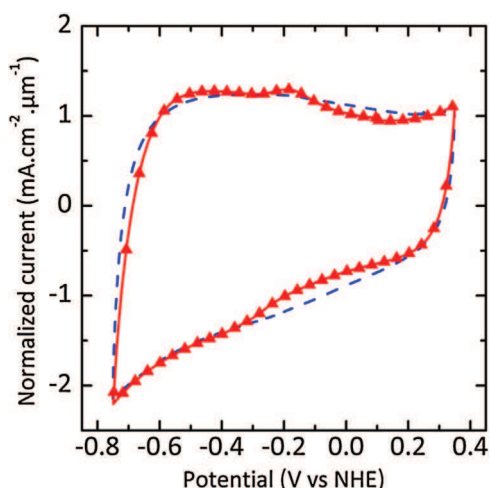


Fig. 1. Cyclic voltammograms of pristine (dashed line) and chemically AQ-grafted 2.0 μm-thick CDC film (solid triangles) recorded at 50 mV.s⁻¹ in 1 M KOH.

into a low AQ loading of 1.6×10^{-12} mol.cm⁻² [20], i.e. less than 1 wt% of AQ molecules grafted onto the CDC film. One can notice a slight decrease of the double layer capacitance from 46 to 41 mF.cm⁻², associated with a blocking of small micropores by the grafting [12]. Indeed, the AQ radicals react predominantly with carbon atoms on the more reactive edge sites at the entrance of the carbon pores [12]. Our 450 °C chlorinated CDC films have a very narrow PSD, with an average pore size of 0.59 nm as confirmed in previous work [47]. Therefore, although small AQ loading was achieved (only 0.89% of the theoretical value expected for the formation of an AQ monolayer [36]) some of the micropores are blocked by the AQ species, thus limiting the capacitive response of the electrode. For comparison, AQ loading of 5.6×10^{-11} mol.cm⁻² was obtained from similar procedure with the same molecule grafted on Vulcan, which contains micro and mesopores [36]. Such low AQ loading on CDC could also be explained by the CDC surface modification occurring during annealing under reductive H₂ atmosphere at high temperature. Indeed, Smith and Pickup [36] studied the competition between covalently bonded and adsorbed AQ and the influence of the carbon surface modification by pre-treatment in either oxidative condition (nitric acid) or reductive conditions (NaBH₄) of activated carbon. They evidenced that the carboxylic acid functional groups formed during oxidative pre-treatments promote the covalent bonding of diazonium cations

[36]. On the contrary, it was shown that the addition of NaBH₄ in the mixture led to less C-AQ covalent bonds and more adsorbed AQ [36]. Moreover, the low grafting loading found for our CDC substrate is consistent with the work of Isikli et al. who reported small loadings of 0.75 wt% and 0.55 wt% for loosely bonded 1,4,9,10-anthracenetetraone on PICA and Vulcan carbons, respectively, through same chemical route [53]. Hence, it is expected that AQ molecules are more likely adsorbed at the CDC surface via physisorption mechanisms through π-stacking between the aromatic rings of AQ and graphitic planes [54].

Another main problem may be the accessibility of AQ molecules to the porosity of CDC. An electrochemical grafting was envisioned to assess if any additional driving force would enhance the grafting yield.

3.2. Determination of the reduction potential of AQ-1-diazonium cations on carbide-derived carbon

Electrochemical grafting is assumed to provide better mobility of the AQ species, allowing higher AQ loadings. To achieve the electrochemical grafting of AQ molecules on CDC films, we first determined the reduction potential of AQ diazonium cations. For this purpose, cyclic voltammetry experiments were performed on Si/SiO₂/Ti/CDC electrode at 50 mV.s⁻¹ in acetonitrile containing 5 mM AQ-1-diazonium and 0.1 M NEt₄BF₄. Same procedure was used with glassy carbon electrode to compare the electrochemical grafting on non-porous carbon and microporous carbon film. Fig. 2A shows the CV corresponding to the reduction of the anthraquinone-1-diazonium on glassy carbon. A broad irreversible cathodic wave is visible at +0.21 V vs NHE during the first potential sweep, corresponding to the reduction of diazonium cations, possibly leading to the formation of covalent bond with the carbon surface [15]. The cathodic current is drastically decreased during the next 4 cycles, indicating that the grafted layer progressively inhibits further electron transfer, in agreement with previous reports [50]. The cyclic voltammogram of the 450 °C chlorinated CDC sample exhibits similar shape, with an intense reduction peak centered at -0.06 V vs NHE (Fig. 2B), evidencing that the reduction of diazonium cations can be achieved on CDC electrode. However, the charge passed through the CDC electrode is similar to that of glassy carbon despite a large difference in the specific surface area (977 m².g⁻¹ for CDC). This might be a first information about the accessibility of the AQ diazonium to the carbon microporosity, which will be discussed in Section 3.3. Aside, the shift in potential compared to glassy carbon electrode can be assigned to the

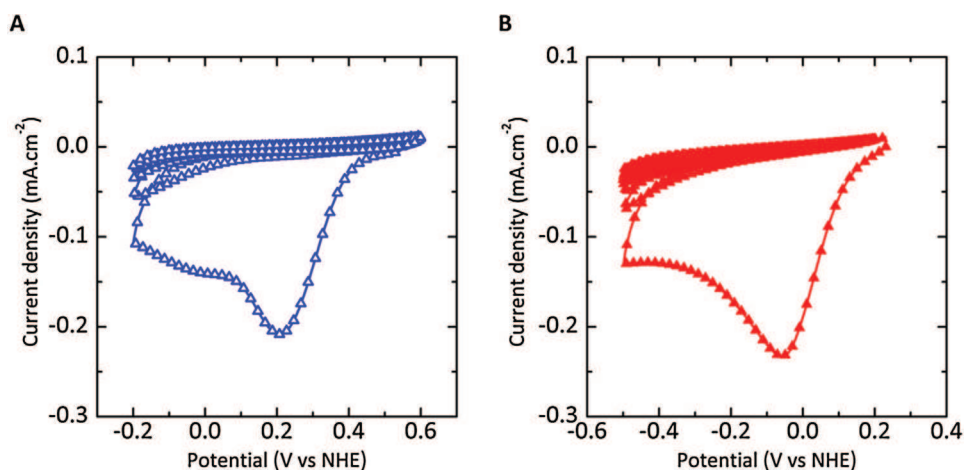


Fig. 2. Cyclic voltammograms of (A) glassy carbon electrode and (B) on-chip CDC film (2.0 μm-thick CDC film) recorded at 50 mV.s⁻¹ in 0.1 M NEt₄BF₄/ACN containing Fast Red Al.

presence of many edge planes due to the specific porosity of CDC electrode. Such shift was already observed in other studies [16].

3.3. Electrochemical grafting of AQ molecules

Pulse potential deposition has been reported in the literature as an efficient technique to tackle mass transport limitations [38]. Therefore, series of rest and grafting steps were used. The potential during the rest step was fixed at the OCV and the grafting step was achieved at $E_{\text{end}} = -0.4 \text{ V}$ vs NHE, that is under cathodic polarization for reduction. E_{OCV} and E_{end} were applied for 90 ms and 10 ms, respectively, for 1 h. It has been shown that the longer the relaxation time, the higher the grafting loading [38]. However, this was observed for *in-situ* generated diazonium cations in aqueous media with NaNO_2 as diazotization agent, where nitrite ions depletion is avoided by longer relaxation time [38]. The influence of the carbon porous structure on the grafting yield was studied, as well as the role of the potential applied during the grafting steps. The cyclic voltammogram recorded at $50 \text{ mV}\cdot\text{s}^{-1}$ in 1 M KOH for the as-prepared 450°C chlorinated on-chip CDC film grafted with AQ is shown Fig. 3A. As for the case of chemical route, rectangular signatures are observed for both pristine (dashed line) and AQ-grafted CDC electrode (solid triangles), with a double layer capacitance decrease from $35 \text{ mF}\cdot\text{cm}^{-2}$ to $27 \text{ mF}\cdot\text{cm}^{-2}$ after grafting. The weak oxidation wave of AQ only brings an additional $0.3 \text{ mC}\cdot\text{cm}^{-2}$ (equivalent to $0.3 \text{ mF}\cdot\text{cm}^{-2}$ if averaged over the potential window) to the double layer current contribution. The low surface coverage measured may originate from a steric effect, since the size of the AQ molecule ($0.388 \text{ nm} \times 0.744 \text{ nm} \times 1.165 \text{ nm}$) [55] is close to the size of most of the CDC pores (mean pore size of 0.59 nm). As a result, AQ molecules could only bond to the outer surface, confirming, as suspected from our previous chemical grafting attempts, that the main issue is the poor pore accessibility. To tackle this limitation, sputtered TiC thin films were chlorinated at higher temperature value (700°C) to prepare on-chip CDC films with larger micropores (mean pore size of 0.85 nm) [47]. Indeed, the porous structure of CDCs can be fine-tuned by adjusting the chlorination conditions. Diameter of 700°C chlorinated CDC pores was reported to reach a maximum value of 2 nm , whereas it is limited to 1 nm as a maximum for CDC films prepared at 450°C [47].

On-chip CDC electrodes chlorinated at 700°C and annealed under H_2 atmosphere were grafted using the same pulsed technique. The CV curves of the 700°C chlorinated on-chip CDC film recorded before (dashed lines) and after (solid circles)

chronoamperometry are shown in Fig. 3B. For comparison, an areal capacitance of $71 \text{ mF}\cdot\text{cm}^{-2}$ ($152 \text{ F}\cdot\text{cm}^{-3}$) was delivered for the pristine CDC electrode. After grafting with AQ, the CV plot of the AQ-grafted CDC film exhibits two intense anodic and cathodic peaks. The apparent redox potential was measured at -0.26 V vs NHE and the associated coulombic charge was estimated to be $18.7 \text{ mC}\cdot\text{cm}^{-2}$ from the integration of the oxidation peak. The AQ surface coverage was calculated to be $0.16 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$, corresponding to $\approx 9\%$ of a monolayer [20]. Furthermore, a double layer capacitance value of $59 \text{ mF}\cdot\text{cm}^{-2}$ ($127 \text{ F}\cdot\text{cm}^{-3}$) is still delivered after AQ grafting (corresponding to only a 17% decrease compared to pristine on-chip CDC film), evidencing that ion adsorption into the CDC micropores is still effective after grafting.

To study the influence of the reduction potential used during pulsed chronoamperometry, the potential E_{end} was switched to the potential of the AQ-1-diazonium reduction peak $E_{\text{red}} = -0.06 \text{ V}$ vs NHE, such as shown in cyclic voltammograms recorded in 0.1 M $\text{NET}_4\text{BF}_4/\text{ACN}$. The pulse step time was kept the same. Fig. 4 presents the CV curves recorded at $50 \text{ mV}\cdot\text{s}^{-1}$ in 1 M KOH for pristine 700°C chlorinated on-chip CDC film (dashed line) and for the as prepared AQ-grafted 700°C chlorinated CDC film (solid circles). An areal capacitance of $20 \text{ mF}\cdot\text{cm}^{-2}$ ($152 \text{ F}\cdot\text{cm}^{-3}$) was delivered at $50 \text{ mV}\cdot\text{s}^{-1}$ for the non-grafted CDC film exhibiting rectangular CV shape. However, after the grafting procedure, two broad redox waves are observed, with an apparent redox potential still located at -0.24 V vs NHE. As a result, a corresponding faradic capacity Q_{AQ} of $28.3 \text{ mC}\cdot\text{cm}^{-2}$ (equivalent to $26 \text{ mF}\cdot\text{cm}^{-2}$ when averaged over the 1.1 V potential window) was calculated. Aside, the double layer capacitance was only slightly decreased of about 10% ($18 \text{ mF}\cdot\text{cm}^{-2}$). Interestingly, the double layer capacitance is less affected by the grafting process achieved at less absolute cathodic potential during chronoamperometry, whereas the AQ surface coverage is increased to $0.88 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$. Using a high cathodic overpotential (absolute value), the growth kinetic is very fast as compared with the diffusion of AQ molecules, although the pulsed deposition technique avoids depletion at the electrode/electrolyte interface [56]; thus, the species available for reduction directly react at the outer carbon surface, leading to preferential grafting at the entrance of the micropores. While decreasing the absolute cathodic overpotential, the more kinetically controlled reduction process allows the AQ to react inside the porous network. For the 700°C chlorinated CDC film, the equivalent of $\approx 50\%$ of a monolayer of AQ molecules is grafted on the surface of the carbon electrode, and the total electrode capacitance is twice higher ($44 \text{ mF}\cdot\text{cm}^{-2}$ after modification, to be compared with 20 mF .

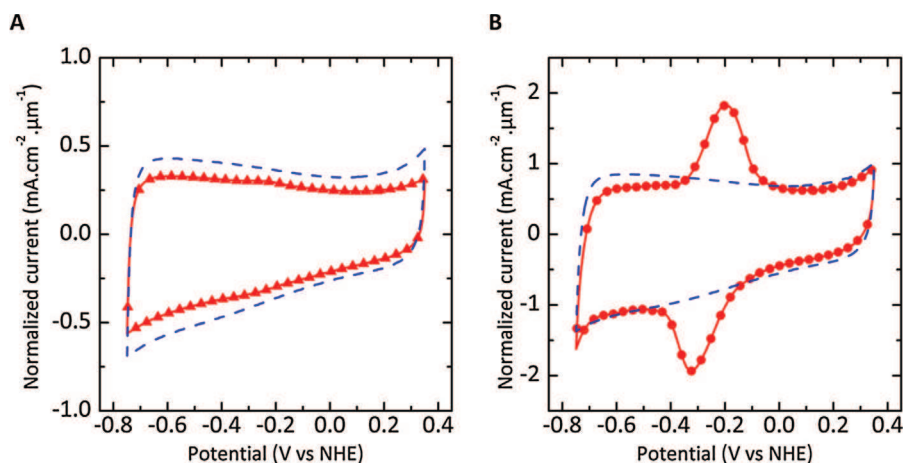


Fig. 3. (A) Cyclic voltammograms recorded at $50 \text{ mV}\cdot\text{s}^{-1}$ in 1 M KOH for the 450°C and (B) 700°C chlorinated CDC electrodes (4.8 and $4.6 \mu\text{m}$ -thick, respectively) before (dashed line) and after grafting (solid symbols) using $E_{\text{end}} = -0.4 \text{ V}$ vs NHE during chronoamperometry.

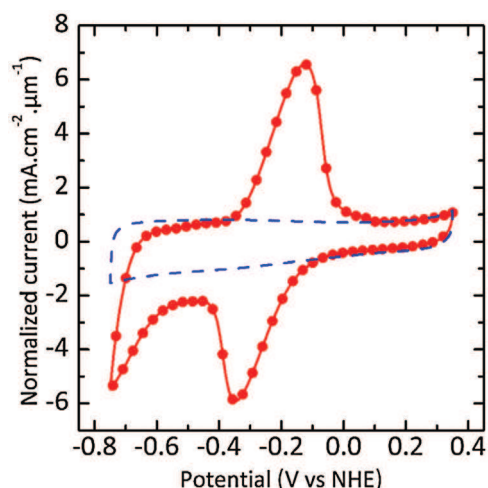


Fig. 4. Cyclic voltammograms recorded at 50 mV s^{-1} in 1 M KOH for a 700°C chlorinated CDC electrode ($1.3 \mu\text{m}$ -thick) before (dashed line) and after (solid circles) electrochemical AQ-grafting using E_{red} during chronoamperometry.

cm^{-2} for the pristine 700°C chlorinated CDC film). This is consistent with previous reports for AQ-modified activated carbons [37,57].

3.4. Evaluation of the stability of AQ in on-chip CDC

The 700°C chlorinated on-chip CDC electrode modified with AQ was further characterized by electrochemical impedance spectroscopy to investigate the influence of the grafted AQ species on the capacitive behavior of the CDC film. The sample was used as working electrode in a three-electrode cell with Pt as counter electrode and Ag/AgCl as reference. EIS was performed in 1 M KOH at $E_{\text{OCV}} = +0.01 \text{ V}$ vs NHE. The corresponding Nyquist plot is shown in Fig. 5A (solid circles). For comparison purpose, the Nyquist plot of pristine 700°C chlorinated CDC film was added (open circles). The high frequency resistance is about $1 \Omega \text{ cm}^2$, which is a conventional value for 1 M KOH electrolyte (inset Fig. 5A); as the frequency decreases, a semi-circle appears as already observed for CDC electrodes [58]. It reveals that ionic mass transport in subnanometer pores is limited due to size effect. However, the semi-circle diameter increases for AQ grafted CDC electrode which suggests that AQ molecules also limit ion diffusion in the porosity due to steric hindrance. In the low frequency range, the quasi vertical line parallel to the imaginary axis, observed for pristine CDC electrode, is typical of a capacitive behavior in agreement with the CVs of Fig. 4. Deviation from the vertical capacitive plot is observed for the grafted sample. Such feature was also reported for AQ-GF, and was assigned to the existence of an additional charge transfer resistance owing to the redox mechanisms involved at such potential [59].

Grafted Si/SiO₂/TiC/CDC electrode was subjected to repeated potentiostatic cycling in 1 M KOH within a 1 V potential window at 20 mV s^{-1} (Fig. 5B). The faradic contribution coming from the redox reactions occurring at the quinone sites is still visible after 500 cycles, although the coulombic charge decreases upon cycling. Also, the difference between the anodic and cathodic peak potentials (ΔE_p) is progressively shifted to higher values, indicating a slower electron transfer. Aside, the double layer capacitance region is kept constant upon cycling. From these features, we were able to plot the change of the pure double layer capacitance C_{EDLC} , estimated from the rectangular part of the CV between 0V and $+0.3 \text{ V}$ vs NHE, and the change of the AQ faradic capacity Q_{AQ} upon

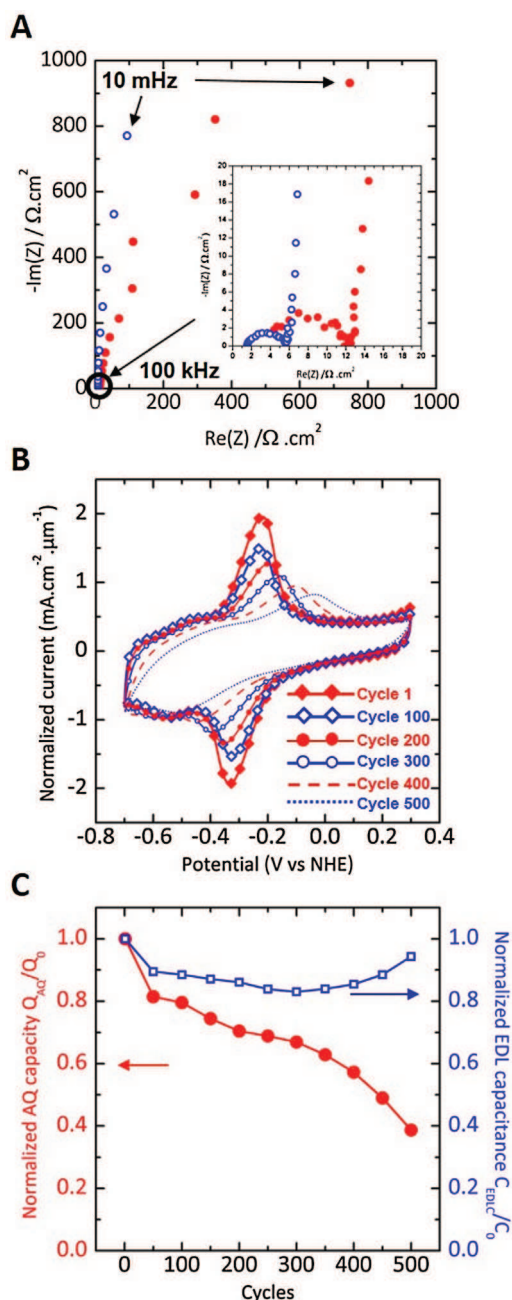


Fig. 5. (A) Nyquist plot of pristine (open circles) and AQ grafted (solid circles) 700°C chlorinated CDC film ($1.3 \mu\text{m}$ -thick); inset: detail of the high frequencies region. (B) Cyclic voltammograms of the AQ grafted CDC film tested in 1 M KOH and recorded at 20 mV s^{-1} during 500 cycles. (C) Change of the normalized AQ capacity (left) and normalized double layer capacitance (right) upon cycling.

cycling (Fig. 5C). As highlighted in similar studies, the AQ capacity drops dramatically during the first 50 cycles. This is usually assigned to the desorption of poorly attached or physically bound AQ molecule from the carbon surface [39]. Then, the faradic contribution due to AQ molecules stabilizes and the AQ-modified on-chip CDC retains 66% of the initial capacity over the following 300 cycles. Meanwhile, the double layer capacitance remains stable, albeit it has slightly decreased from 15%. Then, the AQ contribution starts to decrease sharply, while the double layer capacitance recovers and reaches 94% of the initial capacitance after 500 cycles. AQ-modified activated carbons usually exhibit good capacitance retention over more than 1000 cycles [37]. Such a capacity fade is similar to those reported in the literature [38,53].

After the departure of loosely attached AQ molecules upon the first 50 cycles, the second fade in faradic contribution of AQ after 300 cycles could be due to the repeated formation of quinone dianions upon cycling. It was proposed that the quinone dianions induced from the two electron process occurring in very basic media can endure repulsion interactions toward the negatively charged carbon surface and dissolve in the alkaline electrolyte [60]. This could explain the loss of faradic response recorded after the 300th cycle, as electrostatic repulsion should be exacerbated in such confined micropores. This is supported by the parallel increase in the double layer capacitance value, as AQ dissolution releases the CDC surface and brings back some pore accessibility for the ions of the electrolyte. Also, this is in good agreement with the progressive shifts of the anodic and the cathodic peaks leading to higher potential differences ΔE_p , where slower electron transfer originates from the progressive departure of the AQ molecules due to electrostatic repulsions. Thus, the beneficial effect of AQ grafting in CDC films is balanced by the release of AQ species after only few hundred cycles. Although supercapacitor electrodes are expected to handle fast charge and discharge over thousands of cycles, it is the first time that on-chip carbon electrodes capacity could be boosted by electrochemical grafting of AQ molecules into micropores. The stability of the grafted AQ moieties over charge/discharge cycles might be further improved by changing the orientation of the grafted molecules on the carbon surface, i.e. starting with AQ-2-diazonium precursor, thus modifying the strength of the interactions between the AQ molecule and the substrate [16]. The modification of the CDC electrodes with *in situ* generated diazonium derivatives could also lead to better capacity retention.

4. Conclusion

The modification of on-chip CDC electrodes with AQ molecules was performed by electrochemical route, using 0.1 M $\text{NET}_4\text{BF}_4/\text{ACN}$ solution of AQ diazonium derivative. Using porous carbide-derived carbon (CDC) films with narrow pore size distribution, the grafting yield strongly depends on the average pore size: only 2 nm pore diameter CDC can be grafted with AQ moieties, lower pore size leading to a poorly functionalized electrode. Indeed, for 0.59 nm average pore size, the decrease of the double layer capacitance suggests that the AQ species block the entrance of the small micropores. By increasing the chlorination temperature, the porosity of the CDC films was slightly extended up to 2 nm, thus allowing the access of the carbon porous network during potential pulsed chronoamperometry experiments. High AQ surface coverage of $0.88 \times 10^{-10} \text{ mol.cm}^{-2}$, which represents half of a monolayer, was obtained while the double layer capacitance value was only decreased by 10%. This is the first time that such limitation due to pore diameter is evidenced for carbon electrodes, and that the potential grafting of AQ molecules is evidenced in CDC electrodes.

The cyclability of the AQ-modified on-chip CDC electrode was also investigated. The current which originates from the redox waves of AQ progressively decreased during cycling until only 39% of the faradic contribution was kept after 500 cycles. This decrease has been assigned to electrostatic repulsion of dianionic AQ confined in narrow micropores in the alkaline media. Nevertheless, the grafting strategy has demonstrated a beneficial effect on the total capacitance of the AQ-modified on-chip CDC electrodes that has been doubled compared to the pristine CDC film, leading to high total capacitance value of 44 mF.cm^{-2} (338 F.cm^{-3}). Thus the AQ molecules grafted on the CDC electrode serve as a proof of concept to demonstrate that the modification of microporous on-chip CDC films with electrochemically active species can be a step forward for the improvement of micro-supercapacitors

performance. Other redox molecules have to be tested in order to increase the capacitance of the electrodes while maintaining a good cyclability.

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