# OXYGEN CHEMISORPTION ON WELL CLEANED
# CARBON SURFACES*

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Graphon, a highly graphitized carbon black, was first oxidized to 14.4% weight loss in $O_2$ at 625°C to introduce significant active surface area. Following the cleaning of the activated Graphon surface by heating at 975°C in a vacuum of $10^{-8}$ torr, chemisorption of oxygen between 25-400°C was studied.

The apparatus used was the same as that described previously (1). The reaction system was connected to a modified General Electric mass spectrometer by means of a molecular flow leak. The total volume of the reaction system was $1.3 \times 10^4$ cc. Oxygen was admitted to the closed reaction system and its pressure measured continuously during adsorption. At temperatures below about 300°C, negligible concurrent gasification of the carbon, resulting in the production of CO and $CO_2$, occurred. At the end of a run, the system was first evacuated at reaction temperatures. The carbon was then heated to 950°C, with no pumping, to decompose the chemisorbed oxygen complex. A mass balance showed that 95-100% of the previously adsorbed oxygen could be recovered as CO and $CO_2$ within 6 hr at 950°C. No $O_2$ was found in the degassing products, even at lower temperatures. Since the total carbon consumed per run was very small (only about 0.03% burn-off), the same Graphon sample could be used for a large number of runs.

The maximum amount of oxygen that could be adsorbed on the surface of a 14.4% weight loss Graphon sample was measured between 25-400°C. This was done by exposing the "cleaned" Graphon to a pressure of 500 millitorr of $O_2$ until negligible further adsorption took place. For most temperatures, 24 hr was sufficient. Between 25-250°C the saturation amount of oxygen adsorbed increased only slightly with increasing temperature, between 250-300°C it increased sharply, and between 300-400°C it again increased only slightly. This behavior suggests the presence of at least two types of active sites on the activated Graphon surface. The maximum amount of oxygen adsorbed is estimated to occupy 2.8 $m^2$/g or 2.6% of the total surface. The rate of oxygen chemisorption on the more active sites is given by $dn/dt = k_o C n_\alpha (1-\theta)^2$, where $k_o$ is a rate constant, C is the $O_2$ concentration in the gas phase, $n_\alpha$ is the saturation coverage with oxygen on the more active sites, and $\theta$ is the fraction of the more active sites that are covered at time t. The rate constant equalled $7.14 \times 10^9 \exp(-7,400/RT)$ cc/sec mole $O_2$.

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Following a large number of adsorption-desorption cycles, the Graphon surface was additionally activated to yield (in part) a fraction of very active sites that are not produced at comparable burn-offs by higher temperature activation between 500-625°C.

Rates of oxygen (16-16) and oxygen (18-18) chemisorption on Graphon were compared at 200°C. The rate of oxygen (16-16) chemisorption was 5.3 ±1% greater than oxygen (18-18) chemisorption, which is closely predicted theoretically if the adsorption of oxygen is dissociative and the dissociation is involved in the rate limiting step.

The presence of different active sites on the Graphon surface is discussed in terms of portions of the basal plane being terminated by arm chair or zig-zag configurations and by one or two carbon fragments protruding out from these regular crystallographic configurations.

## References

1.  F. J. Vastola, P. J. Hart, and P. L. Walker, Jr., Carbon, 2, 65 (1964).