Application of the standard porosimetry method for nanomaterials

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Abstract: A new method of Standard Porosimetry (MSP) for investigation of any type of porous materials, including soft, frail, amalgamated materials, films and powders has been developed. The method is relatively simple and non-destructive and can be used for measurements in a wide range of pore sizes from 0.3 nm to 3×10^6 nm. The method is currently being used to study porous materials such as carbon nanotubes, membranes, thin films, ceramics, electrodes for batteries, paper etc., and can be used in other applications, including nanotechnology. The MSP employs numerous manual operations. In order to avoid them, the Automated Standard Porosimeter (ASP) has been developed based on the MSP by POROTECH, Ltd.

Keywords: porous structure; porosimetry; capillary equilibrium; carbon nanotubes; automated porosimeter; porous size distribution; specific surface area; electrodes; non-destructive method; non-toxicity; non-amalgamation.

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Alexander V. Sakars is a Researcher at the Porotech Ltd. Company, Canada. He obtained his PhD Degree in Engineering from the Moscow Power Engineering Institute, Technical University in 1985. He is an expert in mass- and heat-transfer. His current research involves the development of the Method of Standard Porosimetry and devices. He studied a lot of different porous materials such as carbon nano-tubes, activated carbons, membranes; including nano-membranes, thin films, ceramics, and electrodes for batteries. In 2003 he demonstrated the new Automated Porosimeter based on the Method of Standard Porosimetry. He participated in many conferences and exhibits.

Alex A. Volinsky is an Assistant Professor at the University of South Florida, Mechanical Engineering Department. PhD thesis title (University of Minnesota, Materials Science, 2000): *The Role of Geometry and Plasticity in Thin, Ductile Film Adhesion*. Dr. Volinsky held an Engineering Materials Senior Staff Member potion at Motorola's Process and Materials Characterization Lab prior to joining USF. There, he conducted principal research employing XRD, SEM, FIB, FA analytical techniques for advanced technologies development. Professor Volinsky's research interests are thin films processing, mechanical properties and characterisation; thin film porosity, adhesion and fracture. Professor Volisnky's research was recognised by national and international awards.

1 Introduction

The knowledge of structural and surface properties of porous materials is important in many applications, products and processes, such as electrochemical devices (electrodes, separators, membranes, catalysts, active components in batteries, fuel cells, electrolysers, sensors, etc), porous thin films, carbon nanotubes, ceramics, powder-metallurgical products, soils, paper, oil- or gas-bearing strata and rocks, construction materials, etc.

The porous structure can be characterised by integral or differential curves of pore volume distribution vs. pore radius (porosimetric curves or porograms). The following methods for measuring porograms are well known and documented:

- mercury porosimetry mercury intrusion into a non-wettable porous material [1]
- small-angle X-ray scattering [2]
- Electron, Atomic Force and Tunnel Microscopy; centrifugal porosimetry [3]
- displacement of wetting liquids from the pore volume by gas pressure [4]
- capillary condensation [5], and others.

Each of these methods has advantages and limitations. For example, small-angle X-ray scattering can be used only for pore radii ranging from 2 nm to 50 nm and often leads to ambiguous results. Centrifugal porosimetry, optical microscopy and displacement methods are practically useless for $r < 10^3$ nm. Measurements by electron microscopy are associated with difficulties in sample preparation and results interpretation. The method of capillary condensation can be used only in the pore size range from 0.3 nm to 50 nm.

The method of mercury porosimetry (MMP) provides the widest range of measurable pore radii (from 2 nm to 10^5 nm). A great disadvantage of this method is the necessity to apply high pressure of mercury (up to thousands of atmospheres), which can lead to sample deformation or even destruction, as well as the distortion of porograms [5–7]. Other drawbacks of this method are:

- misrepresentation of the results due to amalgamation of most metals [8]
- different values of the mercury wetting angle for different materials [7]
- complexity of the equipment and toxicity of mercury.

All methods of microscopy practically give only half-quantitative information.

Most of the above-mentioned disadvantages are eliminated with the use of the MSP. In addition, it enables measurements in a large range of pore sizes in different kinds of materials, including soft or frail materials, thin films, as well as materials forming amalgams [9–20].

2 Principles of the method

The method is based on the laws of capillary equilibrium. If two (or more) porous bodies partially filled with a wetting liquid are in a state of capillary equilibrium, then the capillary potentials ψ_i for these bodies are:

$$\psi_1 = \psi_2 = \psi_i \equiv \psi, \tag{1}$$

where ψ_i is the capillary potential for the *i*th body.

The MSP measures the dependence of relative liquid content equilibrium, i.e., the liquid volume (V_t) in the test sample as a function of the liquid volume (V_s) in the standard sample:

$$V_t = \phi(V_s). \tag{2}$$

Prior to the measurement, the integral liquid distribution in terms of ψ for the standard sample is established,

$$V_s = f_s(\psi). \tag{3}$$

From equations (1–3), the liquid distribution in terms of ψ for the test sample is obtained:

$$V_t = \phi[f_s(\psi)], \tag{4}$$

with the equilibrium state being attained by liquid and vapour flows. These transport effects are caused by gradients of the capillary potentials formed by: the capillary pressure p_c and the relative vapour pressure of the liquid: $p = p_s/p_o$ (where p_s designates the vapour pressure of the liquid in the system and p_o is the saturated vapour pressure). The capillary pressure can be represented by the Laplace equation:

$$p_c = -2\sigma \cos\theta/r_m,\tag{5}$$

where σ is the surface tension of the liquid, θ the wetting angle and r_m is the maximum radius of pores filled with liquid. Using the value of p_c as a capillary potential, one can derive the radial pore distribution function using equations (4) and (5):

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$$V_t = \phi[f_s(-2\sigma\cos\theta/r)] \equiv F(r).$$
(6)

Employing a measuring liquid with $\theta \sim 0$ (a fully wetting liquid) from equation (6) one obtains:

$$V_t = \phi[f_s(-2\sigma/r)] \equiv F(r). \tag{7}$$

An example of liquid distribution in two porous bodies is given in Figure 1.

Figure 1 Examples for determination of pore size distribution curves by MSP (1) V_s vs. V_t ; (2) pore size distribution curves for the standard sample; and (3) for the test sample



On the left, curve 1 represents the experimental dependence of the volume V_s in the standard sample on the volume V_t in the test sample for different values of V_o $(V_o = V_s + V_t)$. On the right, the integral pore size distribution curves (pore volume as a function of log r) are shown. Curve 2 is the known curve for the standard sample. Let us assume, for simplicity, that the wetting angles of the liquid for both bodies are equal. For a certain total volume of liquid V'_o , the volumes of liquid in both bodies V'_s and V'_t are represented by the coordinates of point C. This point corresponds to point D on curve 2 and to a certain value r' of the maximum radius of filled pores. In the case of capillary equilibrium (under the assumption made), the maximum radius of filled pores in the test sample will be the same. As in this example, the volume of liquid is represented by point B (the line is drawn at an angle of 45°) and the point E is on the pore size distribution curve for the test sample. Thus, by changing the value of the total liquid volume V_o , the overall distribution curve 3 for the test sample can be determined. The specific surface area (S), which is an important parameter of the porous structure, can be obtained from the integral pore radius distribution curve by using:

$$S = 2 \int_{0}^{\infty} (1/r) (dV/dr) dr.$$
 (8)

3 **Experimental**

The amount of liquid in the samples is determined by weighing. Hydrocarbons (octane, decane, etc.) are usually used as a working liquid, which completely wets most of the materials ($\theta \sim 0^{\circ}$). Thus, the assumption of equal wetting angle is fulfilled. In some cases, other liquids are used, e.g., water.

The porous standards and the test sample are prepared in the shape of discs 0.1-3 mm thick. The standards are washed, dried and weighed. Then, they are filled with the liquid (under vacuum). The stack of discs is assembled in a special clamping device (Figure 2), in which they are tightly attached to each other for attainment of capillary equilibrium. In the case of easily compressible (soft) materials, the pressure must be controlled and the clamping device allows it. In the assembly, the test sample (1) is usually placed between two standard samples (2). A small portion of the liquid is evaporated off this assembly through an open surface (3) by heating and/or vacuum treatment with the flow of a dry inert gas. When a certain amount of liquid is removed, the open surface of the samples is hermetically covered and left undisturbed for a certain time (1-30 minutes), allowing a new capillary equilibrium to be established. Subsequently, the stack is disassembled; the samples are placed into individual vials and weighed. Then, the stack is reassembled and all operations are repeated several times until the liquid from the test sample is completely evaporated.

Figure 2 Clamping device assembly: (1) test samples; (2) standard samples; (3) open stack surface



Other possibility for changing the total volume of the liquid is by repeated contact between the test sample and standard samples containing different amounts of liquid.

The attainment of capillary equilibrium can be controlled by using two standard samples, one of which is placed at the open surface of the stack (where the liquid evaporates) and the other one at the closed surface. If during the experiment the amount of liquid in both standard samples corresponds to their known distribution curves, then equilibrium is established throughout the whole stack. In the case of samples with small pores (<10 nm), the stack disassembly is performed in a dry box to prevent adsorption of

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humidity from the air. When samples with large pores $(>10^4 \text{ nm})$ are analysed, the stack is disassembled in a box saturated with the measuring liquid vapour to avoid drying of the stack.

Using this method, porograms can be measured for powdered materials as well. These materials are placed between two sheets of filter paper. Other samples of filter paper with no powder are also assembled in a stack. The pore volume distribution curve for the powder can be determined by subtracting the porograms of the 'empty' filter paper samples from the ones of the test sample. Capillary equilibrium between different porous samples can also be established through a vapour phase (without direct contact with the samples), the so-called method of contactless standard porosimetry. However, in this case, the time for establishing equilibrium increases considerably. The pore size distribution of the standard samples is determined by other methods, e.g., by mercury porosimetry. The materials used must be sufficiently hard and must not be deformed and amalgamated by mercury, such as nickel or ceramic materials. The standard samples must possess sufficiently high pore volume in the pore size range of interest to allow accurate measurement of the mass increase during flooding of these pores. The time needed for the measurement of a porogram depends on the pore properties of the sample (which determine the time of establishing an equilibrium) and varies between 2 and 10 hours.

4 Results and discussion

MSP with appropriate standard samples can be used for measurements of pore sizes in the range from 0.3 nm to 3×10^6 nm. The accuracy of MSP depends primarily on the accuracy of measuring the pore size distribution curve for the standard samples. The accuracy of the method of Mercury Porosimetry (MMP) is about 1% of the total pore volume. As shown by our previous experiments, under suitable conditions, the error (non-reproducibility) of the MSP is <1%.

The sensitivity of the method is illustrated in Figure 3, which represents the results for several practically monolithic samples of carbonate rocks (porosity <1%). Related to the total volume of the sample, the sensitivity in this case was 0.05-0.07% [19].





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Porograms obtained by MSP and MMP for different types of electrodes are shown in Figure 4. The results obtained by these two methods show good agreement, although such a good concurrence is possible only for sufficiently firm and not amalgamated samples.

Figure 4 Integral porograms obtained by MSP and MMP for porous electrodes prepared from a mixture of carbonyl and Raney nickel (1), carbonyl nickel (2) and titanium (3) [18]. Here, V/V_o is the relative pore volume, where V is the pore volume and V_o the total volume of the test sample



Sometimes MMP is used for examining samples with low mechanical strength [6,7]. To reveal the influence of high mercury pressures, the results obtained by MMP and MSP were compared (Figure 5). As an example, differential porograms are shown for a fibrous glass battery separator. It is seen that the changes in MMP curves take place due to sample deformation. The positions of the maxima on these curves are different.

Figure 5 Differential porograms obtained by MSP (1) and MMP (2) for a glass separator



A similar picture (Figure 6) was obtained after measuring a Pb-electrode porous structure by both methods (MMP and MSP). The majority of metals, including Pb, are prone to amalgamation, which explains the distinctions in this case. Thus, MMP does not always give a correct result, as opposed to MSP.



Figure 6 Differential porograms obtained by MSP (1) and MMP (2) for Pb battery electrode

The method of standard porosimetry allows measuring the sample's porosity at fixed compression levels, i.e., under conditions in which they are commonly used in various devices. Porograms at different compression levels reveal additional information of their properties and porous structure.

It should be also noted that MSP allows repetitive measurements of the same sample at different external loading conditions. Indeed, even for soft or frail materials, there is no deteriorative influence of the measurement on the sample (in contrast to MMP) and after drying up the latter fully retains its previous structure.

We have applied MSP to measure the porous structure of carbon nanotubes powder. Integral porograms of two types of carbon nanotubes powder are shown in Figure 7. The results of mathematical data processing, obtained with the PorotechTM special software, are given in Figures 8 and 9. After the special treatment of carbon nanotubes, the specific surface area was increased (Figure 9), in spite of overall decreased porosity (Figure 7). This happened due to increased volume of nanopores in the material and decreased volume of large pores (Figure 8). Thus, MSP allows fixing all structural changes of porous materials in a wide range of pore sizes, while giving concrete technological recommendations. In this case, treatment was useful from the standpoint of a specific surface area.

Figure 7 Integral porograms obtained by MSP for two types of carbon nanotube powders





Figure 8 Differential porograms obtained by MSP for two types of carbon nanotube powders





5 Automated standard porosimeter

In order to avoid numerous manual operations (multiple assembly and disassembly of stacks, weighing of the individual standards and samples), the Automated Standard Porosimeter (ASP), based on the Method of Standard Porosimetry was developed (Figure 10).

Figure 10 Typical automated standard porosimeter (manufactured by POROTECH, Ltd.)



The Automated Standard Porosimeter consists of a clamping device for making contact between the standards and the sample(s), sample holders and an automatic manipulator for moving samples, drying devices, as well as an automatic flow-meter valve for drying gas, a weighing station and a computer.

6 Conclusions

A porosimetric method has been developed, which allows studying all types of porous materials, including soft and frail materials, as well as powders. This method is nondestructive and quantitative, allowing repetitive measurements of the same sample. The method can be used for a wide range of pore sizes from 0.3 nm to 3×10^6 nm, which makes it specifically attractive in nanotechnology applications. The method of standard porosimetry is now widely used in many scientific and industrial fields, including nanotechnology.

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