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

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EXPERIMENTAL SECTION

Synthesis of N-(2-Aminoethyl)-1,8-naphthalimide. The N-(2-Aminoethyl)-1,8-naphthalimide was obtained by reacting an aqueous suspension of 1,8-naphthalic anhydride with an excess of ethylenediamine, according to a published synthetic route (M. Licchelli, A. O. Biroli, A. Poggi, D. Sacchi, C. Sangermani, M. Zema, *Dalton Transactions*, **2003**, 4537).



Schematic representation of the synthetic procedure for the N-(2-Aminoethyl)-1,8-naphthalimide

5g of commercially available 1,8-naphthalic anhydride (25 mmol) partially solubilized in water (25 ml) was added under vigorous stirring to an aqueous solution of ethylenediamine (12 ml, 184 mmol in 60 ml) heated at 70 °C. After 10 min heating at 80 °C, the hot solution was filtered. On cooling the filtrate in an ice bath, a precipitate formed and after filtration and rinsing with a weak volume of cool water, the product was dried overnight at 60 °C. The reaction furnished the desired product in a 80% yield.

¹H NMR (300 MHz, CD₃CN, δ): 8.55 (d, 2H), 8.35 (d, 2H), 7.82 (t, 2H), 4.16 (t, 2H), 2.92 (t, 2H). Anal. calcd for C₁₄H₁₂N₂O₂: C, 69.99; H, 5.03; N 11.66; O 13.32; found: C, 69.12; H, 4.95; N, 11.97; O, 12.99.

Preparation of the naphthalimide-carbon composite used as cathode material. The N-(2-Aminoethyl)-1,8-naphthalimide was attached at surface by spontaneous reaction of the aliphatic primary amine with the carbon. After dispersion of 500 mg of carbon powder in 100 mL of acetonitrile by sonication for 30 min, a suspension of N-(2-Aminoethyl)-1,8-naphthalimide (1 g; 0.1 equiv. versus carbon) in acetonitrile (50 mL) was added under stirring. After stirring the solution at 70 °C during 24 hours, the reaction mixture was vacuum filtered on a Teflon filtration membrane (from Sartorius Stedim) having a pore size diameter of 0.2 μ m. The modified carbon powder was washed successively with acetonitrile (250 mL), DMF (250 mL), methanol (250 mL) and acetone (250 mL) before to be dried overnight at 80 °C.



Schematic representation of the synthetic procedure for naphthalimide-AC composite material

Preparation of the nitroxide-carbon composite used as anode material. The 4amino-2,2,6,6-tetramethylpiperidine-N-oxyl was attached to the carbon surface by peptide coupling reaction in the presence of coupling agent. For having a high density of surface carboxylic acid groups, the carbon powder was previously treated with fuming nitric acid heated at 70 °C for 6 hours. After having cooling the mixture at room temperature, solution was filtered on a Teflon filtration membrane. After thorough rinsing with water (3 x 250 mL) and acetone (250 mL), the chemically oxidized carbon powder was dried overnight at 80 °C.

200 mg of treated carbon powder was dispersed in 30 mL of CH_2Cl_2 by sonication for 5 min and then, a solution of 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl (179 mg) in CH_2Cl_2 (5 mL) was added under argon atmosphere with N-hydroxysuccinimide (120 mg) in CH_2Cl_2 (20 mL). After 10 min stirring, dicyclohexylcarbodiimide (216 mg) solubilized in CH_2Cl_2 (5 mL) was added and the reaction continues during 24 hours at room temperature under argon. Next, the reaction mixture was filtered on a Teflon filtration membrane, thoroughly washed with 200 mL of CH_2Cl_2 , DMF, methanol and acetone, before to be dried overnight at 80 °C.



Schematic representation of the synthetic procedure for TEMPO-AC composite material

Electrodes and cell preparation. Electrochemical experiments were performed in a Swagelok cell assembled inside an Ar filled glove box. Electrochemical tests were evaluated at room temperature in a three-electrode configuration with a VMP-Biologic potentiostat monitored by ECLab software. The working and counter electrodes were separated by a glass fiber separator (Whatman) impregnated with 1 M Bu_4NBF_4 in propylene carbonate as electrolyte. A Silver wire was used as a quasi-reference electrode.

For cyclic voltammetry experiments showed in Figure 2, electrodes were prepared by mixing the carbon powder with poly(vinylidene fluoride) (PVdF, 10 wt% solution in n-methyl pyrrolidinone) and carbon black (superior graphite) with a ratio of 80:10:10 (w:w:w) in 5 mL of n-methyl pyrrolidinone. The mixture was stirred for three days until a homogeneous carbon ink was obtained. Few drops of carbon ink were spread on a gold surface consisting in a disk of 18 mm diameter. After drying at 80 °C for 30 min, thin films of 1-3 mg were obtained.

For Galvanostatic charge–discharge curves showed at Figure 2 and for electrochemical experiments presented at Figure 3, electrodes were prepared by hand mixing the carbon product with PTFE used as binder and carbon black (superior graphite) with a ratio of 80:5:15 (wt/wt/wt) until a homogeneous carbon paste was obtained. 2.5 mg of the carbon paste obtained was pressed for 60 s at 5 tons cm⁻² between two stainless steel grids (80 mesh, 0.127 mm, Alfa Aesar) used as current collector.

Instrumentation and Procedure

X-ray photoelectron spectroscopy (XPS). XPS data have been collected using a Kratos Ultra Axis spectrometer. The X-ray source is Mg K α working at 1253.6 eV and the spot size 0.7×0.3 mm². Semi quantitative XPS analysis has been performed using pseudo-voight function constrained by full width at half maximum (FWMH) ranges typical of each element.

Thermal gravimetric analysis (TGA). TGA analyses were performed with a Netzch STA449 F3 apparatus with 15 mg typical mass of materials.

Transmission electron microscopy (TEM) observations. Specimens for TEM experiments were prepared dispersing the carbon powders in ethanol. An ultrasonic treatment of the suspension has been performed to allow the observation of small carbon nanocomposites aggregates. A drop of the suspension is deposited and dried onto a carbon coated copper grid. The TEM observations were performed using a 200 kV JEOL 2010 FEG transmission electron microscopes fitted with a double tilt sample holder (tilts \pm 42°).