

COMPETITIVE ELECTROSORPTION OF LITHIUM AND VARIOUS IONS BY ACTIVATED CARBONS IN WATER MEDIUM

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Introduction

Porous carbons are extensively used for the recovery of various species, in particular for metallic ions. While heavy metals or transition metals are in general sorbed chemically [1-2], a negative polarization of carbon is necessary for the sorption of alkali ions. Advantage of the later process is a possible desorption of the ions by reversing the current [3]. A mechanism which involves the ionization of the surface groups has been proposed for the reversible electrosorption of lithium [4-5]. The purpose of this work is to investigate the competition of different ions with lithium upon applying an electrical polarization to carbon.

Experimental

We used a physically activated carbon (PA) with a highly developed micropore volume and a BET specific surface area of 1500 m²/g. The main surface groups titrated [6] were lactones (0.1 mmol/g), phenols (0.2 mmol/g) and carbonyls (0.4 mmol/g).

An aqueous mother solution was prepared by dissolving lithium hydroxide in 0.09 mol.l⁻¹ boric acid (H₃BO₃) until lithium concentration reached the value of 7 ppm.

To study the competition of alkali ions (Na⁺ and K⁺) with lithium, sodium hydroxide and potassium hydroxide were introduced into the previous solution to obtain 48.3 ppm of sodium and 56.2 ppm of potassium.

The interference of the 2nd group metal ions was studied for magnesium. Mg(OH)₂ and MgCl₂ were introduced in the lithium solution for getting low or high magnesium concentrations, respectively.

For transition metals we selected either cations i.e. Ni²⁺ or complex ions, i.e. CrO₄²⁻. The interference of nickel ions was studied on mixtures prepared either by stirring the mother solution with nickel oxide NiO to obtain a nickel concentration of 1.5 ppm, or simply by introducing nickel chloride NiCl₂ until the concentration reached 58 ppm. Chromic oxide CrO₃ was used as well to prepare a solution containing 54 ppm of chromium.

Ammonia or phosphoric acid were added to the mother solution in order to reach 16.7 ppm of NH₄⁺, or 40.5 ppm of phosphate PO₄³⁻.

The electrochemical cell included the working electrode from activated carbon (~ 1 g) in tight contact with a graphite rod used as a current collector and a platinum grid which served both as auxiliary and reference electrode. Most of the experiments were performed with 500 ml of the solution to be investigated. In these conditions, the initial amount of each ion was higher than the total concentration of surface groups on the carbon substrate. The cations were trapped with a polarization of -4.5 V, and it was reversed for the desorption.

Small volumes (2 ml) were taken from the solution during the application of a constant polarization. The concentration of the metallic ions was measured by atomic absorption spectroscopy. The ammonium and phosphate concentrations were monitored by UV-visible spectroscopy using the Nessler method and the phospho-vanadomolybdate complex, respectively.

Results and Discussion

In the mechanism of lithium electrosorption which we already established [4-5], electrolysis of water is essential to create a local change of pH on the surface of activated carbon. Upon applying a negative polarization, OH⁻ ions are produced that provoke the dissociation of the surface groups and subsequent trapping of lithium. Reversed polarization depresses the surface pH through water oxidation, and lithium is recovered in the solution. Three parameters should be taken into account for discussing metal ions trapping by an activated carbon in boric acid medium :

- The redox potential :
Metal cations with a relatively high redox potential are reducible electrochemically (transition or heavy metals) or even chemically (noble metals) on the carbon surface. Alkali or alkali-earth metal ions are not reducible in aqueous medium;
- The solubility of the metal borate or hydroxide:
Most of the transition and alkali-earth metal borates or hydroxides are insoluble or very slightly soluble in aqueous solutions ;
- The kind and amount of surface groups :

At pH~7, only carboxylic groups are dissociated and can chemically trap cations. A negative polarization produces a locally high value of pH on the carbon surface, allowing the dissociation of lactones and phenols which become able to trap more cations [4].

Finally we should note that when chloride salts are used, the electroadsorbed cations are replaced by H⁺ in the solution. The pH of the solution decreases to a value of ca ~2.5, while it keeps constant at about 5.15 when hydroxides or borates are used due to the buffer effect of the H₃BO₃/H₂BO₃⁻ mixture when H⁺ are liberated in the solution.

Alkali ions

Alkali ions are not reducible in aqueous medium and their borate salts are soluble. Their trapping mechanism is the same as for lithium. Competitive sorption was measured on the lithium/sodium/potassium mixture. Figure1 gives a plot of C/C₀ for each ion in the solution versus the polarization time; C₀ stands for the initial concentration and C for the concentration after a given time of polarization. Typically of cationic exchangers, the efficiency of electroadsorption increases from lithium to potassium, i.e. with a decreasing radius of solvated ion.

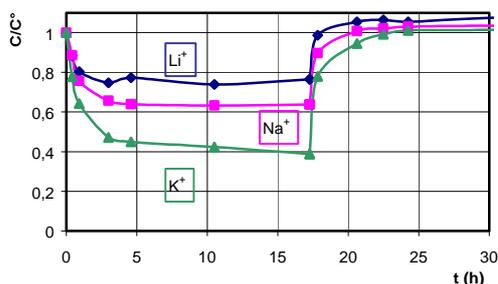


Fig.1. Competitive electrochemical adsorption and desorption in a mixture of Li⁺ (C₀=1mmol/l), Na⁺ (C₀=2.1 mmol/l) and K⁺ (C₀=1.44 mmol/l).

A separate experiment demonstrates also that ammonium is also more electroadsorbed than lithium (Fig.2).

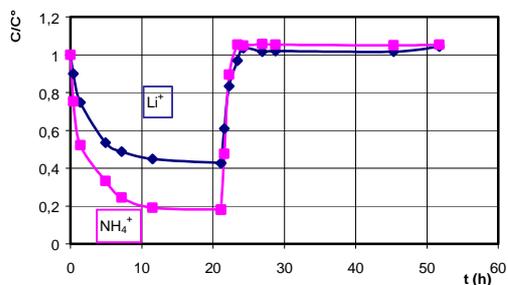


Fig.2. Competitive electrochemical adsorption and desorption of Li⁺ (C₀=1.1mmol/l) and NH₄⁺ (C₀=0.93 mmol/l)

Magnesium ions

All alkali-earth borate and hydroxide salts have a low solubility. Experimentally, magnesium ions are completely adsorbed by the carbon PA negatively polarized, though their amount in solution (1.3mmol) is higher than that of the surface groups (0.7mmol/ g of C) (Fig.3). The high value of local pH on the carbon surface allows magnesium hydroxide and/or magnesium borate to precipitate in the pores producing a total electroadsorption of Mg²⁺.

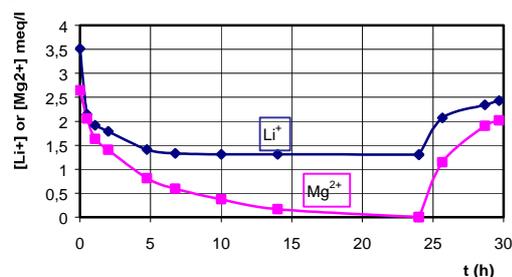


Fig.3. Competitive electrochemical adsorption and desorption of lithium (C₀=3.51 mmol/l) and magnesium (C₀=1.33 mmol/l)

Transition metal ions

The electroadsorption of transition metal ions is much more complicated because of several parameters involved in the mechanism. These ions are either trapped by the surface groups, precipitated in the pores as borate or hydroxide salts, or reduced to a lower oxidation number.

The result of competitive electroadsorption of nickel and lithium is shown in figure 4. Since they are electrochemically reducible in water medium, a metallic layer is formed on the surface of the current collectors through the application of -4.5 V. By reversing the voltage, the nickel concentration increases first as the metal is dissolved in the solution, and a similar process of deposition occurs on the auxiliary electrode which is now at a negative value of voltage.

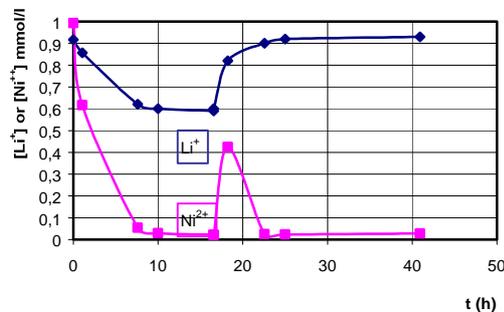
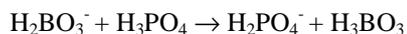


Fig.4. Competitive electrochemical adsorption and desorption of lithium (C₀=0.92 mmol/l) and nickel (NiCl₂; C₀=1 mmol/l of Ni)

Phosphate ions

When phosphoric acid is added to the mother solution which contains lithium hydroxide and boric acid, the following acid-base reaction takes place, showing that only dihydrogenophosphate anions are present :



Hence, the concentration of phosphate species does not change through a negative polarization of the activated carbon (Fig.5), but it is almost totally depressed by a positive polarization of PA.

We have already proved that the contribution of the electrostatic effect to lithium electrosorption is negligible [4]. This property may also be applied to phosphate species. The diffusion of ions in the pores of carbon is rather slow, and a positive polarization creates locally a low pH. This high concentration of hydronium ions in the pores of carbon is neutralized by the migration of H_2PO_4^- ions which progressively disappear from the solution.

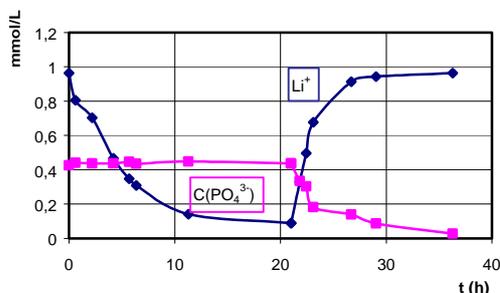


Fig.5. Competitive electrochemical adsorption and desorption of lithium ($C_0=0.96$ mmol/l) and phosphates ($C_0=0.51$ mmol/l)

Conclusion

Lithium and other ions present in an aqueous solution are reversibly trapped when an electrical polarization is applied to activated carbon. The competition is generally comparable to that of cationic exchangers in the case of ammonium and alkali ions. For the other species, several parameters may complicate the phenomenon. In the future, the relation between pore size distribution and ions diffusion should be studied more carefully.

References

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