Bulletin of Electrochemistry 1 (2) Mar-Apr 1985 pp. 195-201

COMPUTER PROGRAM FOR MERCURY PENETRATION POROSIMETER-DATA ANALYSIS

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ABSTRACT

CECRI has a Micromeritics mercury penetration porosimeter for characterisation of porous electrodes. For quick evaluation of the experimental data on porous electrodes, computer programme has been written and tested for reported results. Good agreement on pore size distribution, surface area, and particle size distribution has been observed. The used numerical results and computer results are briefed.

INTRODUCTION

A porous medium is a solid that contains a large number of pore spaces distributed throughout the volume. To characterise the electrodes for electrochemical reaction, pore-size distribution study [1] is made using the physical method, namely, mercury intrusion. With a mercury penetration porosimeter, one can determine size and quantity of void spaces and pores in porous materials. In addition, one can calculate specific surface area and obtain a measure of particle size distribution in the case of powders. The analysis of the data is laborious and the company advises one to follow the calculation sheet to avoid errors. Computer programme has been developed both in Basic and Fortran IV to simplify the entire procedure.

TEST PROCEDURE

The Instruction manual [2] gives the brief description of the experimental procedure. The volume of mercury entering an evacuated porous sample at low pressure is measured and recorded. The pressure is increased and the incremental volume of mercury entering the sample is again recorded. The procedure is continued until the incremental volume is of no further interest. Thus increasing the pressure on a material having a given pore size and/or void space results in a unique pressure-volume curve as shown in Fig. 1.

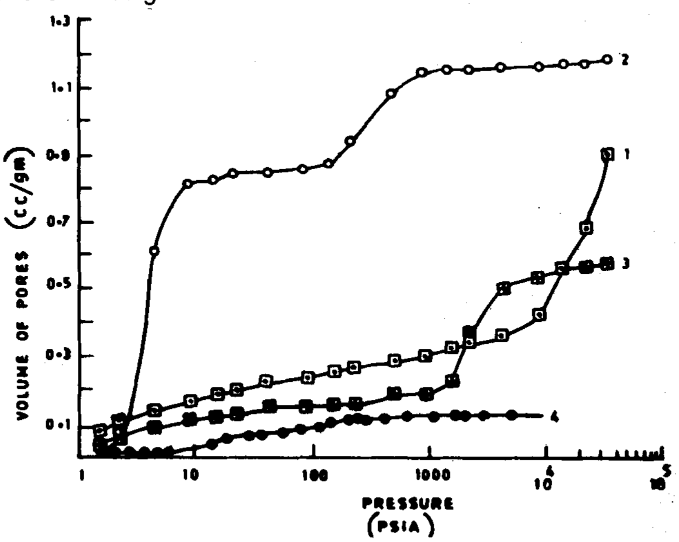

Fig. 1 : Pressure vs volume of pores

Curve 1 represents a catalyst where the volume of pores exceed the volume of void spaces. The pores tend to be predominantly about 0.005 micron in radius while the volume average void space is of the order of 1 micron in radius. The pores and voids thus differ greatly in size. The curve designated No.2 was obtained for a powder with relatively coarse grains. Accordingly the curve consists of two distinct parts. The volume of mercury penetrating the sample at pressures less than 50 psia (344740 N/m^2) went into void spaces among the individual particles, while the volume above 50 psia penetrated pores within the powder grains. Curve 3 is for a mineral having unique structural characteristics. It has pores, for example, predominantly of about 0.04 micron radius. It appears from the figure 1 further that it has a few pores of about 0.01 micron radius. This has been tested in our analysis.

THEORY (2)

Following the theoretical model taken in the instruction manual [2], the following equations are taken for the computation of results.

(a) Pore radius

The pore radius in which mercury will penetrate at an applied P can be determined from

$$r = \frac{-2\,\sigma \cos(\Theta)}{P} \qquad (1)$$

where,

- σ — is the surface tension of mercury
- Θ — is the contact angle
- P — applied pressure in psia
- r — pore radius in microns

(b) Pore size distribution

The pore size distribution of porous electrodes is one of the fundamental parameters determining the extent to which the available surface of electrocatalyst is effective in electrochemical reactions. It is determined by

$$D(r) = \frac{P^2}{2\,\sigma \cos(\Theta)} \times \frac{dV}{dP} \qquad (2)$$

where D(r) is the pore-size distribution function, dV is the volume of pores having radii between r and (r+dr) and dP is the corresponding change in pressure.

D(r) is estimated at each pressure from figure 1 data. Plotting D(r) against r gives the pore-size distribution. If the D(r) vs r curve displays N maxima, each maximum at r(j) (j = 1,2,...N) is assigned, to a large number of pores with the radius r(j). It is said that the porous structure consists largely of N types of pores.

(c) Specific surface area

It is determined using the equation (3)

$$S = -\frac{\int P \, dV}{\sigma \cos(\Theta)} \tag{3}$$

where S is specific surface area over the range of integration.

(d) Particle size distribution

The relationship between particle radius, r and applied pressure P, is [3]

$$r = \frac{68.77 \times P^*}{P} \tag{4}$$

where P* is the so-called breakthrough pressure. It is defined as that pressure required to force mercury through a uniform bed of uniform size particles. Its magnitude depends on the porosity of the bed and the contact angle between the particle and mercury.

ANALYSIS

From recorded pressure data, it can be seen that the pressure readings range from 1 psia to 50000 psia. In any instrument, it is not possible to have pressure control with 1 psia sensitivity. As some of the peaks may lie in the column in which readings are not taken, interpolation technique is used to predict pore size distribution.

To interpolate in the unequal intervals of pressure readings, we have Newton's general interpolation formula and Lagrange's interpolation formula. Mathematics of the formula can be seen in reference [4].

LAGRANGE

The interpolating polynomial passing through unevenly spaced (n+1) points is given by

$$P_n(X) = Y = \sum_{i=0}^{n} y_i \times L_i(X)$$

where

$$L_i(X) = \frac{\prod_{r=0,\ (r \neq i)}^{n} (X - X_r)}{\prod_{r=0,\ (r \neq i)}^{n} (X_i - X_r)}$$

NEWTON

Using divided differences, the values are derived

$$Y = y_0 + (X - X_0)\,\delta(X_0, X_1) + (X - X_0)(X - X_1)\,\delta(X_0, X_1, X_2) + \dots\dots\dots + (X - X_0)(X - X_1)\,\dots\dots\,(X - X_n)\,\delta(X, X_0, X_1, \dots X_n)$$

where $\delta(X_0, X_1) = (y_0 - y_1)/(X_0 - X_1)$ and so on.

Lagrange's interpolation formula offered the best fitting. Each interval between two consecutive recorded readings is divided into three and polynominal upto 3rd degree was used. Program listing 1 briefs the written program. (The entire set of programs in basic and Fortran IV are available at CECRI computer centre). The pressure variable is divided initially and boundary values are evaluated. Later interpolation is done by taking the nearest y value on either side. Using the formulae 1-4, the various required parameters are evaluated. The results are transferred to MAKEGRAF routine available with the computer.

RESULTS

As has been done in the manual, curve 1 in Fig. 1 is used for pore size distribution, curve 2 is used for particle size calculation and curve 3 is used for surface area calculation.

In Fig. 2 the plots of pore size distribution by the two techniques are shown.

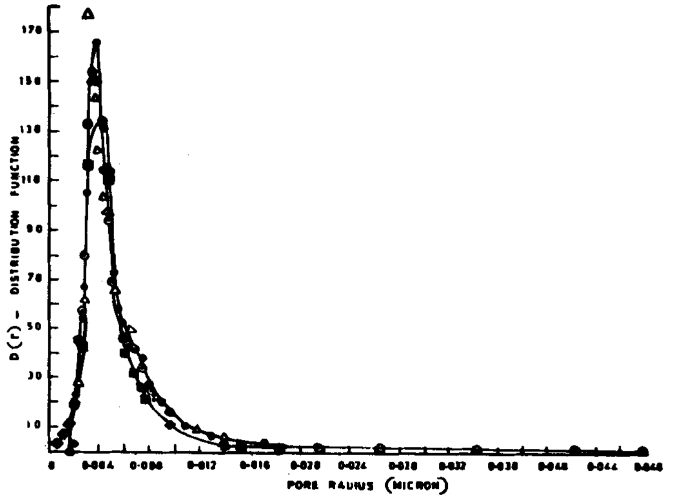

Fig. 2 : Pore distribution (pore radius vs distribution function)
- ⊠ -- *Curve (Ref. 1)*
- △ -- *First order-curve*
- ● -- *Second order-curve*
- ○ -- *Third order-curve*

In the manual, the peak is found to occur at a radius of 0.004 microns as can be seen in curve 1 in Fig. 2. With third order polynomial, the peak is at 0.00343 micron. With second order polynomial, it is at 0.0038 micron and with first order it is at 0.0031 micron. The pores tend to be predominantly about 0.0038 micron. By interfacing with the Graphics utility, we can get the analysed data immediately in the graphical form either on video display unit or in the printed sheet.

In Fig. 3 for curve 2 pore size distribution is shown.

It is found that it contains voids of 21.818 micron and pores of 0.0218/0.09 and 0.21 micron. In Fig. 4 for curve 3 it is found to have pores of 0.04/0.017/0.0075 and 0.00187 micron.

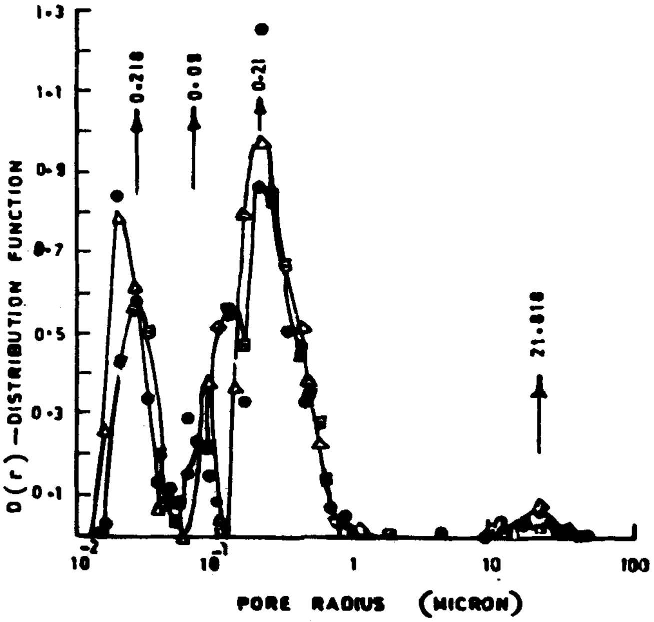

Fig. 3 : Pore distribution (pore radius vs distribution function) (Arrow mark indicates pore radius in microns)

● -- *First order-curve*
□ -- *Second order-curve*
△ -- *Third order-curve*

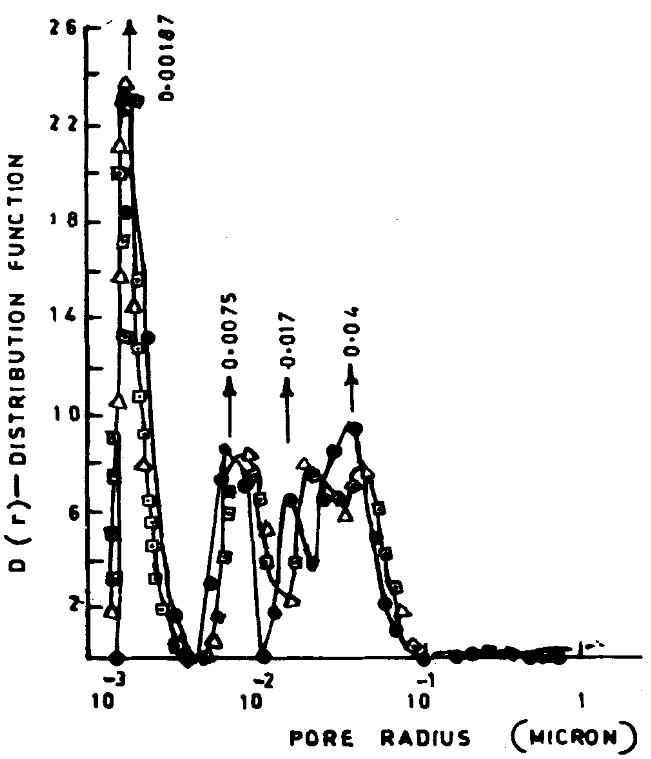

Fig. 4 : Pore distribution (pore radius vs distribution function) (Arrow mark indicates pore radius in microns)

△ , -- *First order-curve*
□ -- *Second order-curve*
● -- *Third order-curve*

For surface area calculation the result with Computer analysis on curve 3 is 30.8 × $10^3 m^2/kg$. Manual's graphical integration result is 29.4 × $10^3 m^2/kg$, and low temperature gas adsorption test result is 31.2 × $10^3 m^2/kg$. In computer analysis, change in degree of polynomial caused a variation of 2%.

For particle size distribution study curve 2 in Fig. 1 has been taken. The results are shown in Table I. Very good agreement with other methods can be noticed.

Table I : Particle size calculation from mercury penetration data

Pressure	Volume fraction greater		% less than (volume basis)		Particle radius MP			
P	M	C	M	C	M	C	Sieving	Sedimentation
2	0.06	0.057	94	94.30	120	120	110	—
3	0.27	0.264	73	73.60	80	80	98	—
4	0.61	0.612	39	38.80	60	60	80	—
5	0.80	0.800	20	20.00	48	48	55	53
7	0.90	0.903	10	9.10	34	34	45	42
10	0.95	0.947	5	5.28	24	24	35	31
20	0.98	0.994	2	0.57	12	12	—	22

M — Readings reported in the manual [2]
C — Result from our computer analysis
MP — Mercury penetration
(Particle radius expressed in micron)

After testing the developed software some of our laboratory experimental readings are tested for pore size distribution. Fig. 5

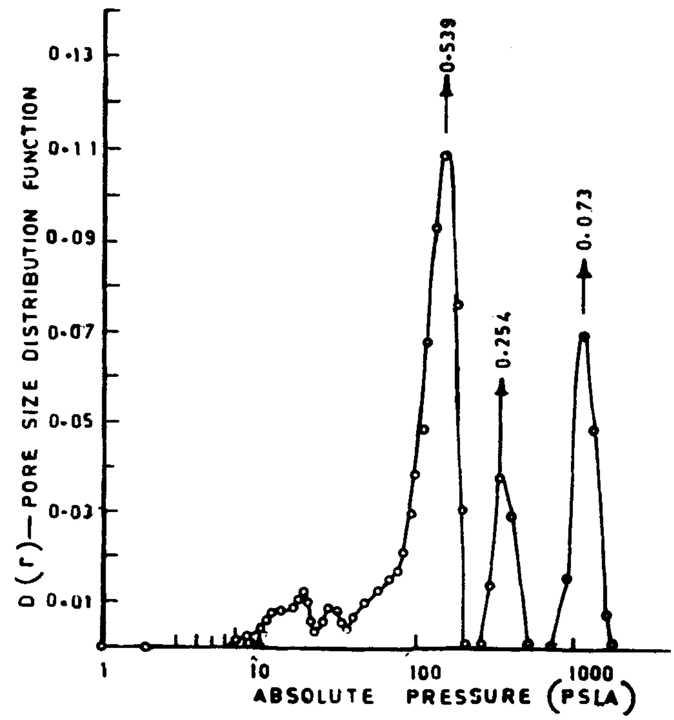

Fig. 5 : Pore size distribution function vs absolute pressure; oxygen electrode No. 623A dual porosity type (Arrow mark indicates pore radius in microns)

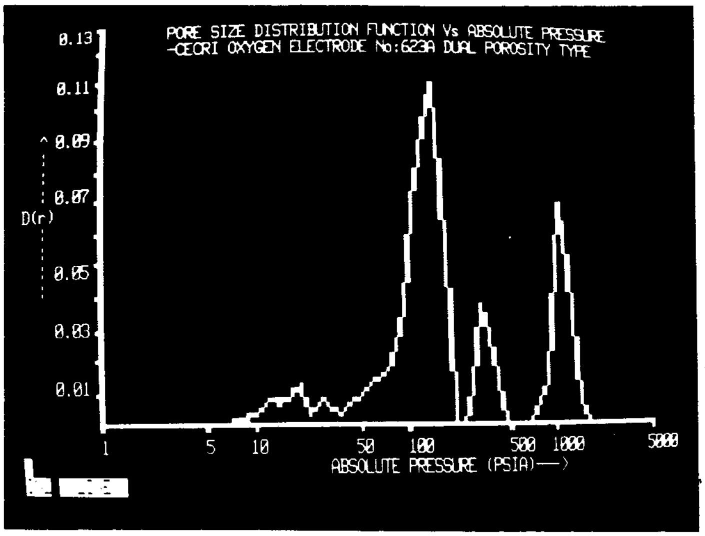

Fig. 6 : VDU — Photograph of Fig. 5.

shows the pore-size distribution of the oxygen gas diffusion electrode of dual porous type evaluated in a short time. It can be seen that the electrode contains predominantly pores of sizes 0.539, 0.254 and 0.073 microns.

ACKNOWLEDGEMENTS : The encouragement received from Shri H N Venkoba Rao, Head of the Electrochemical Instrumentation and Equipment Design Division and Dr V K Venkatesan, Head of in carrying out such type of analysis is greatly acknowledged. We thank Mr Pattabiraman and Mr R Chandrasekaran for referring the problem to us.

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3. R P Mayer and R A Stowe, *J Colloid Sci* **20** (1965) 893.
4. J B Scarborough, *Numerical Methods of Analysis*, Oxford and IBH Publishing Co., Calcutta (1971) Chap III.

FOR PROGRAM LISTING REFER TO THE FOLLOWING THREE PAGES.