

EXPERIMENTAL PART

General

All experiments were carried out in solutions deaerated by extensive N₂ bubbling. All chemicals used were of analytical grade and solutions were prepared with Millipore water. All potentials are quoted the Ag/AgCl electrode. Aerogel pieces were bought from Maketech Inc. They consists in thin films (ca. 500 μm thickness) with macropores. The BET surface area (measured by nitrogen adsorption) of the aerogel is of 580 +/- 40 m²/g.

Probe Beam Deflection

Probe Beam Deflection is a technique that measures the concentration gradient in front of the electrode by monitoring the refractive index gradient with a light beam. The electrochemical charging of the double layer could be accompanied by a ion fluxes due to diffusion and migration. In a binary electrolyte both modes of mass transfer are necessarily coupled and a single binary diffusion coefficient describes the flux. The ion concentration in the solution changes, creating a gradient of refractive index normal to the electrode surface. A beam traveling parallel to the surface suffers a deviation proportional to the concentration gradient, therefore proportional to the extent and direction of ion flux. Positive beam deflection (away from the electrode) corresponds to incorporation of ions into the double layer while negative deflection (towards the electrode) implies release of ions to the solution.

The Probe Beam Deflection (PBD) arrangement is similar to the one described before (R. Kötz, C. Barbero, O. Haas, *J. Electroanal. Chem.*, **296**, 37, 1990.). The basic components of the PBD system are a 5 mW He-Ne laser (Melles Griot, 05 LHP11) and a bicell position sensitive detector (UDT PIN SPOT /2D). The laser beam is focused by a 50 mm lens to a diameter of roughly 60 μm in front of the planar electrode. The electrochemical cell, an optical glass cuvette with 2 x 2 x 4 cm dimensions (1 cm of path length), is mounted on a 3 axis tilt table (Newport). A micrometric translation stage allows for controlled positioning of the sample with respect to the laser beam in 10 μm steps. The position sensitive detector is placed 25 cm behind the electrochemical cell and has a sensitivity of 3 mV/ 1 m, which resulted in a deflection sensitivity of 1 mrad/V. All parts of the system are fixed on an optical rail and the whole set-up is mounted on an optic table (Melles Griot). The deflection signal was processed using a position monitor (UDT 201 DIV). Due to the fact that PBD signal have to be monitored

at long times (> 50 s), the whole system was warmed up for 24 Hs before each measurement to eliminate thermal fluctuations. The signal of the two photodiodes making the bicell detector were subtracted and normalized to the overall signal to eliminate laser intensity fluctuations. A digital multimeter (VOLTCRAFT 96) connected through an RS232 port to a personal computer was used for monitoring the PBD signal during potential step experiments. The chronodeflectometric pulses were fitted using the nonlinear fitting routine of Origin 5.0 (MicroCal).

The glass cell contains a counter electrode of aerogel (with geometrical area 5 times the working electrode) and a Ag/AgCl (3 M NaCl) miniature reference electrode (BAS) separated from the solution with a Vycor diaphragm.

The working electrodes were carbon aerogel (Maketech Inc.) plates (width 2 mm) attached onto Teflon plates with sides and back sealed and the active side unpolished.

The electrode potential, during PBD experiments, were controlled using a potentiostat (AMEL 2049) with a function generator (EG&G PARC M175).

AC Impedance

The AC impedance measurements were performed using a computerized potentiostat (GAMRY PC4) and CM 300 impedance software. The cell configuration has three electrodes with a counter electrode of carbon aerogel (Maketech, geometrical area 5 times of the working electrode) situated parallel to the working electrode and a reference electrode of SCE. The carbon aerogel was used as counter electrode to assure that its electrochemical active area is bigger than that of the working electrode. The measurements were made with a sinusoidal voltage perturbation of 5 mV and a resting time at each potential of 30 min. The circuit simulation and fitting were made using the analysis software in Excel (Microsoft) provided with the equipment.

Resin synthesis

The resorcinol-formaldehyde resins were produced using the molar ratios of resorcinol (R) to formaldehyde (F) of R:F = 1:2.9. The catalyzer (C, Na₂CO₃) to resorcinol ratio is of C:R = 0.005:1).

The viscous solution was impregnated onto the support material (e.g. cellulosic fabric), until saturation, while the fabric is stretched in a wood frame. It is then possible to create multilayer assemblies by adhesion of individual fabric layers. The monolithic materials are produced by curing the resin in petri dishes. To cure the resin, the materials are left by 24 hrs at 70 °C inside a closed glass chamber in presence of a water

saturated atmosphere. Then, the resins were dried in an open oven at 70 °C during 24 hrs. The weight loss during drying is of 45 % in weight.

Resin carbonization

The carbonization of the samples was carried out by pyrolysis in a electric oven (5 kW). The heating program was adjusted via a LabView script (National Inst.) controlling a PC-1200 AD/DA card. The card reads the temperature of a “K” thermocouple and commands an electronic relay that controls the electric power input to the oven. The samples were set in a ceramic recipient. The resin layers were separated with ceramic macroporous thick (> 5 mm) separators which hold the resin in place, avoiding deformation. On the other hand, the pyrolysis gases could leave the plates trough the separators. A nitrogen flow of 0.2 l/min was used to maintain the inert atmosphere. The free spaces in the ceramic recipient were filled with purified wood charcoal to act as sacrificial material in case of oxygen or water contamination. The heating rate used is 40 oC/hr from ambient to the pyrolysis temperature.

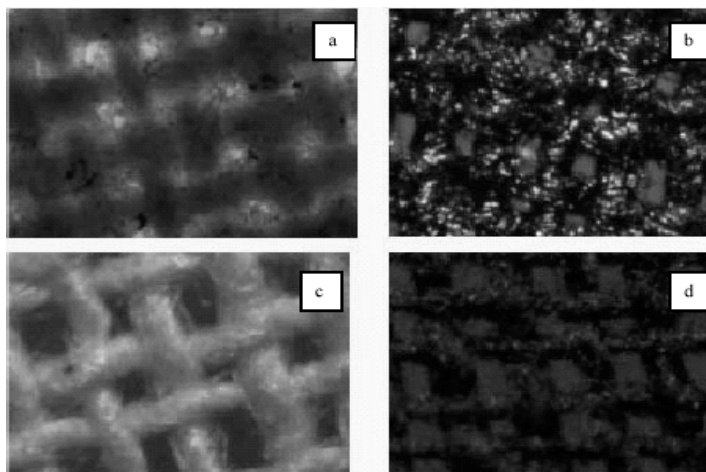


Figure S1.

Optical micrographs (60 X) of:

a) Composite resin, b) Carbon obtained by carbonization of (a),
(c) untreated fabric d) carbonized untreated fabric (x 60).

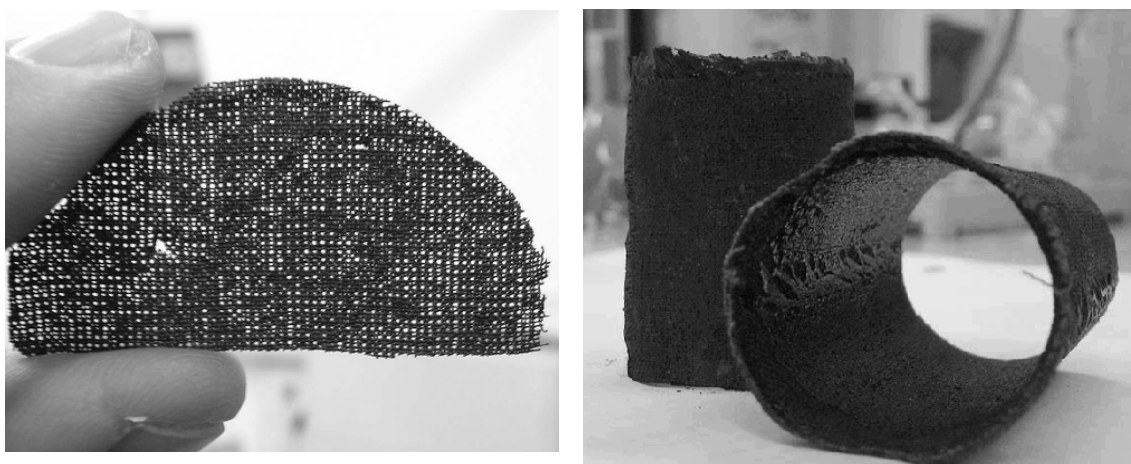


Figure S2

Photographs of one layer of fabric covered with RF resin (left) and tubular shape made of several layers of fabric covered with RF resin (right).

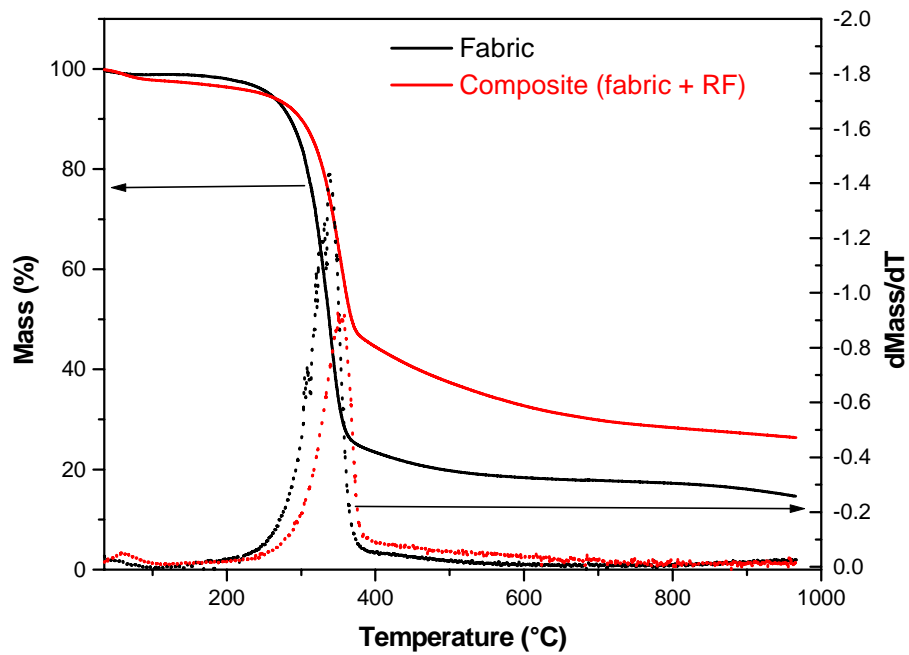


Figure S3: Thermogravimetric plots of fabric alone (black line) and composite resin (red line) during carbonization.

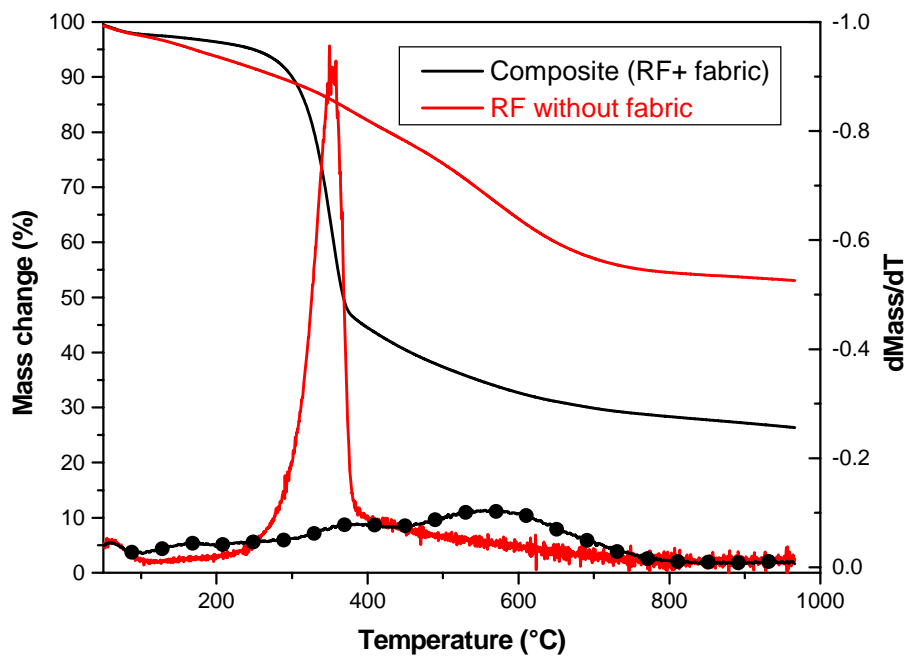


Figure S4 Thermogravimetric plots of composite resin (black line) and RF resin (red line, without fabric) during carbonization.

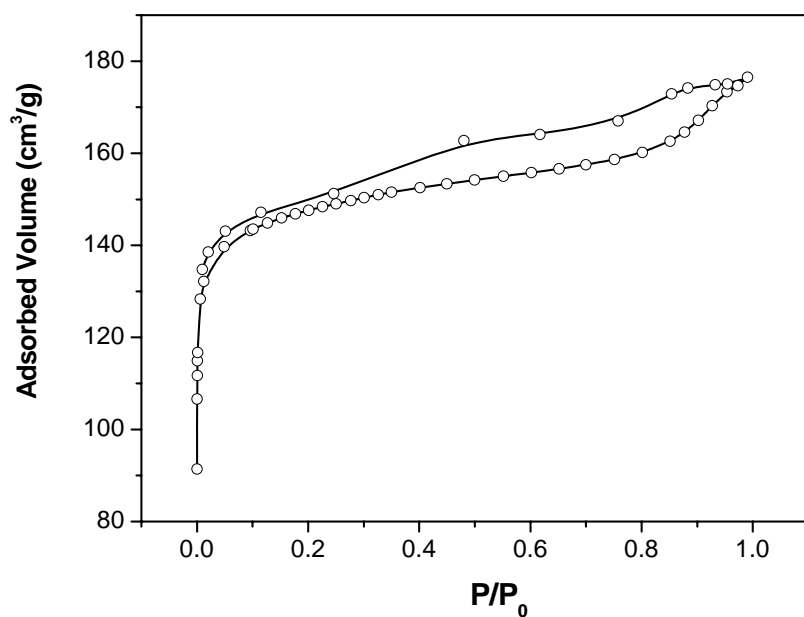


Figure S5:
N₂ adsorption isotherm of a typical carbon composite.

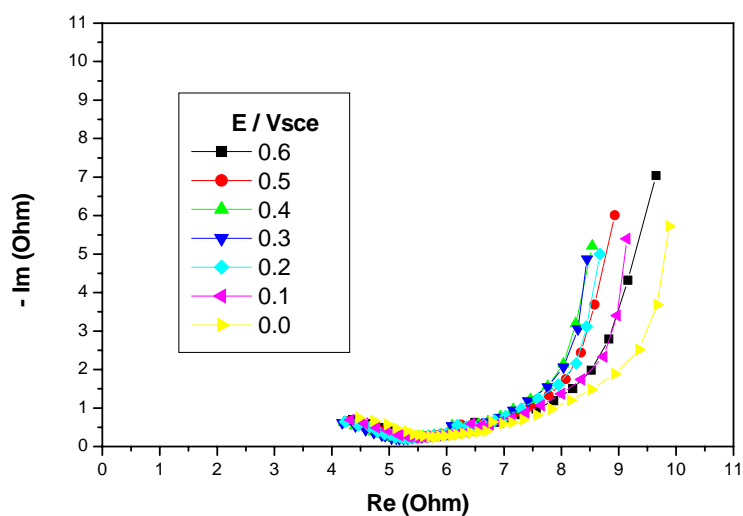


Figure S6:
Complex plane plots of the AC impedance data taken at different frequencies (50 kHz to 3 mHz). Solution = 1 M H₂SO₄.

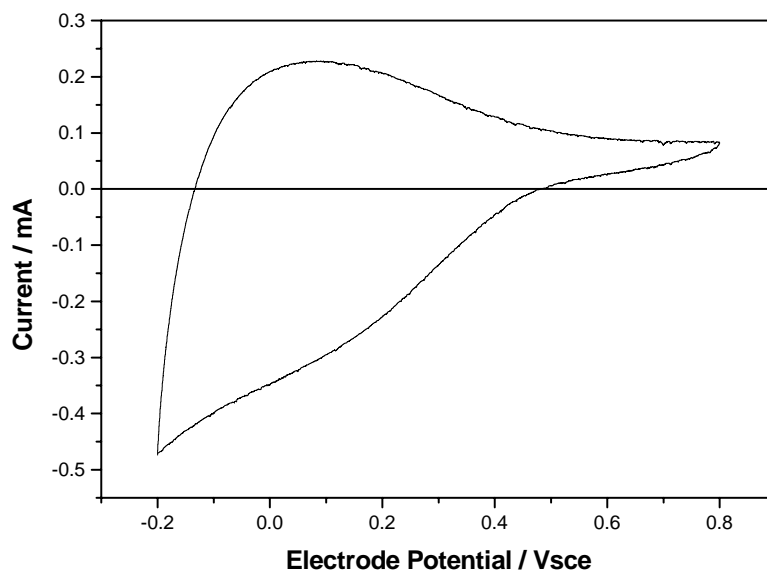


Figure S7

Cyclic voltammogram of a carbonized RF resin deposited on a thin film of cellulose. Scan rate = 1 mV/s. Solution = 1 M H₂SO₄.

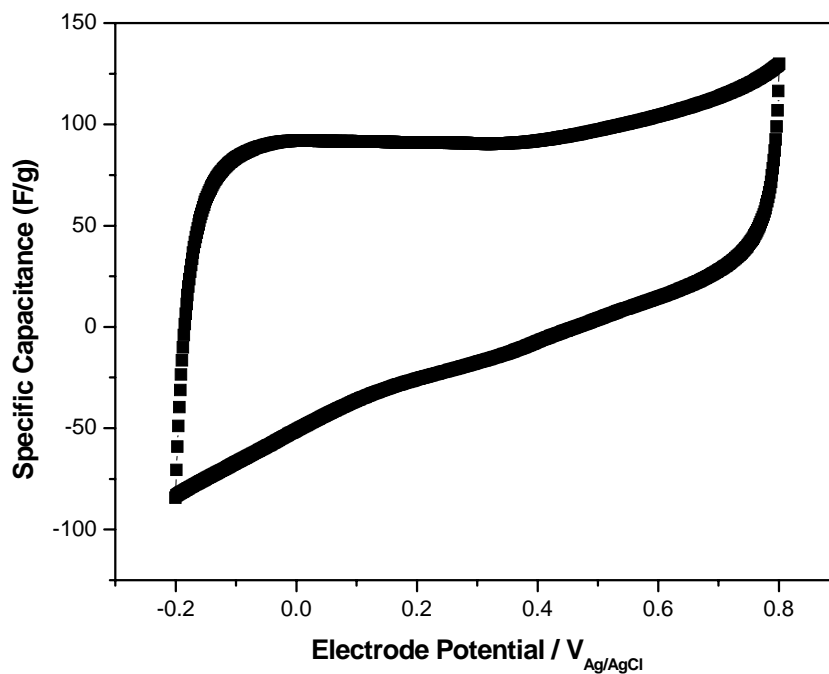


Figure S9: Cyclic voltammogram of a fibre reinforced carbon in 1 M Na₂SO₄. Scan rate = 1 mV/s.