Pore Characterization of Li Ion Battery Separators by Capillary Flow Porometery and Water Intrusion Porosimeter

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Lithum ion Batteries are widely used in many types of consumer electronic devices as they are rechargeable and have high energy density as well as good electrochemical performance. The LIB's use separator which is a permeable membrane placed between battery's anode and cathode. The separator keeps the two electrodes apart to prevent electrical short-circuits while allowing transport of ionic charge carrier to complete the circuit during passage of current in an electrochemical cell.

The market for lithium-ion battery (LIB) separator is expected to register a CAGR of 18.01%, during the forecast period (2019-2024) Source Morodor intelligence. Apart from consumer electronics, like laptops and cell phones, Electric Vehicle manufacturers are becoming one of the most significant customer bases of battery. The key market players Sumitomo Chemical Co. Ltd. Asahi Kasei Corp., Toray Industries Inc., Entek International LLC, SK Innovation Co. Ltd, W-Scope Corp., Ube Industries Ltd., Mitsubishi Electric Corporation , Thermo Fisher Scientific Inc., and few others.

Separator is a critical component of Li ion battery and is generally a polymeric membrane forming microporous layer. Apart from chemical and electrochemical stability, the separator should be mechanically strong to strong to withstand the high tension during battery construction.

The separator has strong impact on cell performance, battery life, safety and reliability. Further Li ion batteries for high power applications is increasing getting widespread, hence it is imperative that industry will demand development of new type of separators

to meet performance, safety and costs targets.

Characterization Requirements of Battery Separator Researchers:

Pore Size of constricted pore as shown in fig1 is important parameter as the separator must have must have good insulation to prevent short circuit between positive and negative contacts or prevent short circuit caused by burrs, particles and dendrites

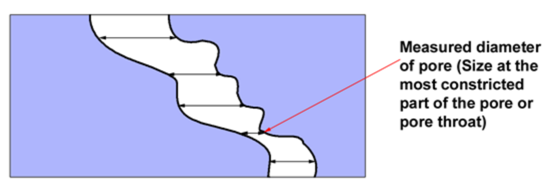


Fig1 : Most constricted part or pore throat

Apart from measurement of most constricted pore size, Porosity and Pore volume of separators give important information on separator resistance and battery capacity

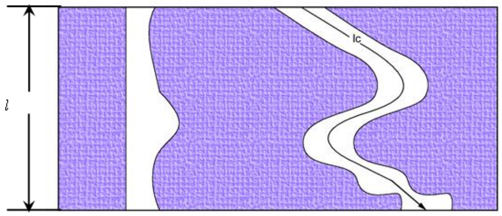


Fig2: Tortuosity of pore

Gas permeability measurement also reflects the separator resistance as the migration of lithium ions is affected by the materials and pores of the separator, so the separator needs to have a high porosity and a uniform distribution of pores. High temperature performance of separator is also critical as the diaphragm should still block the positive and negative poles after the pores have closed in order to avoid internal short circuit.

Capillary Flow Porometery Principle and Measurement of Battery Separator: This technique uses samples with pores filled with a wetting liquid. The gas pressure required to remove the liquid from the pores and the flow rate of the gas through open pores are measured (Fig. 3)

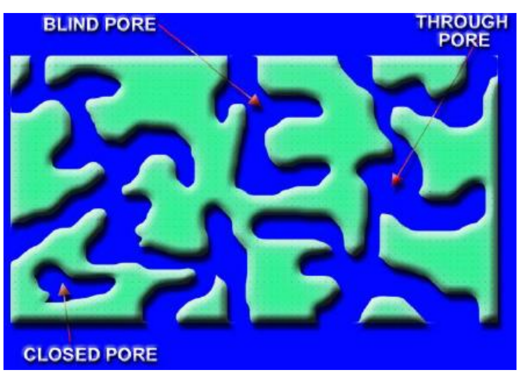


Fig 3: Blind, Through and Closed Pores

The gas pressure is inversely proportional to pore diameter. From such measurements, almost all the characteristics such as the largest pore size, pore size distribution, mean pore size and gas permeability can be measured.

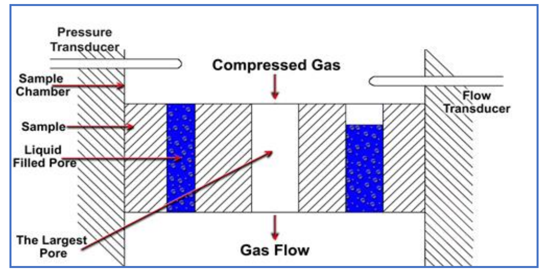


Fig 4: Principle of Capillary Flow Porometery

The schematic representation of Capillary flow Porometery is shown in fig 4. Although it is a versatile technique, it can't measure pore volume or calculate porosity.

PMI Porometer Model iPore-1500AEX as shown in fig 5 was used to measure the constricted pores of battery separator.

Fig 5: PMI Capillary Flow Porometer

The PMI Porometer had pressure range upto 500 PSI with an extra 5 PSI pressure transducer for accurate measurement of large pore sizes. The PMI Porometer with 500 PSI pressure range can theoretically measure through pores upto 0.013 µm. The wetting solution used was Galwick liquid provided by PMI with surface tension of 15.9 dynes/cm. The testing was done under dry up-wet up mode. The pressure increment was precisely controlled through a combination of low and high-pressure gas regulator, further backed up by a motorized valve.

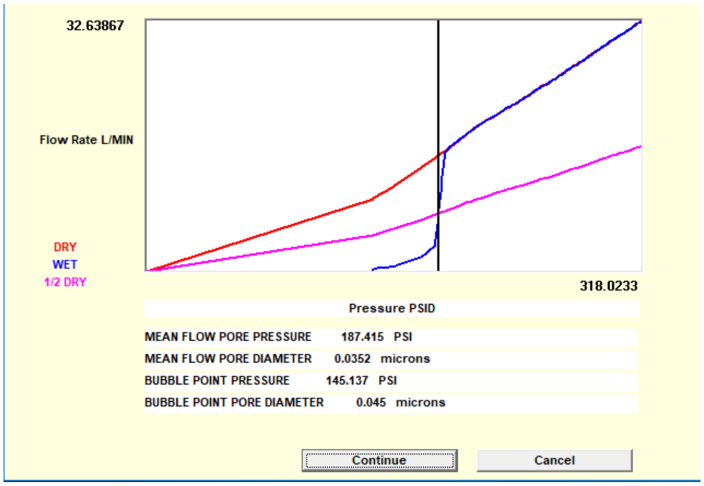


Fig 6: Battery Separator Through Pore Measurement

Bubble Point of 0.045 µm at bubble point pressure of 145 PSI and a Mean Pore size of 0.0352 µm with Mean Flow Pore Pressure of 187 PSI were measured.

The same sample was measured repeatedly as shown in fig 7 to check the repeatability of data.

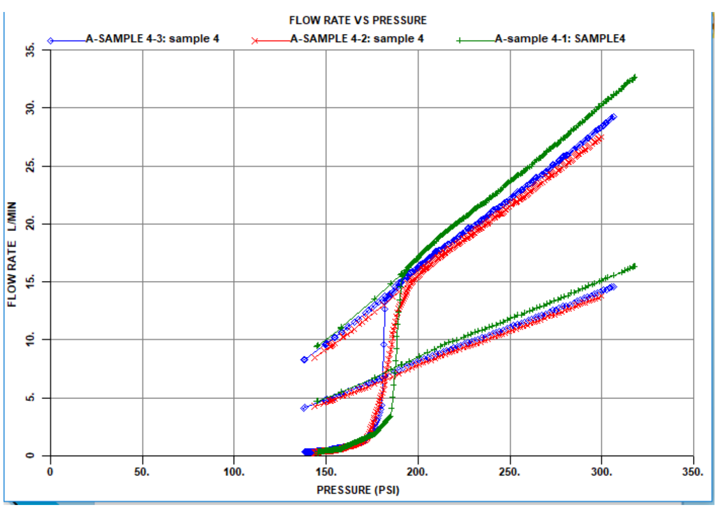


Fig 7: Graph overlay of separator measured three times

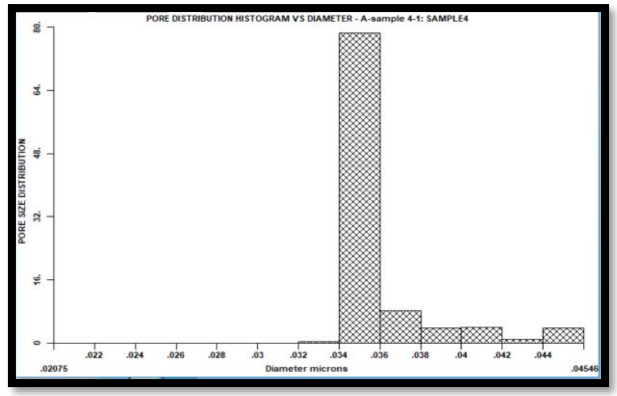


Fig 8: Pore distribution for first round

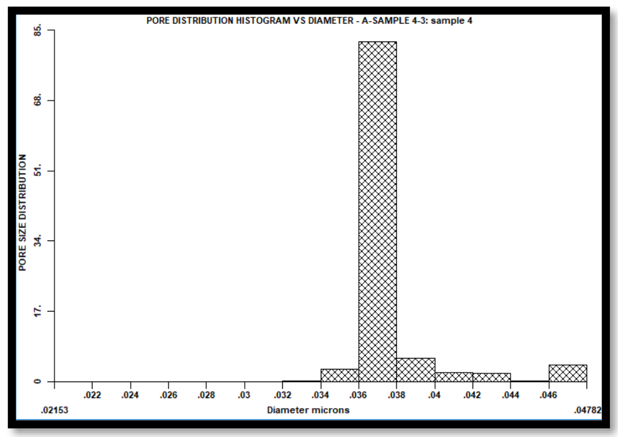


Fig 9: Pore distribution for second round

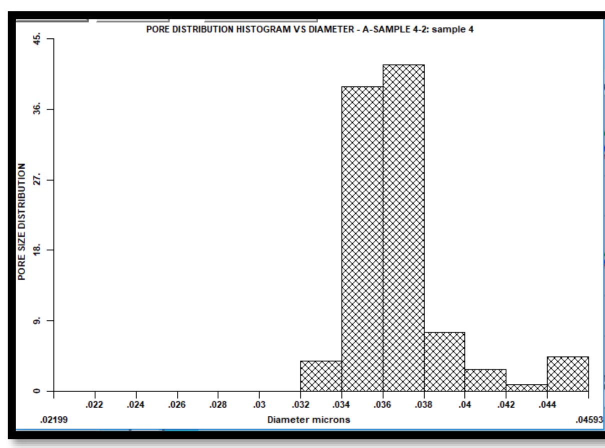


Fig 9: Pore distribution for third round

The pore distribution for all 3 repeat measurements showed a good repeatability without any damage to the separator pore characteristics.

Water Intrusion Porosimeter Principle and Measurement of Battery Separator : It is based on the principle that Water can spontaneously enter the hydrophilic pores of the sample, but cannot spontaneously enter the hydrophobic pores. Application of differential pressure on water can force it in to hydrophobic pores. In water intrusion porosimetry, the sample is surrounded by water and pressure in increased on water to force it in to the hydrophobic pores. The measured intrusion volume of water gives volume of hydrophobic pores and the differential pressure on water gives pore diameter through equation given below :

$$D = - 4 \gamma \cos \theta / p$$

Where D is pore diameter, γ is surface tension of water, θ is contact angle of water and p is differential pressure.

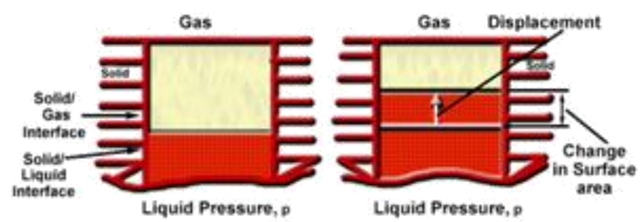
The PMI Aquapore as shown in fig 10 was used in this investigation.

Fig 10: PMI Water Intrusion Porosimeter "Aquapore"

Aquapore™ is a Liquid Intrusion Porosimeter used for hydrophobic pores. Water does not wet hydrophobic pores. Intrusion of water into pores occurs on application of pressure. Measured intrusion volume of water yields pore volume and measured intrusion pressure yields pore diameter

Work done by liquid = Increase in surface free energy

$$(P - p_g)\, dV = \gamma_{s/l}\, dS_{s/l} + \gamma_{s/g}\, dS_{s/g} + \gamma_{l/g}\, dS_{l/g}$$



P	=	pressure of the
p_g	=	nonwetting liquid pressure of gas in pore
dV	=	infinitesimal increase in the volume of nonwetting liquid in the pore
$dS_{s/g}$	=	infinitesimal increase of the solid/gas interfacial area
$dS_{s/l}$	=	infinitesimal increase of the solid/liquid interfacial area
$\gamma_{l/g}$	=	liquid/gas interfacial free energy
$dS_{l/g}$	=	infinitesimal increase of the liquid/gas interfacial area

PMI's Aquapore is a fully-automated water intrusion Porosimeter. It is the safest and highly accurate instrument for measurement of pore structure of battery separators, polymer films, solids, and powder samples. It measures pore volume, pore size distribution, pore volume distribution for through and blind pore.

Water was used to porosity of battery separator. The sample of weight 0.2940 grams with bulk density of 0.4182 g/cc was used for this measurement.

Sample Weight = 0.2940 g
Bulk Density = .4182 g/cc
Liquid = Water
Non-Mercury Contact Angle = 118 Degrees
Non-Mercury Surface Tension = 72 Dynes/cm

Cumulative pore volume in cc/g of sample
% total pore volume = % of total cumulative pore volume belonging to pores of diameter > D
Average pressure = square root of P(I)*P(I-1)
Pore size distribution function is equal to dV/dlog P
Surface area assumes cylindrical pores

Pressure PSIA	Pore Diameter Microns	Cumulative Pore Vol. cc/g	%Porosity	% of total Pore Vol.	Average Pressure PSIA	dV ----- dlogP	Cumulative Surf. area m2/g
55.595	0.3526	0.0	0.0	0.0	55.595	0.017	0.0
63.985	0.3064	0.001	0.043	0.219	59.643	0.0	0.0126
78.885	0.2485	0.001	0.043	0.219	71.045	0.032	0.0126
94.065	0.2084	0.0035	0.147	0.743	86.141	0.0	0.0562
119.955	0.1634	0.0035	0.147	0.743	106.224	0.0	0.0562
143.955	0.1362	0.0035	0.147	0.743	131.408	0.0	0.0562
169.755	0.1155	0.0035	0.147	0.743	156.324	0.0	0.0562
213.705	0.0917	0.0035	0.147	0.743	190.467	0.0	0.0562
258.705	0.0758	0.0035	0.147	0.743	235.131	0.0	0.0562
302.355	0.0648	0.0035	0.147	0.743	279.68	0.168	0.0562
334.005	0.0587	0.0108	0.45	2.276	317.786	1.863	0.526

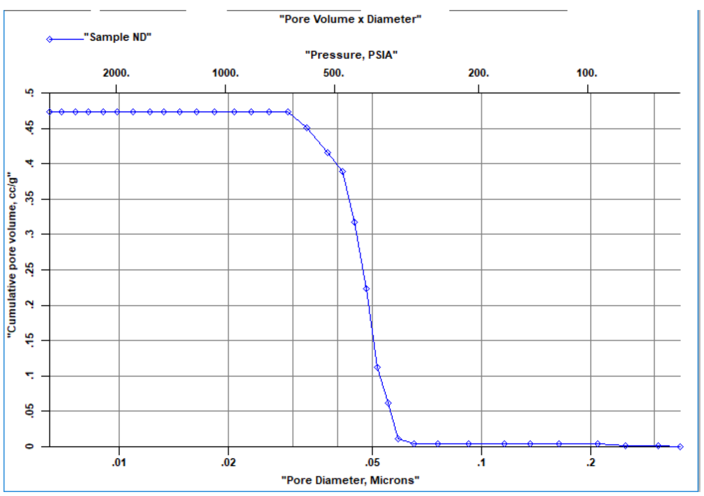


Fig 11: Intrusion Curve for Batter Separator

Figure # 11 shows the intrusion curve for battery separator samples measured using PMI Aquapore Water Intrusion Porosimeter.

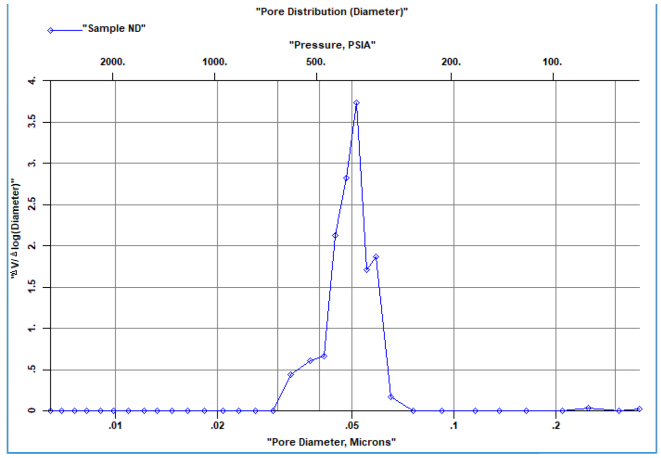


Fig 12: Pore Distribution of Battery Separator

Figure # 12 shows the pore distribution of battery separator using using PMI Aquapore Water Intrusion Porosimeter. The same sample was measured three times to check the repeatability of the measurement.

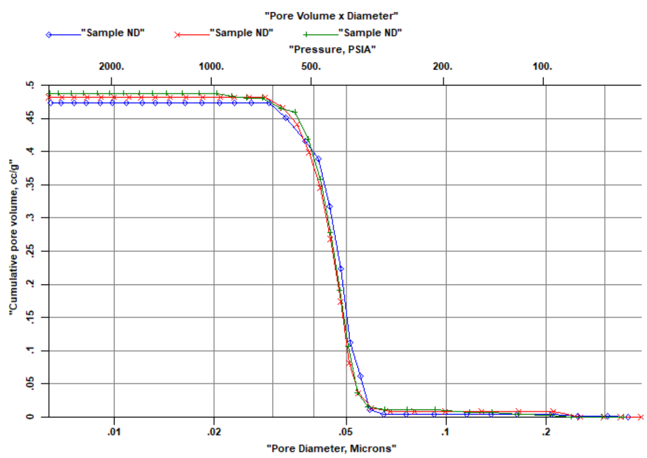


Fig 13 : Intrusion curve overlay

Figure # 13 shows the intrusion curve overlay for three repeated measurements of same sample. The intrusion curves show good measurement repeatability for all three measurements.

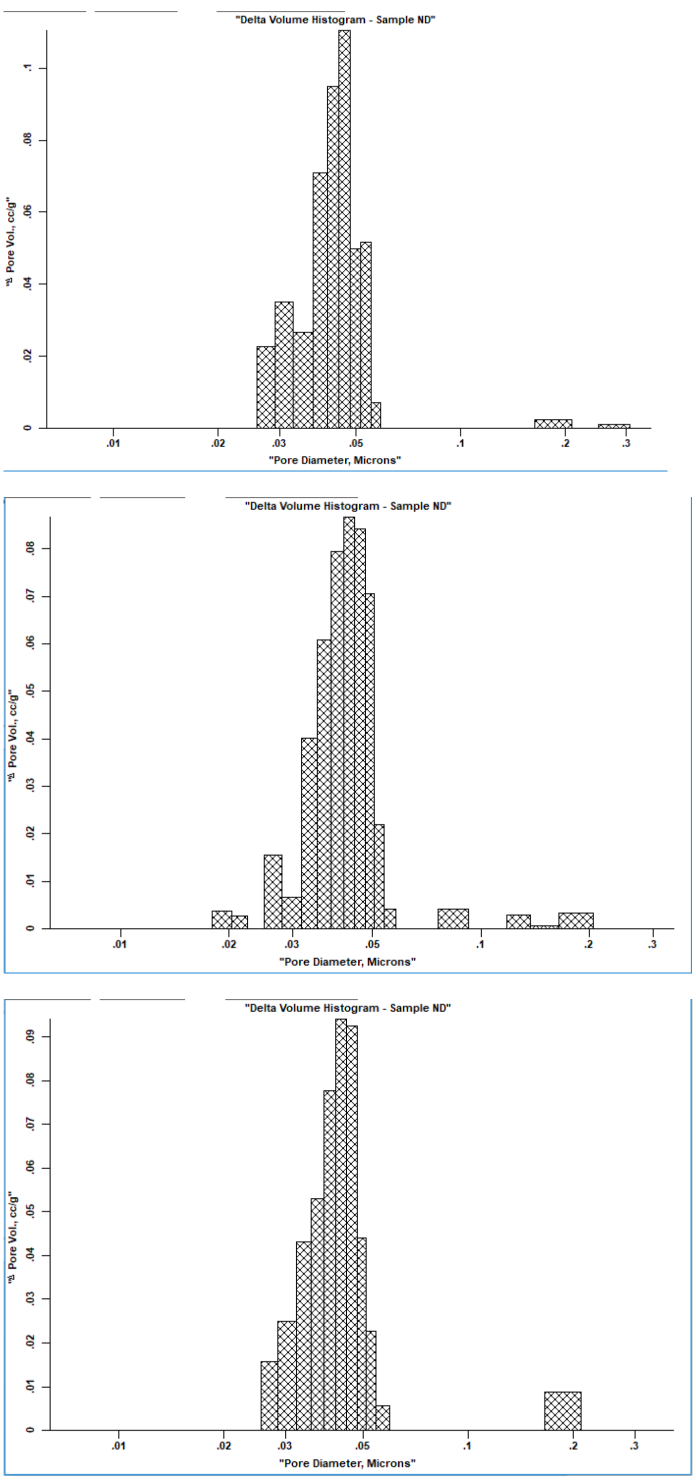


Fig14: The above three graphs are pore size distribution for three repeated measurements of sample. The distribution has good repeatability for all three measurements.

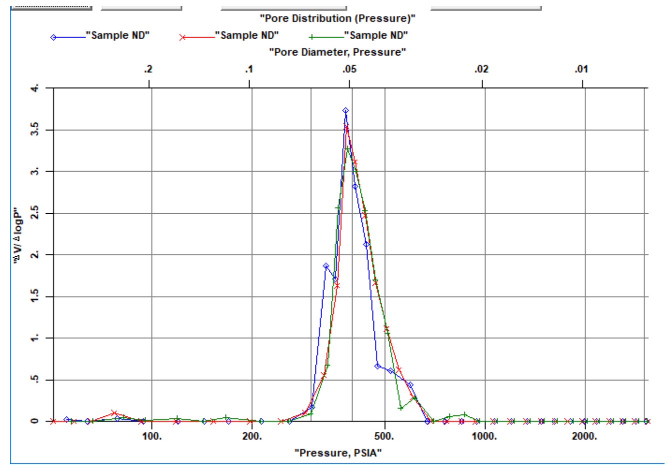


Fig 15: Graphical overlay of all three repeated measurements which show pore distribution against pressure.

The following results were obtained for pore size and porosity in all the three measurements.

Parameter	Run 1	Run 2	Run 3
Intrusion Volume	0.4728 cc/gm	0.4873 cc/gm	0.4824 cc/gm
% Porosity	19.7%	19.8%	19.8%
Pore Median Diameter (based on volume)	0.0476μm	0.046μm	0.0457μm

Excellent repeatability in intrusion volume, porosity and pore diameter was observed. Similarly the gas permeability was measured for

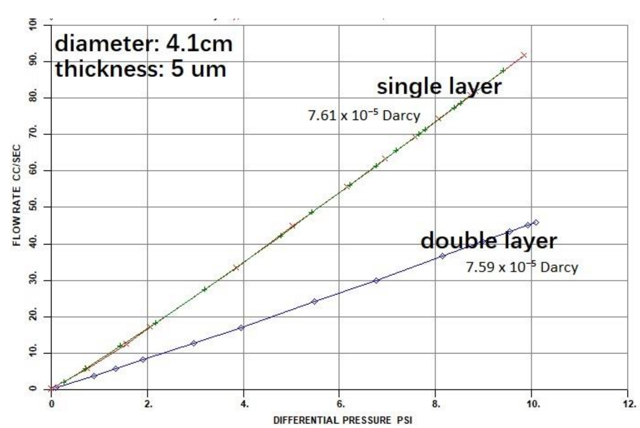


Fig 16: Gas Permeability

Single layer and double layer battery separator as shown in figure 16. The conventional Gurley

Permeability method gives value in seconds and was found to be between 90-450 seconds , whereas the Darcy Permeability was found to be quite similar for single layer and double layer which was 7.61 X 10^{-5} Darcy and 7.59 X 10^{-5} Darcy respectively.

Conclusion: For measurement of Porosity and Pore Volume Distribution, Water Intrusion Porosimeter "Aquapore" provides good repeatability for through and blind pores for hydrophobic pores without any damage to the sample. Also, it is a non-hazardous and safe mercury free technique.

The Capillary Flow Porometer is well suited for measuring constricted pore size of open or through pores and measures pores from 0.013µm

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