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Ext. Abstract

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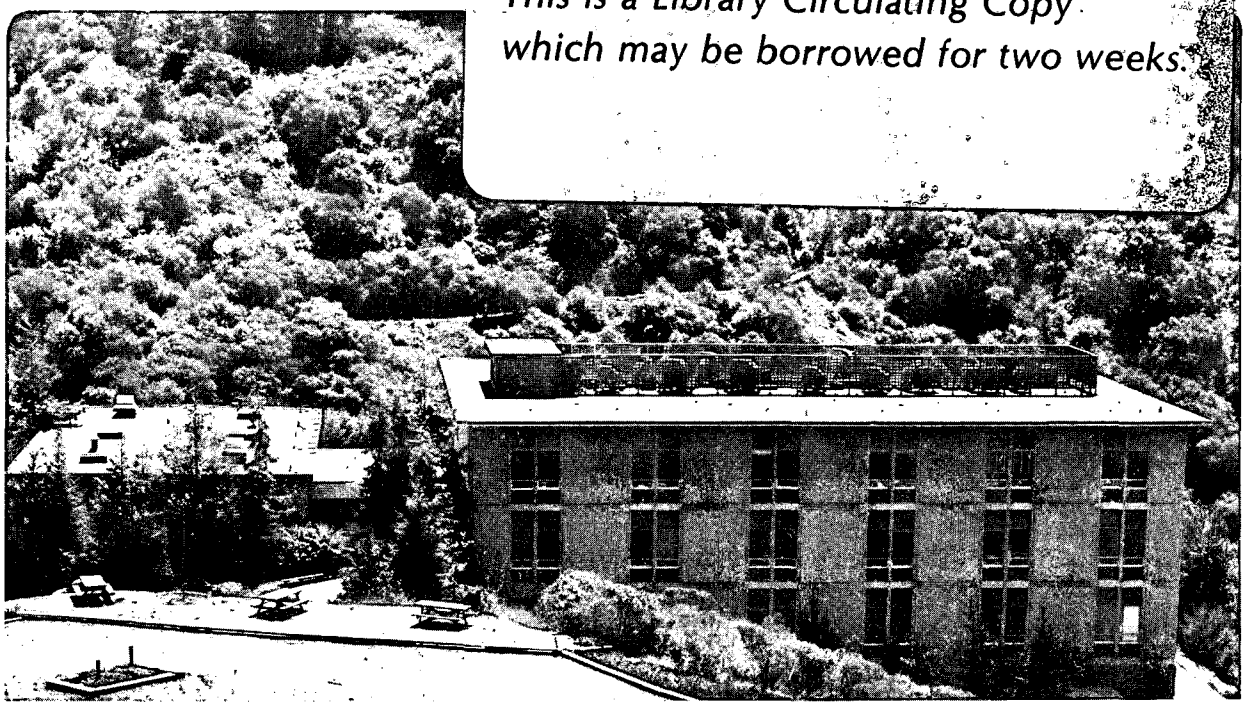

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THE CORROSION OF CARBON BLACK ANODES IN ALKALINE ELECTROLYTE: III. THE EFFECT OF GRAPHITIZATION ON THE CORROSION RESISTANCE OF FURNACE BLACKS

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Extended Abstract

A selection of furnace black carbons of varying surface area and industry type were heat treated in purified helium at 2700°C and the corrosion resistance measured under conditions of oxygen evolution in 30% KOH at 55°C. The extent of graphitization was determined by x-ray diffraction and by high resolution transmission electron microscopy. The experimental methods for corrosion measurement followed those reported previously (1).

Table I lists the furnace blacks studied using the Industry Classification and the ASTM (D1765) Classification where applicable. Also listed are the physical properties of these materials, and their graphitized forms, with which we attempted to correlate the corrosion behavior. The iodine adsorption measurements were performed for us at the Cabot Billerica Technical Center, Billerica MA; these are rubber industry standard measurements designated as ASTM-D1510. The particle size entry refers either to the prime particle size of the furnace black or to the characteristic width of graphitic bands in the graphitized black as observed by TEM.

As seen from the plots shown in Figure 1, separate correlations of the corrosion rate per unit mass with the BET surface area were observed for the furnace blacks and for the graphitized blacks, but each correlation had a relatively high standard deviation. The standard deviation from the best-fit line was greater than precision with which either the BET area or corrosion rate can be determined experimentally. We concluded that BET area was not a unique parameter even within a class of carbons, although it is a qualitative indicator of the rate per unit mass, i.e. a given class or type of carbon does not exhibit a single well-defined value of corrosion rate per unit BET area. Qualitatively, the corrosion rate per unit BET area of graphitized furnace blacks is about one-third that of the precursor furnace blacks.

If the corrosion rate per unit mass for a given material is not solely proportional to its area, then it is likely that some regions of the material are attacked preferentially to others. Chemisorptive methods could be useful in identifying at least the surface sites that serve as the nuclei for the initiation of corrosion reactions. To apply the chemisorption method, one looks for a correlation between the amount of a specific titrant adsorbed and the corrosion rate. As shown by Figure 2, a unifying correlation for both the ungraphitized and graphitized forms was observed between corrosion rate per unit mass and the iodine adsorption number. From this result alone, it appears that there are specific sites on the carbon surface (titrated by iodide) that serve as the initiators for dissolution of the carbon from the surface.

There are a number of conditions that apply to the correlation shown in Figure 2, the most important of these being the time-frame of the corrosion rate measurement. The time dependence of the current-potential relationship for a carbon black in the potential region of +400-600 mV vs. Hg/HgO in KOH is quite complex, as we have described in previous work (1). At any given potential in this region, we could distinguish three different time regimes of behavior: I. $t<10^2$ sec characterized by a corrosion current that decreases exponentially with time with a significant fraction of the anodic current consumed by surface processes (the oxidation products remain on the carbon surface); II. $10^2<t<10^4$ sec characterized by a quasi-steady state current and a material balance between external product and anodic charge; III. $t>10^4$ sec characterized by long period oscillations in corrosion rate and product distribution. The latter observation is new, and is the subject of a future publication. The time-frame applicable to the correlation in Figure 2 is the quasi-steady regime, using the current measured at 550 mV at 10^3 sec (corrected for oxygen evolution measured directly with a mass spectrometer). The current measurements in the short-time regime were not sufficiently reproducible to be used as a basis for correlation.

The correlation of the quasi-steady corrosion rate to the absolute number of surface sites having a specific kind of chemistry implies that these sites remain the points of attack even after a monolayer-equivalent of carbon has been removed from the surface. The chemistry of sites adsorbing iodide (in the ASTM method) is not entirely clear. The systematic variation in BET area to iodine

adsorption number ratio with the degree of graphitization suggests iodide adsorption is specific to edge-plane sites, e.g. in furnace blacks which have no basal planes the ratio is unity, but in the graphitized blacks the ratio is 3-5. However, there is no mention of iodide adsorption as a specific titrant for edge-plane sites on graphitic materials in the carbon chemistry literature. Carbon chemists use the preferential adsorption of n-paraffins from mixtures containing other paraffins to measure the basal plane sites, and adsorption of alcohols to measure the edge-plane sites (2). We have not used the hydrocarbon adsorptions on our materials as yet, so the conclusion that the edge-planes of the graphitized blacks are preferentially attacked, which would be the conventional wisdom, seems premature at this time.

It is clear that graphitization has a beneficial effect on the corrosion resistance of furnace black carbons, and that the effect is fractionally much greater for some types of furnace black. In particular, graphitization of SRF type carbon lowered the corrosion rate by a factor of 7, whereas with other carbons the factor was only 2-3. The degree of graphitization judged from the x-ray diffraction patterns and from the layer plane structures observed by TEM was also the highest for the SRF carbon, e.g. the x-ray diffraction pattern looks identical to that reported by Warren for graphitized Spheron 6 (3), a material usually referred to as Graphon by carbon chemists and regarded as a "standard" for graphitized carbon black. Graphitized SRF type carbons appear to be the most interesting class of carbons for technological applications utilizing carbon materials in oxygen

evolving anodes.

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Table I. Correlation of Physical Properties of Carbon Blacks and Corrosion Resistance.

Carbon Type	BET Area (m^2/g)	Iodine Adsorption (mg/g)	Particle[1] size (nm)	Corrosion[2] rate (% hr^{-1})
HCF-1	560	--	13	>10
HCF-1 Graphitized	220	105	-	0.5
XCF	254	270	30	2.0
XCF Graphitized	128	65	3(L_c)	0.6
SAF (N110)	115	145	-	1.5
SAF Graphitized	85	55	-	0.5
HAF (N330)	80	82	27	1.0
HAF Graphitized	70	32	3(L_c)	0.3
RCF	85	83	25	0.5
RCF Graphitized	70	35	3(L_c)	0.15
SRF (N774)	25	32	80	0.15
SRF Graphitized	32	7	30(L_c)	0.02
Acetylene black	70	35	30	0.10

[1]Size of prime particles determined by electron microscopy.

[2]In 35% KOH at 50°C at 550 mV (Hg/HgO).

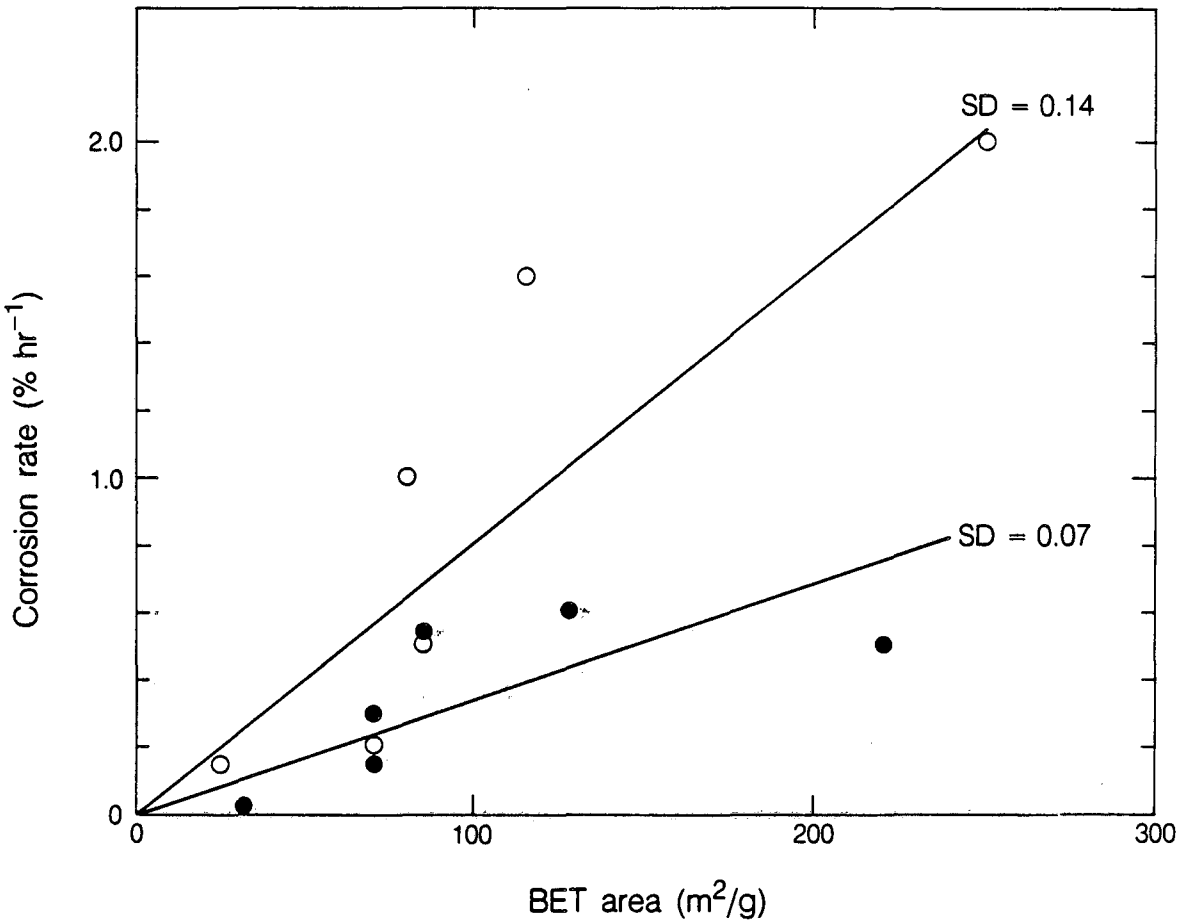

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Fig. 1. Correlation of corrosion rate with BET area for furnace blacks (o) and for graphitized furnace blacks (●).

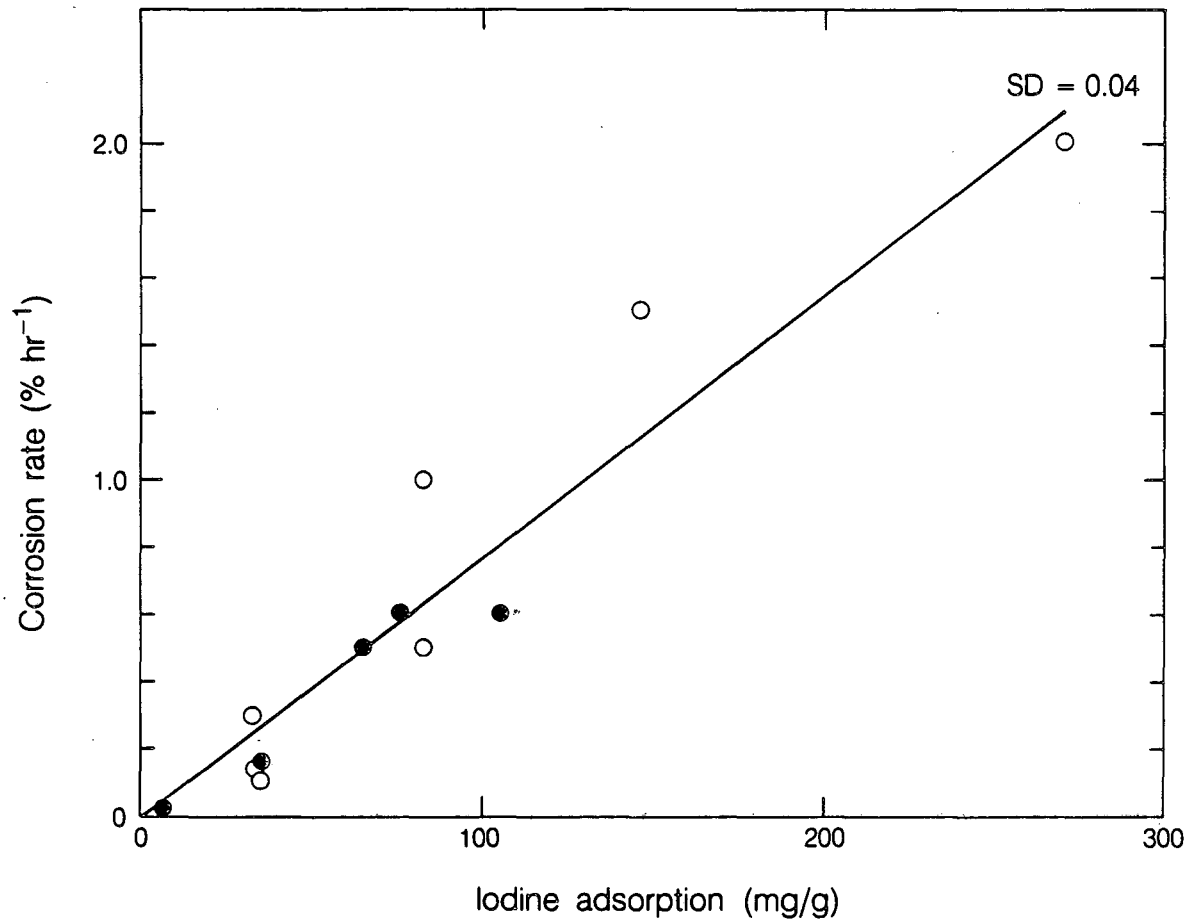

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Fig. 2. Correlation of corrosion rate with quantity of iodine adsorbed (as I^-) for furnace blacks (o) and for graphitized furnace blacks (●)

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