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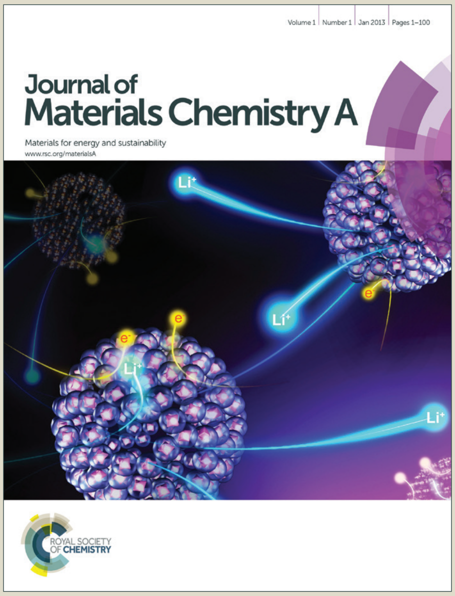

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COMMUNICATION

Toward Fully Organic Rechargeable Charge Storage Devices based on Carbon Electrodes Grafted with Redox Molecules.

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Activated carbon powders modified with naphthalimide and 2,2,6,6-tetramethylpiperidine-N-oxyl were assembled into a hybrid electrochemical capacitor containing an organic electrolyte. The fully organic rechargeable system demonstrated an increase in specific capacitance up to 51 %, an extended operating voltage of 2.9 V in propylene carbonate, compared to 1.9 V for the unmodified system, and a power 2.5 times higher.

The emerging of renewable energies for the production of electricity while minimizing the greenhouse gas emissions, forces us to conceive successful charge storage systems to correct the intermittency of the wind power and photovoltaic. So, powerful electrical charge storage systems having both high energy and power densities, are essential components of this energy transition. At present, electric storage devices range from electrochemical capacitors, which can supply high power, to batteries, which suffer from moderate power but can supply high electrical energy density. In retrospect, a promising approach would consist in combining both the advantages of capacitors and batteries to achieve versatile energy storage systems. Indeed, activated carbons designed for electrochemical capacitors encounter two main limitations: (i) high values of capacitance are obtained for a large BET specific surface area combined with an adequate pore size distribution and surface chemistry that are difficult to control, especially as different pore sizes and surface functionalities are needed for the negative and positive electrodes,[1-4] and (ii) the double layer capacitance is limited by the electrolyte decomposition at positively and negatively charged surfaces due to irreversible electrochemical reactions, which lead to the hysteresis of the charge process.[5-6] Aqueous electrolyte gives the highest capacitance values, but severely limits the cell voltage due to water decomposition. Nevertheless, due to high hydrogen overpotential obtained when activated carbon acts as a negative electrode, asymmetric systems obtained by the combination of a carbon electrode with a positive electrode material showing high oxygen overpotential, allows the asymmetric system to work reversibly at an operating voltage windows approaching 2V in aqueous medium. However, gas evolution at negative and positive electrodes render the system very sensible to the pH and cause a dramatic decrease of the coulombic efficiency beyond a cell voltage of 1.9 V.[7-9] Conversely, in organic based electrolytes, the cell voltage can reach 3 to 4 V, but decrease in double layer capacitance and increase in equivalent series resistance (ESR) are currently obtained.[10-13] The main benefit of replacing an aqueous electrolyte with an organic one is to propose high operative voltage systems for high power applications, but until now, insufficient specific energy density is obtained to be effectively used into such applications.

Very recently, the development in the field of the electricity storage accelerates and parallels the progress accomplished in the photovoltaic during the two past decades; turning determinedly towards organic batteries.[14-15] Resultant organic electrode materials exhibit remarkable characteristics such as (i) high specific capacity due to the extra charge providing from redox-active molecules, (ii) rapid charge-discharge cycling due to the fast redox kinetics and (iii) extension of the cell voltage by the use of appropriate redox groups.[16-18] So, by selection of organic materials desirable for rapid electron rate transfer, high number of exchanged electrons and extreme negative or positive potential values, the molecular approach combines advantages which offer potentialities for maximizing both energy and power densities. Recently, organic electrode materials, including redox radical species, have been reported for electrochemical charge storage application, due to their fast electron-transfer kinetic.[19-22] Unfortunately, these organic materials suffer from poor stability due to high solubility of molecules in common liquid electrolytes, and a large amount of carbon additives is often needed for achieving high power efficiency due to their poor intrinsic conductivity. To circumvent these difficulties, the grafting strategy appears well-suited for retaining the desirable redox properties of electroactive molecules by hindering their release into liquid electrolyte.[23-24] Furthermore, the possibility for robust, dense and permanent surface functionalization offers new opportunities in the organic interfacing of small redox active molecules. Nevertheless, mention of a completely organic rechargeable device is very rare.[25-26]

Here, we propose a promising architecture for the design of organic storage devices at the frontier between electrochemical capacitors and batteries, constructed from generic elements which consist in fast redox-active small molecules having an amine as the surface attachment group, combined to a porous carbon network having a void space that minimize volume changes on cycling. Such combinations permit to build universal electrode materials applicable both for anode and cathode. Our so-called "hybrid system" is tested with a negative electrode prepared by reacting N-(2-aminoethyl)-1,8-naphthalimide with an activated carbon (AC) dispersed in acetonitrile, in series with a positive electrode obtained by peptide attachment of the commercial available 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl (aminoTEMPO) to the surface of a nitric acid treated activated carbon (see experiment details in ESI).

The chemical modification is accompanied by a reinforced contrast and blurry transmission electron microscope (TEM) images compared to the clear and transparent porous texture of the unmodified carbon having a Brunauer-Emmett-Teller (BET) surface area of 1200 m^2 g^{-1} (Figure 1a-c). The grafted organic layers were also analyzed by X-ray photoelectron spectroscopy (XPS) and the formation of bonded molecules with N atoms interacting with the surface was affirmed for the two chemically modified carbon products (Figure 1d). Additionally, TGA experiments contribute to quantify the grafting yield by removing molecules attached to the surface upon heating the carbon products in air to 750 °C at a rate of 10 °C min^{-1} (Figure 1e). The modified carbon products start decomposing above 200 °C with global weight losses at 500 °C equal to 15 % for the Naphthalimide-AC composite and 39 % for the TEMPO-AC composite.

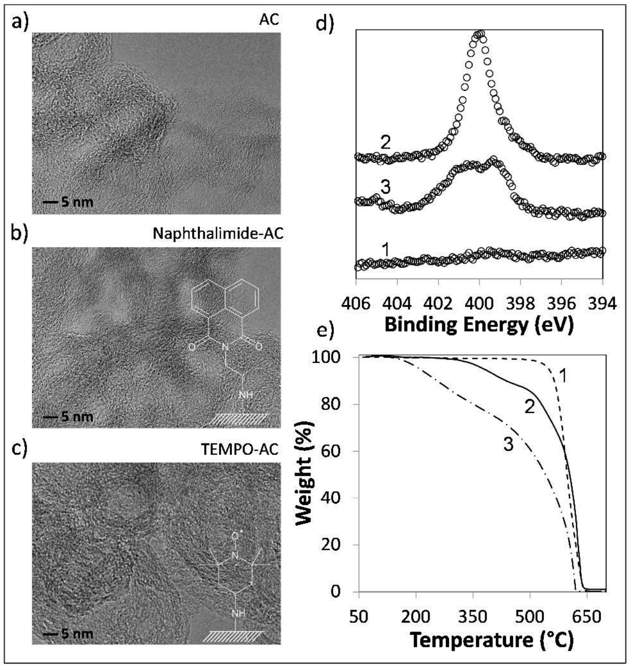

Fig. 1 a-c) TEM images of (a) pristine activated carbon (AC), (b) naphthalimide-AC and (c) TEMPO-AC composites. d) XPS spectra of N1s core level for AC (spectrum 1), naphthalimide-AC (spectrum 2) and TEMPO-AC (spectrum 3). e) TGA decomposition profiles of pristine activated carbon (plot 1), naphthalimide-AC (plot 2) and TEMPO-AC (plot 3) composites.

The electrochemical properties of modified-carbon electrodes were evaluated by cyclic voltammetry (Figure 2a). Both positive and negative materials show intense and well-defined reversible systems located at 1.0 and -1.1 V vs. Ag in addition to the capacitive response of the pristine carbon. In order to assess the capability of grafted molecules to increase the double layer capacitance of activated carbon electrodes, galvanostatic charge/discharge experiments were performed at 0.05 A per gram of active material (without carbon black and organic binder additives) in a half cell composed of a chemically modified electrode in conjunction with a pristine carbon auxiliary electrode (Figure 2b). With naphthalimide-AC and TEMPO-AC composites as working electrodes, attached molecules produce an increase of the global specific capacitance of 80 % at extreme negative potentials and 104 % at extreme positive potentials, where the redox activity occurs.

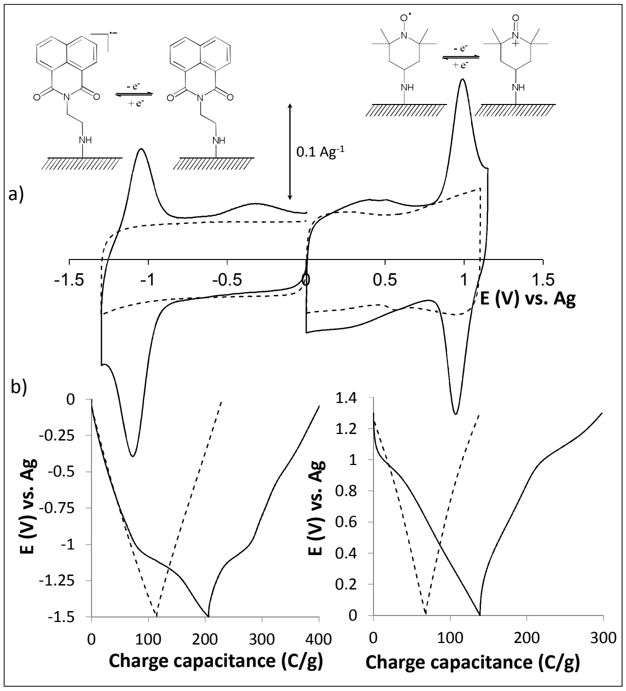

Fig. 2 a) Cyclic voltammograms of the TEMPO-modified positive carbon electrode and the naphthalimide-modified negative carbon electrode recorded in propylene carbonate (PC) + 1 M Bu_4NBF_4 at a scan rate of 1 mV s^{-1}. b) Galvanostatic charge/discharge curves of naphthalimide-AC composite (on the left) and TEMPO-AC composite (on the right) at a current of 0.1 mA.

A fully organic-based hybrid naphthalimide-AC/TEMPO-AC capacitor was evaluated in a three-electrode configuration and the performance of the hybrid capacitor was compared to an AC/AC system obtained by assembling unmodified activated carbon electrodes (Figure 3). In both cases, the masses of negative and positive electrodes were adjusted to ensure a complete charge balance in order to get the maximum cell voltage in full charge.[27] In such conditions, the combination of the two different modified electrodes allowed the specific capacitance per total active mass of negative and positive electrodes to be boosted. The 50th cycle of charge-discharge is showed at Figure 3a. Compared to the AC/AC system, which present a typically triangular shaped charge-discharge galvanostatic cycle commonly observed for conventional activated carbon electrodes, the naphthalimide-AC/TEMPO-AC hybrid capacitor shows distorted potential-capacitance curves, indicating the contribution of a redox-capacitance due to grafted molecules. The capacitance and cycle efficiency of the modified and unmodified capacitors have been tested during 100 cycles using a three-electrode cell configuration. The results obtained are presented in Figure 3c. A decline of the capacitance is obtained with the hybrid capacitor during the first 50 cycles of charge-discharge, probably due to the departure of adsorbed molecules toward the electrolyte, but its gravimetric capacitance remains increased by 51 % in full charge at the 100th cycle. Concomitantly, the cycle efficiency increase during the first 50 cycles to stabilize at a value of 0.94, beyond which the cycle efficiency resembles to that obtained with the AC/AC capacitor. .

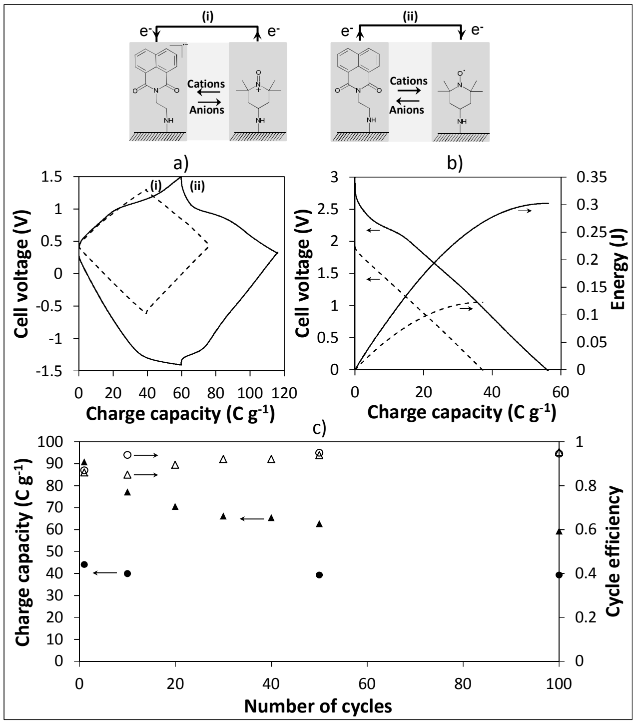

Fig. 3 a) 50th galvanostatic charge–discharge cycle of the fully organic-based hybrid naphthalimide-AC/TEMPO-AC capacitor (solid line) compared to the 50th cycle obtained with the AC/AC system (tilted line) in PC + 1 M Bu_4NBF_4 at a current of 0.1 mA. b) Discharge curves superimposed to the corresponding energy output for the hybrid naphthalimide-AC/TEMPO-AC capacitor (solid line) compared to the AC/AC system (tilted line). c) Evolution of the specific charge capacity (full symbols) and cycle efficiency (empty symbols) with the number of charge/discharge cycles for the naphthalimide-AC/TEMPO-AC capacitor (triangles) and for the AC/AC system (circles).

Beside addition of an extra charge, the molecular activation of carbon materials produced also an unexpected positive effect on the electrochemical stability window (ESW), since the operating voltage in propylene carbonate (PC) + 1 M Bu_4NBF_4 is extended up to 2.9 V, compared to 1.9 V for the AC/AC system (Figure 3a). With porous electrodes like activated carbons, Jow and al. have proposed to evaluate the ESW from cyclic voltammetry by calculation of a Faradaic fraction R defined as the ratio of the irreversible Faradaic charge responsible for the electrolyte degradation to the purely reversible capacitive charge of carbon.[28] Stability limits were so determined for the same organic electrolyte (PC + 1 M Bu_4NBF_4) on the activated carbon electrodes before and after chemical grafting. Before grafting, R = 0.1, which is commonly assumed as an acceptable value, is obtained at 1.3 V vs. Ag, while after grafting, the same value for R is obtained at 1.5 V vs. Ag, suggesting that the grafted electrodes push the anodic decomposition of the electrolyte away from the potential limit obtained with the pristine carbon. It is well-known that porous texture and surface functionalities directly affect the ESW, and authors claim that the macropore surface of the activated carbon plays an active role in the electrolyte decomposition.[24] Since the molecular grafting causes a dramatic loss of the BET surface area in a pore size distribution domain ranging from micro to mesoporosity,[29] it can be assumed that the extension of the ESW probably results from the partial blocking of the mesopore surface by attached molecules. Consequently, considering both the energy density and the operating voltage, the carbon electrodes grafted with redox molecules are found to be superior to the unmodified electrodes.

It is noteworthy that the benefit of the molecular grafting on the ESW can be an interesting alternative to the use of ionic liquids in standard carbon based EDLCs.[30] Due to the enlarged ESW, the electrical energy accumulated in such hybrid organic device is greatly enhanced because the operating voltage has a quadratic effect on the power. So, the specific energy extracted from the hybrid organic system outlined here is 2.5 times higher compared to the AC/AC capacitor in the same electrolyte (Figure 3b).

Conclusions

In conclusion, the fully organic rechargeable charge storage device depicted and tested in this study, exhibits promising potentialities for future eco-friendly systems with both high energy and high power densities. The hybrid capacitor reported is the first rechargeable charge storage system based on carbon electrodes grafted with electroactive molecules working in organic media. With our strategy, the energy density and the operating voltage of modified positive and negative carbon electrodes are found to be superior to the unmodified electrodes.

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Notes

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Table of contents

We present a fully organic rechargeable charge storage device based on carbon electrodes grafted with redox molecules providing combined performance of electrochemical capacitors and batteries.