EXPERIMENTAL PART

General

All experiments were carried out in solutions deareated by extensive N_2 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 m^2/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 trough 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 (geometrical area 5 times of the working electrode) situated parallel to the working electrode and a reference electrode of SCE. 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.

IMPEDANCE MEASUREMENTS

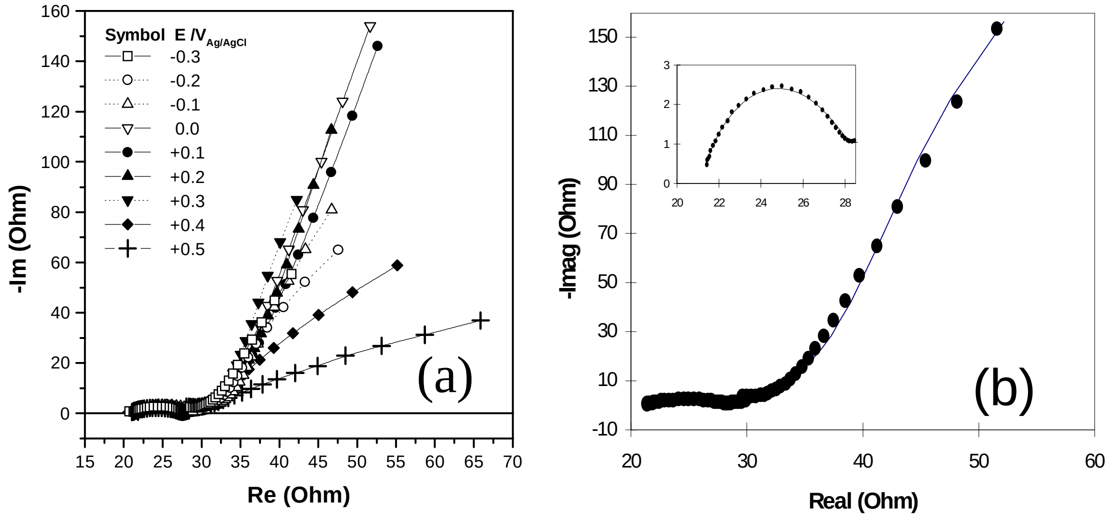
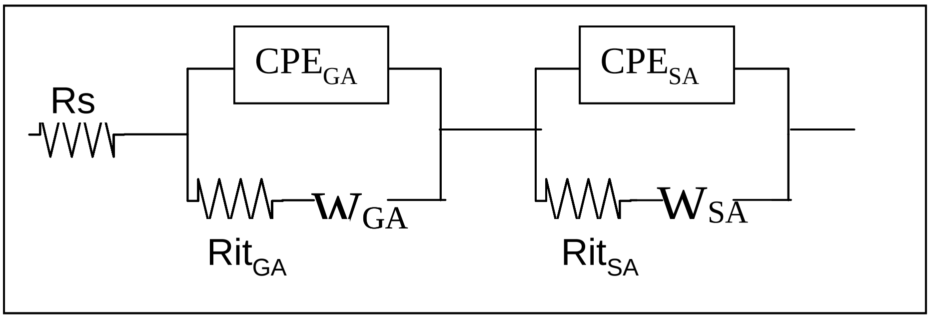


Figure 1:

a) Impedance plane plots of a carbon aerogel electrode in 0.5 M NaF. Potentials in the plot. Frequencies: 30 kHz to 9 mHz

b) Impedance plane plots of a carbon aerogel electrode at –0.3 VAg/AgCl in 0.5 M NaF. Simulation using the circuit described in the text. Expanded view of the high frequency range in the insert. Parameters described in Table 1. Potentials in the plot. Frequencies: 30 kHz to 9 mHz.



Scheme 1: Circuit model for fitting of the AC impedance data of carbon aerogel electrodes

Table 1. Circuit parameters for the best fit of the impedance measurements**.**

Potential ($V_{Ag/AgCl}$) =	**-0.3**	**0.0**	**+0.4**
Circuit Parameter			
Rs	20.8 ± 0.4	21.1 ± 0.4	20.9 ± 0.4
Ce_{GA}	1.1 x 10^{-4}	2.29 x 10^{-4}	2.5 x 10^{-4}
$\propto_{GA}$	0.78	0.74	0.73
Rit_{GA}	7.3 ± 0.5	7.1 ± 0.6	6.5 ± 0.5
W_{GA}	2.9 ± 0.2	6.8 ± 0.7	3.9 ± 0.3
Ce_{SA}	0.4016	0.1692	0.3988
$\propto_{SA}$	1	1	1
Rit_{SA}	2.49 ± 0.13	5.9 ± 0.73	2.51 ± 0.1.7
W_{SA}	0	0	0