

INTERCALATION PROPERTIES OF THE CARBON LINERS OF ALUMINUM REDUCTION CELLS

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Introduction

The carbon lining of Al reduction cells does swell during its life as a cathode. This is believed to be caused by penetration of the carbon layer planes by the sodium produced by the action of Al on NaF. The nature of the solid solutions of Na in various carbons has been studied by Dewing(1) using an electrolytic technique. He found an activity coefficient which increased by a factor of 10^2 over the range of 1200° to 1800°C for the heat treatment of the carbon. He noted that the Fermi level also rises with temperature of treatment and, because Na intercalation involves a transfer of electron charge to the carbon layer planes, he concluded that intercalation would be favored by a low Fermi level and therefore a low temperature of heat treatment. Indeed, he found maximum swelling in the presence of Na for the carbon treated at 1200°C. This influence of temperature on the extent of Na intercalation has been confirmed by Metrot and Herold(2) and by Pflugmacker and Boehm(3). The latter found a surprisingly small increase in average interlayer spacing - only 0.045 nm for the maximum composition of $C_{12}Na$ and less for carbon blacks treated above 1200°C. They concluded that the Na was intercalated in an irregular fashion with preference for those parts of the structure where the distance between layers is wider than the X ray average. This is again in agreement with the work of Dewing(1) who found no steps and therefore no stages of composition in his system.

It is noteworthy that the early work of Fredenhagen(4) showed that K, Rb and Cs all gave C_8M with not only natural graphite but also with charcoal and lampblack. This has recently been confirmed by Salzano(5) for Cs in graphitized and non graphitized carbon blacks. The lack of an effect of graphitization and therefore of Fermi level on composition could be accounted for by the fact that the ionization potential of these three metals is lower than for Na.

It occurred to us that carbons could also be characterized by noting the uptake of an electron accepting intercalator. In this case, the content should be higher for carbons with the higher Fermi level that comes from a higher temperature of treatment. This has indeed been noted for Br_2 . However, the amount of Br_2 intercalated by low temperature carbons is negligible. We therefore chose an electron acceptor which, in natural graphite, has a much lower threshold pressure for intercalation than has Br_2 . This is $AlCl_3$ for which the threshold is $<10^{-6}$ relative to saturation as compared with 0.1 for Br_2 . It will indeed intercalate pot liner carbon and has the added advantage that the amount intercalated can be differentiated from the amount adsorbed on a surface. This is because, in the absence of Cl_2 , no uptake occurs in natural graphite of low surface

area even in saturated $AlCl_3(g)$ at the BP of 180°C(6). The inclusion, however, of <20 torr Cl_2 allows rapid intercalation to give $C_{3.5}AlCl_3 \cdot 0.25 Cl_2$ (6). Hence, in carbons of higher surface area, one run is made on each of 3 samples, all at 180°C. One in $AlCl_3(g)$ just below saturation, a second in pure Cl_2 at 500 torr and a third in $AlCl_3(g)$ just below saturation + 500 torr of Cl_2 . The sum of the first two is assumed to be adsorption and is subtracted from the third one to give the amount intercalated. This has been applied to carbon blacks and fibers(7) and is here applied to cell linings and associated materials.

Experimental

The original liner, the liner used for 3000 days and the electrically calcined anthracite (ECA) were ground, sieved and treated with boiling 6M HCl to constant weight. This required 30 hr. for the used liner, less for the others. The raw anthracite, pitch and tar were heated in a slow stream of N_2 to 500°C for a few hrs, then to 1000°C for 5 hrs. They were then ground and acid treated to constant weight. The % weight losses are shown in Table 1 and appear to be independent of sieve size for the original and used liner carbons. Duplicate samples were also reproduced.

The procedure for the intercalation runs on 0.3 gm samples has been published(7). In each case, any weight increase was treated as if it were $AlCl_3$ in calculating the molar ratios in Table 2. Again, reproducibility and independancy on mesh size were apparent. The expansion that should accompany intercalation was obvious. Thus, both the original and used cell material was, after intercalation, of much greater bulk volume - about a factor of two for the used material. It was also more porous and was blacker than before intercalation.

Discussion

The results for liner carbon are in accord with those of Dewing(1). Just as the electron donor Na was more intercalated by a carbon of low temperature of heat treatment and therefore of low Fermi level, so the electron acceptor $AlCl_3$ is less intercalated. Thus, raw anthracite treated for 5 hr. at 1000°C would not intercalate $AlCl_3$ but after electrical calcining (ECA) at 1700-1900°C would intercalate 19 units on the scale of Table 2. Similarly, whereas the original liner material intercalated 20 units, "use" for 3000 days at an average temperature of 900-950°C (maximum 1000-1050°C, minimum 850°C) raised this to 100 units. In fact the amount intercalated by this used liner carbon was about 80% of the amount intercalated by the highly ordered natural graphite. This is surprising, in view of the relatively low temperature of the liner during its life time. Since the graphitization has been found to occur in these lining materials in a very short period of time(8), it is postulated that free Na is a

prerequisite to such rapid structural changes. Holding anthracite at 1000°C for a short period of time (5 hr) did not produce any evidence of graphitization, and indeed there is no reason to believe that very long periods of time at this temperature would produce any graphitization.

The pitch and tar are interesting in that considerable intercalation of AlCl_3 does occur in samples heated for only a few hours at 1000°C. This is presumably because they initially contain a variety of large, flat, aromatic molecules which are able to align themselves in parallel sheets during the liquid phase of the heat treatment. Anthracites also contain large flat aromatic molecules but do not pass through a liquid phase on treatment of 1000°C. In the absence of the high mobility of a liquid phase, one must either extend the period of heat treatment, as with used liner carbon, or go to a higher temperature than 1000°C as with ECA.

It is of interest that both the original liner and the ECA intercalated 20 units of AlCl_3 . The liner contains 15% pitch and tar and 85% ECA and on a simple composition basis would be expected to intercalate 24 units of AlCl_3 . The difference however, could be caused by the fact that the heating cycle for the pitch and tar in the liner carbon was not the 5 hr at 500°C + 5 hrs at 1000°C used in this laboratory.

Table 1

	500°C	1000°C	6MHC1
Liner, original			
20-40 mesh			0.8
100-170 mesh			1.9
Liner, used			
20-40 mesh			40
100-170 mesh			41
ECA			0.5
Anthracite	4	3	0.6
Pitch	49	7	0.1
Tar	72	5	0.3
Percent weight decrease in N_2 stream or in boiling acid.			

Conclusion

Intercalation of disordered carbons by AlCl_3 is favoured by higher calcination temperatures. It is also enhanced by the prior reordering of the structure by intercalating sodium which occurs in all aluminum reduction cells during electrolysis. It is also favored by a liquid phase during the heat treatment of a pitch or tar. These are all factors that increase both the degree of graphitization and the Fermi level so that intercalation by an electron acceptor is favored. Dewing(1) has shown that such factors would decrease the intercalation of an electron donor such as Na. He therefore finds that a melt of Na_3AlF_6 and Al causes less swelling and hence less Na intercalation, in a carbon that had been heated to a higher temperature. Hence the measurement of AlCl_3 intercalation described in this paper might be of value in characterizing carbons for use as lining materials in Al reduction cells.

References

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Table 2

	1 AlCl_3	2 Cl_2	3 $\text{AlCl}_3 + \text{Cl}_2$	3-2-1 Inter- calated
Acid treated "Carbon"				
Natural graphite	0.0	0.0	120	120
Liner, original				
20-40 mesh	0.7	0.2	21.2	20
20-40 mesh	1.3	0	20.8	19
100-170 mesh	0.9	0.2	21.6	20
Liner, used				
20-40 mesh	2.8	0.1	102	99
3000 days				
20-40 mesh	5.5	0.0	106	100
100-170 mesh	3.0	0.1	96	93
ECA 1800C				
20-40 mesh	1	0	19.6	19
Anthracite 1000C				
20-40 mesh	0	0	0.5	0.5
Pitch 1000C				
20-40 mesh	1	0.3	50.8	49
Tar 1000C				
20-40 mesh	1	0.5	61.2	60

Weight increase as moles AlCl_3 per 1000 moles carbon.