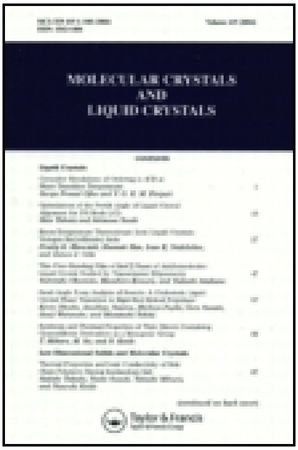

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Sodium Reactivity With Anthracitic Carbons AT 700°C

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SODIUM REACTIVITY WITH ANTHRACITIC CARBONS AT 700°C

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Abstract The reaction of sodium with an anthracite sample is studied at 700°C for various sodium relative pressures and is compared to the simple case of intercalation in a pitch coke. The behaviour of the anthracite sample is similar to that observed with non graphitizing carbon : intercalation and capillary condensation take place simultaneously. The sodium intercalation is found to be very sensitive to the previous heat treatment temperature of the sample, which determines the extent of order, and perfection of the carbon layers.

INTRODUCTION

This work is related to the interaction of sodium with anthracites. Indeed, this particular non graphitic carbon is widely used as a cathodic material in the aluminium electrolysis cells, and there is a general agreement that the penetration of sodium atoms in the carbon lattice is responsible for the swelling and the subsequent destruction of the electrode [1].

The interaction of sodium in non-graphitic carbons have been studied by several authors [2-7], and it has been shown that different phenomena may occur. As regards the graphitizing carbons (pitch-coke, petroleum-coke...), an intercalation is actually observed, and the lower the heat treatment temperature (HTT) of the coke, the greater the intercalation. Such an intercalation is also observed in the non graphitizing carbons. It seems that they behave, with respect to heat treatment temperature as graphitizable carbons do. However, the amount of intercalated sodium, as determined from X-ray diffraction, cannot be considered as being related to chemical analyses. A sodium excess is always evidenced; it can be attributed to capillary condensation in the porosity of the material.

Very few studies [2] are available concerning the intercalation of sodium with anthracitic carbons, which can be assumed to behave like a hard carbon.

We present in this paper some preliminary results about the behaviour of one particular anthracite sample, heat treated between 1000°C and 2400°C with a reaction temperature kept constant at 700°C. The effect of the sodium relative pressure is examined, and the results are compared to the simple case of intercalation in a graphitizable carbon.

EXPERIMENTAL

We made use of two sets of carbon samples : a pitch-coke heat treated from 800°C to 2400°C, and an anthracite heat treated from 1000°C to 2400°C. Heat treatment was carried out in a pure nitrogen atmosphere in a commercial graphitization furnace.

Sodium being liable to react with pyrex glass, the preparations of the sodium-carbon compounds have been conducted in two different reactors made of refractory steel, similar to those described by Metrot [2]. In the first one, the sodium relative pressure is about 0.2 while in the second one, it is about 0.9. In all cases, the carbon temperature is kept constant at 700°C, and the reaction duration is five hours.

The sodium content is determined by means of a boiling-water extraction and a subsequent titration of the resulting alkaline liquor. As the reaction products are extremely sensitive to air, for the X-ray diffraction analysis, we used capillaries the ends of which were stopped by sealing wax. The Co K_α radiation was used.

RESULTS AND DISCUSSION

a)pitch-coke

The variation in the sodium uptake for the pitch-coke, as a function of the heat treatment temperature (HTT) is plotted in fig. 1. The sodium uptake is found to be maximum for a 800°C HTT, after which it decreases, and then becomes insignificant above 2200°C. Also plotted in fig. 1 are the results obtained by Robert et al [7], for a carbon temperature of 380°C and a sodium relative pressure about the unity. Our results are in perfect agreement with the above mentionned ones. X-ray analyses indicate a displacement of the (002) line, with an increase of the c-axis parameter corresponding to an intercalation phenomena. Indexing the (00l) reflexion, using a sodium layer thickness of 1.28 Å and an atomic ratio C/Na of 8, leads to the results listed in table 1. In that case, the sodium uptake is only attributed to the intercalation. Adsorption and capillary condensation can account for only an insignificant fraction of the sodium content. However, it must be pointed out that the formation of regularly stacked stages in particular for high stage numbers cannot be very clearly observed in such poorly organized carbons. It was not possible to observe bands corresponding to sodium, either in a superstructure or in non-epitaxic compounds, as it is found for example in the potassium-carbon compounds.

Finally, our results and those of Metrot et al [2, 5] or Robert et al [7] prove that the sodium content of these products is quite independant of the carbon temperature (from 300°C to 700°C) and the sodium relative pressure (from 0.2 to 0.9).

TABLE I Chemical analyses and stages (determinated by X-ray diffraction) for the intercalation of sodium in a pitch coke.

HTT	Chemical analyses	stage (assumed)
800	NaC_{11}	2
1100	NaC_{22}	3
1400	NaC_{25}	3
1600	NaC_{40}	4 + 5
1800	NaC_{48}	6
2000	$Na C_{120}$	-

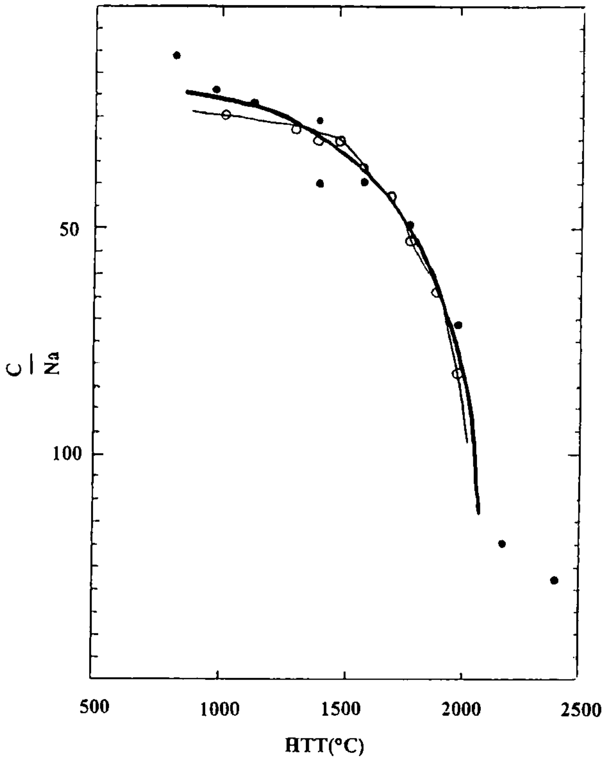

FIGURE 1 Variation in the amount of sodium intercalated in a pitch-coke as a function of HTT.
Full line : data of Robert et al, full circles : this work, $P/P_S = 0.9$, open circles : this work, $P/P_S = 0.2$.

b)Anthracite

The variation in the sodium uptake in the anthracite samples as a function of HTT is plotted in fig. 2. For the low relative sodium pressure, the results are similar to those obtained for a graphitizable carbon, in particular for a HTT lower than 1600°C. Above this HTT, the sodium uptake in slightly higher. For the high sodium relative pressure, only compounds with a composition close to that of NaC_{20} are obtained for the samples heat-treated below 2000°C. X-ray examination of the reaction products also indicates a displacement of the (002) line. These displacements are the same whatever the sodium relative pressure, and in fact, are very similar to those obtained for pitch coke at an equivalent HTT.

Thus, the sodium intercalation, with respect to HTT, is similar in these carbons : less and less sodium is intercalated, as the order and perfection of the carbon layers improve, due to the increase of the HTT. This has been interpreted in terms of position of the Fermi-level :When the Fermi-level is lower, the intercalation is greater. It is clear that the intercalated sodium does not correspond to the whole sodium content in these compounds. As it is known for non-graphitizing carbons, the sodium excess corresponds to the sodium condensed into the carbon porosity.

From the displacement of the (002) carbon line, it is possible to estimate the amount of intercalated sodium and, referring to the chemical analyses, the amount of sodium condensed in the porosity. These values, listed in table 2, show that the amount of sodium condensed in the porosity of the material reachs a maximum near a 1800 °C HTT. This observation must be correlated to the evolution of the microstructure of the anthracites as a function of HTT. It is known from X-ray diffraction [8], or high resolution electron microscopy [9] that anthracites are heterogeneous compounds which behave like non-graphitizing carbons below 1800-2000°C, and like soft or graphitizable carbons above 2200-2500°C. The particular shape of the pores (flat ones) is responsible for this behaviour : it induces a preferential orientation of the carbon planes above 1800°C, which in turn allows a progressive graphitization to occur with a progressive coalescence and collapse of the pores. Small angle X-ray scattering investigations of the pore structures change [10] during the graphitization of an anthracite also indicate a maximum of internal voids near a 1800 °C HTT. Thus, the condensation of sodium reflects the internal porosity of the anthracite.

TABLE II Estimates of the amount of intercalated and condensed sodium in an anthracite.

HTT	Chemical analysis	d_{001} (Å)	Na intercalated	Na condensed	Porous volume (cm^3/g)
1000	NaC_{18}	-	-	-	
1200	NaC_{21}	3.80	NaC_{25}	NaC_{130}	0.02
1400	NaC_{21}	3.77	NaC_{28}	NaC_{84}	0.025
1600	NaC_{19}	3.70	NaC_{40}	NaC_{36}	0.05
1800	NaC_{19}	3.67	NaC_{48}	NaC_{31}	0.06
2000	NaC_{25}	3.56	NaC_{64}	NaC_{41}	0.05
2200	NaC_{47}	3.37	-	NaC_{47}	0.04
2400	NaC_{53}	3.36	-	NaC_{53}	0.035

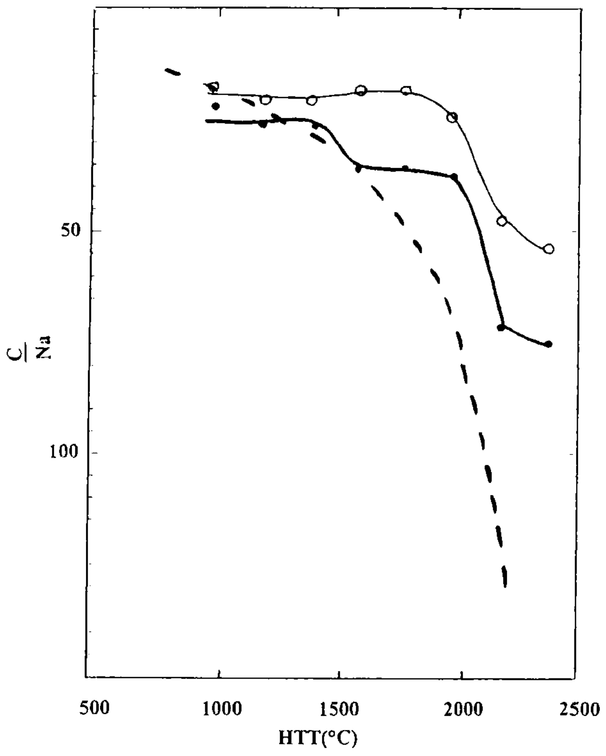

FIGURE 2 Variation in the amount of sodium intercalated in the anthracite sample as a function of HTT.
Full line : data obtained with the pitch-coke, full circles : anthracite samples, P/P$_S$ = 0.2, open circles : anthracite samples, P/P$_S$ = 0.9.

CONCLUSION

Sodium is intercalated in anthracites in quantities which are comparable to those known in graphitizable carbons. Less and less sodium is intercalated, as the order and perfection of the carbon layers improve due to the increase of the HTT.

For the high sodium relative pressures, a sodium excess is evidenced which corresponds to condensation in the porosity of the material. It reflects approximately the internal porosity of the samples. However, more data are necessary to give a complete picture of the formation of sodium-anthracites compounds. Further work will be done in this way, including examinations at different carbon temperatures for anthracites of different origins. The correlation of these data to structural and textural data may provide us with valuable information concerning their use in cathodic materials for aluminium production.

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