

Catechol-Modified Activated Carbon Prepared by the Diazonium Chemistry for Application as Active Electrode Material in Electrochemical Capacitor

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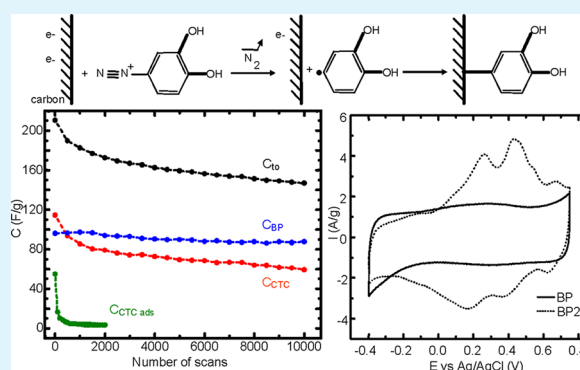
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Supporting Information

ABSTRACT: Activated carbon (Black Pearls 2000) modified with electroactive catechol groups was evaluated for charge storage application as active composite electrode material in an aqueous electrochemical capacitor. High surface area Black Pearls 2000 carbon was functionalized by introduction of catechol groups by spontaneous reduction of catechol diazonium ions in situ prepared in aqueous solution from the corresponding amine. Change in the specific surface area and pore texture of the carbon following grafting was monitored by nitrogen gas adsorption measurements. The electrochemical properties and the chemical composition of the catechol-modified carbon electrodes were investigated by cyclic voltammetry. Such carbon-modified electrode combines well the faradaic capacitance, originating from the redox activity of the surface immobilized catechol groups, to the electrochemical double layer capacitance of the high surface area Black Pearls carbon. Due to the faradaic contribution, the catechol-modified electrode exhibits a higher specific capacitance (250 F/g) than pristine carbon (150 F/g) over a potential range of -0.4 to 0.75 V in 1 M H_2SO_4 . The stability of the modified electrode evaluated by long-time charge/discharge cycling revealed a low decrease of the capacitance of the catechol-modified carbon due to the loss of the catechol redox activity. Nonetheless, it was demonstrated that the benefit of redox groups persists for 10 000 constant current charge/discharge cycles.

KEYWORDS: bifunctional carbon material, catechol, electrochemical capacitor, diazonium, double layer, porous texture



INTRODUCTION

In the last 30 years, electrochemical capacitors have attracted a growing attention as charge storage systems.¹ Advances in materials chemistry have allowed one to exploit and optimize the interfacial properties between the electrode and the electrolyte. Activated carbons are currently considered as the most suitable material for applications in energy storage due to their high surface area, good capacitance, and stability.^{2–5} Thus, improving the capacity and specific energy density of eco-friendly and safe electrochemical capacitors will increase their applicability that already range from portable electronics (weak and moderate power) to hybrid or electric vehicles (high power needs).⁶

Electrochemical capacitors can be divided in two classes, which include the electrochemical double layer capacitor (EDLC) and the redox pseudocapacitor.^{7–9} In the former, the capacitance arises from charge separation and no charge transfer occurs between the electrode and solution species. In the latter, an additional faradaic process takes place due to redox reaction of the active electrode material. For a carbon-based system, coupling its electrochemical double layer

capacitance with a pseudofaradaic and/or faradaic contribution through the addition of heteroatoms,^{10–16} conducting polymers,^{17–19} or metal oxides^{20,21} constitutes an attractive approach to increase the charge storage capability.

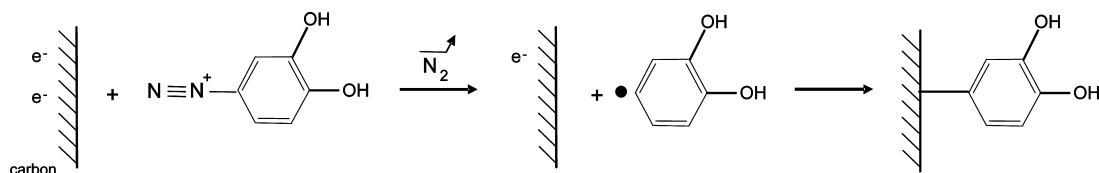
With the recent advances in surface chemistry, simple and flexible ways to introduce appropriate chemical functionalities onto the surface have emerged.^{22,23} In the past two decades, the electrochemical grafting using the diazonium chemistry allows the functionalization of various conducting surfaces.²³ Furthermore, spontaneous covalent derivatization of carbon based on diazonium chemistry also ensures the robust grafting of aryl groups. Therefore, the use of an appropriate modifier allows one to adjust the chemical and electrochemical properties for a specific application. For example, carbon substrates modified with electroactive groups such as anthraquinone and catechol have been used as active electrode materials in electrochemical capacitors.^{24–31} Such modification enables the storage of extra

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Scheme 1. Grafting of Catechol Groups from the Corresponding in Situ Generated Diazonium Cations

Table 1. Reaction Conditions and Chemical, Physical, and Electrochemical Properties of Unmodified and Catechol-Modified Carbons^a

carbon		BP	BP1	BP2	BP3 (ads)	BP4 (ads)
reaction conditions			0.1 eq CTC ^b 0.3 eq NIT ^c	0.2 eq CTC ^b 0.6 eq NIT ^c	0.1 eq CTC 0.3 eq NIT	0.2 eq CTC 0.6 eq NIT
loading of catechol ^d	wt %	0	[3.5] 3.2	[8.4] 8	0.8	2.1
	mol g ⁻¹	0	[3.2 × 10 ⁻⁴] 2.9 × 10 ⁻⁴	[7.6 × 10 ⁻⁴] 7.2 × 10 ⁻⁴	7.3 × 10 ⁻⁵	1.9 × 10 ⁻⁴
	mol cm ⁻²	0	[2.1 × 10 ⁻¹¹] 1.9 × 10 ⁻¹¹	[5 × 10 ⁻¹¹] 4.8 × 10 ⁻¹¹	4.9 × 10 ⁻¹²	1.3 × 10 ⁻¹¹
BET surface area	m ² g ⁻¹	1500	900	270	1100	690
microporous surface area	m ² g ⁻¹	1056	600	105	640	345
	%	70	67	39	58	50
capacitance ^d	C _{tot} (F g ⁻¹)	[150]140	[193] 180	[250] 230	132	177
	C _{DL} (F g ⁻¹)	[150] 140	[140]/[145] ^e 131/135 ^e	[123]/[137] ^e 109/119 ^e	116/117 ^e	131/134 ^e
	C _{CTC} (F g ⁻¹)		[53] 49	[127] 121	16	46

^aThe cyclic voltammograms were recorded in 1M H₂SO₄. ^b4-Aminocatechol: CTC. ^cSodium nitrite: NIT. ^dCapacitance given per mass of active material (BP or PB + catechol) and determined from the cyclic voltammetry data at a scan rate of 5 mV/s (values in brackets for a scan rate of 2 mV/s) and the BET surface area (in the case of the surface concentration, mol/cm²); ^eDouble layer capacitance by taking into account only the mass of BP.

charge, thus leading to an improvement of the energy density of an asymmetric electrochemical capacitor.^{9,25} In addition, covalent grafting of electroactive groups at surface could perhaps promote efficient electronic contact between the redox centers and the carbon that is required for high charging/discharging rate applications. Furthermore, by varying the reaction conditions and time, it has been demonstrated that it is possible to control the quantity of anthraquinone grafted redox centers to obtain adjustable contributions of the double layer and faradaic pseudocapacitance.^{28–30}

Herein, we report on the electrochemical performance of catechol-modified carbons that were obtained by adsorption of catechol and by spontaneous reduction of catechol diazonium cations according to Scheme 1.

The modification with a catechol unit is motivated by the fact that the theoretical specific capacity of the catechol (1750 C/g) is much higher than that of common activated carbons (100–150 C/g), due to its low molecular weight (110.1 g/mol). Furthermore, the two-electron redox reaction and the pH-dependent potential of the catechol species make them a modifier of choice to prepare energy storage systems with increased specific energy and power density. The present study extends the previous short communication from Pickup's group, which described the immobilization of catechol on carbon fabric by the diazonium chemistry and its use as positive electrode material in a hybrid electrochemical capacitor.²⁷ In the present report, a more detailed study is presented for which the specific surface area of the modified carbons was determined by gas adsorption measurements. Furthermore, the specific capacitance and electrochemical stability of catechol-modified activated carbon electrodes were evaluated by cyclic voltammetry and repetitive galvanostatic charge/discharge cycling experiments over a long time period. The effect of catechol loading on the specific surface area of the carbon powders and the faradaic capacitance of the electrodes

were also investigated, and results are compared to the performance obtained for the unmodified carbon.

EXPERIMENTAL SECTION

Reagents. Black Pearls 2000 (BP) was obtained from the Cabot Corporation; 4-aminoveratrole (98 %), boron tribromide (1 M solution in dichloromethane), and sodium nitrite (99.5 %) were purchased from Aldrich. All solutions were prepared using deionized water (Barnstead Nanopure II).

Synthesis of 4-Aminocatechol. A mixture containing 4-aminoveratrole (500 mg; 3.2 mmol) and 1 M boron tribromide solution in dichloromethane (9.6 mL; 2.5 eq) was stirred for 2 h at room temperature under nitrogen. After stirring, methanol (10 mL) was slowly added to the mixture. The crude was concentrated to give a residue, which was recrystallized with a mixture of methanol and ether to afford 4-aminocatechol (375 mg; 3 mmol; 94 %) as a purple solid. Spectral data for 4-aminocatechol: ¹H NMR (300 MHz, CD₃OD): 6.85 (s, 1 H, NH₂), 6.82 (s, 1 H, NH₂), 6.79 (d, *J* = 8.5 Hz, 1 H, CH aromatic), 6.69 (d, *J* = 8.5 Hz, 1 H, CH aromatic), 6.66 (s, 1 H, CH aromatic), 4.88 (s, 1 H, OH), 4.86 (s, 1 H, OH).

Carbon Modification. 4-Aminocatechol (200 mg; 0.1 eq) and sodium nitrite (330 mg; 0.3 eq) were added to an aqueous suspension of Black Pearls carbon (192 mg; 16 mmol) dispersed by a 30 min sonication in 30 mL of deionized water (Barnstead). After complete dissolution, 2 mL of concentrated (37 %) HCl was added under stirring. The reaction mixture was stirred for 24 h at room temperature and then vacuum filtered on a nylon filtration membrane having a pore size diameter of 0.47 μm. The carbon powder (BP1) was washed by successive aliquots of water, *N,N*-dimethylformamide (DMF), methanol, and acetone before being dried under vacuum. For the second sample (BP2), the number of equivalent of reagents was increased 2-fold using the same protocol with only 100 mg of Black Pearls carbon powder. To investigate the effect of catechol adsorption, the procedure described above was repeated using 0.1 (91 mg) and 0.2 eq (184 mg) of catechol for the preparation of BP3 and BP4, respectively. In the latter procedure, the catechol is not a diazonium precursor and no covalent linkage with the carbon substrate is expected. The washing was performed using successive aliquots of water, DMF, methanol, and acetone as for the grafted samples. A

complete characterization of all carbon materials is presented in Table 1.

Adsorption Isotherms and Porosity Analysis. Adsorption isotherms were measured using an Autosorb-1 instrument (Quantachrome Instrument, USA). The porous texture of the carbons was characterized using nitrogen as adsorbent at 77 K. The volume of gas adsorbed for relative pressures ranging from 1×10^{-6} to 1 was recorded. The N_2 adsorption data were used to calculate the BET specific surface area.²⁹

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectra (XPS) measurements were performed with a XPS PHI 5600-ci (Physical Electronics, Eden Prairie, MN, USA) apparatus equipped with a monochromatic Al $K\alpha$ anode (1486.6 eV) at 300 W for survey spectra (resolution 0.8 eV) and a Mg $K\alpha$ (1253.6 eV) anode at 300 W for high-resolution core level spectra (resolution 0.05 eV). The survey spectra do not require the compensation of charge (neutralizer). The data were obtained at room temperature, and typically, the operating pressure in the analysis chamber was below 10^{-9} Torr. Analysis was carried out at an angle of 45° between the sample and the analyzer. The atomic concentrations (at. %) of each individual element were determined from the relative peak areas of the spectra and the corresponding sensitivity factors according to:

$$\text{at. \%} = \frac{A_i/S_i}{\sum_i A_i/S_i} \quad (1)$$

where A_i is the peak area of the element i and S_i is the sensitivity factor for this element. S_i values of 1.0, 1.71, and 2.8 were used for C 1s, N 1s, and O 1s, respectively.

Electrode Preparation and Electrochemical Experiments.

The working electrodes were prepared by mixing the modified activated carbon powder and poly(tetrafluoroethylene) (PTFE), used as binder with a 95:5 (w:w) ratio in a small volume of ethanol until a homogenized paste-like consistency was obtained. A small square of approximately 0.25 cm^2 and 2 mg in weight was placed in a stainless steel grid (80 mesh, 0.127 mm, Alfa Aesar) used as current collector and was pressed for 60 s at $9 \times 10^5 \text{ Pa}$. A three-electrode configuration was used in a one-compartment cell for electrochemical measurements. The counter electrode consisted of a $20 \times 60 \text{ mm}$ piece of carbon paper placed at 20 mm of the working electrode. Deaerated aqueous sulfuric acid (1 M) was used as electrolyte in all experiments at room temperature. An Ag/AgCl electrode placed at 5 mm of the working electrode was used as reference electrode, and all potentials are referred to this electrode. Prior to any measurements, the working electrode was dipped in the electrolyte for 20 min in order to allow the electrolyte to carefully impregnate the electrode porosity.

Cyclic voltammetry (CV) was carried out using a potentiostat electrochemical interface SI480 (Solartron Instruments) connected to a PC, and the electrochemical setups were controlled with DC Corrware software (Scribner Associates, version 2.8d). The gravimetric capacitance, C , expressed in farads per gram (F/g) of carbon paste (carbon modified by catechol and PTFE) and the faradaic charge due to the catechol was estimated by cyclic voltammetry at a scan rate of 2 or 5 mV/s. The faradaic contribution of the capacitance was determined by subtracting the double layer capacitance from the total capacitance.²⁹ It should be noted that the evaluation of the double layer contribution is not always straightforward, as is the case when the redox waves of the catechol species extend close to the potential limits of the cyclic voltammogram. Please note that due to the relatively rapid leaching of catechol species for the adsorbed samples, cyclic voltammograms used to evaluate the catechol loading were recorded at a higher scan rate of 5 mV/s.

RESULTS AND DISCUSSION

The modification conditions and the performance of catechol-modified Black Pearls carbons (BP1 to BP4) are shown in Table 1 and compared to the pristine carbon (BP). The catechol loadings estimated from cyclic voltammetry, by assuming that the catechol oxidation is a two-electron process,

are reported in wt % and mol/g in Table 1. These parameters are considered to be more reliable and meaningful than surface coverage due to the difficulty of choosing an estimate of the appropriate surface area of activated carbons for the calculation. Nonetheless, for comparison purposes, the surface coverages determined from BET adsorption isotherms by taking into account the BET surface area of the unmodified BP are included in Table 1. The evolution of the BET surface area and the pore texture of the carbons will be discussed below. Both the faradaic (C_{CTC}) and double layer (C_{DL}) contributions to the total capacitance (C_{tot}) are estimated from cyclic voltammograms and shown in Table 1.²⁹ Gravimetric specific capacitances are given for the mass of active material (e.g. without PTFE) of the electrode and will be discussed in detail below.

Pore Texture of the Carbons. Figure 1 shows the nitrogen adsorption isotherm for unmodified Black Pearls and

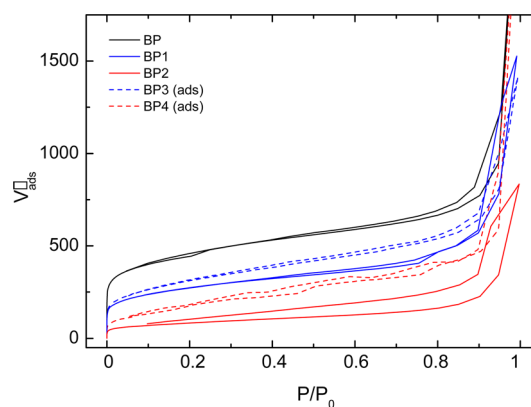


Figure 1. Nitrogen adsorption isotherms for unmodified (black line) and catechol-modified BP carbons (solid line for grafted catechol and dashed lines for adsorbed catechol); modification using 0.1 eq of aminocatechol (blue solid line), 0.2 eq of aminocatechol (red solid line), 0.1 eq of catechol (blue dashed line), and 0.2 eq of catechol (red dashed line).

following modification with various amounts of catechol. Both unmodified and modified carbons present mixed type I and type II isotherms for low relative pressure (P/P_0) and type IV isotherm for high relative pressure.³² Indeed, the isotherms show that a significant volume is adsorbed at low P/P_0 , characteristic of an extended microporous structure (type I isotherm). In the intermediate P/P_0 range, a sloped plateau is observed which is due to a contribution from the outer surface, generally related to the adsorption in the mesopores or larger pores (type II isotherm, for a multimolecular adsorption). Finally, the small hysteresis between the adsorption and desorption branches of the isotherm near the maximum relative pressure (between 0.9 and 1) is characteristic of another mesoporous like behavior (type IV isotherm).

The modification of the carbon surface by the catechol groups, whether it is derivatized by grafting or by adsorption only, causes major changes at the lower relative pressures of the adsorption isotherm with a remarkable drop of the adsorbed volume which becomes more important when the loading increases. Obviously, the presence of the organic molecules at the carbon surface significantly affects the microporous structure. The evolution of the adsorption isotherms in the intermediate P/P_0 range displays the influence of the modification method. The perturbation of the sloped plateau

is much more pronounced (more and more horizontal) when the catechol is chemisorbed to the surface, testifying an influence of the grafted molecules on the multi-molecular adsorption of the gas in the mesopores while the adsorbed catechol molecules do not seem to have such an effect on the adsorption branch of the isotherm. Otherwise, for the BP carbon modified with the largest loading (BP2), the grafted molecules seem to affect the mesopores because the desorption of the gas appears retarded in comparison to its adsorption. These two effects on the micropores and mesopores can be quantified by further analyses of the isotherms, which allow one to determine parameters such as the BET and the microporous surface area (Table 1) as well as the pore size distribution (Figure 2).

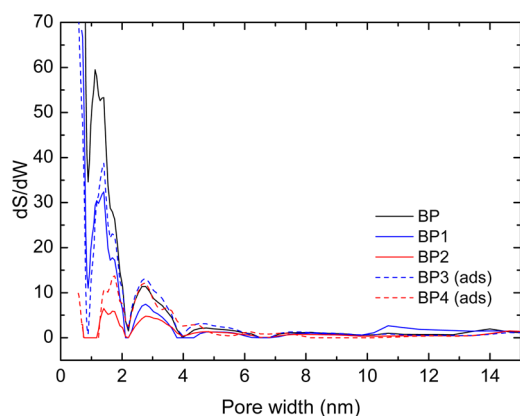


Figure 2. Pore size distribution for unmodified (black line) and catechol-modified BP carbons (solid line for grafted catechol and dashed lines for adsorbed catechol); modification using 0.1 eq of aminocatechol (blue solid line), 0.2 eq of aminocatechol (red solid line), 0.1 eq of catechol (blue dashed line), and 0.2 eq of catechol (red dashed line).

Figure 2 shows the pore size distribution for all the carbons, which is dominated by two types of pores smaller than 4 nm: micropores with size of 1–2 nm and small mesopores between 2 and 4 nm. The change of the pore size distribution following the surface modification depends on the method being used. Firstly, chemical grafting of catechol caused a decrease of all the accessible pores, which is more important for the highest grafting level. Secondly, following adsorption, only the micropores are significantly affected as the pore size distribution for the mesopores is barely modified. It is also important to point out that the loss of the micropores (especially between 1.4 and 2 nm) is not directly related to the amount of catechol when adsorbed and chemisorbed carbons are considered. This observation demonstrates that the type of interaction (adsorption and chemisorption) of catechol does not have the same effect on the porosity of the carbon powders. However, the largest grafting level seems to drastically affect the smallest pores (<1.2 nm) with a complete disappearance of their contribution to the specific surface area as determined by nitrogen gas adsorption.

X-ray Photoelectron Spectroscopy. Some insight in the nature of the catechol species present at the BP surface and their bonding to the surface was obtained by X-ray photoelectron spectroscopy measurements. XPS survey spectra for unmodified and catechol-modified BP carbons are characterized by the presence of C 1s (285 eV) and O 1s (530 eV) peaks, as

expected for a carbon substrate modified by catechol molecules containing carbon and oxygen (Figure SI 1, Supporting Information). In addition, to these two peaks, the chemically grafted samples, especially the one with the highest catechol loading, show clearly the presence of a N 1s peak. Additional information concerning the bonding of the catechol groups can be obtained from the N 1s core level spectra of these samples (Figure 3). A broad peak is clearly observed for the grafted

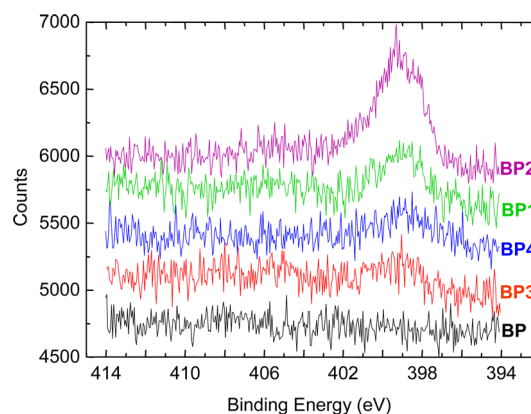


Figure 3. N 1s core level spectra for unmodified (black) and catechol modified carbons.

samples at about 399 eV and can be attributed to the presence of azo bond and thus of a $-\text{C}$ (substrate) $-\text{N}=\text{N}-\text{C}$ (catechol) linkage.^{33,34} The faint N 1s peak, slightly above noise level, for BP with adsorbed catechol is intriguing, but it cannot be attributed to nitrite which is used in the adsorption step because the binding energy for nitrite species is expected at much higher values.³⁵ The atomic composition of the surface of the samples was determined and reported in Table 2. It can be

Table 2. Atomic Composition of the Unmodified BP and Catechol-Modified BP Samples As Determined by XPS

	at. %C	at. %O	at. %N
BP	95.6	4.1	<0.1
BP1	90.6	7.7	1.4
BP2	89.1	7.4	2.8
BP3 (ads)	92.8	6.6	0.3
BP4 (ads)	92.2	6.0	0.5

seen that the oxygen content increases as a result of grafting or adsorption of catechol groups. Correlating the XPS surface analysis data with the catechol loading determined by electrochemistry was not attempted because XPS only probes the surface and not the bulk of the sample.

Electrochemical Properties of the Carbons. Figure 4a shows cyclic voltammograms corresponding to the unmodified BP and BP modified by chemisorption of catechol, recorded in 1 M H_2SO_4 at a scan rate of 10 mV/s. For the unmodified BP, the electrochemical response consists of a nearly perfect rectangular shape cyclic voltammogram (CV) as expected for a material displaying almost pure capacitive behavior. However, a close examination of CV recorded for the unmodified carbon electrode reveals a weak redox system centered at 0.3 V that can be assigned to the presence of oxygenated functional groups as quinone and phenolic or carbonyl oxygen are commonly present at the surface of activated carbon.³⁶ After spontaneous grafting of catechol units, the CV is characterized

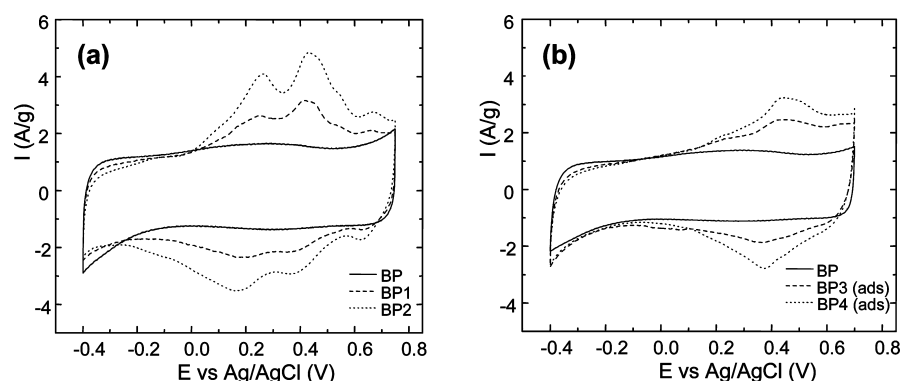


Figure 4. Cyclic voltammograms of unmodified BP (solid line) and catechol-modified carbons (a) by grafting using aminocatechol and (b) by adsorption of catechol (dashed lines for the modifications with 0.1 eq and dotted lines for 0.2 eq).

by three redox systems among which are two well-defined pairs of redox waves centered at 0.2 and 0.4 V and a lower intensity set of peaks centered at about 0.6 V. The cyclic voltammograms for electrodes made with BP modified by adsorption of catechol shown in Figure 4b differ significantly from those of the grafted electrodes and present a set of redox waves centered at 0.4 V which are more intense than the redox waves centered at lower potential. From these observations, it seems plausible to assume that adsorbed catechol could also contribute to the redox waves of the cyclic voltammogram of the grafted electrodes. This will be discussed below in relation with the experiments related to the stability of the electrodes upon cycling.

The shape of the CV of the catechol-modified electrode differs from that reported by Algharaibeh and Pickup in the same electrolyte as the lower potential wave is not observed in their case and the higher potential wave is much more intense.²⁷ Complex CV patterns have been reported for the electrochemistry of catechol modified-carbon electrodes.^{27,37–43} In several cases, two sets of redox waves were observed and several phenomena have been proposed to explain their presence. Firstly, catechol-modified electrodes obtained by oxidative treatment of the carbon electrode will be considered.^{37–43} In these instances, the following combinations have been invoked to explain the 2 pairs of redox waves that were observed when the cyclic voltammograms were recorded in neutral electrolyte instead of acidic electrolyte as is the case in the current report: (i) catechol entrapped in pores and immobilized at surfaces^{37,40} and (ii) chemisorbed and physisorbed (or weakly adsorbed) catechol species.⁴¹ The chemisorbed species could originate from a reaction of catechol with surface carboxylate⁴⁰ or amino groups,⁴² although a recent study seems to have unequivocally ruled out this possibility.⁴³ Instead, Compton and coworkers have proposed that electropolymerization of *o*-benzoquinone formed by oxidation of catechol and/or with *o*-quinone species formed on the carbon electrode upon oxidative pretreatment gave rise to the high potential redox waves.⁴³ In the second case, when the catechol units were grafted on carbon fabric by the diazonium chemistry and the cyclic voltammogram was recorded in the same 1 M H₂SO₄ electrolyte, multiplexes have also been reported and were attributed to bonding of catechol through either a C–C or a C–N linkage.²⁷ We believe that such –C–N– linkage is unlikely in our experimental conditions because the generation of diazonium ions from an amine is usually a fast process, and therefore, the concentration of amine is very small.⁴⁴ Close examination of the cyclic voltammogram of the electrode made

with the chemically grafted BP reveals that the anodic waves are slightly shifted to more positive potential for the highest catechol loading, but the relative intensities of the redox waves are not significantly affected. On the other hand, when catechol is only adsorbed, the lower intensity redox waves at 0.25 V disappeared after a few cycles (not shown). These observations do not allow one to make a definitive attribution for the two pairs of redox waves to either adsorbed or chemisorbed catechol. Moreover, the linear relationship between peak current values and scan rate observed for the two waves, at scan rate slower than about 50 mV/s, changes to a linear dependence with the square root of the scan rate beyond this value for the chemically grafted electrodes (Figure SI 2, Supporting Information). In summary, the electrochemistry of catechol-modified electrode is not fully understood, and a definitive explanation for the presence of the three set of redox waves observed in this study would require further work that is beyond the scope of the present investigation.

Finally, it is worth noting that the capacitive current is only slightly affected (see below) for the catechol loadings investigated in the present study, indicating that the accessibility of the ions of the electrolyte in the porous structure of the carbon is efficient for the charge storage even in the presence of the grafted catechol groups. However, a significant polarization is seen at both negative and positive potential limits for the catechol-modified electrodes, the effect being more pronounced for the highest catechol loading. This could be due to the blocking of the micropores by the grafted molecules (Figures 1 and 2).

Effect of Catechol Grafting on the Specific Capacitance of the Carbons. The energy storage properties of carbonaceous materials used as active electrode materials in electrochemical capacitors are governed by their average pore size and pore size distribution.^{2,4} Micropores are needed for efficient charge storage because they usually provide the most important contribution to the double layer capacitance,^{2–5,45–49} whereas the pore size should also be adapted for the functionalization of the accessible microporous surface area. Thus, the Black Pearls carbon powder used in this study must present an adequate pore size distribution that enables both the access of the electrolyte species and the 4-aminocatechol molecules during the grafting or catechol during the adsorption step. Gas adsorption measurements clearly demonstrated that the pore size distribution is affected by grafting or adsorption of catechol molecules (vide supra). To gain a better understanding of the combination of the faradaic and the double layer

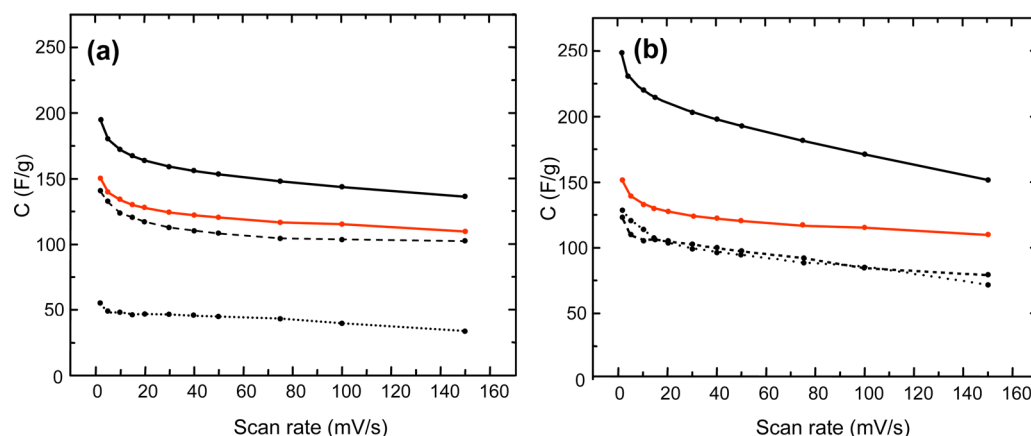


Figure 5. Evolution of the different contributions (double layer (dashed lines), catechol (dotted lines), and total (solid lines)) of the capacitance as a function of scan rate for unmodified carbon (red curve) and catechol-modified carbon with a loading of (a) 3.5 wt % and (b) 8.4 wt %. Capacitance values were extracted from the cyclic voltammograms.

capacitances, the redox activity of catechol moieties and the capacitive current were estimated from cyclic voltammetry considering that the oxidation of catechol is a two-electron process. Both the electrochemical double layer and faradaic contributions of the capacitance were estimated from the CVs recorded at different scan rates for unmodified (BP) and modified Black Pearls carbons (BP1 and BP2). Similar experiments could not be performed with good reliability with the adsorbed samples (BP3 and BP4) due to the rapid desorption of catechol.

Figure 5 shows the evolution of the faradaic and double layer contributions of the total capacitance as well as the total capacitance as a function of the scan rate between 2 and 150 mV/s. A rapid increase of the total capacitance for the unmodified and modified carbons is noticeable at slow scan rate (< 20 mV/s) and is mainly due to the increase of the double layer capacitance. Increasing the scan rate from 20 to 150 mV/s has little influence for the unmodified BP and for the one with the lowest catechol loading. On the other hand, a significant decrease of the total capacitance can be seen for BP modified with the highest catechol loading of 8.4 wt %. In this case, the loss of capacitance associated to the catechol redox system, upon increasing the scan rate, becomes significant.

For the lower catechol loading (3.5 wt %; BP1), the double layer capacitance contribution is slightly smaller than that of pristine carbon (Figure 5a). Above a potential scan rate of approximately 20 mV/s, the double layer capacitance is slightly affected. The rapid increase of the double layer capacitance for slower scan rate is observed because, for this time scale, ions can diffuse in the microporous structure and reach a larger fraction of the available microporous specific area. It is noteworthy that, for scan rate higher than 40 mV/s, the double layer capacitance is only slightly affected by catechol derivatization. This observation might suggest that, for low catechol loading, the grafted molecules cover only the surface of the mesopores and that the micropores that contribute to the double layer capacitance remain accessible to ions. The evolution of the total capacitance for this catechol-modified carbon demonstrates that a faradaic pseudocapacitance can be introduced by surface functionalization without significant detrimental effect to the double layer capacitance. This behavior is in very good agreement with our previous study with anthraquinone-modified carbons.²⁹

In the case of the higher catechol loading (8.4 wt %; BP2), the total capacitance increased further relative to a lower catechol loading, but the double layer and faradaic capacitances are significantly affected by an increase of the scan rate (Figure 5b). Firstly, the double layer capacitance at a slow scan rate of 2 mV/s decreased in comparison to the unmodified or slightly modified carbon (150 F/g for pristine carbon, 140 F/g for BP1, and 123 F/g for BP2 at 2 mV/s). Secondly, the evolution of the capacitances over the whole scan rate domain changes relative to that of BP1 as a strong dependence of both the double layer and the faradaic capacitance on scan rate is noticeable. Presumably, both effects are associated with the presence of a larger amount of grafted catechol molecules which block a larger surface area of the carbon powder and hinders ion transport within the resulting porous structure, in accordance with the dramatic decrease of the surface area measured from the BET adsorption isotherms (Table 1).

Interestingly, the relative decrease of the double layer capacitance following grafting of catechol moieties is much smaller than the loss of the BET surface area (see Table 1). This suggests that most of the surface being lost, which is mainly the microporous one, contributes only very slightly to the double layer capacitance. A similar observation has been recently made for anthraquinone-modified Black Pearls.²⁹ The evolution of the BET surface area and the double layer capacitance with surface coverage is consistent with a nonuniform coating of the surface by the catechol molecules and that the grafting occurs on surface sites that are located close to the entrance of the micropores.

It might be instructive to compare the BET surface measured for Black Pearls carbon containing a 3.5 wt % loading of catechol (e.g. 3.2×10^{-4} mol/g) (Table 1) to that of a 6.7 wt % loading of anthraquinone (e.g. 3.2×10^{-4} mol/g)²⁹ which were found equal to 900 and 985 m²/g, respectively. At first sight, this appears somewhat surprising considering the size of both molecules. The area of a flat-lying AQ molecule is 0.92 nm²/molecule (0.744 nm × 1.165 nm),²⁹ and the maximum surface covered by a monolayer with this orientation would be 177 m²/g or 12 % of the total specific surface area of the carbon. For the catechol-modified carbon, the area of a catechol molecule could be estimated to be 0.28 nm²/molecule (0.509 nm × 0.542 nm). Therefore, a monolayer should only cover 54 m²/g or 3.6 % of the total specific surface of the carbon. If the surface coverage is considered, a low value of 2.1×10^{-11} mol cm⁻² is computed

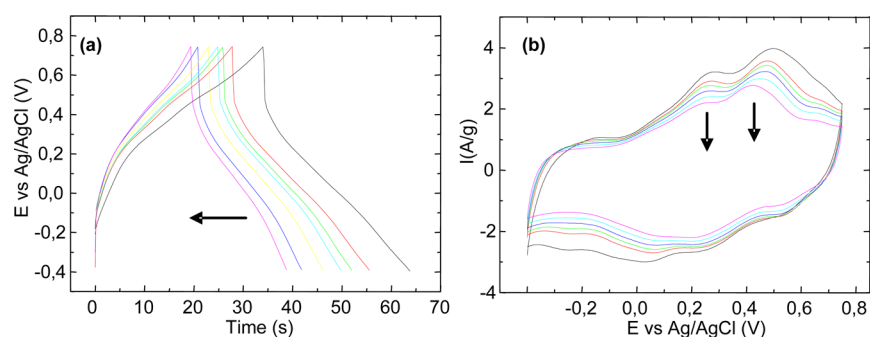


Figure 6. (a) Constant current charge/discharge curves (cycles 1, 500, 1000, 1500, 2000, 5000, and 10 000) in 1M H₂SO₄ at 7.5 A/g for catechol-modified Black Pearls carbon with a catechol loading of 8.4 wt %. (b) Corresponding cyclic voltammograms at 10 mV/s.

for a 3.5 wt % loading of catechol on BP (Table 1). Even if one considers that the surface of the ultramicropores, which is not accessible for grafting, has been estimated to about 300 m² g⁻¹ for BP carbon powder modified with the larger AQ molecules,²⁹ this will still lead to a relatively low surface coverage. These values are much smaller than that expected for monolayer coverage and confirm that the grafting occurs mainly on the microporous surface and presumably at the entrance of the micropores. Interestingly, in a recent study, we have shown that the grafting of a very small amount of AQ molecules, in the range of only 1 wt %, is sufficient to block a significant fraction of the surface area as determined by nitrogen and CO₂ gas adsorption.²⁹

Electrochemical Stability of the Catechol-Modified Carbons. In order to assess the benefit of grafted catechol units, galvanostatic charge/discharge experiments were performed in the potential range of electroactivity of the catechol redox system between -0.4 and 0.75 V range for a current load of 7.5 A/g. Long-time charge/discharge experiments provide information about the stability of an electrochemical capacitor and more specifically of the grafted catechol molecules (Figure 6a). CVs were also recorded at various stages during the charge/discharge cycling experiments and are shown in Figure 6b. Furthermore, the evolution of the total capacitance (extracted from the CV) as a function of the number of charge/discharge cycles is shown in Figure 7 for both chemically grafted and adsorbed catechol-modified BP-based electrodes. At such a current density, the time of charge or

discharge is sufficient to ensure the complete redox interconversion of the catechol redox units (e.g. complete charge/discharge process).

Figure 6a presents selected charge/discharge curves for the chemically grafted BP2 electrode recorded during 10 000 charge/discharge cycles. During the charging step, a steep increase of potential is seen between -0.4 and -0.2 V due to the ohmic drop and the relatively strong polarization. Thereafter, the double layer and faradaic contributions are observed, and their respective potential ranges are identified on the charge/discharge curve (Figure SI 3, Supporting Information). The redox-confined groups yielded a lower slope for the constant current charge curves over the 0.2 to 0.75 V potential range where the catechol units were oxidized. It corresponds to a specific capacitance of 400 F g⁻¹ for the first charge curve. The higher slope for potentials below ca. 0.2 V indicates a lower specific capacitance value of 130 F g⁻¹ for the first charge curve that is contributed by the Black Pearls carbon. These values decrease to 240 and 100 F g⁻¹ after 10 000 charge/discharge cycles, indicating that the beneficial effect of the catechol groups remains even after long time cycling. For the discharge curve, the ohmic drop and polarization are observed between 0.75 and 0.4 V which is followed by two straight lines due to the reduction of the oxidized catechol groups (from 0.3 to -0.2 V) and the double layer contribution of the carbon (from -0.2 to -0.4 V). Electrodes based on catechol adsorbed on BP were characterized by a similar experimental procedure (vide infra).

Figure 7 indicates that the decrease of the total discharge capacitance of BP with chemically grafted catechol can be mainly attributed to the loss of the catechol electroactivity during the first 2000 cycles. Indeed, the double layer capacitance remained stable upon cycling, even for the sample with the highest catechol loading. The similar decrease of the two redox waves of the CVs of Figure 6b suggests that all the catechol moieties, that give rise to these redox waves, are similarly affected during the long term cycling. Nonetheless, the significant shift of the anodic peak to less positive potential might suggest that the remaining catechol species become more electrochemically accessible and the redox processes become less limited by diffusion. This is demonstrated by the smaller polarization loss observed after scan reversal at -0.4 V. A comparison of the decrease of the capacitance of the catechol units for the chemically grafted electrodes with those observed for the adsorbed catechol BP electrodes illustrate some important difference as the decrease is much faster in the later case. These observations suggest that, for BP electrodes with chemically grafted catechol, either the amount of

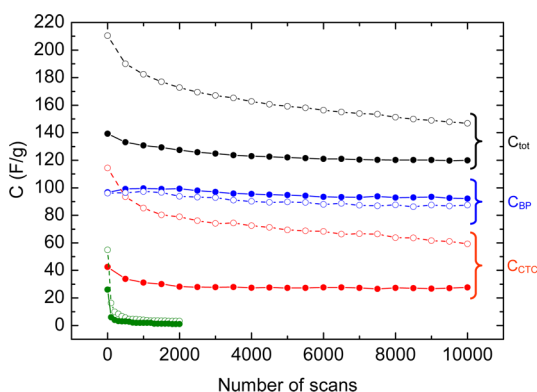


Figure 7. Evolution of the different contributions of specific capacitance for modified carbons BP1 and BP2 containing a catechol loading of 3.5 wt % (solid line) and 8.4 wt % (dashed lines), respectively. The capacitances are extracted from CVs such as those shown in Figure 3b. Specific capacitance of catechol for BP3 and BP4.

“adsorbed only” and ungrafted catechol species is small or that the release of these catechol units is hindered and perhaps that adsorption of catechol may not occur on the same sites as for the chemisorbed species. After the initial 2000 charge/discharge cycles, the performances remains fairly stable with a loss of only 1.5% of the redox capacitance per 1000 charge/discharge cycles for the sample with the highest catechol loading. The relatively good stability is consistent with the fact that the coulombic efficiency for the charge/discharge is about 99.5% and slightly lower for the BP electrode with the lowest catechol loading (Figure SI 4, Supporting Information). In summary, it is noteworthy that the catechol groups allow an increase of the capacitance with very little influence of the double layer capacitance and that the benefit remains after 10 000 charge/discharge cycles.

CONCLUSION

Spontaneous covalent modification of Black Pearls carbon with an in situ produced catechol-substituted diazonium salt allows the preparation of redox-modified carbon surface for application as active electrode material in an electrochemical capacitor. Due to a small molecular size, an efficient faradaic contribution was obtained from the catechol-modified carbon even for a small catechol loading without any significant loss of the double layer capacitance contribution. A 70 % increase of capacitance was reached (250 F/g compared to 150 F/g for pristine carbon) with a catechol loading of 8.4 wt %. Grafted catechol groups provide an extra charge over the 0.2 to 0.75 V potential window. Long-term galvanostatic charge/discharge cycling experiments revealed a decrease of capacitance, which was mainly attributed to the progressive loss of “adsorbed only” and ungrafted catechol moieties during the first 2000 charge/discharge cycles. This catechol-modified carbon constitutes an attractive positive electrode of a hybrid electrochemical capacitor that could be used in conjunction with an anthraquinone-modified carbon as negative electrode.^{27–29} This will be reported elsewhere in a detailed forthcoming paper. It should be noted that this concept has been recently reported in a short communication by Algharaibeh and Pickup.²⁷

ASSOCIATED CONTENT

Supporting Information

Additional figures: XPS survey spectra of unmodified and catechol-modified carbons, scan rate dependence for the two redox waves associated to the catechol groups for BP2 and BP3 electrodes, constant current charge/discharge curves for catechol-modified Black Pearls carbon, and Coulombic efficiency as a function of the number of constant current charge/discharge cycles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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