MORPHOLOGY OF CARBONS DEDUCED FROM PHYSISORPTION ISOTHERMS: I. NUCLEAR GRADE GRAPHITE,

E. Loren Fuller, Jr.

Lorela Enterprises, 1103 Eighth Street, PO Box 355, Stanton NE 68779-0355 USA
Telephone 308 439 2208, email Fullerel@stanton.net

Introduction

Currently, analyses of porous materials by physical adsorption of an inert gas involves comparison to a reference (standard, universal, t, n, α_s, θ, etc.) adsorption isotherm obtained for a chemically similar nonporous substrate(1,2). In this manner any excess uptake is attributed to porosity or other energetic anomalies in the material under analysis. Carbon exists in the form of diamond, graphite, amorphous, chars, activated chars, C60, etc., which are all chemically different in the thermodynamic sense. These substrates can and do inherently contain pores ranging from molecular size upward to large voids which leads to their commercial and academic importance as sorbents, membranes, molecular sieves, aerogels, etc.

Experimental

Nuclear Grade Graphite is, by necessity, free of the chemical impurities found in many carbon materials. This is a report of the nitrogen physical adsorption on H451 graphite that can serve as reference for comparative purposes for porous carbons. Monolithic near-isotropic structural graphite (H451) was obtained by high temperature (2700 °C) treatment of high purity graphitizable carbon in pure argon atmosphere. The nitrogen (99.999%) isotherm (77.2 K) is shown in Figure 1. Data were acquired after in situ 300C overnight outgassing with a Quantachrome volumetric instrument and no hysteresis was detected on desorption.

Results and Discussion

Data analyses with the Autoshielding Potential (ASP) methodology(3) precludes the use of reference (n, t, α_s, etc.) isotherms for the evaluation of relative amounts of internal (pore filling, absorption, etc.) and external (adsorption) sorption processes as presented in Figure 2. The ASP isotherm relates the amount sorbed to the adsorption potential, E:

$$E = -RT \ln [P/P(0)] \qquad \text{Equation 1}$$

to the amount of adsorption, Γ:

$$E = E(zero) \exp[-\Gamma] \qquad \text{Equation 2}$$

The initial linear regime indicates that there may be some microporosity between the graphite grains or other high energy sites on the surface. [note that these data are for pressures, (Γ) below those noted for most reference data]. The extended linear portion (0.04 to 0.94 P(0)) is attributed to unhindered monolayer-multilayer

formation on the surface, followed by pendular ring capillary condensation in mesopores(4) of dimension, d:.

$$d \propto [-RT \ln (P/P(0))]^{-1} \qquad \text{Equation 3}$$

or in dimensionless terms

$$d \propto [E/RT]^{-1} . \qquad \text{Equation 4}$$
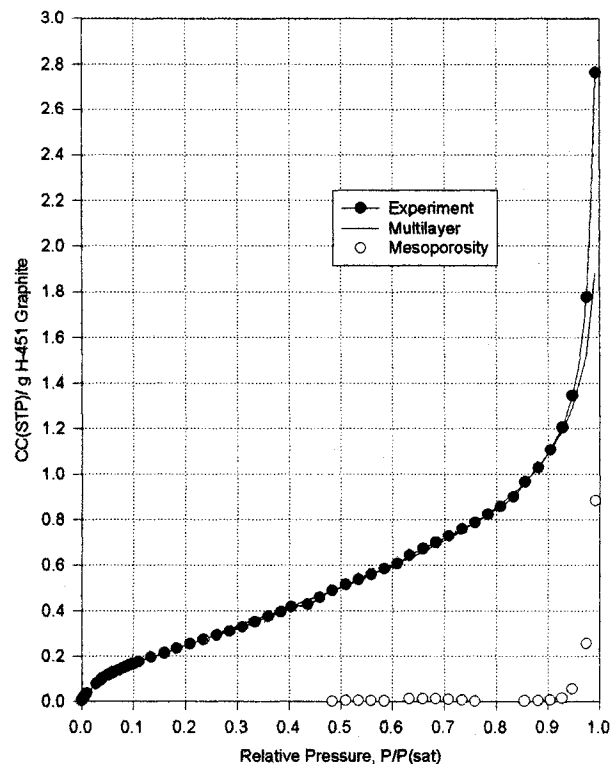
Figure 1. Adsorption Isotherm: Nitrogen on H451 at 77 K.

We can then note the rectilinear relationship of Figure 3, without definition of pore shapes, morphology, liquid density, or surface tension.

Without detailed discussion, we note that the mesoporosity is of low (unity) fractal diminsionality, D:

$$D = d \ln(volume)/d \ln (size) = 1.00 \qquad \text{Equation 5}$$

for the open pores, roughness, facets, convolutions, etc. on the H451 surfaces, where the pore volume and size are proportional to the ordinate and abscissa, restpectively in Figure 3. The parameters and quality of the regression fit for each of the regions of Figures 2 and 3 are presented in Table 1.
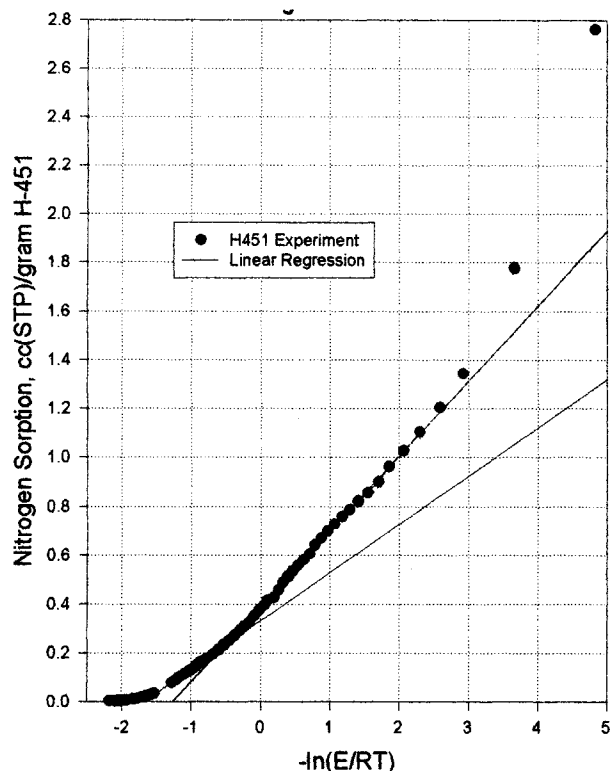
Figure 2. ASP Plot: Nitrogen on H451 at 77 K.

Table 1. Linear Regression Fit Parameters

Fig/#	Intercept	Slope		r squared
2/1	0.3309	0.1976	cc(STP)/g	0.9987
2/2	0.3887	0.3088	" "	0.9996
3/1	-0.0751	7.7375	" "	0.9978

Conclusions

- H451 is a relatively nonporous carbon.
- The isotherm data conform well to the ASP thermodynamic relationships, with
- Excess sorption is due to capillary condensation that exists for all arrays of powders in a gravitational field.
- The ASP isotherm data for porous materials will provide direct adsorption potential distributions for porosity or other high energy surface sites..
- There is no need for standard, reference isotherms. Each isotherm reflects the surface chemistry of the substrate directly.
- There is no adsorption at very low pressures, consistent with a finite vapor pressure (finite sorption potential. for the first adsorbed molecules.
- Mesopore capillary condensation is well defined by the Young-LaPlace thermodynamics.
- Other workers (5,6) have offered standard data that require additional analyses in terms of surface chemistry and morphology.
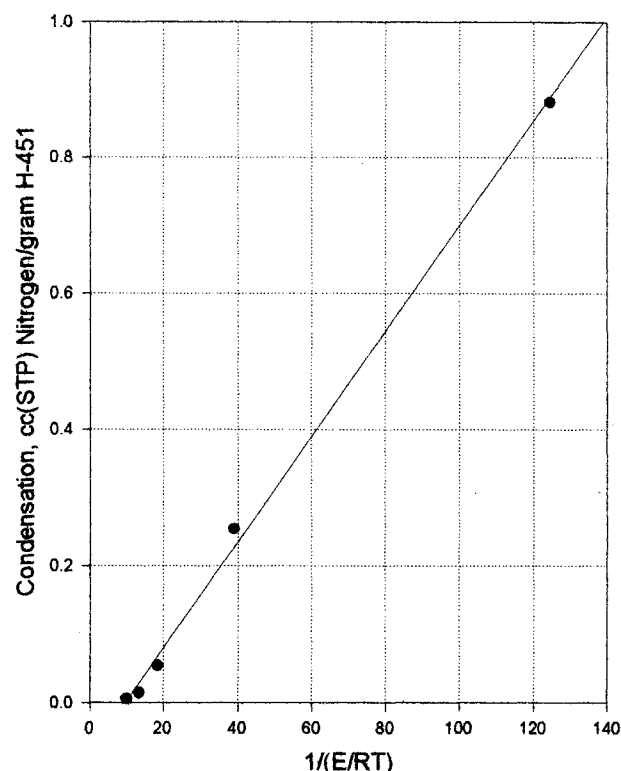

Figure 3. Mesopore Filling: Nitrogen on H451 at 77 K in accord with Young-LaPlace minisci.

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