Pseudocapacitors

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A Redox-Active Binder for Electrochemical Capacitor Electrodes

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Abstract: *A promising strategy for increasing the performance of supercapacitors is proposed. Until now, a popular strategy for increasing the specific capacity of the electrode consists of grafting redox molecules onto a high surface area carbon structure to add a faradaic contribution to the charge storage. Unfortunately, the grafting of molecules to the carbon surface leads to a dramatic decrease of the electrochemical performances of the composite material. Herein, we used the organic binder as an active material in the charge/discharge process. Redox molecules were attached onto its polymeric skeleton to obtain a redox binder with the dual functionalities of both the binder and the active material. In this way, the electrochemical performance was improved without detrimentally affecting the properties of the porous carbon. Results showed that the use of a redox binder is promising for enhancing both energy and power densities.*

Being an attractive material for electrochemical capacitors, high surface area carbons can deliver high specific capacitance provided they have a proper pore texture.[1] Despite their attractive performance, current research effort is aimed at increasing the specific capacitance of the electrode materials. A popular strategy to achieve this goal consists of grafting redox molecules to add a faradaic contribution to the purely capacitive charge storage process. It has been reported that grafting anthraquinone,[2] catechol,[3–5] and phenanthrenequinone[6] on porous carbons yielded a significant increase in their charge storage properties.[7] However, the grafting of molecules is often accompanied by a decrease of the intrinsic performance of the carbon, such as the double-layer capacitance and the ionic transportation within the porous structure.[8–10] To circumvent these difficulties, noncovalent methods have emerged to integrate redox-active materials.[11,12]

Herein, we used the organic binder as a platform for the grafting to increase the overall capacity while minimizing the loading of inactive components in the electrode and preventing damage to the carbon. In this way, the redox binder is expected to have the dual functionalities of both the binder and the active material. This approach is complementary to the one using a conductive binder as both the conductive agent and organic binder to efficiently transfer electrons from the current collector to Si particles of a lithium ion battery anode.[13] Our original approach was demonstrated with a modified binder prepared by reaction between in situ generated O-protected 3,4-dimethoxybenzenediazonium ions and polystyrene (Supporting Information). The charge storage properties of the electrode using the modified binder was compared to those of an electrode based on modified carbon powder to determine the potential usefulness of such a redox-active binder. Figure 1 a illustrates the different combinations of the two modified components used as active materials in this work (activated carbon and organic binder). Unmodified (PS) and modified (PS_{mod}) polystyrene were characterized by ^1H NMR, IR, and X-ray photoelectron spectroscopy (XPS; Figure 1 b–e).

Compared to the broad PS signals in the aromatic and aliphatic region, the ^1H NMR spectrum of PS_{mod} showed peaks at 4.0–3.5 ppm associated with methoxy groups, providing evidence of the grafting of dimethoxybenzene units (Figure 1 b). In addition, the peak splitting and the upfield

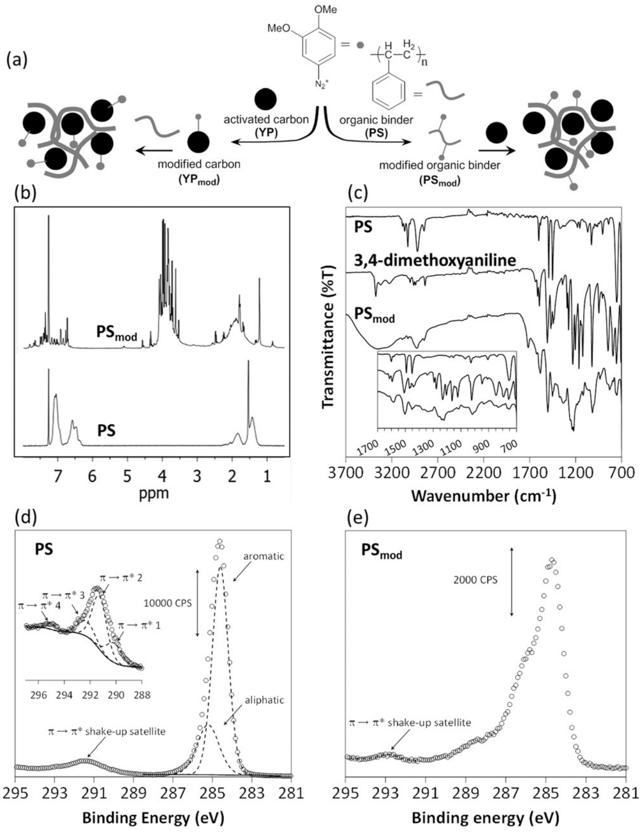

Figure 1. a) The two different routes used for introducing electroactive molecules on the electrode materials. b) ^1H NMR and c) IR spectra of unmodified (PS) and modified (PS_{mod}) polystyrene. d, e) C1s core level peak XPS spectra of PS and PS_{mod}.

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shift of the peaks in the aromatic region following grafting indicated that the phenyl ring in PS was modified. The IR spectra (Figure 1 c) were characterized by a decrease of the sharp aromatic CH stretching bands near 3050 cm^{-1} following grafting, in good agreement with the replacement of C–H bonds by C–phenyl bonds during the grafting reaction involving a radical attack.[14] The bands at 3360 and 1714 cm^{-1} are indicative of adsorbed water.[15] Nevertheless, one of the best frequency regions for the presence of aromatic ring structures is shown in the inset of Figure 1 c. In this 1700–700 cm^{-1} region, there are remarkable similarities between the IR spectra of 3,4-dimethoxyaniline and PS$_{mod}$, verifying that dimethoxy groups were integrated in the polystyrene skeleton.[16] Figures 1 d and e present XPS data obtained for PS and PS$_{mod}$. The C1s core level spectrum of the untreated PS shows a main peak curve-fitted with two components at 284.8 and 285.1 eV, corresponding to aromatic carbon atoms in the pendant phenyl rings and aliphatic carbons in the main chain, respectively. The curve fitting leads to a ratio of 3.1 between the peak contribution of the aromatic and aliphatic carbons that is in good agreement with the polymer molecular structure. The presence of pendant aromatic rings was also confirmed by the π–π* shake-up satellite peak fitting well with four components at binding energies comprised between 290.1 and 295 eV (inset of Figure 1 d).[17] After chemical modification, the decrease of the shake-up peak is consistent with the modification of the phenyl rings.[18] Note that a detailed analysis of the main C1s peak was not made owing to the various carbon–oxygen or carbon–nitrogen functionalities which can contribute to the broad envelope. However, the broad shoulder emerging at around 286 eV is consistent with the introduction of dimethoxybenzene units in the polymer structure.[19]

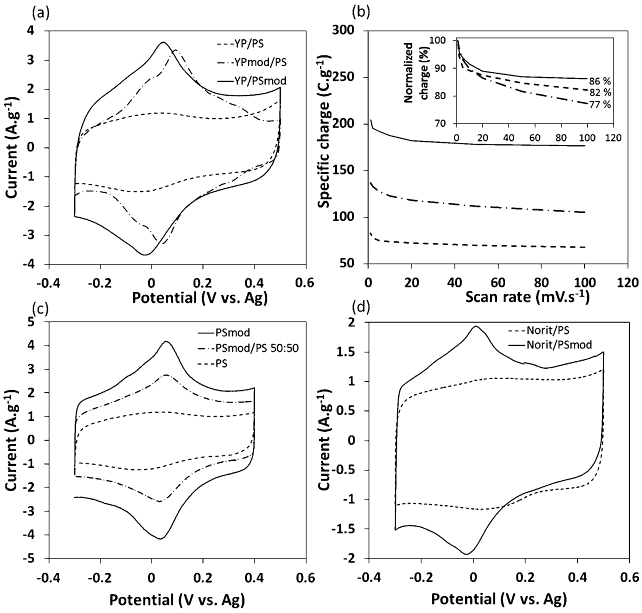

Figure 2. CVs in 1 M H_2SO_4 at 10 mV s^{-1}. a) CVs of YP$_{mod}$/PS, YP/PS$_{mod}$, and YP/PS electrodes. b) Variation of the total specific charge and charge retention (inset) with scan rate for the electrodes of Figure 2 a. c) CVs of YP80 carbon electrodes containing 10 wt % of pure PS, pure PS$_{mod}$, or a 1:1 (w:w) mixture of PS and PS$_{mod}$. d) CVs for Norit/PS and Norit/PS$_{mod}$ electrodes. PS$_{mod}$ was obtained by reacting PS with 0.1 and 1 equivalent of 3,4-dimethoxybenzenediazonium salt for results presented in Figures 2 a and 2 c, d, respectively. The current and charge are reported with respect to the mass of activated carbon and binder (without conducting agent).

To demonstrate the usefulness of the bifunctional modified binder, a composite electrode was prepared by mixing PS$_{mod}$ with the YP80 activated carbon (YP). Electrodes containing modified carbon powder (YP$_{mod}$) with PS or unmodified components (PS and YP) were also tested for comparison. The cyclic voltammograms (CVs) of these electrodes in 1 M H_2SO_4 are presented in Figure 2 a. Prior to these measurements, the carbon electrodes were first cycled between 0 and 1.1 V in 1 M H_2SO_4 to remove the two methyl protecting groups by electrochemical oxidation and recover the well-known redox activity of the catechol.[20] The CV of the YP/PS electrode showed a quasi-rectangular shape characteristic of a nearly pure capacitive behavior, while the modified-carbon electrode (YP$_{mod}$/PS) was characterized by a broad reversible redox system at around 0.1 V. Remarkably, the modified-binder electrode (YP/PS$_{mod}$) revealed a similar redox system with a significantly increased double-layer capacitance (see current values at −0.2 and 0.4 V). The total specific charge, determined by integrating the area under the CV, is 188 C g^{-1}, compared to 76 C g^{-1} for YP/PS and 123 C g^{-1} for YP$_{mod}$/PS. The stability profile presented in Figure S1 (Supporting Information) was different depending on whether carbon or the binder is modified. When the carbon was modified, a loss in specific charge was observed during the first 1000 cycles and was stabilizing, while a progressive decrease was obtained with the modified binder. In the former case, the fade of the charge can be attributed to the release of physisorbed molecules and in the latter, of polymer chains. After 5000 CVs at 10 mV s^{-1}, a 10 % decrease is observed in both cases. By extrapolating these results, the performance of the electrode based on the modified binder remains superior to that of the modified carbon during the first 20 000 cycles. To further improve the stability of these hybrid materials, electrochemical grafting of a quinone on the carbon of the composite electrode was attempted, but it severely complicated the fabrication process.[21] With our strategy, the reticulation of the polymer chains is expected to be a facile way to improve the long-term stability.

The faradaic charge stored by the modified binder-bearing pendant catechol groups was deduced from the CV shown in Figure 2 a by subtracting the double-layer contribution and found to be 35.3 C per gram of activated carbon + binder or the equivalent charge of 319 C per gram of binder alone, approaching the specific capacity obtained with conducting polymers.[22] This corresponds to a catechol loading of 2.5 wt % with respect to the total electrode mass. Note that the catechol-loading for YP$_{mod}$/PS was determined to be equal to 4.3 wt %, implying that polystyrene contains a higher density of grafted electroactive molecules than the carbon powder, because the binder content was only 10 wt % of the composite material in comparison to a carbon content of 80 wt %. It appears that the additional redox charge of the catechol units grafted on PS is not sufficient to explain the increase in the overall charge, which is brought about by a significant increase in the capacitive current. Because the double-layer capacitance of a porous carbon is related to its capability to adsorb ions,[23] it follows that the modified binder likely enhances the wettability of the carbon electrode, increasing the electrolyte-accessible surface and favoring ion adsorption.

Different experiments were performed to verify this assumption: i) the scan-rate-dependence of the voltammetric charge was investigated in Figure 2b; ii) the effect of the catechol-loading in the polymer chain on the double-layer capacitance contribution was evaluated; and iii) another activated carbon with a different pore texture was used to generalize the concept (Figure 2d). When catechol molecules are grafted on carbon (YP_{mod}/PS electrode), the scan-rate-dependence of the specific charge is indicative of a hindered ionic transport. Its retention, given versus that found at a low scan rate of 2 $mV\,s^{-1}$, was less than that of the unmodified YP/PS electrode, decreasing from 82 to 77% at 100 $mV\,s^{-1}$ (inset in Figure 2b). In contrast, when redox-active molecules were grafted to the binder, the resulting YP/PS_{mod} electrode showed a larger specific charge, weakly influenced by the scan rate, with a charge retention as high as 86% at 100 $mV\,s^{-1}$, suggesting a fast ionic transportation within the porous structure of carbon.

The effect of the catechol-loading in the polymer chain on the electrochemical performance was also investigated, first by changing the diazotization conditions for the modification of PS (see the CVs in solid lines in Figures 2a and c), and then by using as binder a mixture of PS and PS_{mod} (1:1 weight ratio; Figure 2c). The data showed that the chemical composition of the polymer has important consequences on the electrochemical double layer of the activated carbon. The capacitive current increased and the polarization became smaller with a higher degree of modification, implying an increase of the electrolyte-accessible surface and faster ionic transportation. Finally, an activated carbon (Norit S50), with a lower BET specific surface area ($S_{BET} = 1231\ m^2\,g^{-1}$ compared to 2140 $m^2\,g^{-1}$ for YP80), was tested with the modified binder. CVs for $Norit/PS_{mod}$ and Norit/PS (Figure 2d) were also characterized by an increase of the capacitive envelope when PS_{mod} acts as electroactive binder material, but to a lesser extent, indicating a direct correlation between the BET surface and the increase in the capacitive current. Thus, the use of an active binder is an interesting approach to improve the charge storage by increasing the double-layer capacitance while providing a faradaic contribution, especially when combined with microporous carbons, such as YP80 and Norit. In these cases, the specific surface area is very sensitive to the grafting as the S_{BET} decreases from 2140 $m^2\,g^{-1}$ to 486 $m^2\,g^{-1}$ when YP80 is grafted and from 1231 $m^2\,g^{-1}$ to 341 $m^2\,g^{-1}$ for Norit. In addition, with YP_{mod}/PS, electrochemical impedance spectroscopy measurement revealed that both an increase in internal resistance and a frequency-dispersed impedance shift the low frequency capacitance towards higher resistance values, whereas the charge process approached that of an ideal electrochemical capacitor when molecules are attached to the polystyrene backbone (Figure 3). The less resistive charge storage obtained with the modified binder resulted in a decrease in the equivalent distributed resistance corresponding to the linear variation of the impedance in the middle frequency range, implying that the improvement of the electrochemical performance is mainly due to a better ionic transportation in the porous structure of the carbon. A complex capacitance modelling of impedance data showed that the relaxation time at a maximum energy dispersion, commonly used as a factor of merit, is in the order $YP/PS < YP/PS_{mod} < YP_{mod}/PS$ (Supporting Information, Figure S2).

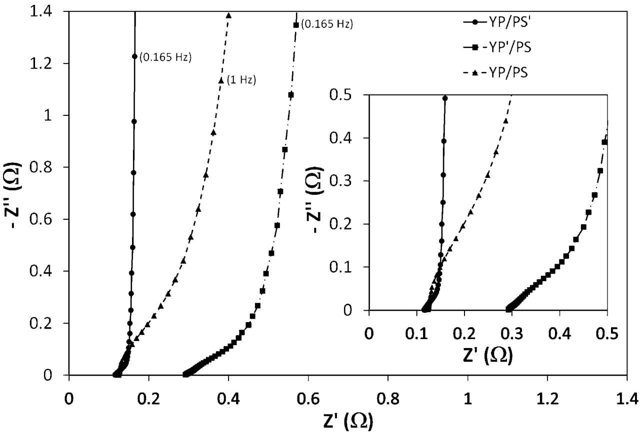

Figure 3. Nyquist plot obtained at 0 V in 1 M H_2SO_4 for YP_{mod}/PS, YP/PS_{mod}, and YP/PS electrodes. The inset shows the magnification of the high-frequency region.

Experimental Section

The chemically modified organic binder was obtained by reacting polystyrene with O-protected 3,4-dimethoxyphenyldiazonium ions generated in situ with tert-butylnitrite in THF. After stirring for 108 hours at room temperature, the residue was purified by chromatography on silica gel and the brown powder obtained was characterized by ^{1}H-NMR, IR, and XPS. The chemically modified carbon powder was obtained by reacting YP80F activated carbon with O-protected 3,4-dimethoxyphenyldiazonium ions in situ generated with $NaNO_2$ in a mixture of acetonitrile-water containing concentrated HCl. After stirring at 50°C for 24 hours, the modified powder was thoroughly washed and dried overnight at 80°C. The electrodes tested were prepared by mixing the carbon powder (YP80 or Norit-S50) with unmodified or modified polystyrene and carbon black (Superior graphite) with a ratio of 80:10:10 (w:w:w) in a small volume of n-methyl pyrrolidinone until a homogeneous carbon ink was obtained. Electrochemical measurements were performed in a three-electrode test cell ECC-AQU (from EL-ELL, Germany). The working and counter electrodes were separated by a glass fiber separator impregnated with aqueous 1M sulfuric acid electrolyte. A silver wire was used as a quasi-reference electrode. Electrochemical impedance spectroscopy experiments were conducted at 0 V with an amplitude voltage of 5 mV from 100 kHz to 10 mHz.

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