

Proton-Selective Environment in the Pores of Activated Molecular Sieving Carbon Electrodes

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In an attempt to form a proton-selective environment in porous carbons that is similar to that of proton-conducting polymers, we used highly oxidized molecular sieving carbons that are covered by oxygen-containing surface groups. Naturally, it would be assumed that the free electron pairs of the surface oxygen atoms are those that provide specific adsorption sites for protons. However, we discovered that selective adsorption of protons takes place within the pores of the molecular sieving carbon electrode, even in the absence of surface oxides.

Introduction

Activated carbons are highly porous solids of high surface area. Their application as adsorbents in both gas and liquid has been known for centuries. Much less recognized are the processes that take advantage of the fact that most of these highly microporous carbons are electrically conductive, so that their performance as adsorbents in electrolyte solutions may be modified electrochemically, by changing the electrochemical potential of an activated carbon electrode vs a reference electrode. In general, a surface excess of electronic charge exists at the electrode side of the electrolyte–electrode interface that is balanced by an opposite and equal ionic surface excess. The two charge layers are separated by a few angstroms, which in fact form a parallel plate capacitor denoted as the electrical double-layer (EDL) system. The two charge layers cannot cross the separation distance to neutralize each other unless a thermodynamic free-energy barrier is overcome. This barrier is, in fact, the oxidation or reduction potential of the corresponding species in the electrolyte solution. Therefore, there is a potential window (about 1–1.5 V in aqueous solutions and 2.5–4.6 V in aprotic solvents) within which only the EDL plays an electrochemical role, and beyond which the more familiar *redox* electrochemistry plays the major role (in addition to that of the EDL).

The basic thermodynamic derivation of the electrical double layer was given by Lippman as early as 1875.¹ The basic molecular presentation was pioneered by Gouy, Chapman, and Stern, using a Boltzman-type interaction field.² Frumkin et al. studied the relation of the EDL with specific adsorption of ionic species on platinum.³ The basic understanding of the EDL is still based on the thermodynamic derivations and correlation with experimental results related to the ideal surface of mercury, developed by Graham and co-workers.⁴

The realization that the electrical double layer exists throughout the micropores in a high surface area activated carbon electrodes was first mentioned by Newman and Tobias,⁵ and then by Soffer and Folman.⁶ Several aspects of EDL of metallic and carbon electrodes, including the influence of surface groups and determination of the potential of zero charge, were studied by Frumkin et al.⁷ and by Soffer.⁸

Two major applications of high surface porous carbon electrodes were developed through the years, because the ion

surface excess vs electronic excess at the EDL can be attenuated by changing the electrode's potential.

1. Electroadsorption and electrodesorption. There are a large variety of potential dependent adsorption processes of EDL carbon electrodes that may be very useful in the separation of science and technology, especially for water purification⁹ and desalination.¹⁰

2. Production of unique capacitors of extremely high capacitivities. In fact, a porous carbon electrode in an electrolyte solution is always an EDL capacitor with a surface area of hundreds of square meters per gram of carbon. The EDL capacitance of carbon electrodes in aqueous solutions was estimated to range from 3 to 60 $\mu\text{F}/\text{cm}^2$. The lower value stands for the basal plane of graphite and the higher one for the edge plane.¹¹ The capacitance for various types of carbons falls in the range of 8–35 $\mu\text{F}/\text{cm}^2$, depending on the type of carbon and electrolyte.¹² Assuming a capacitance of 10 $\mu\text{F}/\text{cm}^2$, and a surface area of 1000 m^2/g typical of activated carbons, we obtained $C = 100 \text{ F/g}$, a tremendous, but experimentally verified value.

Currently, EDL capacitors (also termed electrochemical or super capacitors) are a rapidly growing technology conducted by several major companies engaged in electrochemical energy storage devices.¹³

Molecular Sieving Effects. The electroadsorption capacity of a porous carbon electrode is obviously a function of its surface area. Large surface areas may be obtained by increasing the concentration of small pores on the electrode's surface. When the pore size approaches the molecular size of the adsorbate, molecular sieving effects in electroadsorption can be obtained.¹⁴ It is possible to control the pore size and pore concentration of porous carbon electrodes by applying different activation procedures, all of which are essentially controlled burnoff processes by oxidizing agents, which increase the surface area and pore size. Chemical vapor deposition (CVD) of carbon can then be applied to reduce the pore size,¹⁵ and, as a result, the accessible surface area. We can define “normal” adsorption processes from the gas phase or electroadsorption processes from the electrolytic solutions when the pores are significantly larger than the adsorbate size. However, once the pores are adjusted, using the techniques above, to approach the adsorbate-effective size, *molecular sieving* effects are observed.

Some Implications of Carbon Molecular Sieves. In the past, adsorption molecular sieving effects on activated carbons were developed and applied for gas separation by adsorption–desorption cycles. Later on, novel carbon molecular sieve membranes for gas separation were invented.¹⁶ Molecular sieving carbon electrodes were developed with various pore dimensions and pore size calibrated by means of the gas-phase adsorbability of probe molecules having a known size. These calibrated carbon molecular sieves were demonstrated as tools for estimating the effective dimensions of different ionic species in solution.¹⁷ Under this category, we were able to show that the singly charged alkaline cations are adsorbed in their hydrated state, so that their effective dimension while electroadsorbed into a porous carbon electrode is much larger than their ion size in the crystalline state. On the other hand, singly charged anions were shown to be electroadsorbed predominantly in the nonhydrated state. Doubly charged cations and anions were found to acquire a significantly larger hydration sheath than the alkaline cations. In these studies, we were able to establish a scale of effective ionic dimensions in pores, from which one may readily deduce on the corresponding ionic dimensions in the bulk solution.¹⁷

The Objectives of the Present Work. The studies of the molecular sieving effects in carbon membranes and carbon electrodes of molecular size pores were performed in the gas phase,¹⁴ in neutral aqueous electrolyte,¹⁷ and in aprotic solvent electrolyte media.¹⁸ However, acidic and basic media are expected to exhibit a different behavior. In this paper, the behavior of protons in pores of molecular dimensions was studied for the first time. Of special interest is the question whether a selective protic environment can be obtained in activated carbons. If this is achievable, molecular sieving carbon electrodes could be developed for regenerative electroseparation of acids from aqueous electrolyte streams. By the term selective protic environment, we imply a chemical environment of strong hydrogen-bonding moieties that are confined to a small free pore volume, which does not allow the insertion of other cations rather than protons. Such a consideration is based on the prerequisite that the effective size of the protic cation is smaller than that of the alkali ions studied previously. It is the aim of this study to prove or disprove this assumption.

A proton-selective environment is highly important in several chemical systems. Examples are the proton-conductive polymers, currently a fast-growing topic in the area of membrane separators in hydrogen and methanol fuel cells. These systems typically comprise cation-exchange sites in a dense polymer which excludes non-hydrogen-bonding cations. Others comprise nitrogen basic groups that can be protonated, dragging a counteranion into the protic environment. In this paper, we attempt to mimic a situation of a protic environment in polymers with molecular sieving carbons. The uniqueness of a carbon membrane is in substituting the counteranion by electronic negative charge at the other side of the EDL.

Experimental Section

For this study we used integral carbon electrodes. (No metallic current collectors were needed.) The methods of preparation of the carbon cloth from cellulose-based cloth precursor and then its activation with CO₂ (to obtain the desired porosity), as well as scanning electron and scanning tunneling microscopic images of the carbon electrodes, were presented previously.²⁰ Activation with nitric acid solutions at room temperature and at 80 °C was conducted simply by dipping pieces of carbon-cloth samples into the nitric acid (60%) at the desired temperature and duration,

then washed with excess amounts of deionized water and dried in a vacuum at 80 °C. Activated carbon cloths from which the surface groups were removed by heat treatments were also studied. One heat treatment included heating the carbon samples activated by HNO₃ solutions at 1000 °C. The other treatment included heating the activated carbon samples at 1000 °C under a flow of highly pure argon gas (1 atm) containing 5% H₂. Cyclic voltammetry (CV) measurements were made with 0.1 N each of aqueous sodium chloride, hydrogen chloride, and sulfuric acid, in this sequence. The first solution used was the NaCl one, which ensured neutral pH for the measurements with this solution.

Instrumentation for the electrochemical measurements and the structure of the electrochemical cell were described previously²⁰ (standard, computerized potentiostat/galvanostat work stations). The thermal stability of the carbon cloth was monitored by thermogravimetric analysis (Mettler Toledo, TGA/SDTA851) by heating under a N₂ flow (30 cm³/min) from 30 °C to 500 °C (10 °C/min).

In this work, the main interest was assessing the dependence of the electroadsorption of each ion separately on the electrode potential. The electrodes' charging states were measured by cyclic voltammetry. We judged whether cations or anions are adsorbed to the electrodes by comparing the electrode's potential with the potential of zero charge (PZC). We assume that at potentials negative to the PZC, mainly cations are adsorbed and that adsorption of anions occurs mainly at potentials positive to the PZC.

The value of the PZC was taken as the *immersion potential*, namely, the potential measured shortly after wetting a dry, high surface area electrode with an electrolytic solution. The action of wetting the electrode creates the electrical double layer throughout the internal electrode surface area, thus bringing about a tremendous increase in the capacity of the electrode without charge supply, leading to a negligible charge density per unit area, as illustrated in Figure 1. The coincidence of the immersion potential and the PZC, and the limitation of the relevant assumptions were discussed elsewhere.¹⁸ The immersion potential was measured only after first wetting with the sodium chloride solution. The data obtained with the acidic solutions cannot be easily interpreted on the basis of the immersion potential of NaCl. In these cases, therefore, we used the triangular shape of the chemical vapors (CVs) which are usually measured with the H₂SO₄ solutions. This unique shape of the CVs is due to the molecular sieve rejection of the large sulfate ion at positive potentials. The PZC in this case was taken as the potential at which there is a significant drop in the electrodes' capacity as the potential is swept anodically. The immersion potentials for the various experimental series are indicated on the cyclic voltammograms presented.

Results and Discussion

Creating Proton-Selective Absorbing Electrodes. We presume that the key parameters for producing a proton-selective environment within the micropores of carbon electrodes are:

1. High density of hydrogen-bonding sites. This implies creation of surface sites that can behave as Lewis bases.
2. Groups having electron donor sites. A first choice is, in general, the addition of chemibound oxygen to the carbon surface. This is obtained by using strong oxidizing agents in aqueous solutions, water being the resource of the –OH surface groups which act as electron pair donors.
3. Narrow pores that should reject hydrated ions by virtue of their size. Here we emphasize *hydrated* cations, on the basis of

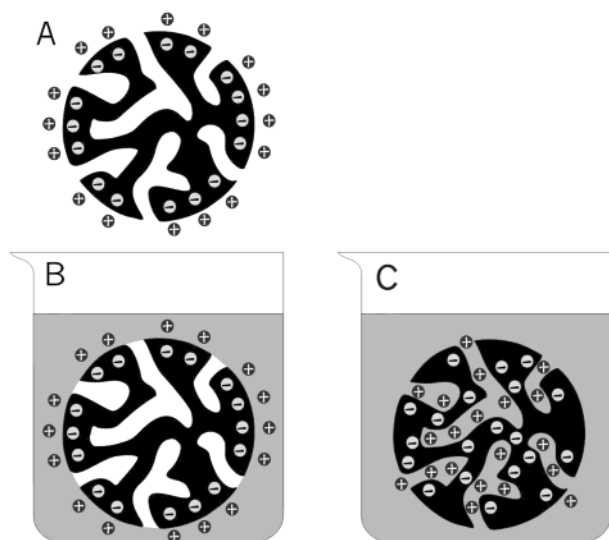


Figure 1. The capacitance of a dry porous carbon electrode sphere (A) is $4\pi r\epsilon_0 = 1.1 \times 10^{-12}$ F for $r = 1$ cm (ϵ , the permittivity of vacuum $= 8.85 \times 10^{-10}$ F/cm). When immersed without pore penetration (B) in an electrochemically inert electrolyte solution, the surface capacitance of the sphere becomes that of the EDL, about $10 \mu\text{F}/\text{cm}^2$, or $4\pi \times 10^{-5}$ F, about 10^8 -fold capacity growth. Because the outer surface of the electrode is highly sensitive to impurities, the condition of electrochemical inertness may be violated. However, if the electrolyte penetrates the micropore system (C), typically acquiring 1000 m^2 for the mentioned sphere radius, the capacitance is further multiplied by $10^7/4\pi$, which renders the immersion potential to be more reliably equal to the PZC.

our recent discovery that alkaline and alkaline earth cations are inserted at negative potentials into the micropores while considerably hydrated (i.e., the pores with which they interact must be as large as the hydrated cations).¹⁷

Our approach was to achieve these two goals in one treatment: activation of a nonporous carbon by concentrated nitric acid which, if limited in duration, is assumed to create only pores of molecular dimensions, as was found in gas-phase activation.¹⁹

Below we present cyclic voltammograms for carbons treated with nitric acid for different durations and temperatures. The electric current at the ordinate of the voltammograms is normalized per gram of electrode material and per unit sweep rate. This makes the cyclic voltammograms become plots of the differential capacitance of the electrodes:

$$C = I/(dV/dt) \quad (1)$$

where I is in amperes per gram of electrode material, V is the electrode potential in volts; t is the time (in seconds); and C is a capacity magnitude in farads per gram. The latter value is the most convenient mode of normalized current because it gives an approximate differential capacity value defined by the width of the cyclic voltammograms.²⁰ Because the voltage scan rate was always 1 mV/s , the ordinates in the CV graphs (amperes per gram) should be multiplied by 1000 to obtain the capacity in farads per gram.

The presentation of the main results, i.e., those for HNO_3 -treated carbons, are compared herein with the behavior of other reference carbons that have large pores, so that the effects of the surface treatments on the selectivity of the electrodes are demonstrated.

Figure 2 depicts a first reference cyclic voltammogram of a well-activated electrode using CO_2 at 900°C . This electrode presents a reference behavior of a porous electrode with

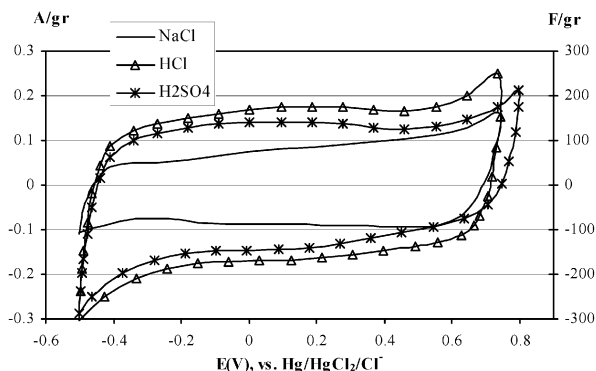


Figure 2. Cyclic voltammetric curves (1 mV/s) for a carbon electrode that was highly activated with CO_2 at 900°C .

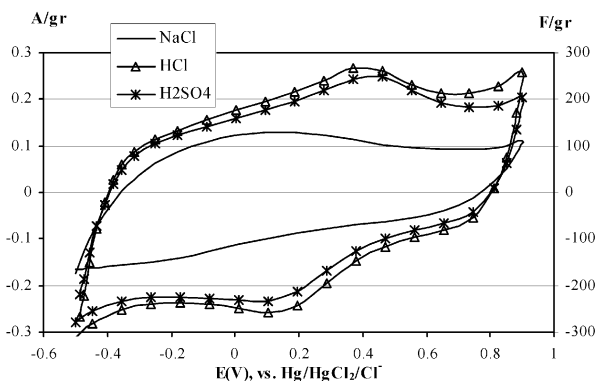


Figure 3. Cyclic voltammograms (1 mV/s) of a carbon cloth that was activated with HNO_3 at 80°C for 3 h.

relatively large (yet microporous in size) pores. Whereas different ions are adsorbed equally well, preference to proton adsorption is evident. This could be explained in two ways: (1) The hydrated Na^+ is somewhat larger than the hydrated H_3O^+ (the size of H_3O^+ is about that of hydrated potassium ion, as discussed below). (2) The pore distribution function is nonhomogeneous so that there is a fraction of pores that are sufficiently large to accommodate H_3O^+ but not hydrated Na^+ ions.

The behavior of an electrode that was deeply activated with nitric acid (3 h, 80°C , Figure 3) is our second reference case. It is basically similar to that of the carbon activated by carbon dioxide. In both cases, electroadsorption of all ions seems to be equally possible. Note the pair of corresponding anodic and cathodic peaks in the voltammograms of Figure 3, which relate to the acid solutions (HCl , H_2SO_4) centered around 0.3 V . These corresponding peaks appear only in voltammograms of the carbons treated with HNO_3 and not with CO_2 , which takes place at high temperatures where surface oxides are unstable and degas as carbon oxides, and probably belong to the quinone-hydroquinone surface redox couple.²¹ These peaks always appear in well-oxidized carbon surfaces and are independent of pore size.

Another observation is that the currents seen in the CV curve of the NaCl solution are higher at the more negative potentials in HNO_3 -activated electrode (Figure 3). This reflects the effect of the surface dipole of oxygen surface groups formed by the HNO_3 activation: The dipoles' negative sides face the solution, and therefore they attract cations and repel anions. On the other hand, the CO_2 -activated carbon (Figure 2), which is much lower in oxygen surface groups, as was found from thermogravimetric analysis of these carbon samples (see Figure 4), exhibits an opposite behavior: the currents seen in the CV curve are higher

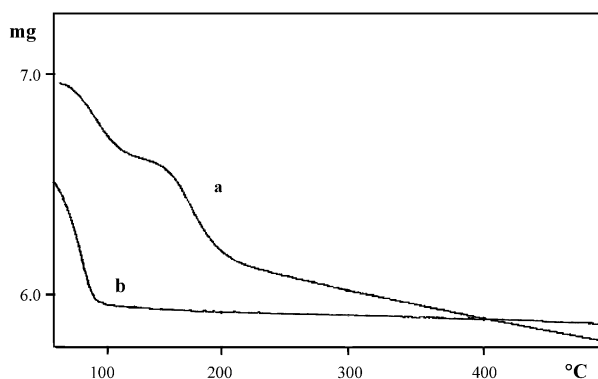


Figure 4. Thermogravimetric analysis of: (a) A carbon-cloth sample activated for 30 min at 80 °C in a nitric acid solution (70%); (b) a carbon-cloth sample activated by CO₂ at 900 °C, 1 atm for 30 min. The drop in weight seen up to 80 °C relates to loss of physisorbed water. The drop in weight between 80 and 170 °C is caused by desorption (degassing) of oxygen from surface groups. It is evident that this drop is the most significant for the carbons activated by the HNO₃ solution.

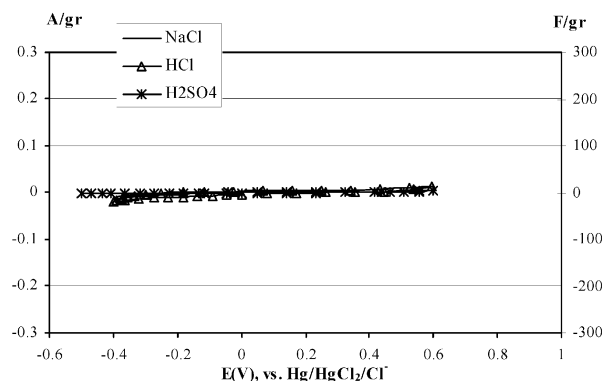


Figure 5. Cyclic voltammogram (1 mV/s) of a nonactivated carbon-cloth electrode in the presence of 0.1 M each of H₂SO₄, HCl, and NaCl.

at the more positive potentials. Similar behavior was also observed previously with other types of carbons.¹⁴

In Figure 5 we show cyclic voltammograms of our third reference carbon, which is as-received, nonactivated, carbon cloth. The EDL capacity is negligible considering the above-mentioned figure of 100 F/g. Obviously, this is because the nonactivated carbon has no pores that are large enough to accommodate any of the four ions studied. The remaining capacity should be attributed to the outer surface area of the carbonized cotton fibers whose roughness is typical of natural fibers. The increase in the currents at the extreme potentials are typical of the initiation of redox reaction processes, which determine the EDL window of potentials. The increase in the current at the extreme potentials is also seen in the well-activated electrode cases, Figures 2 and 3, but here in Figure 5 it is more pronounced on the background of the low currents appearing in the CVs in the middle of the potential window (i.e., at the EDL activity).

In Figure 6, the CV curve of a carbon electrode that was treated to provide a molecular sieving protic environment is shown. Activation was obtained with concentrated nitric acid at room temperature for 15 min. The high H⁺ electroadsorption selectivity is clearly demonstrated at the negative branch of the curve, comparing the response for H⁺ and Na⁺, and at the positive branch, compared with the response of Cl⁻ and SO₄²⁻.

We may conclude that the selective protic environment has been accomplished, as expected, by activation of the carbon with nitric acid. At this point, the question about the effective

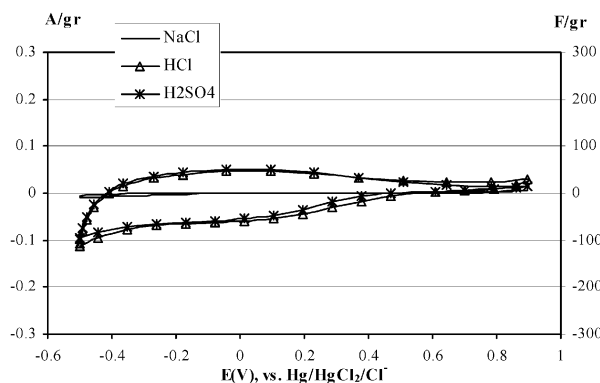


Figure 6. Cyclic voltammograms (1 mV/s) of a slightly activated (15 min, room temperature) carbon-cloth electrode. Very high selectivity of H⁺ electroadsorption is obtained. Compare with the nonselective behavior exhibited by the deeply activated samples shown in Figures 2 and 3.

dimension of the protic ion H₃O⁺ should be addressed in light of previous discussion on the size of ions adsorbed into porous carbons.^{17,20} Considering what is known from the electrochemistry of aqueous solutions, the protic ion has more-or-less the dimension of hydrated K⁺ (i.e., not much smaller than that of Na⁺).²² Therefore, the pronounced selectivity of H⁺ vs Na⁺ observed cannot be attributed to specific pore size distribution.

It may be possible to weigh the roles of the two factors that lead to the protic selective environment, namely, molecular sieving by possible nanopores and oxygen-containing surface groups, by removing the surface groups from the carbon surfaces while still retaining the pores in the molecular sieving size, and observing the effect on the electrochemical (EDL) response.

The Molecular Sieving Factor. In Figure 7a–d, CV curves are shown for a series of samples activated at 80 °C with concentrated HNO₃ for progressively longer times. Thus, the pores are gradually enlarged by carbon burnoff,¹⁸ but are likely to stay at a similar status of high concentration of surface oxides.²³ The first experiment of this series is in fact the nonactivated carbon shown in Figure 5, and its end is in the 3-h activated carbon shown in Figure 3.

Figure 7a shows behavior similar to that in Figure 6, namely, strong molecular sieving or high electroadsorption selectivity for H⁺. Figure 7b shows that a 5-min activation time at 80 °C enables weak and slow Na⁺ electroadsorption, thus slightly breaking the selectivity that is due to the molecular sieving effect of the electrodes for H⁺. This trend is developed further upon activation as shown in the 10-min activated sample (Figure 7c). At a longer activation time, Figure 7d, the H⁺/Na⁺ selectivity drops further, and also the electroadsorption of the Cl⁻ anion commences in the HCl solution, as is evident from the current increase at the anodic (more positive) branch of the CV curve. Chloride adsorption becomes even more significant in the 1-h HNO₃-activated carbon (see Figure 10a, below).

In the course of this sequence of pore widening, the chloride anion, which was previously shown to be close in size to Na⁺, using pore-size-calibrated carbon electrodes developed by CO₂ activation,¹⁷ could not be electroadsorbed into pores having the size of Na⁺, as shown in Figure 7b,c. Chloride electroadsorption could be clearly obtained only after pore enlargement considerably beyond that of Na⁺ size (Figure 7d). This difference in the possibility to adsorb anions between the CO₂- and HNO₃-activated carbons can be explained in light of the very high concentration of surface oxides in the latter carbon, which creates anion-rejecting surface dipoles.

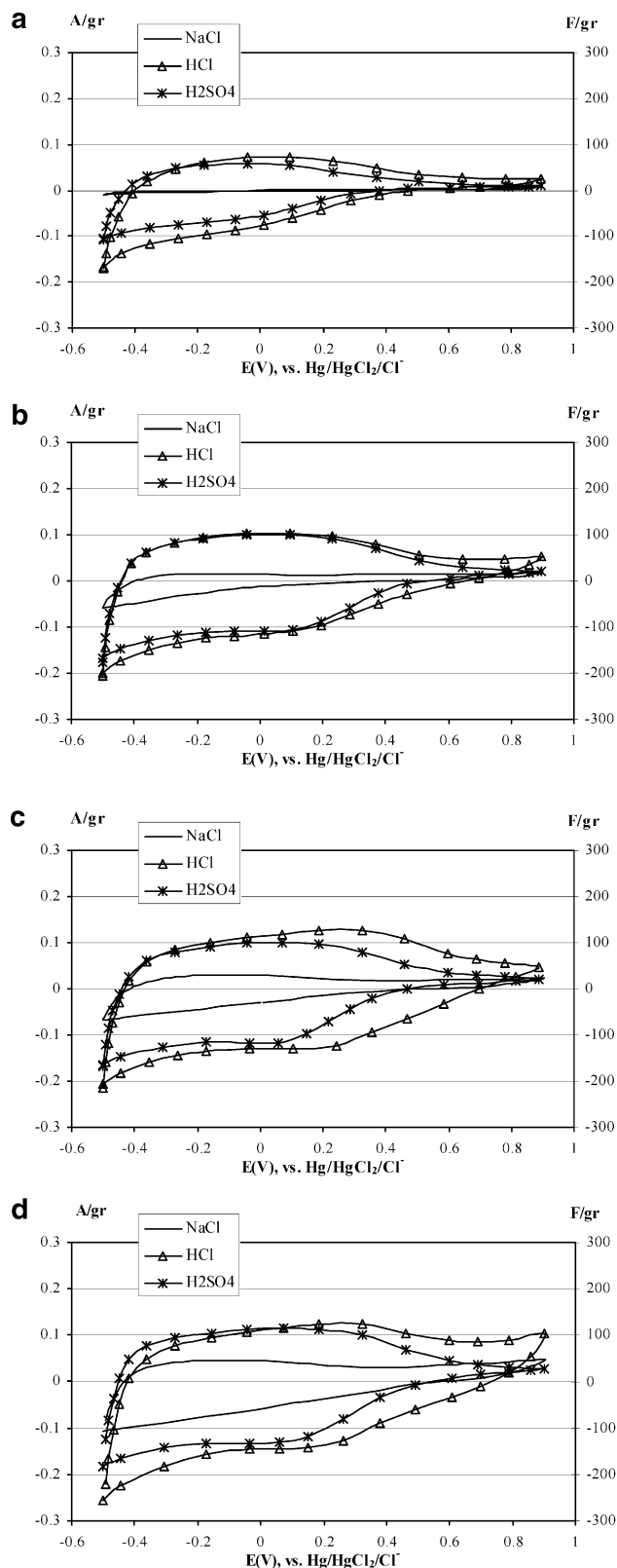


Figure 7. Cyclic voltammograms (1 mV/s) of carbon-cloth electrodes gradually activated in a HNO_3 solution at 80 °C for different times, starting from short immersion in the hot acid, up to 30 min. (a) Short immersion (min); (b) 5 min; (c) 10 min; (d) 30 min.

Finally, the highly hydrated bivalent anion SO_4^{2-} , is, as expected, the most difficult to be electroadsorbed, as seen in Figures 2, 3, 6, and 7.

The Effect of the Oxygen-Containing Surface Groups. The removal of the surface oxides is supposed to destroy the protic

selective environment (where H_3O^+ is preferentially adsorbed in the EDL over any common cation), which was formed by oxidation with the nitric acid solutions at temperatures below their boiling point. This can be achieved by high-temperature (300–1000 °C) degassing of the activated carbons in a vacuum or under flow of inert gas. It is most important to mention that besides the loss of the electron donor surface oxides, the removal of oxygen containing surface groups has three additional effects:

1. Shifting the immersion potential negatively. As mentioned earlier, the immersion potential helps in estimating whether the major ionic species present at the solution side of the EDL at a given potential are the anions or the cations. This is a general feature and is not specific to the molecular sieving effects of the fine pores.

2. Shifting the surface dipole negatively. In active carbons that have pores of molecular dimensions, electroadsorbed ions have to come closer to the electrode surface, thus they are rendered sensitive to the local surface dipoles. Explicitly, anions can be excluded out of pores having dipoles with the negative pole facing the solution. The effect is specific to pores that are about the size of the ionic species and disappears once the pores are considerably larger than the ion size. It is therefore not equivalent to changing the immersion potential. This feature had previously been encountered several times^{14,17,18} and is not discussed further, but it must be kept in mind upon analyzing the effect of surface oxides removal.

3. Pore enlargement. It is well-known that thermal removal of surface oxides proceeds as evolution of carbon monoxide (at 600–1000 °C) and carbon dioxide (at 300–600 °C). Thus, carbon atoms are abstracted from the pore's walls, leading to pore enlargement. This effect is also well-known and has been exploited in the past.^{16,20}

Surface oxygen-containing groups were removed in two ways: heating the activated carbons in a vacuum at 1000 °C, or under Ar/H_2 flow (5% H_2) at 1000 °C (1 atm). The latter treatment exchanges, at least partially, the oxygen surface groups with C–H bonds. As shown previously,¹⁸ this treatment shifts the immersion potential further negatively because of the addition of the short surface dipoles at the C–H bonds with their positive side facing the solution.

Figure 8a,b shows CV curves of carbon-cloth electrodes that were activated in HNO_3 at room temperature for 15 min, then heat-treated in a vacuum (Figure 8a) or in Ar/H_2 atmosphere (Figure 8b). This is the electrode that exhibits a very high H_3O^+ adsorption selectivity (Figure 6) before the heat treatments. Comparing the CV curves in Figures 6 and 8a related to NaCl solutions, we see that a slight increase in the EDL capacity occurs at the negative potentials (to the PZC), and it increases further at the more positive potentials. This behavior corresponds to the pore enlargement that occurred because of the removal of the surface oxygen groups. We suggest that the shift in the surface dipole moments due to the heat treatment gives a slight advantage to Cl^- adsorption at the positive branch of the CV curve. This trend is even more significant in the H_2 -treated electrode presented in Figure 8b. As mentioned above, heat treatments in the presence of H_2 forms a C–H bond that should have an opposite effect on the surface dipole, compared with removal of oxygen-containing surface groups only (by heat treatment in a vacuum). Of special interest is the behavior of the HCl solution in Figure 8b: Despite the almost total rejection of Na^+ , the currents in the CV related to the HCl solution is high at both branches of the cyclic voltammograms.

It is surprising that the selective protic environment expressed by the H^+/Na^+ high adsorption ratio (Figure 8a,b) was *not*

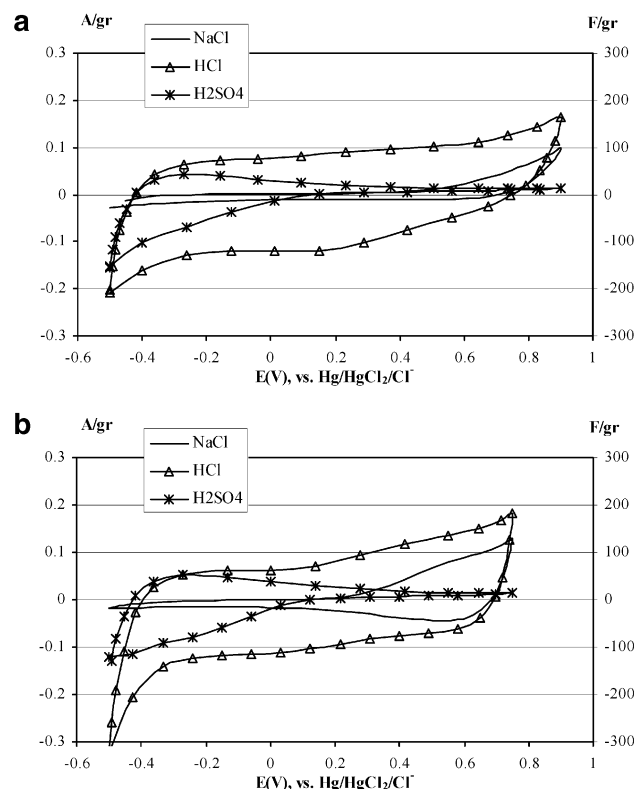


Figure 8. (a) Cyclic voltammogram curves (1 mV/s) of carbon cloth activated by concentrated nitric acid at room temperature for 15 min, then vacuum-treated at 1000 °C. (b) Cyclic voltammogram curves (1 mV/s) of carbon cloth activated by concentrated nitric acid at room temperature for 15 min, then treated at 1000 °C with a flow of argon gas containing 5% hydrogen in argon at ambient pressure.

destroyed, although most, if not all, of the electron donor oxygen surface groups were removed by the heat treatments. In the sulfuric acid solution, the sulfate anion is too large to be electroadsorbed, giving rise to the triangular shape of the CV curves related to the H_2SO_4 solution (Figure 8a,b). The fact that the chloride anion (NaCl curve, Figure 8a,b) is adsorbed significantly while Na^+ is rejected, implies that there is a good fit of the average pore size to that of the Cl^- ions, in addition to the anion-attracting dipole of the vacuum and the H_2 -treated electrodes, respectively.

Figure 9a,b relates to more intensively activated electrodes than those related to Figure 8 (30-min activation time in the HNO_3 solution at 80 °C compared with 15 min in this solution at room temperature). The differential EDL capacities of the more activated electrodes in the HCl solutions in all cases (activated, heat-treated, etc.) are, as expected, greater than those of the less activated electrodes whose CVs are presented in Figure 8a,b.

Comparing the medium-activated electrode (Figure 9a) with the less activated one shown in Figure 8a, we observe a strong decrease in the H^+/Na^+ selectivity, as a result of pore enlargement. More interesting is the behavior of the medium-activated and $\text{Ar}/5\%\text{H}_2$ heat-treated electrode, as shown in Figure 9b (compare with Figure 9a). Besides the almost total loss of the H^+/Na^+ selectivity, the sulfate ion exhibits significant adsorption while it was previously negligible. We may attribute this effect to the attraction of the highly charged anion to the local C–H dipole (positive pole facing solution) formed by the H_2 HTT treatment. In any event, we were able to present a very interesting phenomenon, namely, a protic selective environment

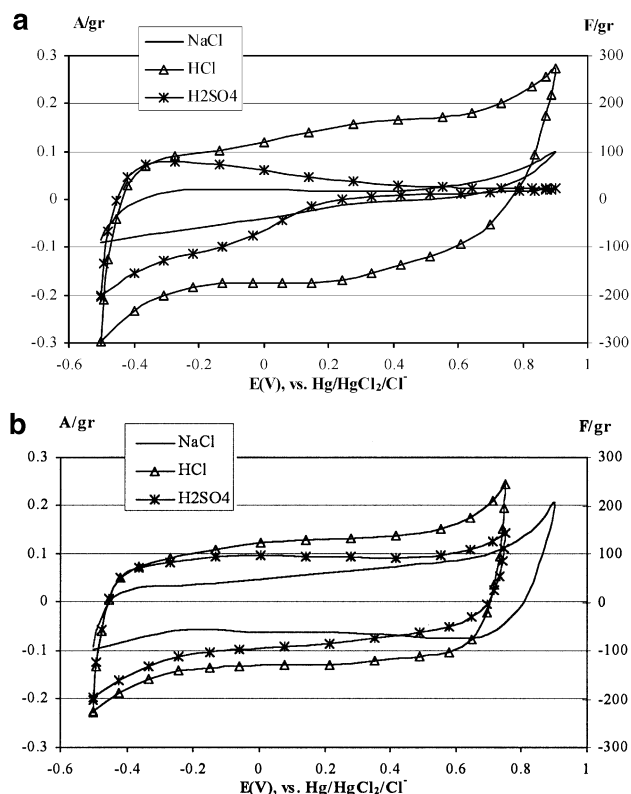


Figure 9. (a) Cyclic voltammograms of carbon electrodes in HCl , NaCl , and H_2SO_4 solutions, as indicated. The carbon electrode was activated by immersion for 30 min in a HNO_3 solution at 80 °C, and then vacuum-treated at 1000 °C. (b) Same as Figure 9a. The electrode was heated after activation at 1000 °C in a flow of argon containing 5% H_2 at 1 atm.

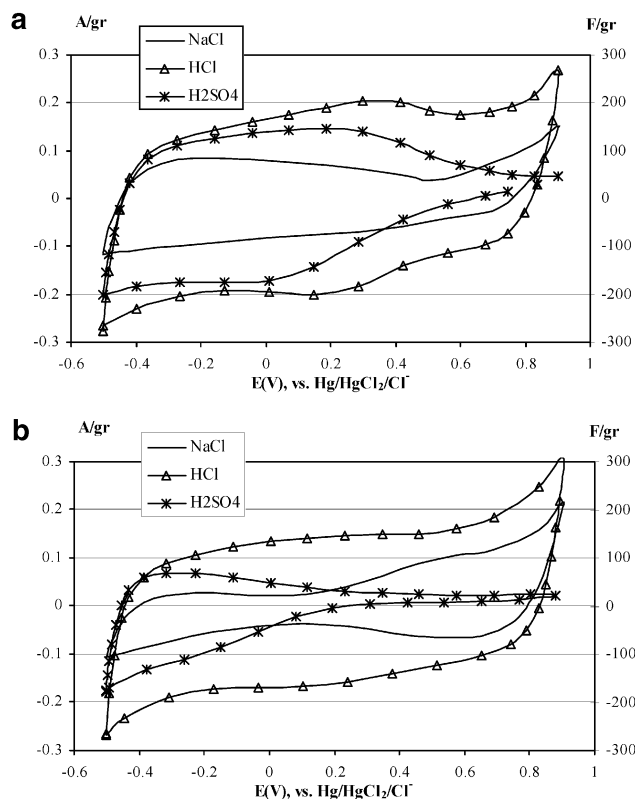


Figure 10. (a) Cyclic voltammograms (1 mV/s) of carbon-cloth electrodes activated in a HNO_3 solution at 80 °C for 60 min. (b) Cyclic voltammograms (1 mV/s) of carbon-cloth electrodes activated in a HNO_3 solution at 80 °C for 60 min, and then vacuum-treated at 1000 °C.

that exists at porous carbon electrodes, even in the absence of oxygen-containing surface groups.

Finally, we examine the behavior of carbon electrodes with further, deeper activation by the HNO₃ solution, as shown in Figure 10a,b. We see here that, for both heat-treated and nonheat-treated electrodes, all the molecular sieving effects, namely the surface dipole effect and the exclusion of ions because of the size of the pores, are minimized as far as NaCl is concerned. However, in the larger SO₄²⁻ ion, the average pore size is still too small, and hence, the possibility of their adsorption is very limited, as seen by the CVs of Figure 10b.

Conclusion

Aqueous protons, in size-confined pore systems of activated carbon electrodes, exhibit an effective size that is remarkably smaller than that of regular anions and hydrated cations. This implies that, unlike other ions, hydrated protonic species can be stripped of most of their hydration sheath upon electroadsorption into small pores a few Å in diameter. This highly endothermic loss of hydration shell is assumed to occur in exchange with the gain of interaction at close proximity of the proton with the opposite walls of the nanopores on the carbon electrodes. Such interactions between ions and carbon walls in sub-nanopores is not possible with regular ions, thus leading to a very high electroadsorption stereoselectivity of H⁺ over other ions. This phenomenon enables the use of nanoporous carbonaceous materials in proton-selective membranes for a wide variety of applications.

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