

LITHIUM ELECTROSORPTION ON ACTIVATED CARBONS

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Introduction

Activated carbons are interesting sorbents which are able to trap trace amounts of metallic ions such as copper, lead, zinc, cadmium, mercury and chromium [1-2]. The amount and the nature of the surface groups generally exert stronger influence than surface area and porous texture in the adsorption of inorganic compounds from aqueous solution [3]. There are only few studies reporting the sorption of alkali metals in trace amounts on activated carbons, or the use of electrical polarization to improve this phenomenon [4-6]. Here we give the results of reversible electrosorption of low concentration lithium solutions by activated carbons.

Experimental

For the electrosorption experiments, the working electrode was the activated carbon in tight contact with a graphite rod used as current collector. A platinum grid served both as an auxiliary and a reference electrode in order to avoid the pollution of the solution by other ions which could diffuse from a classical reference electrode. The activated carbon used was a highly microporous physically activated carbon with a BET surface area of 1500 m²/g. For the electrosorption of lithium ions, a fixed polarization of -4.5 V was applied, and it was reversed for the desorption.

Aqueous lithium solutions were prepared from lithium hydroxide monohydrate, LiOH.H₂O, dissolved in 0.09 mol.l⁻¹ boric acid, H₃BO₃. Most of the experiments were realized with 100 ml of 7 ppm lithium solution and 1 g of carbon. The evolution of lithium concentration during sorption/desorption on carbon was monitored by atomic absorption spectrometry (Perkin Elmer 3300) on samples of the solution (2 ml) taken out at various times.

The concentration of carbon surface groups was determined according to Boehm method of titration [7]. In some cases their amount was varied by oxidation with 69 % nitric acid for 3 or 4 hours at 80°C.

Pulse galvanostatic and potentiostatic methods were used for the determination of electrolyte resistance and electric capacitance of carbon, using 7 ppm and 78 ppm lithium solutions. An electric model was applied in which the double layer capacitance and the charge transfer resistance are in parallel, and in series with the electrolyte resistance. After the resolution of differential equations, the analytical solutions were compared to the experimental recorded curves in order to optimize the values of the three elements of the electric circuit.

Results and Discussion

According to the results of surface groups titration, the total acidity, especially of carboxylic type, is enhanced by nitric acid oxidation (table1). Phenolic groups are more numerous after washing of the raw material. This could be due to the elimination of some ionic impurities which were linked to these groups and/or to the hydrolysis of ethers or lactonic groups.

Table1. Concentration of surface groups in meq/g of activated carbon after different treatments.

Sample	raw	washed	oxidized 3h	oxidized 4h
COOH	0	0	0.7	0.7
Lactonic	0.1	0	0.4	0.5
Phenolic	0.2	0.5	1	0.9
Carbonyl	0.4	0.4	0.5	0.6
Total	0.7	0.9	2.6	2.7

Without applying a polarization, the pristine carbon sample could not reduce the concentration of lithium ions (figure1). After oxidation by nitric acid, the sorption efficiency was enhanced even if surface area was reduced to 1250 m²/g: 93 % of the lithium ions were sorbed from the 7.1 ppm solution within less than 4 hours, i.e. 0.1 meq/g of carbon.

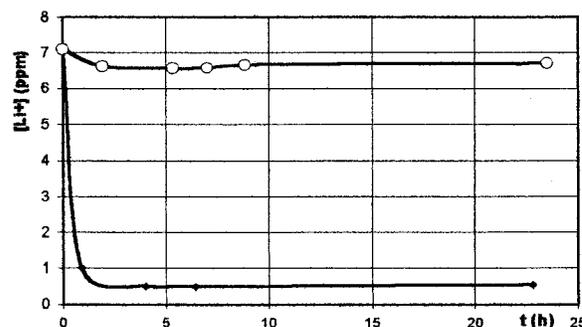


Figure 1. Chemical adsorption from 7.1 ppm lithium solution (100 ml) on 1g of activated carbon : (o) raw; (•) oxidized 3 hours.

If a polarization of -4.5 V was applied on the raw carbon material, the concentration of lithium in the solution was easily depressed and reached 0.6 ppm (0.095 meq of lithium adsorbed/g of C) after 25 hours (figure 2). In the same conditions, the oxidized sample gave a little bit better efficiency than without polarization, and only 0.1 ppm of

lithium remained in the solution (1.0 meq Li trapped per g of C) after 3.5 hours (figure 3). The most remarkable observation however, whatever the kind of carbon, oxidized or not, is that reversed voltage allowed to control quickly the desorption of trapped lithium, even if it was previously chemically adsorbed (figures 2 and 3).

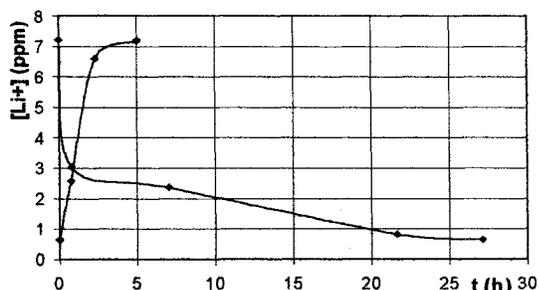


Figure 2. Electrochemical adsorption and desorption from a lithium solution (100 ml, initially 7.2 ppm) by 1g of activated carbon.

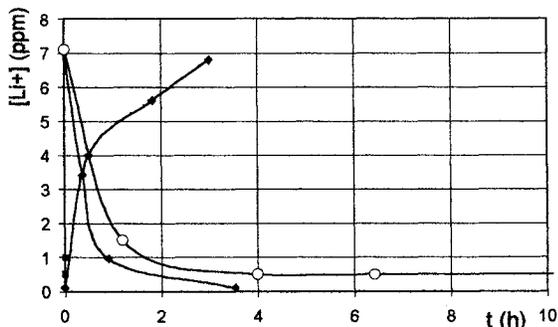


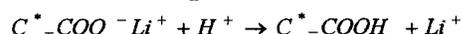
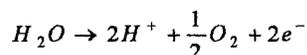
Figure 3. Chemical adsorption (○) and electro-chemical (◆) adsorption/desorption from a lithium solution (100 ml, initially 7 ppm) by 1g of oxidized activated carbon.

For an estimation of the electric parameters of the cell, pulse galvanostatic and potentiostatic methods were used for non oxidized carbon only, in order to reduce the effects of chemical sorption which would modify lithium concentration in the solution, and consequently its conductivity. The estimated electrolyte resistance was 280 Ω for the 7 ppm lithium solution, and 30 Ω in the case of 78 ppm. The value of charge transfer resistance was 2000 Ω and it did not noticeably change with concentration. The double layer capacitance varied from 25 to 55 mF/g by changing lithium concentration from 7 to 78 ppm. Consequently, a polarization of -4.5 V charges an electrical double layer ($Q=CV$) of 1.2×10^{-3} meq/g and 2.6×10^{-3} meq/g of carbon for the two solutions respectively. The number of lithium ions cumulated by this process is much more lower than the values observed. On the other hand, charging an electric double layer is a fast phenomenon which does not need hours.

If the oxidized carbon was stirred for 18 hours with 100 ml of 200 ppm solution of lithium, 0.7 meq of lithium / g of carbon were adsorbed. It shows that only the carboxylic groups (table 1), with the highest acidic strength, were saturated. Hence we can expect these groups to be responsible for the chemical sorption by protonic exchange.

In another experiment, the oxidized sample (1 g) in contact of 100 ml of 200 ppm lithium solution was polarized during 4 hours and it offered an adsorption of 1.1 meq of lithium / g of carbon. By comparison with table 1, we can suggest that carboxylic groups share the sorption with other surface groups, such as phenolic and lactonic.

In the case of electrodesorption of lithium, the following reactions take place, where *C stands for the carbon substrate:



The results presented here tend to demonstrate that surface groups are mainly responsible for lithium electro-sorption. However, we noticed that some other activated carbons with rich surface functionality could not adsorb lithium efficiently. As already suggested, the porous texture may interfere in this phenomenon [6]. Therefore in the future, relation between pores distribution and lithium sorption should be studied more carefully.

Conclusion

Reversible electrosorption of lithium ions in aqueous solution by activated carbon was successfully realized. Charging an electric double layer is not the main reason for the sorption, and the high value of charge transfer resistance may be a sign that electrochemical ionic exchange is a slow reaction. Carboxylic and more weak surface groups participate in this phenomenon, provided that use of polarization favors their dissociation.

References

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