



HAL
open science

Electrochemical evidence of the modification of carbon materials with anthraquinone moiety by a Diels Alder process

Mathieu Deschanel, Frédéric Favier, Olivier Fontaine, Steven Le Vot

► **To cite this version:**

Mathieu Deschanel, Frédéric Favier, Olivier Fontaine, Steven Le Vot. Electrochemical evidence of the modification of carbon materials with anthraquinone moiety by a Diels Alder process. *Electrochimica Acta*, 2020, 361, pp.137027. 10.1016/j.electacta.2020.137027 . hal-02991016

HAL Id: hal-02991016

<https://hal.umontpellier.fr/hal-02991016>

Submitted on 21 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Electrochemical evidence of the modification of carbon materials with anthraquinone moiety by a Diels Alder process

Mathieu Deschanel, ¹ Frédéric Favier, ^{1,2} Olivier Fontaine, ^{1,2} Steven Le Vot ^{1,2*}*

¹ ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

² Réseau sur le Stockage Electrochimique de l'énergie (RS2E), FR CNRS 3459, France

Abstract

Interfaces play a key role in electrochemical energy storage. They are directly responsible for performances (and thus indirectly costs), safety and lifetime of the batteries and electrochemical capacitors. A way to improve devices is to control these interfaces and one attractive approach to achieve this goal is to modify electrodes by grafting molecules bearing desired moieties (hydrophilic/hydrophobic, redox...). Diazonium (electro)chemistry is the most popular modification technique in the field of energy storage but it has some limitations. Two major drawbacks are the lack of control on the grafted layer (structure and morphology) and the chemical nature of the diazonium itself that could, in some cases, makes it difficult to manipulate. Thus, our objective is to propose an alternative option to modify electrodes and, particularly this work aims to validate the use of the Diels Alder reaction to modify carbon materials with redox molecules for electrochemical storage purposes. A new molecule (propargyl anthraquinone) was synthesized to make this Diels Alder reaction possible. The modification was evidenced by electrochemical characterizations, comparing carbon electrodes modified with the synthesized propargyl anthraquinone and other commercial anthraquinone derivatives. The modified carbons were stable in both acidic and buffered neutral conditions and rate capability similar to unmodified carbon. Very interestingly, the electrochemical behavior of our electrodes is comparable to those fabricated by the state-of-the-art diazonium chemistry. In this study, we investigated and validated the possibility to use the Diels Alder reaction to modify carbon for electrochemical storage application. This is a critical input because it allows to expand modification methods suitable to tune interfaces for electrochemical storage applications.

Introduction

Electrochemical capacitors and batteries are key devices in the competitive field of electrochemical energy storage (EES). Even if already commercial since decades, these devices face today the huge challenge of large scale implantation whether for mobile[1, 2] or stationary[3, 4] applications. There are real needs to improve EES technologies particularly to allow the development of renewable energies such as wind or solar, that are intermittent and unpredictable and to support the electrification of transports. Of course, many strategies have been considered and, among them, surface modification appears to be very promising. The basic idea is straightforward: to tune and thus control interfaces in electrochemical devices. Potentially, huge benefits could be expected in many fields. For example, some researches focus on designing artificial SEI for better cyclability in Li-ion batteries[5-9]. In the growing field of redox-flow batteries[10-14], carbon surfaces are modified to improve wettability and thus performances. For electrochemical capacitors[15-19], redox moieties were grafted on carbon surfaces to add Faradaic contribution to the capacitive one to enhance the capacity (and thus the energy) of the device.

In the latter case, quinones have attracted such an interest after it was reported that 2-nitro-1-naphthol grafted on carbon black led to higher capacity[20]. Few years later, this approach was also considered to enhance performances of carbon-based electrochemical capacitors capitalizing on attractive low redox potential of anthraquinone (AQ) molecule which was expected to boost capacity of negative electrodes[15, 18, 21-23]. AQ based electrochemical capacitors were largely investigated and it was demonstrated that AQ coverage could reach 10 wt% without significantly altering the carbon double layer capacitance[22, 23]. Interestingly, AQ has brought Faradaic contribution that allowed doubling the capacity of electrodes that can be cycled in acidic media but are not stable in alkaline electrolytes[24]. In fact, looking at their electrochemical behavior, pH dependence of grafted AQ is now well known and it was proven that only acidic or fully neutral buffered media lead to desired electrochemical performances[25, 26]. Nowadays, this strategy to practically enhance electrochemical capacitor performances is not considered anymore, mainly because of the progressive loss of the electroactivity of redox moieties upon cycling[23]. However, beyond performances, these studies are very interesting because they provide guidelines for surface modification adapted to electrochemical purposes.

In the field of electrochemistry, most of the surfaces have been modified using the very popular diazonium chemistry which is nowadays very well known. Indeed, countless papers have been reported since Pinson and Saveant published in the early 90s' the covalent modification of carbon surfaces using diazonium salts[27]. The groups of Bélanger and Pickup used this method to modify porous carbon with AQ to improve performances of electrochemical capacitors. At the same time, the group of Bartlett reported original strategies to modify carbon nanotubes[28] and anthracene[29], also with anthraquinone but not targeting electrochemical energy storage. Even if very attractive, diazonium grafting involves formation of radicals and leads to poorly controlled thick coatings (multilayers). Moreover, diazonium chemistry is very sensitive and can be difficult to manage in some cases[30]. Thus, it might be of great interest to investigate and develop new surface modification strategies applied to electrochemical energy storage.

Carbon is a very common material for which many surface modification strategies have already been developed. Each one requires different chemical functions and intrinsically possesses advantages and drawbacks that are presented in Table S1 which summarizes most used grafting methods. Among these strategies, the Diels Alder reaction appears to be an interesting alternative to diazonium chemistry. It is a one-step reaction, with no pretreatment, involving molecules containing diene or dienophile moieties. The Diels Alder grafting method was first used with carbon nanotubes [31-33] and this modification process was then extended to graphene and graphite [34]. More recently, it was adapted to activated carbon [35] acting as a diene (condensed benzene rings) whereas the grafted molecules acted as the dienophile (propargyl function, maleic anhydride, vinyl methyl ketone...). Readers can refer to figure 1 to get schematic representation of this reaction. In this study, propargyl approach was chosen because this function can easily be attached to a redox molecule via a simple and versatile chemical process (see experimental part and Fig. S1 for details).

We report herein, a study that evaluates the opportunity to use Diels-Alder reaction to modify a carbon surface for electrochemical energy storage applications. The strategy was the following one. First, we synthesized the redox molecule (dienophile) highlighting that it is a simple and versatile process. Then, this molecule was used to modify different carbons. Glassy carbon served as a model flat surface and acetylene black and Black Pearls were used as more realistic electrode materials. Finally, the electrochemical behavior of the modified carbons was deeply investigated. For this matter, studies of Bélanger and Pickup, dealing with redox-enhanced electrochemical capacitors, were used as standards.. Comparison between our

results and these studies allowed to conclude that Diels Alder reaction is suitable to add redox molecules on carbon for electrochemical purposes. Nevertheless, it is important to clarify herein, that our point is to validate a strategy to tune carbon surface but not to develop new performant electrochemical capacitors

Experimental section

Chemicals. 2-(hydroxomethyl)anthraquinone, sodium hydride (60 %wt stabilized in organic oil), propargyl bromide (80 %wt in toluene), tetrahydrofuran (anhydrous) were all received from Sigma Aldrich. Chloroform (pure stabilized with ethanol) were purchased from Carlo Erba. DMF (reagent grade) comes from Fischer laboratory.

Synthesis and purification of AQP molecules. In a typical experiment, 1 g of 2-(hydroxomethyl)anthraquinone (4.2 mmol) was dissolved in THF. Then sodium hydride (6.3 mmol) was carefully added by little portion. The mixture was stirred at room temperature for 1 h. Propargyl bromide was then added (5.04 mmol) and the mixture was stirred at room temperature for 24 h. After being dried (rotary evaporator) the resulting powder was dissolved in 300 ml of chloroform, sonicated for 10 min and filtered on a 0.22 μm PVDF membrane. The resulting solution was dried (rotary evaporator) and a solid residue was purified by chromatography (silica column with a 9/1 chloroform/acetone eluent). ^1H NMR, mass spectroscopy and FTIR (fig S2, S3 and S4, respectively) allowed to validate this synthesis procedure.

Carbon modification. Three different carbons were used: glassy carbon (BASi[®], 3 mm diameter), acetylene black (Sigma Aldrich, Compressed 75 m^2/g) and Black Pearls 2000 (Cabot corporation). To modify powders, 200 mg of AQ derivative (AQ, AQOH or AQP) was dissolved in 100 mL of DMF. 100 mg of carbon were added and the suspension was stirred for 16 h at room temperature. The modified powder was filtered on a 0.22 μm nylon membrane and dried at 80 $^\circ\text{C}$ overnight. Washing was achieved by sonication (20 min) in DMF (100 ml) to desorb molecules weakly bonded to the carbon surface. Filtration, followed by drying overnight, allowed to obtain desired modified powders. Scheme S1 summarizes this carbon modification procedure. To modify glassy carbon electrodes (Basi d=3mm), 5 mg of AQ derivative was dispersed in 10 ml of DMF, thus respecting the same ratio used to modify powders. Glassy carbon was immersed in the suspension that was stirred at room temperature for 16 h. To wash the electrode, it was carefully rinsed in DMF for 5 min and then sonicated

for 5 more min in a new DMF solution. Finally, it was abundantly rinsed with ultrapure water before being used as electrode.

Electrochemical measurements. Self-standing electrodes were obtained mixing 75 %wt of modified carbon (active material), 15 wt% of acetylene black (conductive additive) and 10wt% of PTFE (binder). 9 mm disks were cut in the composite film leading to mass loading ranging from 9 to 12 mg cm⁻² (mass refers to electrode and not to active material only). Electrochemical experiments were performed using a VMP-3 potentiostat-galvanostat from Biologic. In a three-electrode setup, modified carbon (pressed into stainless steel grid), Ag/AgCl and oversized porous carbon were used as working, reference and counter electrodes, respectively. Electrodes were immersed in the electrolyte for 15 min prior to electrochemical measurements to ensure good impregnation. All solutions were prepared with ultrapure water (> 18 Ω cm⁻¹) and were degassed with nitrogen for at least 20 min.

Data reporting. Because of anthraquinone Faradaic response, capacities (expressed in C g⁻¹) have to be considered. However, for comparison purposes (published literature), capacitances (in F g⁻¹) have eventually been calculated and reported in this study (in addition to capacities in C g⁻¹). When acetylene black is used as active modified carbon and conductive additive, capacities/capacitances were normalized by the total mass of carbon in the electrode whereas for Black Pearls capacities/capacitances they were normalized using the mass of active material (*i.e.* Black Pearls).

Results and discussion

Our work aims to study the potential of the Diels Alder reaction to graft redox active moieties for electrochemical purposes. This reaction involves a cycloaddition between a diene and a dienophile. Carbon acts as the diene function whereas propargylanthraquinone molecule (bond line structural formula is available in table 1) provides the dienophile function. The first step was to synthesize the dienophile molecule from the commercial 2-(hydroxomethyl)anthraquinone (AQOH, see table 1).

Full name	Propargyl anthraquinone	2-(Hydroxymethyl)anthraquinone	Anthraquinone
Referred as	AQP	AQOH	AQ

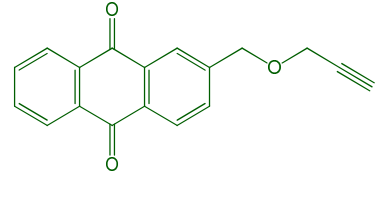
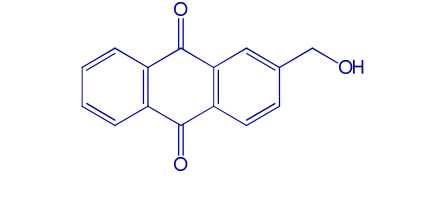
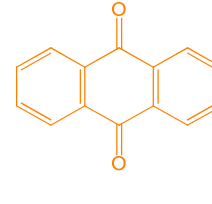
Bond line structural formula			
---------------------------------------	---	--	---

Table 1. Name and bond line structural formula of the three AQ derivatives used in this study

Detailed protocol is described in the experimental part and is illustrated in figure S1. ^1H NMR, mass spectroscopy and FTIR proved that pure targeted molecule was obtained (see S2, S3 and S4).

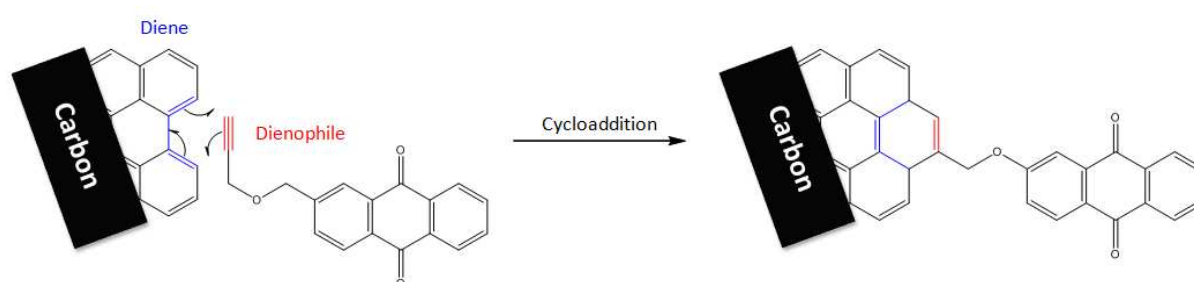


Fig. 1. Schematic modification of carbon substrate. Carbon surface serves as a diene while functionalized AQ molecule acts as a dienophile in a Diels-Alder type cycloaddition.

Fig. 1 illustrates the mechanism theoretically involved to form a covalent bond between the carbon surface and the synthesized molecule. It is important to notice that this mechanism is the expected one according to the Diels Alder reaction. However, Fig. 1 should not be understood as a claim that covalent bonds were definitely formed during this study. Even if it was not the main objective of this work to fully optimize the modification process, influence of several experimental parameters were investigated. Concentration of anthraquinone-based molecules, time of the modification reaction and the choice of the solvent are discussed in supporting information (Figs S5-S7). Moreover, to highlight the role of the dienophile function (propargyl), surface modifications were performed with two others AQ derivatives 1) AQOH that was used as precursor for the synthesis of AQP and 2) the pristine commercial AQ molecule. Interestingly, despite the fact that AQ derivatives are known for their natural tendency to adsorb on carbon substrate [24, 36, 37], different electrochemical behaviors were observed.

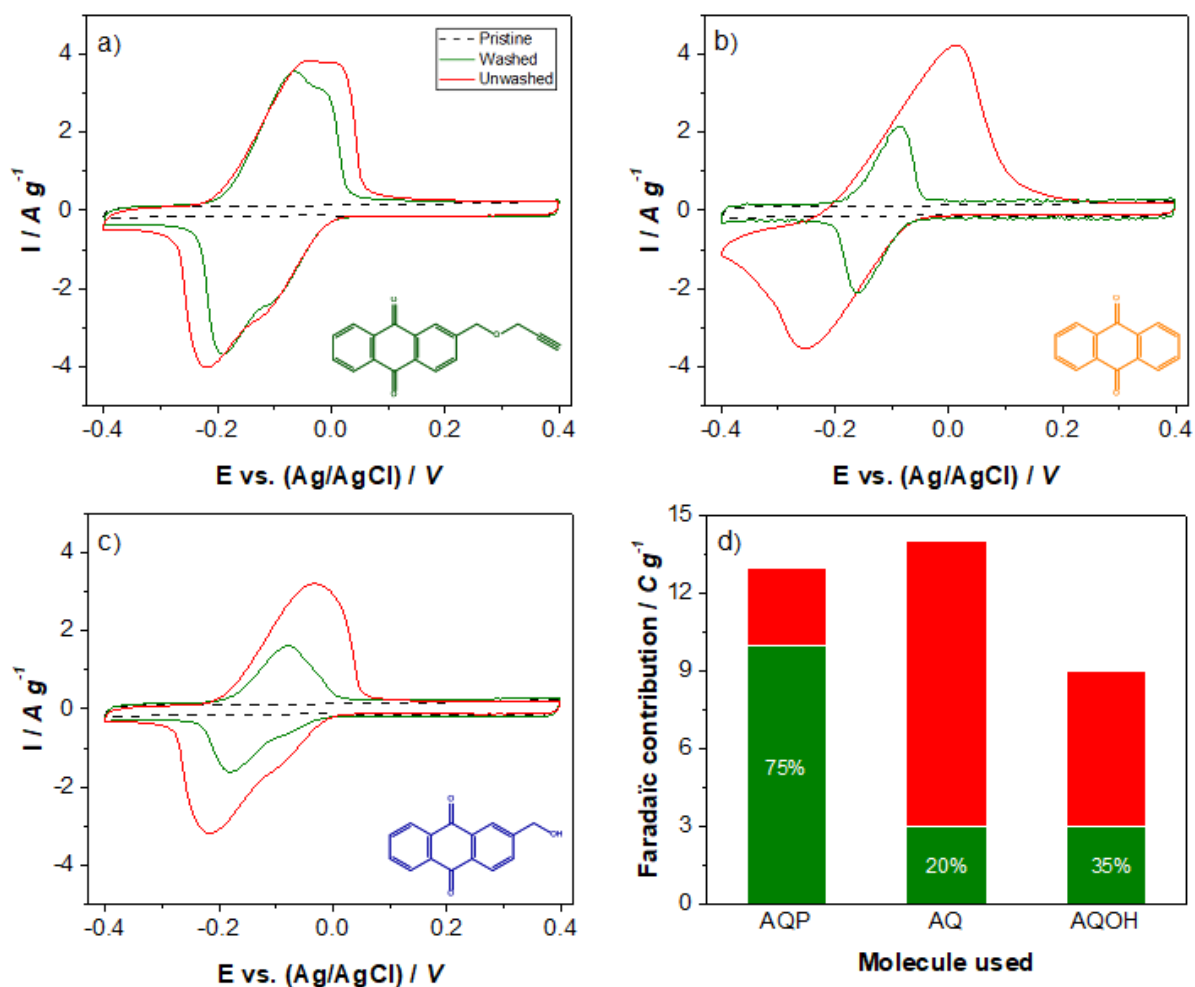


Fig. 2. Comparison of the cyclic voltammetry before (red) and after (green) washing of a) AQP modified electrode b) AQ modified electrode and c) AQOH modified electrode. Electrolyte is $[H_2SO_4] = 0.5 \text{ M}$ and applied scan rate is 50 mV s^{-1} d) Faradaic contribution of the anthraquinone derivatives. Green part represents the remaining contribution after washing while red part represents the lost one.

Cyclic voltammetry (CV) (Fig. 2) were recorded straight after surface modification (red line - unwashed samples) and after a washing procedure aiming to remove weakly adsorbed species (green line – washed samples). Additionally, unmodified carbon powder CV is shown in black dashed line. For the three molecules, redox waves between -0.3 and 0.1 V vs. Ag/AgCl are observed and correspond to the oxidation and the reduction of anthraquinone derivatives[22, 23, 37-39]. It can be noticed that double layer capacitance (rectangular shape between 0 and 0.4 V) is not affected under our experimental conditions. It is not surprising using this low specific surface area carbon substrate that does not possess microporosity. Before being washed AQP, AQ and AQOH electrodes shows Faradaic contributions of 13, 14 and 9 C g^{-1} , respectively. Interestingly, after the washing process only the electrode modified using AQP molecule retained good capacity compare to the two other molecules (see quantification on Fig 2d.).

To go further in the CV analysis, washed modified electrodes were studied at scan rates ranging from 5 to 200 mV s⁻¹. In figure 3, peak current (oxidation) was plotted versus the scan rate (log-log scale). Slope were determined for each electrodes and value between 0.8 and 1 were obtained. In electrochemistry, using potential sweep method (*i.e.* voltammetry) i-E curves are divided in two categories[40]. The first one corresponds to the case for which electroactive species diffuse from the bulk electrolyte to the surface (so-called semi-infinite linear diffusion). Current peak depends on many factors and different equations describe reversible (fast kinetics) and irreversible (slow kinetics) processes but in every case, it evolves linearly with the square root of the scan rate ($v^{1/2}$ dependence). The second case corresponds to both adsorbed layers and thin layer. In these cases, the peak current is directly proportional to the scan rate (v dependence). These two electrochemical behaviors are often reported as “diffusion limited process” and “surface reactions”[41]. One can easily understand that slope of a log-log curve of the peak current as a function of the scan rate will be very useful to investigate the electrochemical interface[42]. A slope of 0.5 is characteristic of linear semi-infinite diffusion whereas a value of 1 is characteristic of an adsorbed layer. Herein, slopes between 0.8 and 0.96 were obtained for the three modified electrodes, clearly suggesting that anthraquinone signal to come from surface redox processes and not from diluted molecules present in the bulk electrolyte. One could notice that AQ and AQOH values differs from 1, as it should be for an ideal system. There might be two explanations. The first one, the most likely in our opinion, is that this deviation from the ideality comes from the irregular nature of the surface (irregular porous carbon) combined to the presence of thick multilayer of adsorbed quinones. CV peaks are not ideal and thus it is reasonable to concede that Faradaic current corresponding to a defined redox process might be tricky to determine. Another possible explanation could be a loss in reversibility at higher scan rates. Considering usual formalism for cyclic voltammetry, switching from reversible to irreversible process while increasing the scan rate would lead to a slope smaller to the theoretical one, whether for diffusion limited processes or surface reactions.

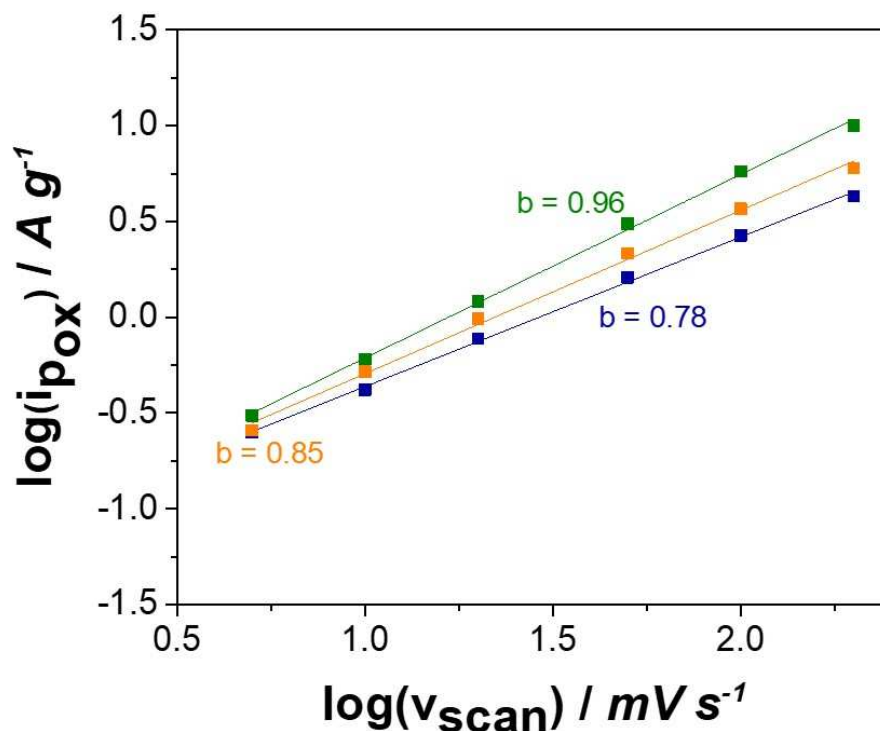


Fig. 3 Log-Log graph showing the evolution of the peak current (oxidation) as a function of the scan rate from CV experiments in 0.5 M H₂SO₄. Green data correspond to AQP modified electrode, orange one to AQ, and blue one to AQOH.

Now that it is proven that molecules are adsorbed on carbon surface and going back to cyclic voltammeteries shown on figure 2, one could notice that redox waves are not pure Gaussian as it should be. Even more, in some cases, two overlapped peaks appeared. This is even more pronounced at lower scan rate (Fig S8). This unclear electrochemical behavior has already been observed in the literature and all attempts to explain it refer to adsorption energy and surface heterogeneities. In other words, depending where at the surface, AQ molecules are in different environments and thus, oxidation and reduction processes do not occur at a single potential. It is suggested that this phenomenon might come from oxygen functionalities involved in hydrogen bonding between two closely-spaced molecules [23]. It is also suggested elsewhere[43, 44] that overlapping (2-peaks separation) might be due to the presence of strongly (near surface) and weakly bonded redox moieties that behave differently due to different adsorption strengths.

What can be assumed from this electrochemical analysis is that propargyl function lead to significantly stronger interaction between AQ derivative and carbon. We are suggesting the following hypothesis to explain these observations: grafting process successfully occurs and a first layer (likely a monolayer) of covalently bonded anthraquinone moieties is formed (our hypothesis). Then, AQP are adsorbed, propargyl functions favoring stronger interactions. Unfortunately, this hypothesis seems to be very difficult to confirm with direct experimental proofs. However, two indirect arguments could be used to support this hypothesis. One “issue” when grafting quinones, is that they spontaneously tend to strongly adsorb at the carbon surface, making very tricky every attempt to discriminate covalently bonded molecules (often called grafted molecules in literature) and those physisorbed (referred as adsorbed molecules in many publications). However, a first argument is that it has already been reported in the literature that molecules containing propargyl moieties, but without any strong adsorption site, have been already grafted on porous carbon using Diels Alder process[35]. A second issue, in the present case, is that acetylene black possesses a very irregular and surface making difficult any data interpretation. To tackle this issue, glassy carbon electrodes were modified using AQP and AQ molecules. Figure 4 presents cyclic voltammograms obtained after modification and washing procedures. For the AQP modified electrode (Fig. 4a), a redox wave centered around -0.1 V vs Ag/AgCl is characteristic of AQ oxidation and reduction. These redox contributions are not visible when electrodes were modified with commercial AQ (Fig. 4b). Interestingly, figure S9 shows that redox signal observed for AQP modified electrode remains stable even after 250 cycles. These observations showing that modification was only successful in the case of AQP molecule strongly suggest that more than a simple adsorption to occur.

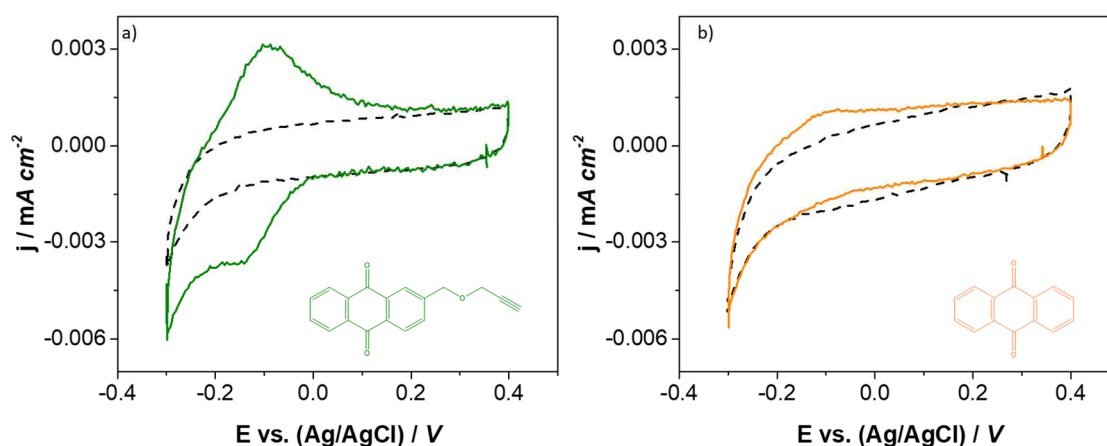


Fig. 4. Cyclic voltammetry of glassy carbon electrode modified with a) AQP (green) and b) AQ (orange). In both cases, black dashed line correspond to unmodified glassy carbon. 0.5 M H₂SO₄, 100 mV s⁻¹.

Another point that seems important to clarify is the following one: could solubility of molecules explain the behavior difference observed by cyclic voltammetry (Fig. 2)? In other words, what if AQP is insoluble (or almost) in washing solvent whereas AQOH and AQ are indeed significantly more soluble. If so, it would make sense that more AQP moieties remain adsorbed on carbon after washing. To eliminate any doubts raised by this question, solubility tests were performed using UV-Visible spectroscopy. Measurement procedure is detailed in supplementary information (see also associated figure S10 and S11). Solubilities of 575, 40 and 645 mM were measured respectively for AQP, AQ and AQOH molecules. On one hand, the highest solubility is obtained for AQOH but the tiny difference with that for AQP cannot explain the difference in capacity retention observed after washing. On the other hand, AQ molecule is more than ten times less soluble than the others in the series. This set of experiments confirmed that capacity retention is related to interaction strengths and cannot be explained by the solubility of the molecules in the washing solvent (DMF).

After being tested in acidic medium which is known to be favorable to anthraquinone electrochemical behavior, modified electrodes were investigated under neutral and alkaline conditions in which stability issues were previously reported[24, 25]. For that purpose, modified AQP electrodes were cycled 250 times in four different electrolytes: an acidic, an alkaline, a neutral and a buffered neutral solution. ~~Recorded voltammograms are shown in fig-5 and the evolution of electrode capacities upon cycling is given in fig. S12.~~ Recorded voltammograms and the evolution of electrode capacities upon cycling are shown in fig. 5. The first cycle is in dashed line while last cycle (250th) is in plain line. Whatever the considered electrolyte, a Faradaic signal, characteristic of the grafted molecule was observed, but the electrode stability was shown to strongly depend on the electrolyte nature. Fig. 5a shows that electrode is not stable in alkaline medium (50 % capacity loss after 250 cycles). As expected, the redox potential in alkaline media is shifted towards more negative potentials (about -0.8 V vs Ag/AgCl) compared to acidic electrolyte. In acidic conditions (Fig. 5b) a stable signal with 98 % capacity retention is obtained and the redox potential is about -0.11 V vs Ag/AgCl.

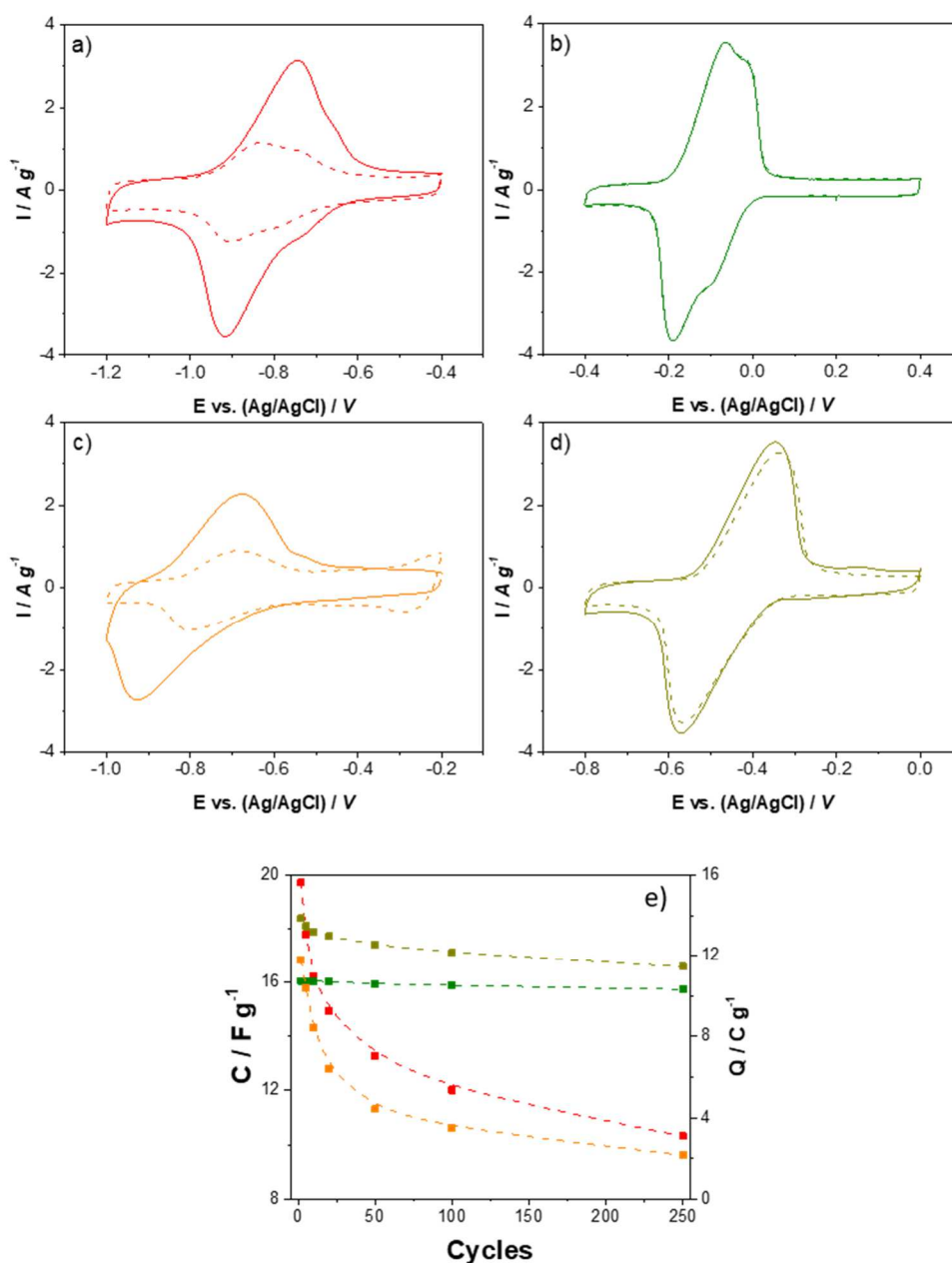


Fig. 5. Stability of acetylene black modified with AQP in different electrolytes. CV are recorded at 50 mV s^{-1} . Full line represent the 1st cycle whereas dashed line represent the 250th cycle. Electrolytes are a) 1 M NaOH. b) 0.5 M H₂SO₄ c) 1 M Na₂SO₄ and d) 1M Na₂SO₄ + pH 7 buffered solution ($[Na_2HPO_4] + [NaH_2PO_4] = 0.2 \text{ M}$). figure 5e plots the evolution of capacities upon cycling for all electrolytes.

Under neutral conditions (fig. 5c), a capacity retention of about 55 % was found after 250 cycles, pointing out stability issues just like in alkaline medium. Moreover, the shape of the Faradaic contribution seems far from the ideal Gaussian shape (as expected for diffusion-constrained redox species). The redox peaks seem broader when compared to fig. 5b) and 5d) and the redox potential is about -0.8 V vs Ag/AgCl which corresponds to that measured in

alkaline media. On the other hand, in neutral buffered electrolyte (fig. 5d), a more stable signal was observed with capacity retention of 91% over 250 cycles. The shape of the CV is more conventional and the inter-peak potential is lower when compared to measurement in unbuffered medium. Moreover, a redox potential of -0.45 V vs Ag/AgCl is observed which is in good agreement with the one expected in neutral electrolyte.

AQ modified electrodes have already been studied and have shown distinct behaviors in acidic and alkaline electrolytes that were explained through different redox mechanisms (scheme S2). In alkaline medium a dianion is formed and AQ could be desorbed because of very strong electrostatic repulsions. When moving to neutral medium, a more unexpected behavior is observed. Indeed, based on pKa of AQ in its reduced form, reduction should involve the formation of dianions only at pH greater than 10[45]. Thus, at pH 7 their formation should not occur and electrodes should remain stable. However, it has been reported that pH at carbon AQ-modified electrode surface could be altered by 5 or 6 units because of local alkalination during electrochemical reduction[26]. This phenomenon leads to undesired alkaline conditions involving dianion formation during AQ reduction and explaining the unexpected capacity decay. Experimentally, redox potentials of -0.84 and -0.80 V were measured in alkaline and neutral unbuffered media, respectively. This confirms the undesired alkalisation of local pH at the electrochemical interface during reduction of AQ in neutral media. The addition of a buffer addresses this issue by preventing dianions formation and therefore originate for the good stability of the modified electrodes. For strongly buffered electrolytes a difference of 340 mV is observed when compared to acidic medium. It is consistent with the theoretical 60 mV per pHunit expected by the Nernst equation for a two protons/ two electrons redox mechanism.

Stability tests were also performed using AQOH and AQ modified electrodes and it was found that all electrodes behave the same in a given electrolyte (CV in acidic media are presented in figure S12). AQP allows to improve the amount of adsorbed species but does not avoid stability issues in alkaline and unbuffered media. It is important to mention that this observation is consistent with previous hypothesis suggesting that a first monolayer of AQP might be covalently grafted on carbon[35].

After being validated using acetylene lack and glassy carbon, the modification process was adapted to carbon with large specific surface area (*i.e.* porous activated Black Pearls). This carbon allows direct comparison with literature data[22, 23].

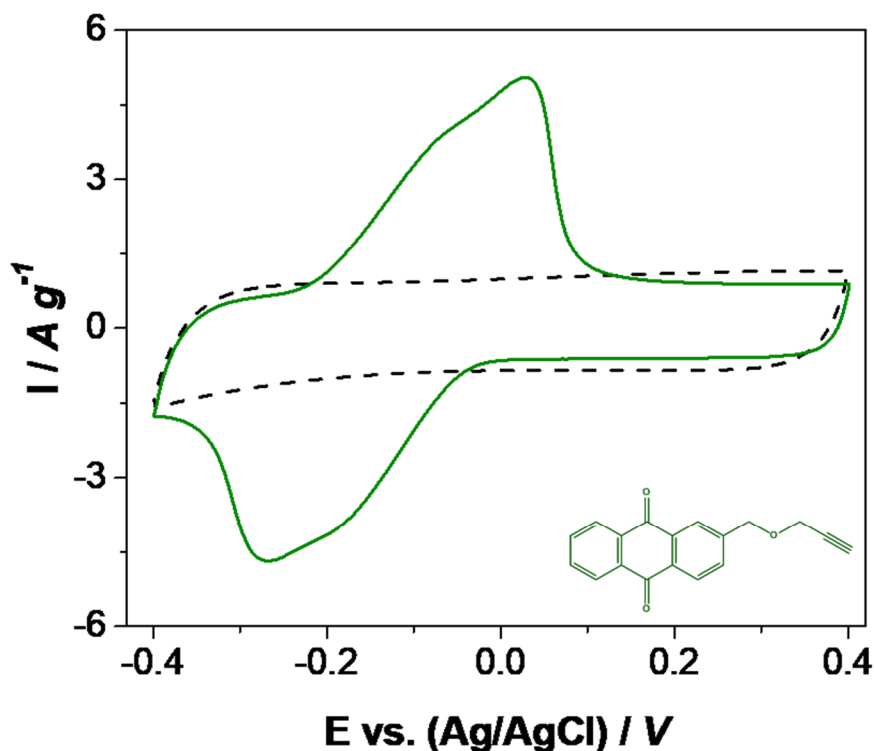


Fig. 6. Cyclic voltammetry of Black Pearls modified with AQP (green full line) and Black Pearls pristine electrode (black dashed line) in 0.5 M H_2SO_4 . Scan rate is 10 mV s^{-1} .

Figure 6 shows the cyclic voltammogram of pristine activated carbon and AQP-modified activated carbon. As expected, for modified electrode, a Faradaic contribution is observed at about $-0.1\text{ V vs. Ag/AgCl}$ and a capacity of 136 C g^{-1} (170 F g^{-1}) is obtained. This corresponds to a capacity increase of 110 % when compared to the unmodified activated carbon electrode. However, a slight decrease of the electrochemical double layer capacitance can be observed between 0 and 0.4 V. This can be explained by a blocking effect of the grafted layer that impede ion accessibility to the carbon microporosity [22]. As a reminder it was not the case using acetylene black (see *e.g.* fig 2). Figure S5 illustrates well the difference between the two carbon substrates when looking at the influence of modification on double layer capacitance. N_2 adsorption isotherms (fig. S13), show a type I isotherm at low relative pressure (P/P_0) whereas a type II isotherm is observed at greater relative pressures. This isotherm is characteristic of a complex porosity, mixing micro and mesopores. In this study, the BET surface of the pristine Black Pearls was $1580\text{ m}^2\text{ g}^{-1}$ whereas the one of the modified powder was only $720\text{ m}^2\text{ g}^{-1}$. More precisely, for pristine powder, microporosity accounts for $630\text{ m}^2\text{ g}^{-1}$ and mesoporosity for $950\text{ m}^2\text{ g}^{-1}$. For modified Black Pearls, the mesoporosity is

not so much affected when compared to microporosity. A decrease of $220 \text{ m}^2 \text{ g}^{-1}$ (25 %) was observed for the mesopores contribution whereas for the micropores contribution, a drastic decrease of $550 \text{ m}^2 \text{ g}^{-1}$ (90 %) was observed. TGA and contact angle measurements are available in figures S14 and S16.

Galvanostatic measurements (4000 cycles) were performed on Black Pearls modified electrodes to evaluate their stability. A capacity decay of about 30 % was observed either in acidic and buffered media (fig. S16). Looking closely to the evolution of the capacity with time it can be noticed that capacity quickly fades down during the first hundred cycles then signal tended to stabilize at about 100 C g^{-1} (140 F g^{-1}). It is important to notice that capacity of unmodified carbon is 80 F g^{-1} and thus the quasi stabilized value of 140 F g^{-1} involves that an important part of AQ moieties remains upon cycling.

Impact of the grafted layer on rate capability of the electrodes was also investigated. CV (fig. S17) were performed at scan rates ranging from 1 to 200 mV s^{-1} and electrode capacity was calculated for every applied scan rate for pristine and modified Black Pearls. Interestingly, a comparable behavior is observed for modified and bare carbon up to 100 mV s^{-1} showing that grafting is not affecting the rate capability of the electrode material. These electrochemical observations are in good agreement with existing literature.

Based on all these observations, similar results were obtained when compared with the diazonium approach both for electrochemical and physical properties highlighting that Diels Alder reaction could be a promising alternative to design interfaces for electrochemical applications.

Conclusion

This work aimed to develop an original approach to modify carbon surfaces for electrochemical applications and more specifically for electrochemical energy storage. To support our argumentation, it was chosen to compare our results to reference literature on AQ-modified carbons for electrochemical capacitors[46]. We have shown the possibility to add redox functions to carbon using Diels Alder reaction. To that extend, the synthesis of a AQ derivative containing a dienophile moiety was achieved using a simple and versatile protocol. A one-step method, by simple stirring at room temperature, was developed to graft this redox molecule on various carbon substrates. We are unfortunately not able to definitely prove that a covalent bonded is formed between AQ moieties and carbon, however many observations

resulting in a body of indirect evidences converge to this conclusion (at least for the first grafted layer). Anyway, it makes no doubt that interactions between carbon and AQ-based molecules are far stronger when propargyl function is present. Modified electrodes were found to be stable either in acidic medium and buffered neutral medium. The electrochemical and physical characterizations of the modified electrodes were compared to the literature related to the diazonium grafting approach and very interestingly Diels Alder leads to comparable results. In this study, we investigated and validated the possibility to use the Diels Alder reaction to modify carbon for electrochemical storage application. This is an important conclusion because it allows expanding modification methods suitable to tune interfaces for electrochemical storage applications.

Acknowledgments

The authors thank the French National Research Agency for its support to through the Labex STORE-EX project (ANR-10- LABX-76-01).

References

- [1] C. Liu, F. Li, L.-P. Ma, H.-M. Cheng, *Advanced Materials for Energy Storage*, *Advanced materials*, 22 (2010) E28-E62.
- [2] M. Beidaghi, Y. Gogotsi, *Capacitive energy storage in micro-scale devices: recent advances in design and fabrication of micro-supercapacitors*, *Energy & Environmental Science*, 7 (2014) 867-884.
- [3] B. Dunn, H. Kamath, J.-M. Tarascon, *Electrical Energy Storage for the Grid: A Battery of Choices*, *Science*, 334 (2011) 928-935.
- [4] S. Koochi-Kamali, V.V. Tyagi, N.A. Rahim, N.L. Panwar, H. Mokhlis, *Emergence of energy storage technologies as the solution for reliable operation of smart power systems: A review*, *Renewable and Sustainable Energy Reviews*, 25 (2013) 135-165.
- [5] F. Tanguy, J. Gaubicher, A.-C. Gaillot, D. Guyomard, J. Pinson, *Lowering interfacial chemical reactivity of oxide materials for lithium batteries. A molecular grafting approach*, *Journal of Materials Chemistry*, 19 (2009) 4771-4777.
- [6] A. Mauger, C. Julien, *Surface modifications of electrode materials for lithium-ion batteries: status and trends*, *Ionics*, 20 (2014) 751-787.
- [7] G. Ma, Z. Wen, M. Wu, C. Shen, Q. Wang, J. Jin, X. Wu, *A lithium anode protection guided highly-stable lithium-sulfur battery*, *Chemical communications*, 50 (2014) 14209-14212.
- [8] G. Ma, Z. Wen, Q. Wang, C. Shen, J. Jin, X. Wu, *Enhanced cycle performance of a Li-S battery based on a protected lithium anode*, *Journal of Materials Chemistry A*, 2 (2014) 19355-19359.
- [9] D.A. Dalla Corte, A.C. Gouget-Laemmel, K. Lahlil, G. Caillon, C. Jordy, J.-N. Chazalviel, T. Gacoin, M. Rosso, F. Ozanam, *Molecular grafting on silicon anodes: artificial Solid-Electrolyte Interphase and surface stabilization*, *Electrochimica Acta*, 201 (2016) 70-77.
- [10] Z. He, Y. Jiang, Y. Li, J. Zhu, H. Zhou, W. Meng, L. Wang, L. Dai, *Carbon layer-exfoliated, wettability-enhanced, SO₃H-functionalized carbon paper: A superior positive electrode for vanadium redox flow battery*, *Carbon*, 127 (2018) 297-304.
- [11] Z. He, A. Su, C. Gao, Z. Zhou, C. Pan, S. Liu, *Carbon paper modified by hydrothermal ammoniated treatment for vanadium redox battery*, *Ionics*, 19 (2013) 1021-1026.
- [12] B. Sun, M. Skylas-Kazacos, *Chemical modification of graphite electrode materials for vanadium redox flow battery application—part II. Acid treatments*, *Electrochimica Acta*, 37 (1992) 2459-2465.
- [13] X. Wu, H. Xu, Y. Shen, P. Xu, L. Lu, J. Fu, H. Zhao, *Treatment of graphite felt by modified Hummers method for the positive electrode of vanadium redox flow battery*, *Electrochimica Acta*, 138 (2014) 264-269.
- [14] Y. Xie, Z. Cheng, B. Guo, Y. Qiu, H. Fan, S. Sun, T. Wu, L. Jin, L. Fan, *Preparation of activated carbon paper by modified Hummer's method and application as vanadium redox battery*, *Ionics*, 21 (2015) 283-287.
- [15] Z. Algharaibeh, P.G. Pickup, *An asymmetric supercapacitor with anthraquinone and dihydroxybenzene modified carbon fabric electrodes*, *Electrochemistry Communications*, 13 (2011) 147-149.
- [16] N. Delaporte, R.L. Belanger, G. Lajoie, M. Trudeau, K. Zaghib, *Multi-carbonyl molecules immobilized on high surface area carbon by diazonium chemistry for energy storage applications*, *Electrochimica Acta*, 308 (2019) 99-114.
- [17] A.A. Ensafi, H.A. Alinajafi, B. Rezaei, *Adenine decorated@reduced graphene oxide, a new environmental friendly material for supercapacitor application*, *Journal of Alloys and Compounds*, 735 (2018) 1010-1016.
- [18] K. Kalinathan, D.P. DesRoches, X. Liu, P.G. Pickup, *Anthraquinone modified carbon fabric supercapacitors with improved energy and power densities*, *Journal of Power Sources*, 181 (2008) 182-185.
- [19] E. Touzé, F. Gohier, B. Daffos, P.-L. Taberna, C. Cougnon, *Improvement of electrochemical performances of catechol-based supercapacitor electrodes by tuning the redox potential via different-sized O-protected catechol diazonium salts*, *Electrochimica Acta*, 265 (2018) 121-130.

- [20] K.W. Leitner, B. Gollas, M. Winter, J.O. Besenhard, Combination of redox capacity and double layer capacitance in composite electrodes through immobilization of an organic redox couple on carbon black, *Electrochimica Acta*, 50 (2004) 199-204.
- [21] Z. Algharaibeh, X. Liu, P.G. Pickup, An asymmetric anthraquinone-modified carbon/ruthenium oxide supercapacitor, *Journal of Power Sources*, 187 (2009) 640-643.
- [22] G. Pognon, T. Brousse, D. Bélanger, Effect of molecular grafting on the pore size distribution and the double layer capacitance of activated carbon for electrochemical double layer capacitors, *Carbon*, 49 (2011) 1340-1348.
- [23] G. Pognon, T. Brousse, L. Demarconnay, D. Bélanger, Performance and stability of electrochemical capacitor based on anthraquinone modified activated carbon, *Journal of Power Sources*, 196 (2011) 4117-4122.
- [24] A. Le Comte, T. Brousse, D. Bélanger, Simpler and greener grafting method for improving the stability of anthraquinone-modified carbon electrode in alkaline media, *Electrochimica Acta*, 137 (2014) 447-453.
- [25] M. Weissmann, O. Crosnier, T. Brousse, D. Bélanger, Electrochemical study of anthraquinone groups, grafted by the diazonium chemistry, in different aqueous media-relevance for the development of aqueous hybrid electrochemical capacitor, *Electrochimica Acta*, 82 (2012) 250-256.
- [26] C. Batchelor-McAuley, B.R. Kozub, D. Menshukau, R.G. Compton, Voltammetric Responses of Surface-Bound and Solution-Phase Anthraquinone Moieties in the Presence of Unbuffered Aqueous Media, *The Journal of Physical Chemistry C*, 115 (2011) 714-718.
- [27] M. Delamar, R. Hitmi, J. Pinson, J.M. Saveant, Covalent modification of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts, *Journal of the American Chemical Society*, 114 (1992) 5883-5884.
- [28] M.A. Ghanem, I. Kocak, A. Al-Mayouf, M. AlHoshan, P.N. Bartlett, Covalent modification of carbon nanotubes with anthraquinone by electrochemical grafting and solid phase synthesis, *Electrochimica Acta*, 68 (2012) 74-80.
- [29] M. Sosna, J.-M. Chrétien, J.D. Kilburn, P.N. Bartlett, Monolayer anthracene and anthraquinone modified electrodes as platforms for *Trametes hirsuta* laccase immobilisation, *Physical Chemistry Chemical Physics*, 12 (2010) 10018-10026.
- [30] J. Agullo, S. Canesi, F. Schaper, M. Morin, D. Belanger, Formation and Reactivity of 3-Diazopyridinium Cations and Influence on Their Reductive Electrografting on Glassy Carbon, *Langmuir*, 28 (2012) 4889-4895.
- [31] J.L. Delgado, P. de la Cruz, F. Langa, A. Urbina, J. Casado, J.T. Lopez Navarrete, Microwave-assisted sidewall functionalization of single-wall carbon nanotubes by Diels-Alder cycloaddition, *Chemical communications*, (2004) 1734-1735.
- [32] C.-M. Chang, Y.-L. Liu, Functionalization of multi-walled carbon nanotubes with furan and maleimide compounds through Diels-Alder cycloaddition, *Carbon*, 47 (2009) 3041-3049.
- [33] S. Munirasu, J. Albuerné, A. Boschetti-de-Fierro, V. Abetz, Functionalization of Carbon Materials using the Diels-Alder Reaction, *Macromolecular Rapid Communications*, 31 (2010) 574-579.
- [34] S. Sarkar, E. Bekyarova, S. Niyogi, R.C. Haddon, Diels-Alder Chemistry of Graphite and Graphene: Graphene as Diene and Dienophile, *Journal of the American Chemical Society*, 133 (2011) 3324-3327.
- [35] H. Kaper, A. Grandjean, C. Weidenthaler, F. Schüth, F. Goettmann, Surface Diels-Alder Reactions as an Effective Method to Synthesize Functional Carbon Materials, *Chemistry – A European Journal*, 18 (2012) 4099-4106.
- [36] K. Shi, K.-K. Shiu, Adsorption of some quinone derivatives at electrochemically activated glassy carbon electrodes, *Journal of Electroanalytical Chemistry*, 574 (2004) 63-70.
- [37] H. Yoon, H.-J. Kim, J.J. Yoo, C.-Y. Yoo, J.H. Park, Y.A. Lee, W.K. Cho, Y.-K. Han, D.H. Kim, Pseudocapacitive slurry electrodes using redox-active quinone for high-performance flow capacitors: an atomic-level understanding of pore texture and capacitance enhancement, *Journal of Materials Chemistry A*, 3 (2015) 23323-23332.
- [38] M. Boota, K.B. Hatzell, E.C. Kumbur, Y. Gogotsi, Towards High-Energy-Density Pseudocapacitive Flowable Electrodes by the Incorporation of Hydroquinone, *ChemSusChem*, 8 (2015) 835-843.

- [39] D.M. Anjos, J.K. McDonough, E. Perre, G.M. Brown, S.H. Overbury, Y. Gogotsi, V. Presser, Pseudocapacitance and performance stability of quinone-coated carbon onions, *Nano Energy*, 2 (2013) 702-712.
- [40] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980.
- [41] V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.-L. Taberna, S.H. Tolbert, H.D. Abruña, P. Simon, B. Dunn, High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance, *Nat Mater*, 12 (2013) 518-522.
- [42] H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt, S.-E. Lindquist, Li⁺ Ion Insertion in TiO₂ (Anatase). 2. Voltammetry on Nanoporous Films, *The Journal of Physical Chemistry B*, 101 (1997) 7717-7722.
- [43] A.S. Kumar, P. Swetha, Simple adsorption of anthraquinone on carbon nanotube modified electrode and its efficient electrochemical behaviors, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384 (2011) 597-604.
- [44] X. Chen, H. Wang, H. Yi, X. Wang, X. Yan, Z. Guo, Anthraquinone on Porous Carbon Nanotubes with Improved Supercapacitor Performance, *The Journal of Physical Chemistry C*, 118 (2014) 8262-8270.
- [45] C. Batchelor-McAuley, Q. Li, S.M. Dapin, R.G. Compton, Voltammetric Characterization of DNA Intercalators across the Full pH Range: Anthraquinone-2,6-disulfonate and Anthraquinone-2-sulfonate, *The Journal of Physical Chemistry B*, 114 (2010) 4094-4100.
- [46] T. Brousse, C. Cougnon, D. Bélanger, Grafting of Quinones on Carbons as Active Electrode Materials in Electrochemical Capacitors, *Journal of the Brazilian Chemical Society*, 29 (2018) 989-997.

For Table of Content Only

