The standard contact porosimetry

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Abstract

A new porosimetric method — the Method of Standard Contact Porosimetry (MSP) is described which allows the investigation of the structure and the properties of all kind of porous materials including soft, frail, amalgamated materials and also of powders. This method is relatively simple, nondestructive, is not connected with the use of mercury and can be applied for measurements in a wide range of pore sizes from about 1 to $3 \times 10^5$ nm. This method is very informative. It has been used for measuring the pore volume and the pore surface area distribution in terms of the pore radii and the pore shapes, the distribution of liquids in porous materials in terms of the liquid-sample free energy and the capillary pressure, and also for the measuring of adsorption isotherms, of structural changes during contraction and swelling of the samples in different liquids, of different properties of multicomponent hydrophilic-hydrophobic systems etc. The results obtained by applying the MSP for investigating different processes in porous systems are discussed. The following processes were investigated; swelling and ion exchange polymeric materials (membranes, conducting polymers); pressing of powdered materials (PVC, Raney silver); the influence of temperature on the porous structure; the influence of pore-forming agents; chemical and electrochemical sintering of catalysts; deposition of solid products in the pore volume of the cathode during reduction of SOCl₂ in lithium batteries; structural changes during formation and cycling of lead and silver oxide electrode, etc. The MSP includes different manual operations. In order to avoid them on the base of MSP, an automated standard porosimeter (ASP) was developed which includes a computer, an electronic balance, an automatic manipulator, and a device for a controlled drying of the porous samples. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The structural and surface properties of different porous materials; separators, membranes, catalysts, battery electrodes, ceramics, powder-metalurgical products, soils, oil- or gas-bearing strata and rocks, building materials, etc. have a great influence on their performances.

The porous structure can be characterized by integral or differential curves of pore volume distribution in terms of the pore radii (porosimetric curves or porograms). The following methods for measuring porograms are well known; mercury porosimetry-mercury intrusion into nonwettable strata
ing [2]; electronic or optical microscopy; centrifugal porosimetry [3]; displacement of wetting liquids from the pore volume by gas pressure [4]; capillary condensation [5].

Each of these methods has its merits and its limitations. Low-angle diffraction can be used only for pore radii from 2 to 50 nm and often leads to ambiguous results. The centrifugal, optical microscopy and displacement methods are practically useless for \( r < 10^{3} \) nm. Measurements by electronic microscopy are associated with difficulties in pretreatment of the samples and in interpretation of the results. The method of capillary condensation can be used in the pore size range from 1 to 50 nm.

The widest spectrum of measurable pore radii (from 2 to \( 10^{5} \) nm) is found in the method of mercury porosimetry (MMP). A great disadvantage of this method is the necessity to apply high pressures of mercury (up to thousands of atmospheres), which can lead to a deformation or even destruction of the samples and to a distortion of the porograms [5–7]. Other drawbacks of this method are: distortion of the results owing to amalgamation of most metals [8], different values of the mercury wetting angle for different materials [7], complexity of the equipment, toxicity of mercury.

In the A.N. Frumkin Institute of Electrochemistry of the Russian Academy of Sciences, a new method — the method of standard contact porosimetry (MSP) was developed in which most of these disadvantages are eliminated and which gives the possibility of measurements in a large range of pore sizes and with different kinds of materials including soft or frail materials or materials which are amalgamated by mercury [9–19].

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 the state of capillary equilibrium the values of the capillary potentials \( \psi \), for these bodies are equal:

\[ \psi_1 = \psi_2 = \ldots = \psi_i = \psi, \]  

where \( \psi_i \) is the capillary potential for body \( i \).

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

\[ V_i = \phi (V_s) \]  

Having found from independent measurements the cumulative (integral) liquid distribution in terms of values of for the standard sample,

\[ V_s = f_s (\psi), \]  

we obtain from Eq. (1) to Eq. (3) the liquid distribution in terms of values of for the test sample:

\[ V_i = \phi [f_s (\psi)]. \]  

The equilibrium state is attained by liquid and vapor flows. These transport processes are caused by gradients of the capillary potentials which are characterized by; the capillary pressure \( p_c \) and the relative vapour pressure of the liquid \( p = p_s/p_o \) (where \( p_s \) is the vapour pressure of the liquid in the system and \( p_o \) — its saturated vapour pressure). The capillary pressure can be represented by the Laplace equation

\[ p_c = -2\sigma \cos \frac{\theta}{r_m} \]  

where \( \sigma \) is the surface tension of the liquid, \( \theta \) is the wetting angle, \( r_m \) the maximum radius of pores filled with the liquid. For instance, when using value of \( p_c \) as a capillary potential from Eqs. (4) and (5) we obtain the pore radii distribution function:

\[ V_i = \phi \left[f_s \left(-2\sigma \cos \frac{\theta}{r}\right)\right] \equiv F (r) \]  

By using for measurements a wetting liquid with \( \theta \sim 0 \) we obtain from Eq. (6);

\[ V_i = \phi \left[f_s \left(-2\sigma \right)\right] \equiv F(r) \]  

For this case in Fig. 1 an example for the distribution of a liquid in two porous bodies is given. In the left part curve 1 represents the experimental dependence of the volume of the
liquid in the standard sample $V_s$ on the volume $V_t$ in the test sample for different values the overall volume of the liquid $V_o (V_o = V_s + V_t)$. In the right part, the integral pore size distribution curves-dependence of pore volume on $\log r$ 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 given overall volume of the 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 defined value $r'$ of the maximal radius of filled pores. In the case of a capillary equilibrium (under the assumption made), the maximum radius of filled pores in the test samples will be the same. As in this sample the volume of liquid is represented by point B (the line is drawn at an angle of $45^\circ$) the point E corresponds to a point on the pore size distribution curve for the test sample. In a similar manner by changing the value of over-all volumes $V_o$ of the liquid, the whole 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 [19]; from the integral pore radius distribution curve, using the expression (assuming cylindrical shaped pores)

$$S = 2 \int_0^{r'} \left( \frac{1}{r} \right) \left( \frac{dV}{dr} \right) dr \quad (8)$$

3. Experimental

3.1. Method of measurement

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

The porous standard and test samples are prepared in the shape of discs with thickness 0.1–6 mm. They are washed, dried, weighed; after this they are filled (under vacuum) filled with the liquid. The stack of porous samples is assembled in a special clamping device (Fig. 2) in which the samples are tightly pressed to each other for attainment of the capillary equilibrium. In the case of readily compressible (soft) materials, the pressure must be controlled, (e.g. by sylphon bellows). In the assembly, the test samples (1) are usually placed between two standard samples (2).

From this assembly a small portion of the liquid is evaporated through the open surface (3) by heating and/or vacuum treatment or by a flow of dry inert gas. When a certain amount of liquid is removed the open surface of the samples is closed up with a plug and the assembly is stored.
for a certain time (1–30 min) to allow the establishment of a new capillary equilibrium. Afterwards the stock is disassembled, the samples are placed into individual glass bottles and weighed. After this the stock is reassembled and all listed operations are continued periodically until all the liquid has practically completely evaporated from the test samples.

There exist also other possibilities for changing the overall volume of liquid, e.g. by repeatedly contacting the test sample with the standard sample, containing different amounts of liquid.

The attainment of the capillary equilibrium can be controlled by the use of 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 amounts of liquid in both standard samples correspond to their (known) distribution curves, the equilibrium is established throughout the whole stack.

In the case of samples with small pores (<10 nm), the disassembling of the stack is performed in a dry box in order to prevent absorption of humidity from air. When making measurements involving large pores (>10⁴ nm) the stack is disassembled in a box saturated with vapor of the measuring liquid in order to avoid drying of the stack.

With this method, porograms can be measured also for powdered materials. These materials are placed between two sheets of filter paper. Other samples of filter paper without powder are also assembled in the stack. By subtracting the porograms of the 'empty' filter paper samples from the porograms of the test sample the pore volume distribution curve of the powder can be determined.

The capillary equilibrium between different porous samples can also be established through the vapor phase (without a direct contact of the samples) — the method of contactless standard porosimetry. But in this case the time for the establishing of the equilibrium rises sharply.

The standard samples must fulfill the following condition; their pore volume in the corresponding pore size range must be sufficiently high as to allow an accurate measurement of the mass increase during flooding of these pores.

The time needed for the measurement of a porogram depends on the pore characteristics of the sample (which influences the time of establishment of the equilibrium) and varies between 2 and 10 h.

4. Results and discussion

4.1. Limits, accuracy and sensitivity of the method

MSP with suitable standard samples can be used for measurements of pore sizes in the range from ~1 to 3 × 10⁵ nm. The accuracy of MSP depends primarily on the accuracy of measuring the pore size distribution curve of the standard samples. By MMP this curve can be measured with an accuracy of about 1% of the total pore volume. As was shown by special experiments, under suitable conditions the error (nonreproducibility) of the results due to MSP itself is less than 1%.

The sensitivity of the method is illustrated by Fig. 3, which represents the results for different practically monolithic samples of carbonate rocks (porosity less than 1%). When referred to the overall volume of the sample the sensitivity in this case was 0.05–0.07%.

In Fig. 4, the porograms measured by MSP and by MMP for different types of electrodes are shown. It can be seen that there is a good agreement between the results obtained by these two methods. \( \vartheta = \frac{V}{V_o} \) is the relative pore volume (porosity), where \( V \) is the volume of pores, \( V_o \) is the total volume of the test sample.

Fig. 3. Integral porograms for different carbonate rocks of the Vuktyl region [20] (measured with octane).
4.2. Porosimetry of deforming samples

Sometimes MMP is used for investigation of samples with a low mechanical strength [6,7]. To reveal the influence of high mercury pressures the results of measurements by MMP and MSP for such samples were compared. The effect of deformation depends on the nature of the material. As an example in Fig. 5 differential porograms are shown for a fibrous filter material FPIAN-5 which is used as separator in batteries (measured with octane).

It can be seen from Fig. 5 that the deformation changes the shape of the curves; the number and the position of the maxima on these curves is different. They coincide only in the pore size range $10^2–10^3$ nm; this indicates to a rigid microporous structure within the fibers.

MSP gives the possibility to perform measurements of samples at fixed levels of compression, i.e. in conditions in which they are used in different devices. By measuring porograms at different levels of compression, additional information on the properties of the porous structure can be obtained.

It should be also noted that MSP allows repeated measurements on the same sample, which gives the possibility to investigate structural changes under the influence of different external factors, e.g. the structure of the same electrode at different depths of charge or discharge. Indeed even for soft or frail materials there is no deteriorating influence of the measurement on the sample (in contrast to MMP) and after drying up it fully retains its earlier structure.

4.3. Measurement of the total pore volume

When measuring the total porosity of porous bodies, an error is often introduced due to a thin liquid film on the surface of the sample or to a deficiency of liquid after attempts to remove this film. On the base of MSP a method was developed [19] with a new procedure of filling the sample with the wetting liquid. The test sample is contacted with an auxiliary sample whose volume of coarse pores $V_2$ is higher than the total volume of the test sample $V_1$, the volume of liquid, which is added to the sample, is greater than $V_1$ but lower than $V_2$. Under these conditions the pores of the test sample will be completely filled with the liquid without the forming of a film on its surface.

4.4. Investigation of samples with corrugated pores

The corrugation of pores influences to a great extent processes of mass- and heat-transfer and of current flow in porous materials. For such materials the porograms measured in forward and reverse directions (from smaller pores to larger ones and vice versa) usually do not coincide and it is difficult to evaluate the true shape of the porogram. MSP gives the possibility to measure the true pore size dependence with taking into account of pore corrugation [16,19]. The quantitative description of such a porous structure is given by the statistical distribution function of the vol-
Fig. 6. Integral porograms for electrodes made from carbonyl nickel measured by MSP via; (1-I) capillary impregnation, (1-E) evaporation starting with complete flooding, and (1, 2...k-1, k) evaporation starting with different degrees of flooding [19].

To evaluate this function it is necessary to measure the porograms by two methods; (a) by filling of the pores with liquid, and (b) by evaporation of the liquid beginning from different degrees of filling. In Fig. 6 such a set of porograms for an electrode from carbonyl nickel is shown (measured with decane).

In Fig. 7 plotted in coordinates log $r_{tr}$, log $r_{tr}$, the lines connect points with equal values of the distribution function (dimensionless, for relative porosity). The line at an angle of 45° is characteristic for without corrugation. From this figure it follows that the pores of this electrode can be divided into three groups; (1) coarse pores with radii 30–70 μm and with a low degree of corruga-

tion, formed by special pore forming additives, (2) pores in the range 2–15 μm with a high corrugation degree, located between individual particles of the carbonyl nickel, and (3) a low volume of small pores (below 1 μm) with a low degree of corrugation, located inside the nickel particles. Such kind of distribution functions has not been yet described in literature.

4.5. Measurement of wetting angles

The measurement of wetting angles for porous materials is connected with difficulties especially if these materials can not be prepared with a smooth surface, (e.g. carbons, soil samples, building materials etc.). MSP gives such a possibility for liquids with wetting angles of $\theta_l < 90^\circ$. For this purpose porograms with the test liquid whose wetting angle must be determined and with a standard liquid (s) whose wetting angle is known, (e.g. hydrocarbons with $\theta_s \approx 0^\circ$) are measured. The results of measurements are plotted as indicated above, i.e. without taking into account the change of the value of $\cos \theta_l$. In this case the curves for the two liquids will be shifted along the log $r$ axis. For a given amount of liquid $V$ the value of $\cos \theta_l/r = (p_l/2\sigma)$ in both cases will be the same. Therefore, the value of the shift will be $\log[\cos \theta_l/\cos \theta_s]$ or when $\theta_s \approx 0^\circ$, $\log \cos \theta_l$. If the value of $\theta_l$ for the sample is not constant but depends on the pore size, then there will be not only a shift
but also some deformation of the porogram. From the values of the shift for different values of \( V_t \) the dependence of \( \theta_t \) on the pore size can be found. In Fig. 8 porograms are shown for a porous sample of pressed polytetrafluoroethylene (PTFE) powder measured with cyclohexanone, isopropyl alcohol and decane. From Eq. (8) we have:

\[
\log \cos \theta_t = \log \left( \frac{2\sigma_L}{p_c(V_L)} \right) - \log \left( \frac{2\sigma_s}{p_c(V_s)} \right)
\]

(10)

or

\[
\cos \theta_t = \frac{\sigma_L}{\sigma_s} \frac{p_c(V_s)}{p_c(V_L)}.
\]

(11)

where \( V_L = V_s \), \( V_L \) volume of test liquid of L, \( V_s \) volume of practically ideal wetting (standard) liquid.

It can be seen from Fig. 8 that there is an almost parallel shift of the curves without deformation. Assuming that for decane \( \theta_L \sim 0^\circ \) we find for cyclohexanone \( \theta_L = 52^\circ \) and for isopropyl alcohol \( \theta_L = 20^\circ \). These values are close to values measured for a smooth PTFE surface [21].

The situation is different for samples of activated carbon. In Fig. 9 porograms for carbon samples SKN-1 and SKN-4M are presented which were measured with decane and water. It can be seen that the micropores are practically hydrophilic. With increasing pore radius up to 10 nm the wettability with water decreases (wetting angle \( \theta_t \) increases). Almost all the pores with \( r > 10 \) nm are hydrophobic.

### 4.6. Investigation of multicomponent porous bodies

Multicomponent porous materials with a mixed water wettability (hydrophobic–hydrophilic materials) are widely used as electrodes in fuel cells and other electrochemical devices, as well as in other fields (glass reinforced plastics, composite materials, etc.). MSP gives the possibility to have a complete information on the structure and surface properties of such kind of materials. For this purpose measurements are performed with several liquids with a different wettability of each component of the material. Let us consider a two-component system of a catalytic active electrode consisting of platinum black and PTFE particles.

Let us denote the wetting angle of water with the hydrophilic and hydrophobic component as \( \theta_1 \) and \( \theta_2 \), respectively. Such a material contains interconnected systems of purely hydrophilic pores (between Pt particles), purely hydrophobic pores (between PTFE particles) and mixed pores, which are filled with water only in the case when for the mean value of \( \cos \theta \) the condition

\[
\cos \theta \equiv ((1 - \rho) \cos \theta_1 + \cos \theta_2) > 0
\]

is fulfilled [23]; \( \rho \) is the fraction of the pore surface occupied by the hydrophobic material.

In order to evaluate the structure type of this electrode the dependence of the amount of liquids in the electrode as function of their wetting angles with PTFE \( \theta_p \), was measured by hydrostatic weighing the electrode in different liquids that wet platinum (\( \theta = 0^\circ \)). It can be seen from Fig. 10 that...
kind of functions have not yet been described in literature.

MSP was also applied for investigation of two-component negative electrodes of solid oxide fuel cells (SOFC), consisting of nickel particles and solid electrolyte particles [24].

4.7. Absorption isotherms

The ability of highly dispersed (colloidal) porous systems to absorb or to release liquids can be investigated by the method of capillary condensation and is usually characterized by absorption isotherms, i.e. equilibrium relations between the amount of liquid bound in the body and the relative vapor pressure of the liquid \( \tilde{p} = p_s/p_o \), where \( p_s \) the vapor pressure of the liquid in the system and \( p_o \) is its saturated vapor pressure. The upper limit for this method is at a pore size of about 50 nm, where \( p_s \approx p_o \).

By using standard porosimetry measurements it is possible to extend the notion of absorption isotherms to a broader range of porous systems. For this purpose it is convenient to use the parameter ‘free binding energy liquid-sample’ \( A \) (capillary potential, differential work of wetting). This parameter is related to the structural (\( r \)) and surface properties (\( \theta \)) of the system which can be determined by MSP and also to the relative vapor pressure (method of capillary condensation) via the Kelvin equation:

\[
A = -RT \ln \left( \frac{p_s}{p_o} \right) = 2\sigma \cos \theta \frac{V_m}{r} \quad (13)
\]

Absorption or desorption isotherms expressed as dependence of amount of liquid in the system on free binding energy allow the comparison of the behaviour of any kind of porous systems, investigated by different methods, even of lyophobic systems for which the values of \( A \) are negative. A number of water desorption isotherms are presented in Fig. 12 as plots of the volume of filled pores against \( A \), and for comparison, versus \( \tilde{p} \) and versus \( r \). Very diverse samples have been examined including hydrophilic, hydrophobic and mixed materials, typically porous samples and samples of colloidal type (pine wood, peat). The spectrum of \( A \) values measured is rather wide

Fig. 10. Dependence of the flooding degree on the wetting angle with different liquids for electrodes of; (1) platinum + 6% PTFE, (2) platinum + 16% PTFE, (3) nickel + 4.8% PTFE [18].

Fig. 11. Differential pore distribution function in terms of pore radii \( r \) and in terms of hydrophobicity factors \( \rho \) for a platinum electrode containing 16% PTFE [18].
here; six orders of magnitude in the hydrophilic region and three orders of magnitude in the hydrophobic region. It can be seen that isotherms measured by MSP give a very complete information concerning the uptake of liquids by porous systems.


The described MSP includes a great amount of manual operations; multiple assemblage and disassemblage of the stack, weighing of the individual test and standard samples etc. In order to exclude manual operations on the base of MSP an automated standard porosimeter (ASP) was developed which includes the following parts; a computer for the management of the measuring process, data accumulation and processing; an electronic balance `Sartorius` for weighing of the test and standard samples; an automatic manipulator for the assembling and disassembling of the stack of samples and for transfer of the samples to the balance; a device with electromagnetic valves for a controlled drying of the samples by a flow of dry inert gas $r$.

4.9. Investigation of the formation of porous structures

The laws of formation of porous structures with given properties or of modifications of the porous structure resulting from external influences or from technological processes are not as yet studied in detail. One of the reasons for this circumstance is connected with the fact that the most widespread porosimetric method, MMP is a destructive method and does not give the possibility of repeated measurements of one and the same sample. MSP is free from this drawback.

This part describes the some results of MSP and ASP measurements during formation processes of porous structures.

4.9.1. Nondestructive measurements of structural changes

The possibility of repeated measurements on one and the same sample excludes for instance the influence of technological nonreproducibility of the parameters of different samples and substantially increases the accuracy and sensitivity of the measurements. This can be illustrated by the results of measurements on the negative electrode of lead-acid batteries [25]. At different stages of their
functioning the storage cells were disassembled, one of the negative electrodes was washed, dried and mounted in a special device for porosimetric measurements. After the measurements, the electrode was again assembled in the storage cell for further cycling. In Fig. 13 porograms for three electrodes after a starter discharge at $-20^\circ$C are shown. The manufacturing process for all three electrodes was the same. In Fig. 14 porograms for one of this electrodes after different technological and charging-discharging processes are shown. It can be seen that the scattering of the structure for different electrodes is comparable with the scattering induced by these processes.

4.9.2. Swelling of porous materials

When a porous material with an insufficient rigid structure is soaked with a wetting liquid a volume increase (swelling) under the influence of the liquid’s capillary pressure is possible. If such a material is used in a liquid medium it is important to know its porous structure just in this medium. The process of swelling depends on the nature of the liquid. In absence of a specific interaction between the porous material and the liquid, the capillary pressure is proportional to the surface tension $s$ of the liquid.

The structure of chrysothyl asbestos widely used as separator in different electrochemical devices (electrolysers, fuel cells etc.) was studied. As working liquids octane ($\sigma = 21.7$ mJ m$^{-2}$), water ($\sigma = 72.5$ mJ m$^{-2}$) and a solution of 7 M KOH ($\sigma = 92$ mJ m$^{-2}$ [26]) were used. For alkaline solutions, the method described in [12] can not be used since during water evaporation or condensation the solution concentration changes. A modified method was developed in which the amount of liquid in the porous bodies is changed by capillary soaking or drying. In the first case the dried test sample is contacted with several standard samples filled with different amounts of liquid. In the second case the completely filled test sample is contacted with dried standard samples. In Fig. 15 differential porograms measured by this method are shown. In octane (curve 1), there is practically no swelling of the asbestos and the porogram is characteristic for its native porous structure. In water (curve 2), swelling is due to an increase of the volume of pores with radii in the range from $10^3$ to $4.5 \times 10^4$ nm. In the alkaline solution (curve 3), there is a further volume increase in the range of the largest pores.

In the case of ion exchange membranes (solid polymer electrolytes), a different kind of swelling
4.9.3. The influence of preliminary soaking and evaporation memory effects

When investigating the porous structure of polyaniline in the form of emeraldine chloride or sulfate, a peculiar ‘memory’ effect can be observed which manifests itself in a well pronounced shape change of the porograms during successive measurements with water as working liquid (Fig. 17) [29]. As a result of pore volume increase in the range of micropores, the specific surface of the sample increases substantially. A similar behaviour was observed for the system poly(para-phenylen)--acetonitrile [30]. This phenomenon can be tentatively explained by a loosening and subsequent shrinkage of the labile porous structure of these materials during successive soaking and vacuum drying during measurement. This effect is of great practical significance as the value of the specific surface area influences the electrochemical properties of conducting polymers [31].

4.9.4. The influence of ion exchange

Fig. 18 shows porograms for an ion exchange membrane MA-41 in the initial sulfate form (curve 1) and after ion exchange in dodecyl ether of sulfoacetic acid (curve 2), in sodium dodecyl sulfate (curve 3) and in sodium decylsulfate (curve...
It can be seen that the porous structure depends upon the nature of the counter-ion and the pore volume significantly decreases upon transition from inorganic to organic anions.

A similar but even more pronounced behaviour can be observed for polyaniline in the form of emeraldine salts [33]. In Fig. 19, integral porograms measured with water for chemically synthesized emeraldine chloride (curve 1), and of this salt after ion exchange in sulfuric acid (curve 2) and fluoroacetic acid (curve 3) are shown. It can be seen that the porosity of the chloride form is substantially higher than that of the sulfate form. For the fluoroacetic form in water there is practically no hydrophilic porosity, i.e. this form becomes hydrophobic.

The effect of the degree of doping, the nature of counter-ions, and type of the polymerization (chemical or electrochemical) on poly(aniline) structure were also studied [28]. It was shown that all poly(aniline) forms impregnated with GBL had high porosities of several dozen per cent, high specific surface areas of 80–400 m² cm⁻¹, pore radii of 1–100 nm, and average fibril radii of 2–10 nm.

MSP was also applied for a detailed investigation of the porous structure and sorption properties of swollen in water Naion® proton-exchange membranes [34,35].

4.9.5. The influence of pressure on the porous structure

Porous materials are often manufactured by pressing of powders. MSP (unlike MMP) gives the possibility to investigate the structure of porous and dispersed materials at fixed values of pressure. In Fig. 20 porograms for a fixed amount of Raney silver (used as catalyst for oxygen electrodes) during a successive pressure increase are shown. While increasing the pressure from 0.05 to 5 MPa, first the volume of the largest pores diminishes, and then the volume of smaller pores in the range from 2 × 10⁴ to 3 × 10² nm. These pores are located between individual particles of
the silver catalyst. The structure inside the particles with pores of lower radii (the primary structure) is not altered at these values of pressure. However, when increasing the pressure to 10 MPa and higher, a second stage of compressing is reached connected with a destruction of the individual particles. In this case the border between the primary and the secondary structures corresponds to pore radii about $3 \times 10^2$ nm. Thus, MSP gives the possibility to investigate separately the porous structure of individual primary particles and the secondary structure of agglomerates of particles.

A behaviour analogous to Fig. 20 was observed also for other powder samples, e.g. for PVC [36].

4.9.6. The influence of temperature on the porous structure

MSP, in contrast of the MMP can be used for investigation on porous structure under different temperatures. In [34], MSP was used for the first time for porosimetric measurements of Nafion® proton-exchange membranes swollen in water at temperatures (80°C) higher than room temperature. For this purpose a thermostatically controlled cell was used, where a high humidity was provided by nitrogen which preliminarily was bubbled through water heated to the same temperature. A clamping device (see Fig. 2) was assembled in the cell and used to fix a contact of the membrane specimen with two standard ones during a period sufficient to achieve capillary and thermal equilibrium.

Fig. 21 gives a comparison of the porous structure of a Nafion 117 membrane measured at 20°C (curve 1) and at 80°C (curve 2). It can be seen that the heating leads to a significant change of the porous structure, in particular, a decline in pore volumes only for pores larger than 10 nm [34].

4.9.7. The influence of pore-forming agents

When manufacturing porous products by pressuring of powders, special additives are often used for increasing the amount of coarse pores or for the formation of bidisperse structures.

The influence of pore-forming agents was studied for porous titanium electrodes [37]. These electrodes were prepared by pressing powders of titanium and of NH₄HCO₃ (45 m) at 4.5 MPa and subsequent removal of the pore-forming additive at 100°C. In Fig. 22 the porograms measured with decane for different concentrations (wt.%, $c_p$) of the pore-forming agent are shown. It can be seen that the porous structure of the electrode is bidisperse. The primary structure with pore sizes below 1 m is formed between titanium particles and the secondary structure with greater pore sizes-by the pore-forming agent. An increase of this agent’s amount by 1% leads to an increases of the pore volume by about 1.1%.

These results were obtained by using MSP with evaporation of the working liquid. Therefore, they reflect the radii of the blocking pores or ‘necks’ $r_b$ between trapped pores formed by the additive (see Fig. 22. Integral porograms of titanium electrodes prepared with different concentrations (wt.%) of a pore-forming agent; (1) 0, (2) 5, (3) 10, (4) 15, and (5) 20 [37].

Fig. 21. Curves of integral pore-volume distribution in terms of radii for Nafion 117 membrane measured at 20 (1) and 80°C (2) [34].
Section 4.7). The steep rising sections of the porograms practically correspond to the highest values of $r_b$. When $c_p$ is increased from 5 to 20% the value of $r_b$ increases from 1.3 to 8 μm though the particle sizes of the pore-forming agent did not change.

4.9.8. The structure of dispersed platinum

During measurements of samples of dispersed platinum, e.g. platinized platinum, a large amount of micropores with radii less than 1 nm were found (Fig. 23, curve 1). For platinized platinum these micropores account for more than half of the total pore volume; the radii of most of the remaining pores do not exceed 3 nm. This circumstance is very important since the size of such micropores is comparable with the thickness $d$ of the electrical double layer, and also with the size $a$ of many molecules and ions, especially organic. Both these factors influence adsorption and kinetic properties of the deposits, particularly their intrinsic catalytic activity. Such phenomena were observed in [38–41].

The electrochemical sintering of dispersed platinum during polarisation for several hours at 0.3 V (RHE) in 0.5 M H$_2$SO$_4$ was investigated for electrodes prepared by platinum deposition on platinum gauze or by pressing platinum black powder at 150 MPa [42]. Fig. 23 shows that for the first sample (curve 1) the mean pore size increased from 20 to 40 nm, the specific surface area decreased from 28.6 to 17 m$^2$ g$^{-1}$ and overall porosity decreased more than two-fold. For second sample (curve 2), porosity did not change and the mean pore size of the primary pores increased from 10 to 16 nm, and that of the secondary pores from 20 to 55 nm. The specific surface area decreased from 13.8 to 6.5 m$^2$ g$^{-1}$. These results show that electrodes prepared from pressed platinum black unlike electrodes from platinized platinum have a rigid structure, which prevents shrinkage during polarization.

4.9.9. Deposition of solids in a porous body

In [14], the changes in the structure of a carbon black electrode during thionyl chloride reduction and deposition in the pores of the reaction product LiCl were investigated. In Fig. 24 porograms which were measured during discharge at current density 5 mA cm$^{-2}$ up to different values of depth of discharge (DOD) are shown. It can be seen that the formation of the deposit leads to a significant decrease of the larger pores. At the same time a slight increase of the volume of very small pores can be observed which is due to the filling of large pores with LiCl crystals. The porosity of the filled pores (which is represented by curve 5 and can be calculated by subtraction of curve 4 from curve 1) is only 3.4%. This dense deposit leads subsequently to an increase of the thickness of the electrode.

For electrolytic metal deposition on a porous substrate a different behaviour is observed as in this case the deposit is formed not in the bulk of the solution contained in the pores but directly at the pore surface. In Fig. 25, porograms of an electrolytically platinized porous titanium ele-
trode are shown [37]. It can be seen that platinizing leads to a shift of the maximum of the distribution curve towards smaller pore sizes and to a gradual lowering of the radii of practically all pores. During platinizing there is a gradual increase of small pores with radii less than 100 nm inside the platinum deposit.

4.9.10. Solid state reactions in storage cells

The investigation of structural changes of battery electrodes during discharge and during cycling is of great importance for a better understanding of their properties. As most of the metals used in such electrodes (lead, cadmium, silver, etc.) are easily amalgamated, MMP can not be used for this purpose.

From the porogram for the negative electrode of the lead acid cell (Fig. 14), it can be seen that the freshly pasted electrode (curve 1) has a bidisperse structure with a great amount of pores with radii between 7 and 300 nm and a lower amount of pores between 6 and 10 μm. After formation (curve 2) of the electrode, the main amount of pores corresponds to a narrow range between 800 and 3200 nm while the remaining amount is spread over the range between 5 and 800 nm. The significant part of pores in the range 800–3200 nm is maintained for all states-of-charge of the electrode during cycling. Thus, the main effect of the forming process of lead electrodes is the development of pores in this range. It seems that these pores are important for the transport of \( \text{HSO}_4^- \) ions, particularly at high current densities. The localization of the structural changes in a narrow range of pore sizes is probably beneficial for the reversibility of the structure during cycling and thus for enhancing the cycle life of the storage cell. The great difference of the overall porosity in the charged and discharged states is due to the high ratio of the densities of metallic lead and lead sulfate (1.8:1).

For silver electrode in silver-zinc batteries the main parameter is the efficiency of silver utilization (transformation into AgO) during charging. This efficiency increases with decreasing charging current density and with increasing discharge current density. These observations can be compared with structural changes. In Fig. 26 porograms are shown for electrodes manufactured from commonly used silver powder (1, 1′) and from fine-grained powder prepared by reduction of AgCl (2, 2′) both before formation (1, 2) and after formation (1′, 2′) during two cycles [43]. For the initial electrodes 1 and 2, the values of the specific surface area calculated from the porograms were 0.2 and 2.19 m² g⁻¹ and the efficiencies 47 and 77%, respectively. After formation, the corresponding values were 0.87 and 1.14 m² g⁻¹ for the specific surface area and 72 and 73% for the efficiency. Thus, after formation the properties of the electrodes and their structure are leveled. Recrystallization during cycling leads to a loss of the ‘memory’ of the initial structure of the electrode.

The increase of efficiency with increasing discharge current density can be attributed to an increase of the specific surface of silver.

MSP was also applied to several other materials and processes, e.g. the polymerization of...
vinylchloride to polyvinylchloride [36], the sintering of porous titanium electrodes [37], the storage of electrodes of the silver–zinc storage cell, the preparation of an ion exchange membrane from the corresponding ion-exchange resins [32], etc.

5. Conclusion

A porosimetric method was developed which allows the investigation of all kinds of porous materials including soft or frail materials and powders. This method is nondestructive and allows repeated measurements on one and the same sample. The method can be used for a wide range of pore sizes from 1 to $3 \times 10^5$ nm. The use of different working liquids allows the evaluation of wetting angles and of the water wettability of multicomponent porous materials. No complex devices and high pressures are needed for this method. The method of standard porosimetry is now widely used in many scientific and industrial laboratories throughout Russia and other countries for the investigation of porous materials used in electrochemical devices (electrodes, membranes) as well as of other types of porous materials.

The results obtained by applying the MSP for investigation of different processes in batteries, fuel cells and other electrochemical devices are discussed. The following processes were investigated; swelling and ion exchange polymeric materials (membranes, conducting polymers); pressing of powdered materials (PVC, Raney silver); the influence of temperature on the porous structure; the influence of pore-forming agents; chemical and electrochemical sintering of catalysts; deposition of solid products in the pore volume of the cathode during reduction of SOCl$_2$ in lithium batteries; structural changes during formation and cycling of lead and silver oxide electrode, etc.

The MSP includes different manual operations. In order to avoid it, an automated standard porosimeter (ASP) was developed based on MSP. This ASP includes the following parts: a computer, an electronic balance, an automatic manipulator, a device with electromagnetic valves for a controlled drying of the porous samples by a flow of dry inert gas.

References