Substrate-dependent performance of supercapacitors based on an organic redox couple impregnated on carbon

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ABSTRACT

Two different carbon electrodes have been modified with 1,4,9,10-anthracenetetraone (AT) in order to produce composite electrodes combining the double layer capacitance of carbons and the redox capacity of the organic redox couple. Electrodes were prepared by impregnation of AT on both commercial high surface area functionalized carbon and on carbon black.

Optimum loading amount, redox activity, and electrochemical potentials of AT were determined to be dependent on the substrate used, and the respective performances were characterized by cyclic voltammetry at different scan rates, and galvanostatic charge discharge experiments.

Immobilized AT improves more than 50% of the total capacitances of both bare carbons, even after 1000 cycles at $200 \, mA \, g^{-1}$. This increase is attributable to the use of AT, which can exchange up to four electrons, but is also surprisingly effective taking into account that no efforts were undergone to achieve covalent bonding. Although substantial loss of capacitance is observed for both modified carbons at higher rates, the results here discussed are a step forward to determine the contribution of covalent bond to carbon electrode performances and its benefits compared to loosely bound molecules, with the aim of optimizing supercapacitor electrodes based on this combination of materials.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, are energy storage devices with very high specific power and long durability upon hundreds of thousands of cycles without significant deterioration. The early commercialization of capacitors for memory back-up in consumer electronics and storage systems for micro solar power generators is expected to be broadened to high power/energy applications, such as hybrid and electric vehicles, power quality systems and smart grids, but higher energy densities are needed to achieve this goal [1].

Charge storage mechanism of EDLCs consists of electrostatic charge separation at extremely small distances within the electrical double layer at the electrode/electrolyte interface; hence their capacitance is mainly governed by the surface area of the electrodes. Carbons are widely studied electrode materials in these devices due to their high surface area, suitable electric conductivity, and low cost [2].

The main drawback of EDLCs upon comparing with batteries is the remarkably low energy density that they can store. So the study of modified carbon electrodes in order to enhance their energy density has currently become the focus of many research efforts. One of the most active areas to achieve this goal proposes the combination of high surface area carbons with materials having faradaic-type charge transfer [3]. As it has long been known that at certain carbons pseudocapacitance by redox contribution of naturally occurring surface functionalities such as phenols, carboxylic acids, lactones and quinonoid structures [4] is added to the carbon electrical double layer capacitance, many studies have been based on covalent modification of electrode surfaces by redox active species in order to attain higher energy densities.

Particularly, quinone derivatives are well-known redox couples in terms of their high reversibility, and Saveant et al. demonstrated for the first time electrochemical reduction of a wide variety of aromatic diazonium salts on carbon electrodes such as glassy carbon or highly oriented pyrolytic graphite, leading to the covalent attachment of the corresponding aromatic radicals [5]. Later, Compton's group presented a chemical method to carry out homogeneous reduction of diazonium salts by hypophosphorous acid, providing an easy methodology for the derivatization of carbon powder. They demonstrated the derivatization of carbon particles with anthraquinone and nitrobenzene diazonium salts throughout a covalent bonding [6].

Since then several studies have been presented by applying similar methodologies to different carbon supercapacitor electrodes. Specifically, Pickup's group has presented various recent studies on this subject, reaching improved energy and power density for

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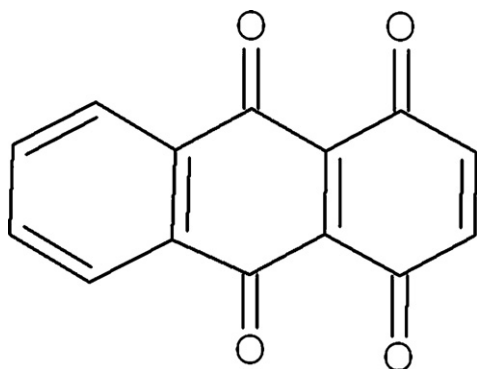 *E-mail address:* suheda.isikli@imdea.org (S. Isikli).

Fig. 1. Molecular structure of AT.

Fig. 2. Amount of AT grafted vs. time on (a) Pica electrodes and (b) Vulcan electrodes.

anthraquinone modified carbon fabric as negative supercapacitor electrode relative to asymmetric unmodified carbon fabric [7], ruthenium oxide [8], and 1-2-dihydroxybenzene [9] as positive electrodes. Also, Bélanger at al. studied a series of high surface area activated carbon powders modified with various loadings of electroactive anthraquinone groups, reaching almost double capacitance values for the modified electrodes compared with unmodified carbons [10].

In some of these studies, in addition to the covalently bound species, it has already been pointed out the presence of loosely bound species which, in some cases, may diminish the coverage by covalently bound molecules [11]. Nevertheless, no "blank" study regarding the influence of only loosely bound molecules has been undergone. Here, we try to point out the effect of adsorption by using electroactive 1,4,9,10-anthracenetetraone (AT) (see Fig. 1) on different carbons. For that, two different carbons were impregnated with AT. Porous structure, pore size distribution and surface area alterations of the electrodes before and after modification will be discussed. This, together with electrochemical measurements, will show a substrate-dependent AT redox activity which establishes significant differences on the amount and stability of AT present, and more importantly on the performance of supercapacitor device.

2. Experimental

1,4,9,10-Anthracenetetraone (AT) was purchased from Sigma–Aldrich and used without further purification. Vulcan XC-72R (CABOT Corporation) (hereby referred as "Vulcan") and Picactif BP 10 (PICA) (hereby referred as "Pica") are commercially available activated carbons and used as received as well. Glassy carbon (3 mm in diameter) was purchased from BASI Corp. and used as working electrode for electrochemistry of AT in solution. Before experiments, this electrode was polished with 0.1 and 0.05 μm alumina slurry polishing solution and then rinsed with copious amounts of purified water (Milli-Q system, Millipore). Polytetrafluoroethylene (PTFE 60 wt.% dispersion in water, Sigma–Aldrich) was used as binder and acetylene black (carbon black, acetylene, 100% compressed, >99.9%, Alfa Aesar) was added as conductive agent for carbon paste preparation.

Carbon (70 wt.%), acetylene black (20 wt.%) and PTFE (10 wt.%) were mixed and grinded using 2-propanol (>99.5%, Scharlau) until reduced to pasty mass. The paste was coated on a coin shape stainless steel mesh current collector (AISI 3024, 97% open, Goodfellow) (1 cm in diameter). The electrodes were then pressed with a uniaxial press (CARVER model 3853-0) applying a pressure of 450 kg cm^{-2} and dried at room temperature overnight. Average mass of dry electrodes was 15–20 mg cm^{-2}. Pristine carbon electrodes were soaked in 5×10^{-3} M AT in acetonitrile (>99.5%,
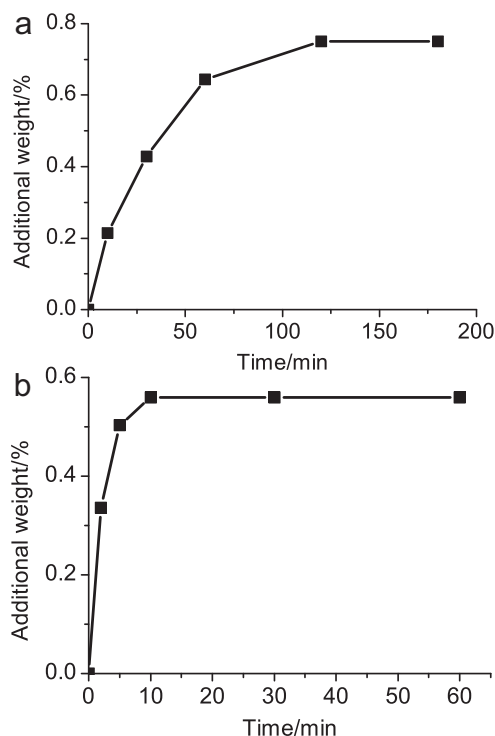
Sigma–Aldrich) with different immersion periods and dried at room temperature around 3 h.

Porous texture of the modified and unmodified electrodes was analyzed by N$_2$ adsorption at 77 K (Autosorb-1, Quantachrome Instruments). The analyses were performed using whole electrode paste material including binder and acetylene black. Before the measurements, the sample was outgassed under vacuum at 120 °C overnight. The specific surface area was calculated from the isotherm by applying the BET equation (S_{BET}). The micro and meso pore volume and the pore size distribution were obtained from N$_2$ adsorption isotherm by applying the QSDFT model.

Cyclic voltammetries (CV), and galvanostatic charge–discharge tests were performed using Biologic VMP3 multichannel potentiostat–galvanostat (Biologic, France). All electrochemical experiments for supercapacitor performance were performed in 0.5 M H$_2$SO$_4$ (95–97%, p.a., Scharlau) aqueous electrolyte.

CV experiments were run with a three electrode configuration (Ag/AgCl reference and Pt grid counter electrode) at scan rates ranging from 10 to 200 mV s^{-1}. Symmetric cells were constructed by balanced weights and AT doping ratios in a two electrode Swagelok® cell configuration. Electrochemical performance of the cells was tested by galvanostatic charge–discharge at 200 mA g^{-1}.

3. Results and discussion

3.1. Optimization of AT loading on different carbon substrates

The electrodes can be loaded up to a maximum of 0.75 and 0.55 wt% AT for Pica and Vulcan respectively, where they reach an equilibrium in which adsorption–desorption rate between substrates and soaking solutions becomes equal. Pica electrodes reach constant weight after 180 min immersion time (Fig. 2a), while Vulcan electrodes reach equilibrium after only 5 min (Fig. 2b). After each immersion time, the specific capacitances of modified electrodes were measured for both carbons and can be correlated with the amount of AT adsorbed (Supporting information, Fig. S1).

Table 1
Peak values extracted from Fig. 4b.

Scan rate(mV s^{-1})	$E_{1/2}$(I)(V)	$E_{1/2}$(II)(V)	ΔE(I)(V)	ΔE(II)(V)
10	0.120	0.630	0.044	0.058
50	0.120	0.630	0.141	0.100
200	0.160	0.640	0.320	0.200

The fast AT adsorption kinetics showed by Vulcan may be attributed to both a different affinity, possibly through a different adsorption mechanism than that taking place at Pica, and also to the lack of diffusion limitations through micropores, as further discussed below.

Taking into account these results, all the experiments below were performed with either pristine electrodes or electrodes modified with the maximum possible amounts of AT (0.75 wt.% for Pica and 0.55 wt.% for Vulcan).

3.2. Porous texture and pore size distribution of modified and unmodified electrodes

Fig. 3a demonstrates the nitrogen adsorption isotherms of pristine and AT grafted Pica carbon, both curves are well correlated with both type I and type IV isotherms within the IUPAC classification of adsorption isotherms [12]. Substantial volume adsorbed at low P/P_0 is a characteristic of extended microporous structure [13]. After modification, significant volume decrease was detected at low P/P_0. Pore size distribution graph (Fig. 3c) confirms the presence of micropores (<2 nm) and the contribution of a significant amount of mesopores (2–4 nm) to the total surface area as well. Additionally, both BET and DFT surface area decreases from 1782.76 to 1304.06 m^2 g^{-1} and 1536.8 to 971.8 m^2 g^{-1} respectively upon grafting. The total and micropore area loss were calculated according to DFT model. Most of the total DFT area lost (36.8%) comes from micropores (Fig. 3d) which may be blocked by AT molecules.

Nitrogen adsorption isotherm of Vulcan electrodes is presented in Fig. 3b. The shape of isotherm shows a type III curve, which describe the adsorption on mesopores and macropores. Vulcan carbon is not a microporous carbon and it has very small BET and DFT surface area (Fig. 3d). The loss of 20% DFT surface area can be attributed to AT adsorption.

3.3. Electrochemical characterization

3.3.1. Capacitance relation with cycling rate

Cyclic voltammetries were performed at different scan rates by using 0.5 M H$_2$SO$_4$ electrolytes for all electrodes. Fig. 4a and b illustrates the scan rate dependence of the capacitance of AT grafted Pica and Vulcan carbon electrodes. As can be clearly observed, in the case of Pica electrodes the CV shapes are distorted even at 50 mV s^{-1}. Compared with pristine Pica electrodes, the decrease of the total capacitance is much more important for the modified carbon at higher scan rates (Fig. 4c), indicating poorer kinetics for the AT redox processes on Pica carbon substrate.

Vulcan electrodes exhibit excellent cycling rate stability up to very high scan rates such as 200 mV s^{-1}, even after AT modification (Fig. 4b). Nevertheless, AT redox peak separation increases with the scan rate (Table 1), thus showing kinetic limitations which are confirmed when extracting capacitance values at different rates (Fig. 4d), but which are much less important than those present on Pica electrodes.

Previously, Bélanger at al. reported that for covalently bound species the decrease of the total capacitance becomes much more important for the highest anthraquinone loaded electrodes and at high scan rates [10].
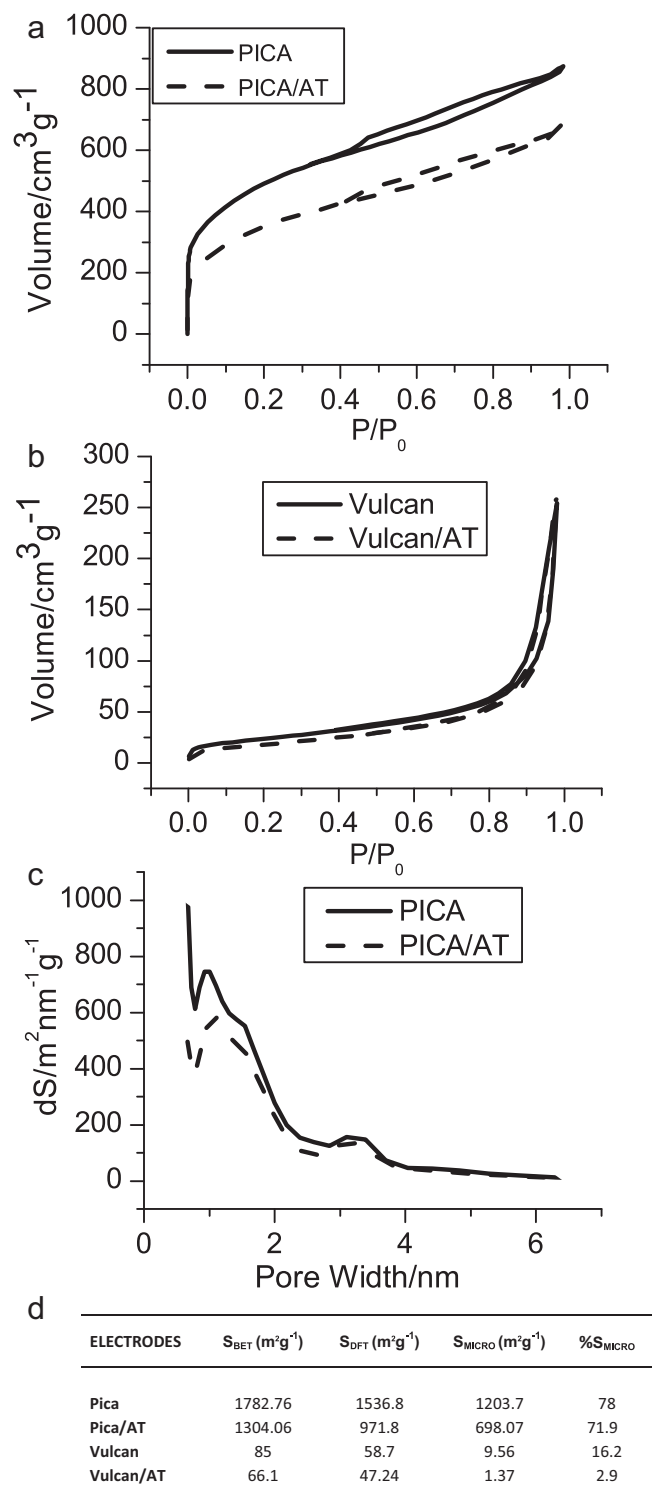

ELECTRODES	S_{BET} (m^{2}g^{-1})	S_{DFT} (m^{2}g^{-1})	S_{MICRO} (m^{2}g^{-1})	%S_{MICRO}
Pica	1782.76	1536.8	1203.7	78
Pica/AT	1304.06	971.8	698.07	71.9
Vulcan	85	58.7	9.56	16.2
Vulcan/AT	66.1	47.24	1.37	2.9

Fig. 3. N$_2$ adsorption isotherms of unmodified and AT-modified (a) Pica electrodes for loading of 0.75 wt.% and (b) Vulcan electrodes for loading of 0.55 wt.%; (c) pore size distribution of unmodified and AT-modified Pica electrodes for loading of 0.75 wt.% and (d) textural properties for all electrodes.

3.3.2. Cyclic voltammetry of 1,4,9,10-anthracenetetraone in aqueous acidic solution

To gain more insight on the electrochemical behavior of impregnated AT on the two different carbons and the reasons of the features exhibited in cyclic voltammetries, we examined for comparison the electrochemistry of an aqueous solution of AT using glassy carbon working electrodes.
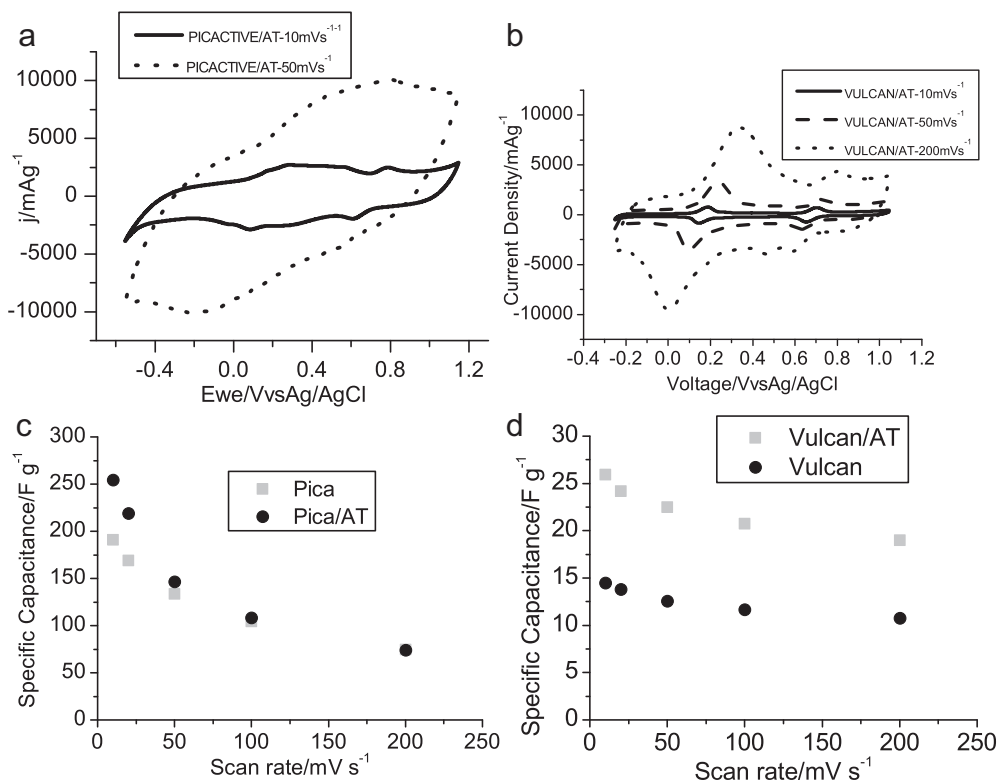
Fig. 4. Cyclic voltammetries of AT modified (a) Pica and (b) Vulcan electrodes in aqueous H_2SO_4 (0.5 M) electrolyte; capacitance values extracted from CVs at different scan rates of unmodified and AT modified (c) Pica and (d) Vulcan electrodes.
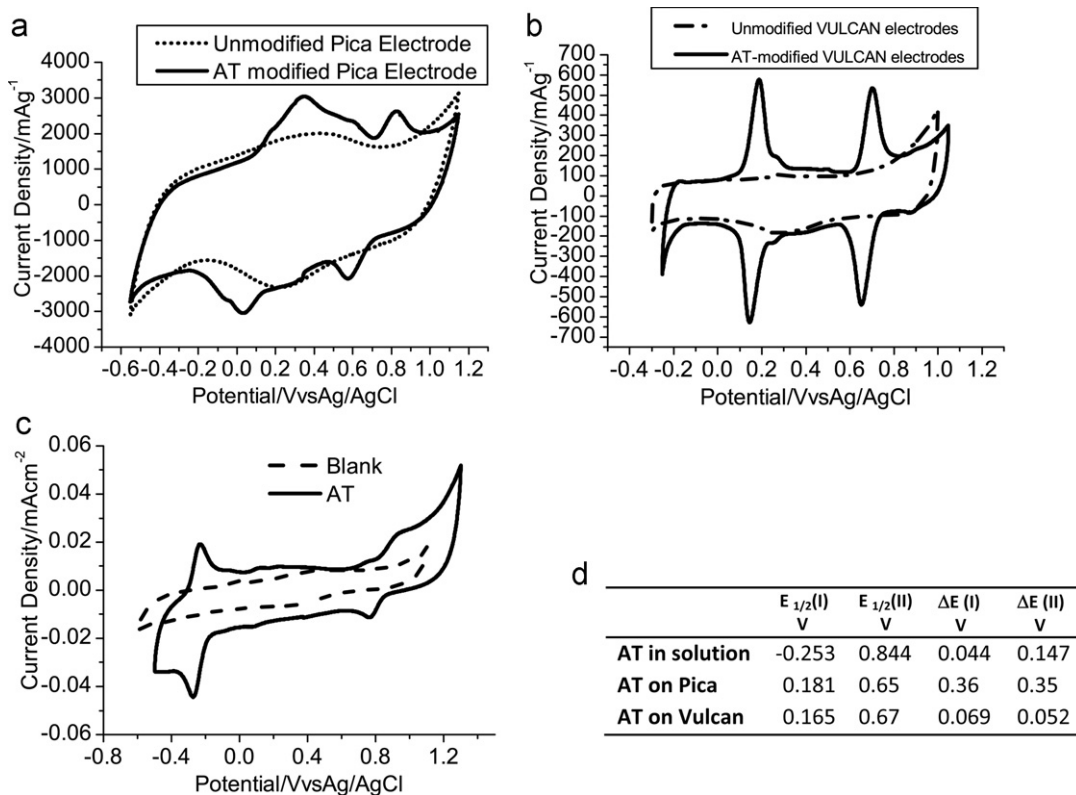

	$E_{1/2}(I)$ V	$E_{1/2}(II)$ V	$\Delta E (I)$ V	$\Delta E (II)$ V
AT in solution	-0.253	0.844	0.044	0.147
AT on Pica	0.181	0.65	0.36	0.35
AT on Vulcan	0.165	0.67	0.069	0.052

Fig. 5. Cyclic voltammetries in aqueous H_2SO_4 (0.5 M) electrolyte: unmodified and modified Pica (a) and Vulcan (b) electrodes at optimum grafting time. Scan rate: $10\,mV\,s^{-1}$; (c) 1.67×10^{-4} M AT using glassy carbon working electrodes at $50\,mV\,s^{-1}$; (d) half wave potentials and peak separations extracted from CV experiments.
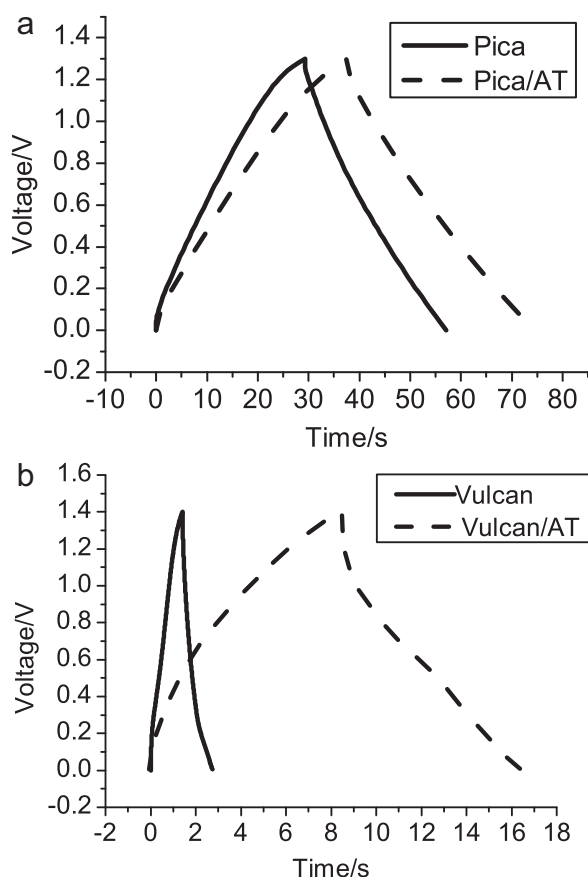
Fig. 6. Potential vs. time charge/discharge curves during galvanostatic cycles of the symmetric cells at 200 mA g^{-1} with (a) unmodified and AT modified Pica electrodes; and (b) unmodified and AT modified Vulcan electrodes.

Fig. 7. Discharge capacitance as a function of cycle number for the symmetric cell in H$_2$SO$_4$ (0.5 M) aqueous electrolyte at 200 mA g^{-1} with unmodified and AT modified (a) Pica and (b) Vulcan electrodes.

The redox chemistry of quinones in aqueous solution had been well described as a one-step 2e$^-$, 2H$^+$ reaction giving the hydroquinone as the final product [14]. Fig. 5 shows the cyclic voltammetry of AT in 0.5 M H$_2$SO$_4$ solution with sweep rate of 50 mV s^{-1}. Highly reversible and quasi-reversible redox waves were observed around −0.253 V and 0.844 V (vs. Ag/AgCl) with peak separations 44 mV and 147 mV respectively (Fig. 5d). These results suggest that AT redox mechanism follows the characteristic of aqueous redox mechanism of typical para-benzoquinone (p-BQ) type but since it has two quinonoid units, every single molecule allows 4 electrons transfer.

Compared to the voltammetries of AT-grafted carbons also shown in Fig. 5, half wave potentials ($E_{1/2}$) of first and second redox couple at modified electrodes are shifted towards less negative and less positive values in comparison with aqueous electrolyte results respectively. Thus, AT grafting on both carbons difficults the oxidation of AT, while later the first radical anion is slightly desta-bilized. This kind of behavior can be attributed to a partial charge transfer from AT to the carbon support. Moreover, the remarkable positive potential value for the second redox unit (0.844 V), can be attributed to a better stabilization of the anion radical in AT due to the more extended π-conjugation of this molecule. It is also note-worthy the wider anodic/cathodic peak separation and the broad redox peaks for redox reaction on Pica, which may respectively be attributed to an additional kinetic barrier and slow electron transfer on this particular substrate.

3.3.3. Galvanostatic discharge capacitance

Electrodes were further investigated by galvanostatic charge/discharge experiments at 200 mA g^{-1}. Fig. 6a presents
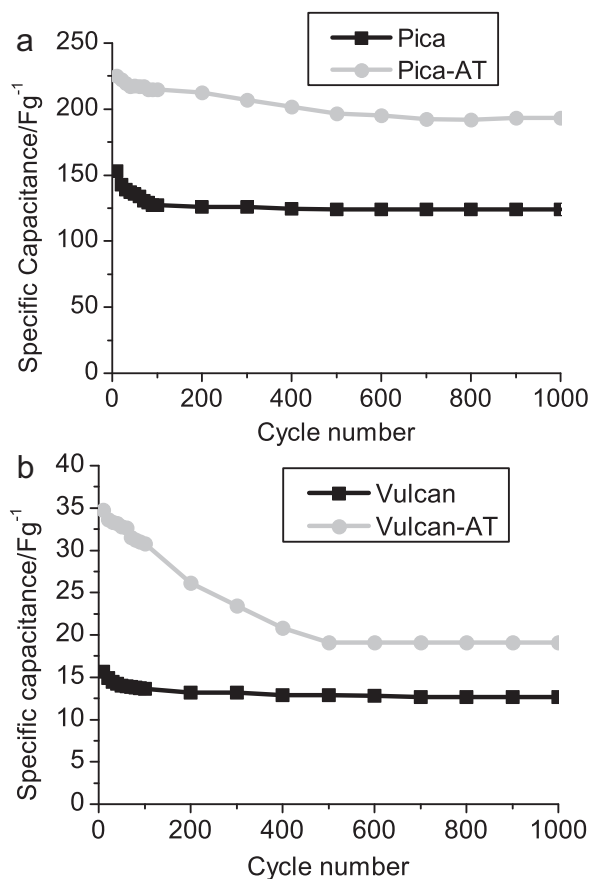
potential–time plots recorded for a Pica and AT-modified Pica carbon electrode with a 0.75 wt.% AT loading, while Fig. 6b presents potential–time plots recorded for a Vulcan and AT-modified Vulcan carbon electrode with a 0.55 wt.% AT loading. In both cases, the influence of additional charge storage due to AT electrochemistry is seen as a gentler slope in the curves.

The variation of the capacitance of pristine electrodes and AT loaded Pica and Vulcan electrodes during 1000 charge/discharge cycles is shown in Fig. 7. Modified Pica electrodes lose 10% of the initial specific capacitance during the first 700 cycles (Fig. 7a), and afterwards capacitance is quite stable up to 1000 cycles, while pris-tine Pica loses 3% of its capacitance after 1000 cycles under the same conditions. The small amount of additional capacitance loss in modified Pica indicates very effective immobilization and excellent chemical stability of the redox system on this substrate.

The capacitance fades out quite rapidly for modified Vulcan electrodes, and after 500 cycles it loses approximately 40% of its ini-tial capacitance, afterwards stabilizing up to 1000 cycles, whereas the capacitance of unmodified Vulcan decreases by 7% upon 1000 cycles (Fig. 7b). This reveals the fact that Vulcan carbon is less able than Pica to adsorb this redox species effectively. One possible rea-son may be a process resembling an electrochemical grafting taking place on the physical mixture of Pica (a highly functionalized car-bon) and AT [15], different from the case of the non-functionalized Vulcan carbon, which would have more weakly adsorbed AT species that would desorb after the initial charge/discharge cycles. Nev-ertheless, even after 1000 cycles the specific capacitance of both AT modified Pica and AT modified Vulcan are around 50% higher than those of pristine carbons, thus showing the good stability and capacitance improvement present in both modified electrodes.

4. Conclusion

The redox chemistry of AT allows the transfer of 4 electrons. This multiple electron transfer capability makes this redox couple appropriate for carbon modification for high energy density supercapacitor applications.

Herein, impregnation method was used for grafting AT on the surface of different carbon substrates. High surface area functionalized Pica carbon and low surface area Vulcan carbon electrodes were grafted with different loadings of AT (maximum of 0.75 wt.% for Pica and 0.55 wt.% for Vulcan electrodes).

Variations of redox peak potentials and reversibility were observed on carbon-supported AT in comparison with AT in solution. Those differences were attributed to different properties of each carbon.

Extended charge/discharge cycling behavior shows a loss of 10% of total capacity for modified Pica carbon and 40% for modified Vulcan carbon after 1000 cycles at $200\,mA g^{-1}$, compared to a 3% and 7% loss of unmodified carbons in the same conditions. Thus, the mesoporous structure and non-functionalized surface of Vulcan carbon give rise to a more unstable grafting, while Pica carbon shows a fairly stable grafting. For both, total capacitance is nearly doubled after modification with AT even after 1000 cycles at $200\,mA\,g^{-1}$.

These results are comparable to those reported for covalent bonding, and the main difference is that, as expected, here both Pica and Vulcan modified electrodes loose performance in a more dramatic way at higher rates. Nevertheless, the results here reported call for new strategies to promote full coverage by covalently bound species to take full advantage of this approach.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2012.01.088.

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