

Comparison of Mercury Porosimetry and Flow Porometry for the Testing of Battery Separator Materials

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ABSTRACT

Control of porosity is very important for proper functioning of battery separators. Specifications of mean pore size and percent porosity are commonly an integral part of separator acceptance criteria. To date most testing of these parameters has relied on mercury intrusion porosimetry. Recently, a new technique, flow porometry, has been introduced which has the potential of more accurately predicting product performance. This technique categorizes pore structure based on flow rates through the membrane and is specially useful in locating pore structure defects, which can be a chief cause for product failure, and malfunctioning. Data from both mercury intrusion and flow porometry analyses on different types of separator materials are critically examined and discussed. It is proposed that the battery industry could benefit by using information created by flow porometry to augment its reliance on mercury porosimetry data.

Introduction

Battery separators are sheets of porous material. The porous structure of battery separators allows flow of electrolytes in batteries. Permeability, strength and ability to maximize ionic conductivity are characteristics of separators. Therefore, testing of battery separators and control of their pore characteristics are important requirements for proper functioning of batteries. Mercury porosimetry is normally used to characterize the separators in terms of percentage porosity and mean pore size. Recently, a novel technique, Capillary Flow Porometry has been developed to characterize battery separators. This instrument can measure a number of characteristics of battery separators such as size of the pore at its most constricted part, the largest pore size, pore size distribution, permeability and envelope surface area. In this investigation, both of these techniques have been used to characterize battery separators and the results have been critically examined.

Technique

Mercury porosimetry: In this technique, the sample is evacuated and surrounded with mercury. Mercury is non-wetting to the separator material. Therefore, mercury does not flow in to the pores in the sample. On increase of pressure on mercury, it flows in to the pores in the sample. The pressure required for intrusion of mercury in to a pore of diameter, D is given by the following relation (1).

$$D = - (4\gamma \cos \theta) / p \quad (1)$$

where D is the diameter of the pore assuming the pore to be cylindrical, p is the differential pressure, γ is the surface tension of the non-wetting liquid, mercury and θ is the

contact angle of mercury. Accurate measurement of pressure and volume of intrusion yields pore volume and pore volume distribution.

Capillary Flow Porometry: In this technique (2), the sample is brought in contact with a wetting liquid, which fills the pores in the sample spontaneously. Gas pressure on one side of the sample is slowly increased to remove the liquid from pores and increase gas flow. The pressure required to displace liquid at a location in the pore is given by the following equation (2).

$$D = (4\gamma \cos \theta) / p \quad (2)$$

where D is the diameter of the pore at the location assuming the pore to be cylindrical at that location, p is the differential pressure, γ is the surface tension of the wetting liquid and θ is the contact angle of the wetting liquid. It follows from this relation that the largest pore is emptied at the lowest pressure and initiates gas flow. With increase in pressure, smaller pores are emptied and the flow rate increases. The flow rate measured as a function of gas pressure yields many characteristics of separator material. Fig. 1 shows the capillary flow porometer. It uses state-of-the-art components, innovative designs and windows based software to increase pressure in small intervals and measure pressure and flow rates accurately to yield highly reproducible, accurate and reliable data (3). Typical results obtained with a separator are shown in Fig.2

The wet and dry curves in Fig.2 correspond to wet and dry samples respectively. The half-dry curve is calculated from the dry curve to yield half of the flow rate at any pressure. The pressure at which the flow starts is known as the bubble point pressure. This pressure corresponds to the largest pore

diameter. The intersection of the half-dry curve with the wet curve gives the mean flow pressure corresponding to the mean flow pore diameter. Flow through pores larger than the mean flow pore diameter is half of the flow through the sample.



Fig. 1 (a) Capillary Flow Porometer

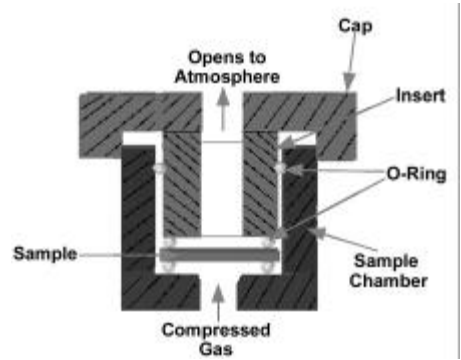


Fig. 1 (b) Sample chamber.

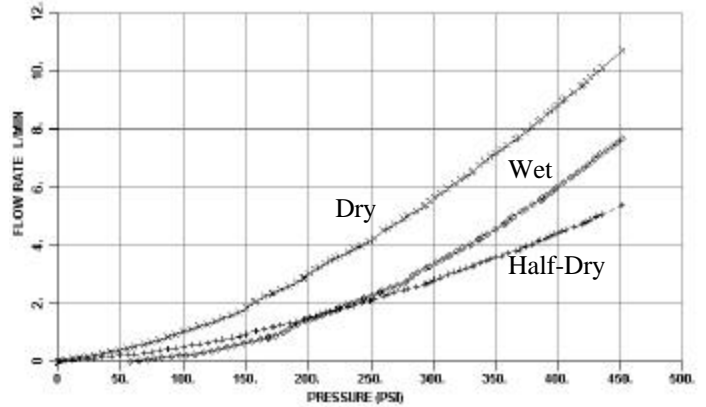


Fig.2 Variation of flow rate with gas pressure for wet and dry samples of a battery separator.

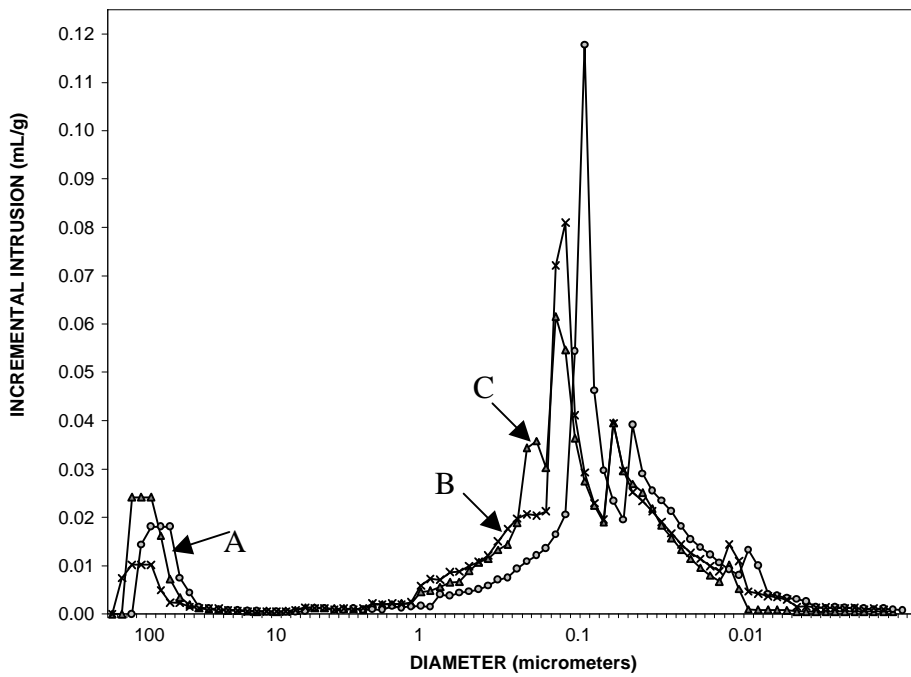


Fig. 3 Pore volume distribution of three separators. (a) A incremental volume. (b) B incremental volume. (c) C incremental volume.

Results

Mercury porosimetry: The results of mercury intrusion carried out on three different samples are presented in Table I. The pore volume distributions of the three samples are presented in Fig.3.

Table I Mercury intrusion data

Characteristics	Samples		
	A	B	C
Pore Volume, ml/g	0.7633	0.7964	0.7586
Surface Area, sq-m/g	43.074	45.255	35.616
Median Pore Diameter (volume), μ	0.1458	0.1491	0.1642
Porosity, %	47.76	48.15	46.35

Capillary flow porometry: The results obtained with the three separators are listed in Table II.

Table II Pore size by flow porometry

Sample	Diameter, microns	
	Largest Pore	Mean Pore
A	0.1134	0.0295
B	0.1256	0.0237
C	0.1275	0.0327

The pore size distribution is obtained from the flow rates through wet and dry curves. The flow rate through the sample can be expressed in terms of the equations for viscous flow (4):

$$F = [\pi\beta / (128 \mu / 2p_s)] [p_i + p_0] [\sum_i N_i D_i^4] [p_i - p_0] \quad (3)$$

where;

F = flow rate in volume at STP

β = a constant

μ = viscosity

l = sample thickness

p_s = standard pressure

p_i = inlet pressure

p_0 = out let pressure

N_i = number of pores of diameter D_i

It follows from this relation that the ratio of flow rate through wet sample F_w and the flow rate through dry sample F_d measured at the same pressure p_i is independent of pressure. The ratio depends upon pore number and pore diameter.

Pore size distribution, f is defined as:

$$f = - d[100 \times (F_w / F_d)]_{p_i} / dD \quad (4)$$

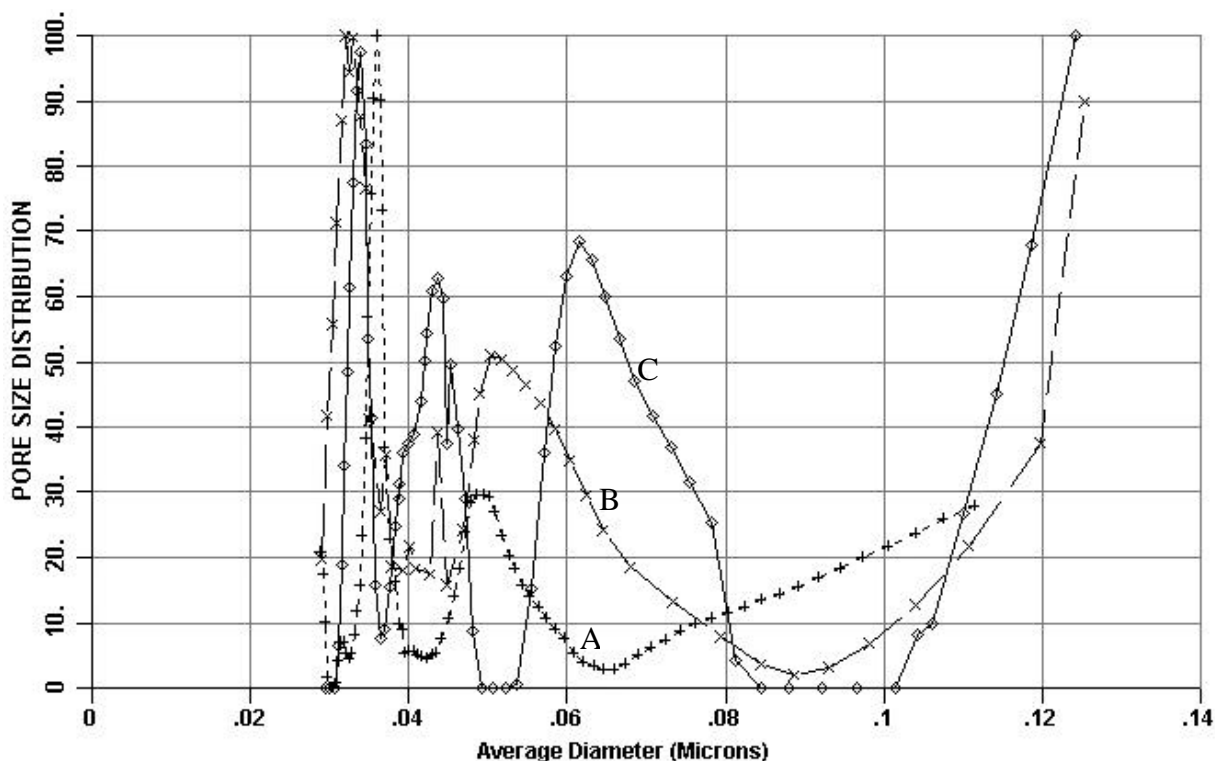


Fig.4 Pore Size distribution of the three samples.

The leading negative sign on the right hand side of this equation is due to the fact that decrease in pore diameter increases the flow rate. The % flow through any desired pore size range is given by the area under the distribution function–diameter curve. Pore size distributions of the three materials are shown in Fig.4

Discussion

Pore size: The size of a pore varies along its length. Therefore, pore sizes measured by different instruments are different. Fig. 5 shows a wetting liquid filled pore whose size varies along its length. The gas pressure required to displace the liquid in the pore changes with change in the pore size along the length of the pore. Gas pressure required to displace the liquid in the most constricted part of the pore is the maximum. Only when gas pressure is equal to this maximum pressure will the gas displace the liquid in the pore and completely empty the pore allowing gas flow to occur. Flow porometry measures this maximum pressure of the gas that permits gas flow. Therefore, the measured pressure gives the pore diameter, D at the most constricted part of the pore.

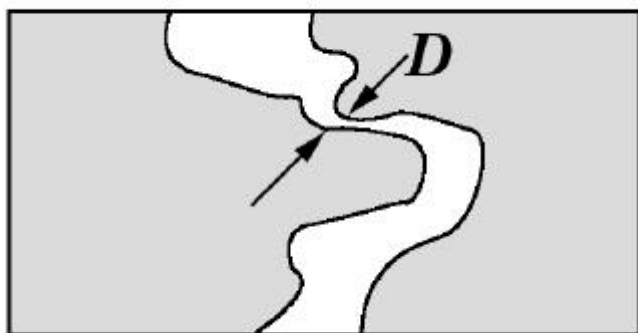


Fig. 5 Variation of pore diameter

Porosimetry measures the volume of intrusion. Therefore, the single pore in Fig.5 is measured by porosimetry as many pores within a range of pore diameters. The constricted pore diameter measured by flow porometry is the most appropriate for evaluation of barrier characteristics of separators for particles and ions.

The largest pore size: Flow porometry can measure the largest pore diameter very accurately. The pore diameter is required when a particle or ion of a given size is prevented from passing through the separator. If there is a defect in the separator, that is also detected as the largest opening in the separator. The largest pore size cannot be detected by porosimetry

Pore volume: Total pore volume, porosity and bulk density are measurable by porosimetry. However, these properties cannot be measured by flow porometry.

Surface area: For determining surface area by porosimetry the term, $\int p dV$ is evaluated. Since small pores having large surface areas are associated with large p and very small dV , the measured surface area is generally not very accurate. Also, presence of blind pores can give an over estimation of surface area as illustrated in Fig.6. Flow porometry cannot measure total surface area, but envelope surface area (surface area of through pores only) and average particle size or fiber diameter can be measured by flow porometry (5).

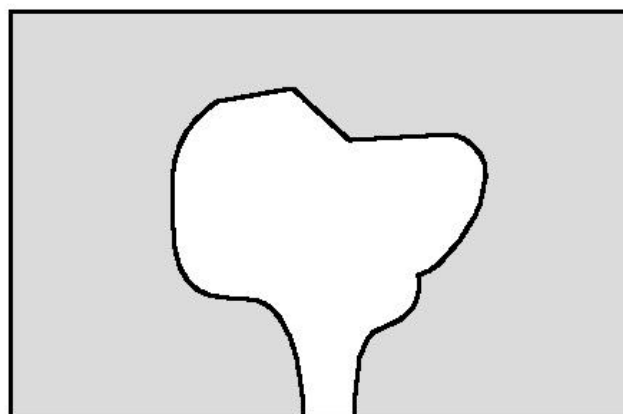


Fig.6 Blind pore that results in over estimation of surface area.

Pore distribution: Pore distribution data obtained from porosimetry and flow porometry (Figs, 3 & 4) show considerable difference between the two sets of data on the same material. Porosimetry shows large pores of appreciable volume where as porometry shows very small pores. Let us consider the pore morphology shown in Fig.7. The pore has a small constriction, but wide mouth. This pore will be detected by flow porometry as a single pore of small diameter. However, porosimetry will measure the wider parts of the pore as large pores of considerable volume and the constricted part of the pore as a small pore of small volume associated with the narrowest part of the pore. This is consistent with our observations. Flow porometry shows that the largest pore has a size of about 0.12μ and pores are appreciable below 0.06μ , while porosimetry shows appreciable pore volume in the much higher size ranges of about $0.01-1 \mu$ and $15 - 150 \mu$.

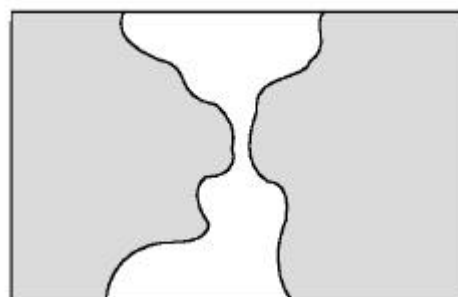


Fig.7 Pore shape

Future work

The pore distributions of the three materials obtained by porosimetry are very close to each other. However, the pore distributions obtained by flow porometry for the same three materials show more details and many interesting features (Fig.4). The largest pore within two of the samples is much greater when compared with that of the third sample. Each sample shows almost bimodal distribution corresponding to two groups of pores. However, the pore groups in different materials appear at different pore diameters. For example the first peak in the distribution curve occurs at about 0.063, 0.052 & 0.049 μ in materials C, B, & A respectively.

Observation of bimodal distribution, distribution peaks at different pore diameters and wide range of the largest pore size is consistent with the different morphologies of separator materials produced during manufacturing. Porosimetry cannot as easily differentiate between these features.

Mean pore size: The mean pore diameters in Tables I & II suggest that the average pore size measured by porosimetry based on volume is almost an order of magnitude greater than that measured by flow porometry. This result suggests that the pores have wide mouths as illustrated in Fig.7.

Permeability: The dry curve in Fig.2 gives the permeability of air through the battery separator and the envelope surface area. The instrument can also give permeability of liquids and chemicals through the battery separator.

Conclusion

- Three battery separators were tested by mercury porosimetry and the new technique, capillary flow porometry.
- Porosimetry yielded pore volume, surface area, mean pore diameter and pore distributions, which were almost identical.
- Flow porometry gave the largest pore diameter, mean flow pore diameter and pore distribution. The distributions as well as the largest pores were appreciably different amongst the samples.
- Pore volume and total surface area measurable by porosimetry are not measurable by flow porometry.
- Constricted pore diameter, the largest pore diameter, permeability and envelope surface area measurable by flow porometry but cannot be measured by porosimetry.
- Flow porometry provides more applicable characterizations of battery separators given its ability to provide both gas and liquid permeability in a manner most like the actual functioning of a membrane in battery use.

This is the first in a series of papers relating to the study of microporous battery separators. Future work will further compare separator types and show how materials and manufacturing processes can alter the porous structure.

References

1. Washburn, E.W. *Proceedings of the National Academy of Sciences*, U.S. **1921**, 7, 115-16.
2. Jena, A.K.; Gupta, K.M. *J. Power Sources*, **1999**, 80(1-2), 46-52.
3. Gupta, Vibhor; Jena, A.K. *Advances in Filtration and Separation Technology, American Filtration and Separation Society*, **1999**, 13b, 833-44.
4. Scheidegger, C.R. *The Physics of Flow Through Porous Media*, Macmillan, New York, **1957**
5. Sanders, Howard; Jena, Akshaya *Ceramic Industry*, **2000**, 3(November), 1-4.