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# Carbon materials as electrodes for electrosorption of NaCl in aqueous solutions

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**Abstract** Different porous carbons (MWCNT, a carbon aerogel, an activated carbon cloth and a chemically activated carbon) were evaluated as electrode material for the electrosorption of NaCl. The results obtained from the chronoamperometric experiments were correlated to the surface area and the size of the pores present in each carbon. These results indicate that all the surfaces are equivalent for the electrosorption process, demonstrating that both, mesopores and micropores, are equally effective. Nevertheless, the kinetics of the process is influenced by the pore size distribution of the carbon, although it is rather fast for all the carbons studied. The chemically activated carbon seems to be the most suitable carbon material for electrosorption of NaCl due to the combination of a high surface area and an appropriate pore size distribution.

**Keywords** Electrosorption · Activated carbon · MWCNT · Carbon aerogel

## 1 Introduction

Porous carbons, in particular activated carbons, are used in a wide range of applications related to their adsorption capabilities due to the high surface areas, different pore size distribution and variable surface chemical composition that they can possess. Activated carbons used in gas-phase applications (gas purification and separation, solvent recovery, catalytic uses, gas storage, etc.) have usually a well developed microporosity to provide a high adsorptive capacity and selectivity for gases and organic vapors. Liquid-phase applications (water treatment including both industrial waste water and drinking water, purification of chemicals and pharmaceuticals, removal of odor or color causing contaminants in the food and beverage processing, etc.) require activated carbons with a larger pore size than gas-phase uses, in order to assure a rapid diffusion of the liquid into the interior of the carbon particles and also due to the large size of many dissolved molecules to be retained (Rodríguez-Reinoso et al. 1997).

Other application in the liquid phase that has emerged during the last decade is the use of porous carbons as electrodes for supercapacitors or electrochemical double layer capacitors (Qu 2002; Pekala et al. 1998). In this application, energy is stored at the electrical double layer formed between the surface of the carbon electrode and the ions of the electrolyte when an electric field is applied. Therefore, the surface area available to the electrolyte ions determines the amount of charge that can be stored. Furthermore, depending on the electrolytic media, the surface chemistry of the carbon can play a significant role through faradaic reactions involving electroactive sites (Ruiz et al. 2007, 2008; Pandolfo and Hollenkap 2006).

Although electrochemical ion separation on high surface carbons has been mainly addressed to energy storage, it can also be used for other purposes, such as capacitive deionization (CDI), which is a typical electrosorption application for removing inorganic ions from aqueous solutions (Li et al. 2010; Seo et al. 2010). The main uses of CDI are water purification and desalinization (Oren 2008; Yang et al. 2005). Compared to other desalinization processes like reverse osmosis, CDI is expected to be more energy efficient, this being the main driving force for research in this field.

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The work reported herein examines the behavior of different porous carbons as electrode materials for the electrosorption of NaCl. The results obtained from the chronoamperometric experiments are correlated to the surface area and the size of the pores present in each carbon material.

## 2 Experimental

### 2.1 Carbon materials

The carbon materials used in this study were a commercial activated carbon cloth (Cloth) purchased from ACTITEX©, a carbon aerogel (Aerogel) from *Marketech International*, multiwalled carbon nanotubes (MWCNT) from *Sigma-Aldrich*, and an activated carbon (KOH-AC) obtained by chemical activation of a commercial mesophase pitch with KOH. A detailed description of the procedure followed to obtain this sample can be found in Ruiz et al. (2007), Villar et al. (2010).

### 2.2 Characterization of carbon materials

Physical adsorption of $N_2$ at 77 K was carried out in order to characterize the porous texture of the different carbon materials. The specific surface area was determined from the $N_2$ adsorption isotherm using the BET equation (Barrett et al. 1951). The total micropore volume ($V_{\text{micro}}$) was calculated from the application of the Dubinin-Radushkevich (DR) equation to the isotherm (Dubinin 1975). The microporous surface area was obtained from the equation: $S_{\text{mic}}$ $(\text{m}^2\,\text{g}^{-1}) = 2000 V_{\text{micro}}\,(\text{cm}^3\,\text{g}^{-1})/L_0$ (nm), where $L_0$ is the average micropore diameter calculated from the equation proposed by Stoeckli and Ballerini (Stoeckli and Ballerini 1991) $L_0 = 10.8/E_0 - 11.4$ ($E_0$ is the characteristic energy in kJ/mol obtained from the DR equation). The total pore volume was obtained from the $N_2$ adsorption at $P/P_0 = 0.99$, except for the MWCNT ($P/P_0 = 0.82$). The volume of mesopores was calculated by subtracting the total micropore volume from the total pore volume. The pore size distribution in the different carbons were estimated by the Density Functional Theory (DFT) Jaroiec and Solovyoc 2006; Kruk and Jaroniec 2002, assuming slit-shape pores.

### 2.3 Electrode preparation, cell assembly and electrochemical characterization

The electrosorption characteristics of each carbon material were studied on disk type electrodes, 12 mm in diameter. Cloth was directly cut from the purchased sheet. Aerogel, MWCNT and KOH-AC were mixed with a binder (PVDF, 10 wt.%) and pressed into pellets. The electrochemical tests were performed in PFA (polyfluoroalkoxy) "T"-type Swagelok® cells, using a BioLogic multichannel potenciostat/galvanostat. Chronoamperometric experiments were performed for each unit cell in 0.6 M NaCl solution by applying a 1 V voltage for 10 minutes. Both current and specific charge were measured during the polarization time. Each material was cycled up to 100 times (Villar et al. 2010).

## 3 Results and discussion

### 3.1 Textural properties

The carbon materials selected for this study have rather different textural properties, as indicated by their different capacity to adsorb nitrogen and the shape of their nitrogen isotherms (Fig. 1). The shape of the Cloth isotherm indicates that this material is mainly microporous (Type I) with a negligible volume of mesopores (Table 1). The apparent

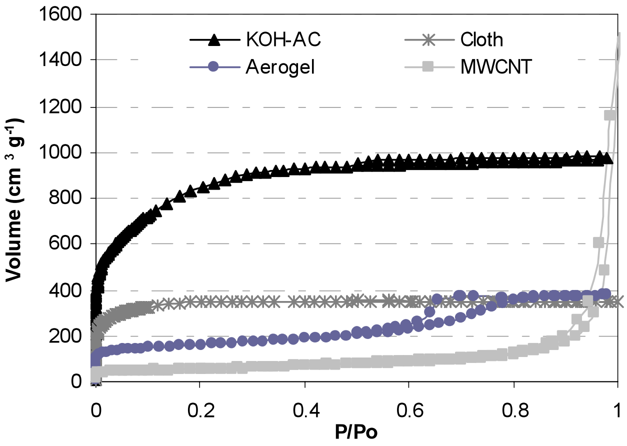

Fig. 1 Nitrogen adsorption isotherms

Table 1 Textural properties of carbon materials

| | $V_T$[a] | $V_{\text{micro}}$[b] | $V_{\text{meso}}$[c] | $L_0$[d] | $S_{\text{mic}}$[e] | $S_{\text{BET}}$[f] |
|---|---|---|---|---|---|---|
| KOH-AC | 1.51 | 1.02 | 0.49 | 1.51 | 1171 | 3091 |
| Cloth | 0.48 | 0.45 | 0.03 | 1.18 | 767 | 1199 |
| Aerogel | 0.59 | 0.23 | 0.36 | 1.14 | 396 | 560 |
| MWCNT | 0.19 | 0.08 | 0.11 | 2.07 | 87 | 210 |

[a] Total volume of pores $(\text{cm}^3\,\text{g}^{-1})$

[b] Total volume of micropores $(\text{cm}^3\,\text{g}^{-1})$

[c] Volume of mesopores $(\text{cm}^3\,\text{g}^{-1})$

[d] Average pore size (nm)

[e] Microporous surface area $(\text{m}^2\,\text{g}^{-1})$

[f] Apparent BET area $(\text{m}^2\,\text{g}^{-1})$

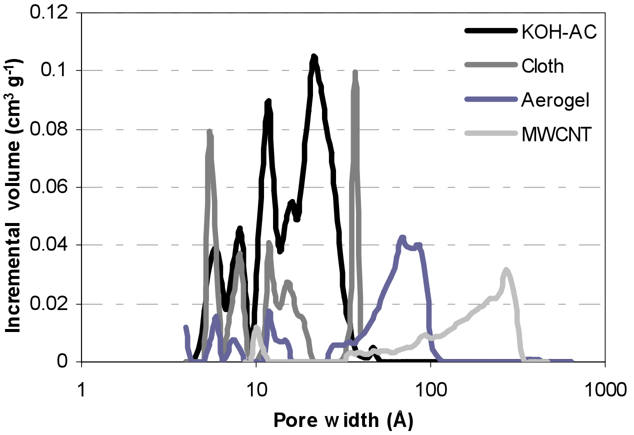

**Fig. 2** Pore size distribution of carbon materials calculated by DFT method

BET area for this sample is 1199 $m^2\ g^{-1}$, which is reasonably high.

The activated carbon KOH-AC also showed a Type I isotherm, but with a relatively broader knee (Fig. 1), indicative of the presence of large size pores. In fact, the volume of mesopores estimated for this sample is 0.49 $cm^3\ g^{-1}$ (Table 1). The volume of micropores (1.02 $cm^3\ g^{-1}$) is also higher in this sample, which results in a wider pore size distribution (Fig. 2). The apparent surface area of this sample is significantly higher (over 3000 $m^2\ g^{-1}$) than that of Cloth.

The isotherm obtained for Aerogel (Type IV) is characteristic of mesoporous solids (Fig. 1). The volume of mesopores (0.36 $cm^3\ g^{-1}$) is higher than the volume of micropores (0.23 $cm^3\ g^{-1}$, Table 1). The volume of nitrogen adsorbed by Aerogel is similar to that adsorbed by Cloth, but the apparent BET area is nearly half of that obtained for Cloth (560 vs. 1199 $m^2\ g^{-1}$).

The nitrogen isotherm of the MWCNT indicates that this sample is also mainly mesoporous, their average pore size being higher than 2 nm (Table 1). The volume of pores is rather low and its apparent BET area is also the lowest (210 $m^2\ g^{-1}$).

The analysis of the isotherms by DFT (Fig. 2) illustrates the pore size distribution of each sample. As mentioned before, the pores present in the MWCNT are significantly higher than those observed for the rest of the samples. The carbon aerogel also has pores of large size, but it contains a fraction of smaller size pores as well. As discussed before, pores in KOH-AC and Cloth are significantly smaller than for the other two samples, but the size distribution is significantly broader for KOH-AC. Cloth essentially contains pores of small size.

### 3.2 Electrochemical performance

Chronoamperometric curves are shown in Fig. 3a. When the experiment starts (1 V is applied), a rapid increase of the current occurs due to the migration of the NaCl ions from the solution to the carbon surface. Thereafter, a relatively rapid decay of current is observed until the double layer is completely formed. As observed in Fig. 3b, there are some differences in the decay of intensity to reach the equilibrium depending on the sample. As will be discussed below, this different behavior is expected to be related to the pore size distribution of the carbon materials.

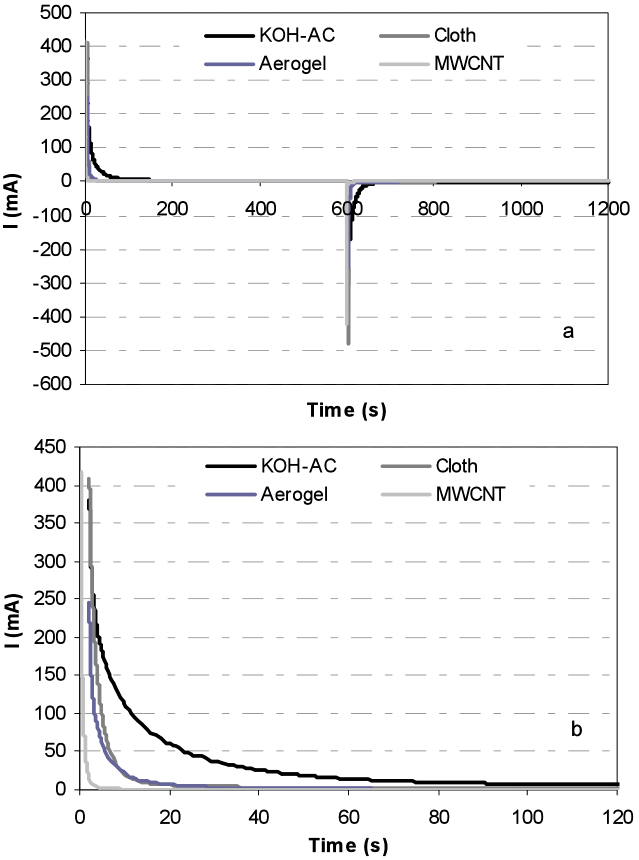

**Fig. 3** (**a**) First cycle amperometric curves of carbon materials, (**b**) Zoom

In all cases, the adsorption equilibrium is reached rather fast, the great majority of ions are electrosorbed in less than 2 minutes (Fig. 3b). In Fig. 3a the behavior during depolarization can also be observed (after 600 s), this being also a rapid process.

The specific charge ($C\ g^{-1}$), related to the amount of ions adsorbed on the electrode surface, is calculated from the chronoamperometric experiments, which have been repeated up to 100 cycles. The results are shown in Fig. 4. The values obtained for all the cycles are nearly constant except for the first one. In this first cycle, the specific charge is higher than for the following ones, due to some irreversible reactions occurring on the surface of the carbon. During depolarization the results were almost the same, the efficiency of the charge-discharge process being close to 100%. The amount of ions adsorbed is very different for each sample, as

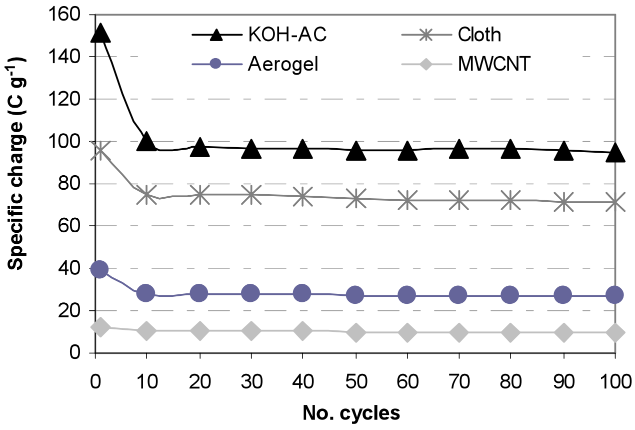

**Fig. 4** Specific charge per cycle (1V)

**Table 2** Charge by unit of surface area

| | $Q_{\mathrm{BET}}$[a] | $Q_{\mathrm{micDR}}$[b] |
|---|---|---|
| KOH-AC | 0.03 | 0.08 |
| Cloth | 0.06 | 0.09 |
| Aerogel | 0.05 | 0.07 |
| MWCNT | 0.05 | 0.11 |

[a] Charge by unit of BET surface area ($\mathrm{C\,m^{-2}}$)

[b] Charge by unit of DR surface area ($\mathrm{C\,m^{-2}}$)

could be expected considering the great differences in their textural properties discussed above. Thus, KOH-AC has the highest capability to adsorb ions and the MWCNT the lowest.

In order to evaluate if all the surface area available for gas adsorption is effectively participating in the electrosorption process, the data provided by the chronoamperometric experiments were normalized by unit of surface area (using the values obtained from both BET and DR calculations). The results are summarized in Table 2. When BET surface area is used for normalization, the values are very similar (0.05–0.06 $\mathrm{C\,m^{-2}}$) except for KOH-AC (0.03 $\mathrm{C\,m^{-2}}$). This might not be due to the different electrosorption behavior of the sample but to the overestimation of area resultant from the application of the BET equation to such a highly microporous sample (Molina-Sabio et al. 1994). Meanwhile, when the areas obtained from the DR method are used, KOH-AC becomes very similar to the other carbons, except to the MWCNT. Again this could be due to the unsuitability of the model used to calculate the area (DR suits microporous solids but not mesoporous ones, Dubinin 1975). Taking into account these considerations, it is reasonable to say that all the carbon surfaces tested are equivalent in the electrosorption of NaCl and that both mesopores and micropores participate in the process. Nonetheless, the differences in pore size have an influence in the kinetics of the process, as mentioned above (Fig. 3b).

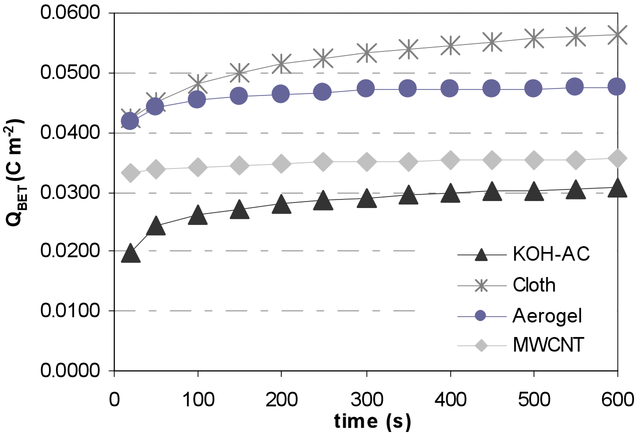

**Fig. 5** Charge by unit of BET surface area vs. time

Figure 5 shows the evolution of the specific charge ($\mathrm{C\,m^{-2}}$) with time for one cycle. For all the samples most of the charge is stored very quickly after polarization. While this initial charge remains almost constant for the MWCNT (95% of the adsorption occurred in the first 20 s) and the carbon aerogel, it steadily increases with time for the other two samples. In fact, for Cloth less than 75% of the adsorption occurs in the first 20 s. This behavior is due to the different porosity present in the carbons. At very short times, the adsorption occurs in the accessible area, which is most of the surface for MWCNT and the aerogel. At longer times, the adsorption involves less accessible surface with some restrictions to the diffusion of ions into the narrower pores. These observations perfectly match with the pore size distributions obtained by DFT (Fig. 2).

## 4 Conclusions

The surfaces from the different carbon materials studied are equivalent for the electrosorption of NaCl. It has been demonstrated that both, mesopores and micropores, are equally effective in the adsorption process. Nevertheless, the kinetics of the process is influenced by the pore size distribution of the carbon, although it is rather fast for all the carbons studied. The chemically activated carbon, KOH-AC, seems to be the most suitable for electroadsorption of NaCl due to the combination of a high surface area and suitable pore size distribution.

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