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Double layer properties of carbon aerogel electrodes measured by probe beam deflection and AC impedance techniques†

Gabriel A. Planes, María C. Miras and César A. Barbero*

Probe beam deflection (PBD) and AC impedance are used to quantitatively evaluate the double layer properties of carbon aerogel electrodes in aqueous media (NaF). The measurements allow determination of the potential of minimum charge of the material.

Electrochemical double layer supercapacitors (EDLC) consist of a pair of electrodes, made of high surface area conductive materials, separated by a porous dielectric material filled with electrolyte.[1] Different porous carbon materials have been used in EDLC: activated carbon powder,[2] activated carbon fibre cloth,[3] electrochemically activated carbon[4] and carbon aerogels.[5] Carbon aerogels are materials produced by carbonisation of resorcinol–formaldehyde aerogels, which are usually produced by supercritical drying. The carbonisation process produces a glassy carbon solid which has high surface area (> 500 m^2 g^{-1}) and is mechanically rigid, making it especially suitable for use in capacitors and other energy storage devices.[6]

To design such devices, the double layer properties of the materials, specifically the potential of minimum charge (*pmc*), should be known. The knowledge of double layer properties is of even more interest when aerogel electrodes are used for electrochemical deionisation applications[7] where ions present in salty water are trapped into the double layer of the electrodes, producing deionised water.

However, while extensive testing of EDLC devices using those materials has been performed, few studies deal with the electrochemical properties. By blocking the pores with epoxy resin, it was shown that carbon aerogels have surface electrochemical properties similar to glassy carbon materials.[8] Similarly, capacitive[9] and surface properties[10] of electrochemically activated glassy carbon have been studied. Soffer *et al.*[11] studied the exchange of ions of high surface porous carbon upon potentiostatization in aqueous solution using ionic conductivity. Similar studies were performed with carbon aerogels at low salt concentration.[12]

Probe beam deflection (PBD) is a novel optical technique which could measure electrochemically driven ion fluxes to/from the electrode surface by monitoring refractive index gradients. It has been extensively used to study ion exchange in electroactive polymers,[13] redox oxides[14] and, more recently, self assembled redox multilayers.[15]

In the field of double layer measurements, it has been shown previously that potential changes during a cyclic voltammogram in the double layer region of a flat gold electrode show a small deflection signal.[16] Also, specific adsorption of anions on Pt electrodes[17] has been detected. The PBD technique has also been used to study surface phenomena such as under potential deposition (UPD) of metals[16] or hydrogen.[18]

PBD appears to be especially suitable to investigate the double layer properties of high surface area electrode materials, such as carbon aerogels. When a conductor is immersed in an electrolyte solution, an electric double layer appears at the interface. The ion population at a given potential is linked to the surface charge. If the electrode potential is changed, the ion population is modified and ion fluxes to/from the electrode occur, which could be detected by PBD.

It has been shown[19] that a way to quantitatively evaluate PBD data consists of measuring the temporal evolution of the PBD signal when the potential of the electrode is pulsed (chronodeflectometry). For a potential pulse driving an instantaneous or discontinuous process, like charging–discharging a double layer, the experimental deflection signal follows.[19]

$$\theta(x,t) = \left(\frac{l}{n}\frac{\partial n}{\partial C}\right)\frac{C_s}{\sqrt{\pi D_o t}}\frac{x}{2D_o t}e^{-x^2/4D_o t} \qquad (1)$$

where C_s is the effective (taking into account the surface area) concentration of ions exchanged on the electrode surface, D_o is the diffusion coefficient of the mobile species, x is the beam–electrode distance, l is the beam pathlength, n is the refractive index of the solution and $\partial n/\partial C$ is the change of refractive index with concentration for the mobile species.

In Fig. 1 is shown the chronodeflectometric profile of a carbon aerogel electrode in 0.5 M NaF aqueous solution.

The PBD signal is monitored while the potential is stepped (from -0.125 to -0.050 V$_{Ag/AgCl}$ in Fig. 1) during 200 s. NaF is used as electrolyte due to its low specific adsorption on carbon.[4]

As can be seen, the curve simulated for the discontinuous process tracks closely the experimental values, while the simulated curve for a continuous process departs completely from the experimental data. This means that all the change of ion population inside the aerogel occurs in a negligible time span compared with the occurrence of the film. Therefore, the aerogel electrode could be considered a very thin layer. Additionally, the good fit suggests that continuous secondary reactions (*e.g.* faradaic reactions) are minimal.

Based on the good fitting, it is possible to use eqn. 1 to evaluate the dependence of ion concentration with potential, by measuring the amplitude of the PBD maximum signal. It is known that the

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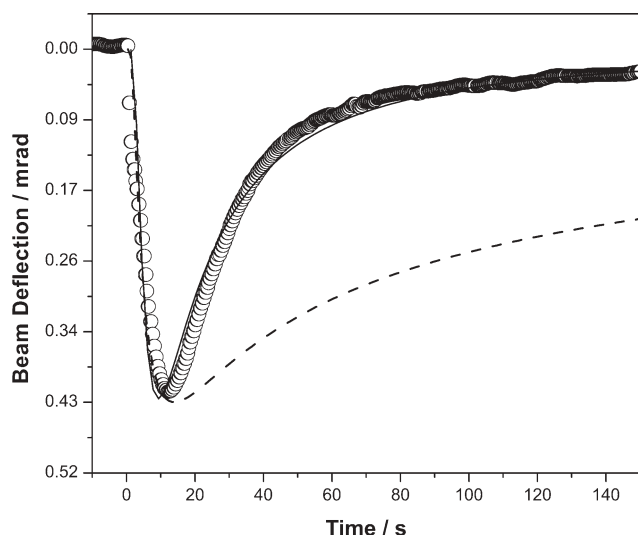
Fig. 1 Chronodeflectometry of a carbon aerogel electrode in 0.5 M NaF ($\Delta E = 0.075$ V). The full line is simulated using eqn. 1 with $D_o = 1.8 \times 10^{-5}$ cm^2 s^{-1} and $x = 462$ μm. The dashed line is simulated using the equation for a continuous reaction (eqn. 4 of Ref. 19) with $x = 280$ μm and $D_o = 1.8 \times 10^{-5}$ cm^2 s^{-1}. Both simulated curves are normalized with the experimental value.

time to reach maximum PBD signal, in a discontinuous process is equal to[19,20]:

$$t_{\max} = \frac{x^2}{6D_o} \qquad (2)$$

Replacing (2) into (1) renders:

$$\theta(E)_{x,t_{\max}} = \left(\frac{l}{n}\frac{\partial n}{\partial C}\right)\left(\frac{6^{3/2}}{2\sqrt{\pi}}\frac{e^{-3/2}}{x^2}\right)C_s(E) \qquad (3)$$

Therefore, the changes of ion population ($C_s(E)$) could be evaluated[20] by measuring the maximum PBD signal ($\theta(E)$) when the electrode potential is pulsed from a fixed initial potential to various more positive potentials.[21]

In Fig. 2 is shown the plot of $\theta(E)$ for a carbon aerogel electrode in NaF. The values are calculated from the maximum of the chronodeflectometric plots like the one depicted in Fig. 1. Each pulse has a duration of 200 s, starts at -0.125 V$_{Ag/AgCl}$ and the potential step increases by 25 mV on each pulse. The plot has a parabolic shape, with a minimum value at 0.09 V$_{Ag/AgCl}$ which should correspond to the potential of minimum charge (pmc[22]) of the material.

The retention of ions is closely related to the charge storage in the aerogel electrodes. While we could use cyclic voltammetry to evaluate the charge storage, the measurements could be affected by dynamic effects. To evaluate the charge storage in the steady state, we used AC impedance.

The impedance plots (*supp. inf.*) reveal a complex behaviour which could be associated with two circuits in series (*supp. inf.*). One corresponds to the high frequency regime and is related to the double layer capacitance of the external electrode area (outside the pores). The other is related to the low frequency behaviour and is associated with the capacitance of the whole surface area,[23] therefore related to the ion retention inside the pores which is measured by PBD.
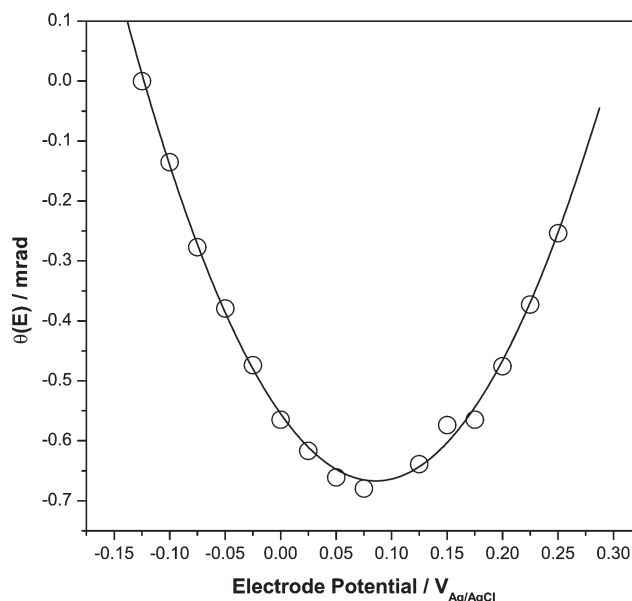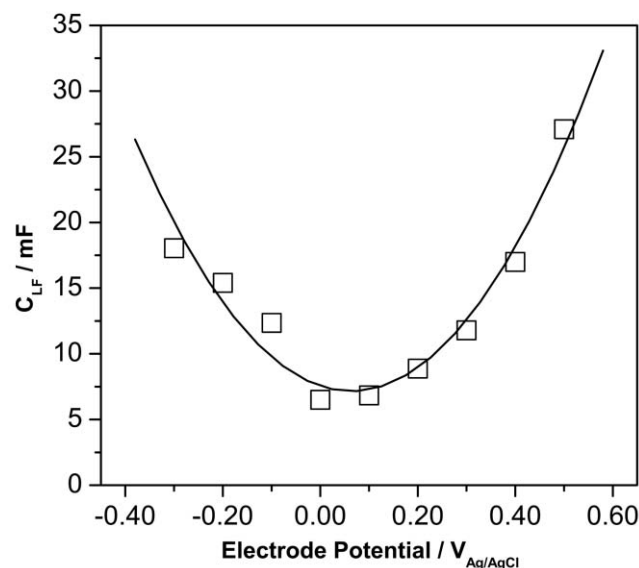

Fig. 2 $\theta(E)$ signal of a carbon aerogel electrode in 0.5 M NaF.

From the impedance at the lowest frequency (9 mHz), it is possible to calculate the dependence of the low frequency capacitance (C_{LF}) with potential (Fig. 3). The capacitance shows a parabolic dependence on potential, with a minimum at *ca.* 0.09 V$_{Ag/AgCl}$. The value corresponds to the *pmc* of the material.

The agreement between the *pmc* values determined by PBD and AC impedance suggests that the modelling of the carbon aerogel electrode is correct.

Preliminary results indicate that PBD techniques could also be used in nonaqueous media, where the *pmc* value also coincides with a minimum in the capacitance of the porous electrode.[24]

Probe beam deflection seems to be a very useful technique to measure double layer properties of high surface area electrodes.

Fig. 3 Low frequency capacitance (C_{LF}) as a function of the potential of a carbon aerogel electrode in 0.5 M NaF aqueous solution.

Gabriel A. Planes, María C. Miras and César A. Barbero*

Departamento de Química, Universidad Nacional de Rio Cuarto, Agencia postal N° 3, 5800, Rio Cuarto, Argentina.
E-mail: cbarbero@exa.unrc.edu.ar; Fax: +54 358 4676233;
Tel: +54 358 4676 157

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