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Characterisation of porous carbon electrode materials used in proton exchange membrane fuel cells via gas adsorption

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ABSTRACT

Porous carbon materials are typically used in both the substrate (typically carbon paper) and the electrocatalyst supports (often platinised carbon) within proton exchange membrane fuel cells. Gravimetric nitrogen adsorption has been studied at a carbon paper substrate, two different Pt-loaded carbon paper electrodes and three particulate carbon blacks. N_2 BET surface areas and surface fractal dimensions were determined using the fractal BET and Frenkel–Halsey–Hill models for all but one of the materials studied. The fractal dimensions of the carbon blacks obtained from gas adsorption were compared with those obtained independently by small angle X-ray scattering and showed good agreement. Density functional theory was used to characterise one of the carbon blacks, as the standard BET model was not applicable.

1. Introduction

The varieties of carbon [1] include activated carbon, carbon black, carbon fibres and carbon cloth, with clear definitions of these and all the forms of carbon as a solid described by Fitzer et al. [2]. In most catalytic applications, including proton exchange membrane (PEM) fuel cells [3], carbon-containing composites are the substrates under consideration. Carbon paper is often chosen as the substrate in PEM fuel cells and is usually prepared from the random weaving of carbon fibres, with the extent and nature of the surface area and porosity being dependent upon the precursor material and its manufacturing history.

Carbon blacks are often used as the support material for precious metal electrocatalyst coatings. Carbon blacks play a major role in structural components, conductive supports, and electrocatalysts in batteries and fuel cells. Such materials possess a relatively high surface area which is derived from the fine particle size of the material, rather than from porosity. Optimising the structural properties of carbon blacks is an important area of research due to their importance in fuel cell applications.

The characterisation of carbon blacks has previously been determined using a comparison of nitrogen and carbon dioxide adsorption at 77 and 298 K, respectively [4], atomic force microscopy [5], Raman and neutron scattering [6], X-ray diffraction [7], small angle X-ray scattering (SAXS) [8], transmission electron microscopy and small angle neutron scattering [9]. Xu et al. [10] used various gas adsorbates to investigate the structural properties of different grades of carbon blacks. Analysis of the data using the work of Pfeifer and Avnir [11] and Halsey [12] determined the fractal dimension of the materials.

Carbon fibre materials tend to have carbon content greater than 90%. Since the final carbon fibres contain almost 100% carbon, any fibrous material with a carbon backbone can potentially be used as a precursor which would yield a carbonaceous residue. Rayon and polyacrylonitrile are precursors for many of the commercial fibres that are produced, although other precursors such as pitch (a by-product of the petroleum or coal-coking industry), phenolic resins and polyacetylenes have also been used [13]. Gas adsorption is a common technique in the study of structural properties of carbon fibres; a review by Do and Do [14] has considered the adsorption of supercritical fluids (Kr, Ar, N and CH_4) on different porous and non-porous carbons. Studies using Kr [15–17] and N_2 [18,19] have also been performed. Techniques such as scanning electron microscopy and atomic force microscopy [20], X-ray diffraction and Raman spectroscopy [21], scanning tunnelling microscopy [22,23]

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Nomenclature

C	BET constant
d	fractal dimension
E_i	energy of adsorption
E_L	liquefication energy
n	amount of gas adsorbed (mol)
n_m	molecular capacity
N_A	Avagadro constant (6.023×10^{23} mol^{-1})
P	applied pressure (bar)
P_0	saturation pressure (bar)
R	molar gas constant (8.314 J mol^{-1} K^{-1})
T	temperature (K)
V	volume of gas adsorbed at equilibrium pressure (m^3)
V_m	volume of gas in monolayer (m^3)

Greek letter

σ	molecular cross-sectional area (nm^2)

and SAXS [24] have been used to investigate the structure and physical properties of carbon fibres.

The work presented here aims to interpret isothermal data, using a selection of established models, for a variety of important carbon materials that are typically and routinely used in PEM fuel cells. The materials include a carbon paper substrate for electrocatalysts and also two Pt-loaded electrodes. In addition, three carbon blacks, which are used as the electrocatalyst support, are examined. The results aim to give a quantitative and accurate description of the structural properties of these materials. Both classical and recently developed adsorption models are considered and the paper represents an ambitious attempt to fit these models to standard isotherms of practical PEM fuel cell carbons. Features of this paper include: (a) a quantitative consideration of several adsorption models, (b) classical adsorption models are complemented by modern, (e.g., modified fractal) ones, (c) adsorption data on carbon materials in the paper have not previously been reported, (d) not all of the materials can be fitted to simple adsorption models and (e) problems in applying adsorption models to certain carbons are highlighted.

2. Theory

2.1. Determination of surface area—the BET method

2.1.1. The BET model

The most popular technique for the determination of the surface area over a wide range of porous materials (the BET model) is the method proposed by Brunauer et al. [25]. According to the BET model, the molecules in one layer can act as possible sites for the adsorption of molecules in the next layer. When the rate of condensation (adsorption) is equal to the rate of evaporation (desorption), an equilibrium pressure, P, is achieved at a given temperature, T. For adsorption in each layer, the following expression applies:

$$a_i P\theta_{i-1} = b_i\theta_i \ \exp\left(-\frac{E_i}{RT}\right) \tag{1}$$

where θ_{i-1} and θ_i are, respectively, the fractions of surface covered by the $i-1$ and i layers, a_i and b_i are adsorption and desorption constants and E_i is the energy of adsorption for the ith layer. Each layer has a different set of values of a_i, b_i and E_i but it is assumed that for all layers after the first, these parameters remain constant and also that $E_i = E_L$, the liquefaction energy. Also, the assumption is made that E_i is not dependent on surface coverage, θ_i. This implies both a uniform array of surface sites and the absence of lateral interactions between the adsorbed molecules. A further assumption is made to the model, which is that the multilayer has an infinite thickness at $P/P_0 = 1$. This assumption allows the simplification of the summation of the amounts adsorbed in all layers and allowed the production of the BET equation:

$$\frac{P/P_0}{n(1-P/P_0)} = \frac{1}{n_m c} + \frac{C-1}{n_m c}\frac{P}{P_0} \tag{2}$$

where n_m is the monolayer capacity and C is an empirical constant.

According to the BET theory, the constant C is related exponentially to E_1 by the simplified equation:

$$C \approx \exp\left[\frac{E_1 - E_L}{RT}\right] \tag{3}$$

where the quantity $E_1 - E_L$ is termed the net molar energy of adsorption. The value of C is an indication of the adsorbent–adsorbate interactions, with high values ($C > 100$) indicative of high interaction strengths, whilst medium (<80) and low values (<20) represent medium and low interaction strengths.

The validity of the original BET equation is always confined to a limited part of the isotherm, which is seldom above $P/P_0 = 0.3$. The BET model does not take into account lateral interactions between the adsorbed molecules in the first layer, and assumes that all higher layers have liquid-like properties. Another prerequisite of the model is that the surface sites are all equivalent (i.e. a uniform surface) and that the surface is flat. Although the BET method includes assumptions and limitations, it is widely used for the evaluation of the surface area from physisorption isotherm data.

2.1.2. Determination of surface area

Two stages are involved in the evaluation of the surface area. Firstly, it is necessary to construct the BET plot and to derive a value of n_m. The next stage is the calculation of the specific surface area, a(BET), which requires knowledge of the average area, σ, occupied by each molecule in the completed monolayer. The value of n_m and C can be solved by plotting $(P/P_0)/[n(1-P/P_0)]$ against P/P_0. The usual range of linearity of the BET plot is $0.1 < P/P_0 < 0.3$. This range varies, depending on the material investigated. Sufficient experimental points on the adsorption isotherm must be determined to select the region providing the best linear fit. The second stage in the application of the BET method is the calculation of the specific surface area, a(BET), from the monolayer capacity n_m:

$$\alpha(\text{BET}) = n_m N_A \ \sigma \tag{4}$$

where N_A is the Avagadro constant (6.023×10^{23} mol^{-1}) and σ is the average area occupied by each adsorbed molecule in the completed monolayer. Varied values of σ are found in the literature; the value of σ is, to some extent, dependent on the adsorbent-adsorptive system and temperature and not just on the adsorbate. If the adsorbent–adsorbate interactions are strong and the temperature is low, the monolayer is likely to be localised and, under these conditions, the monolayer structure tends to be controlled by surface chemistry.

The most widely used adsorptive for surface area determination is nitrogen (at 77 K) as it is considered to be the most suitable adsorptive for the determination of the surface area of nonporous, macroporous, or mesoporous solids. It is assumed that the BET nitrogen monolayer is close-packed, giving a $\sigma(N_2) = 0.162$ nm^2 at 77 K [26].