



BATTERY ELECTRODES & SEPARATORS - PORE ANALYSIS BY MERCURY POROSIMETRY

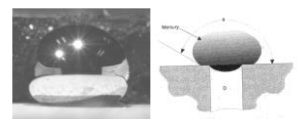
Introduction

Battery materials like electrodes and separators are porous materials. Homogeneous distributions of well-defined pore sizes are an important factor for optimum and reliable battery performance. Since the pores are in the range of a few 100 nm up to several microns, these cannot be detected by gas adsorption techniques, they are too large. Therefore, Mercury Intrusion Porosimetry (MIP) is the proper and suitable technique.

Basics of Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry is described in the ISO standard ISO 15901-1. The non-wetting mercury is forced into the pores at ambient temperature with pressures up to 414 MPa entering pores down to ca. 3.6 nm pore diameter (Figure 1). The pore volume corresponds to the intruded amount of mercury. According to the Washburn equation, the pore size (radius, diameter) is inversely proportional to the applied pressure.

$$r = - \frac{2\gamma \cos \theta}{p}$$



with pore radius r [m], surface tension of mercury $\gamma = 0.48$ N/m, and intrusion pressure p [Pa].
With a contact angle $\theta = 141.3^\circ$ a simple estimation for the pore radius is obtained

$$r \approx 0.7500/p.$$

BELPORE - the Device for Safe Mercury Intrusion Porosimetry



The BELPORE mercury porosimeters can measure pore diameters from 3.6 nanometers up to 1 millimeter. They consist of 3 models: **BELPORE LP** as mercury filling device and for low pressures, **BELPORE MP** for medium-high pressures, and **BELPORE HP** for high pressures, details see Figure 1.

The BELPORE mercury porosimeters work according to the P.A.S.C.A.L. principle which is not only a pressure unit. In the BELPORE porosimeter, it means the equilibrium-controlled and optimized control of the pressure build-up by "Pressurization by Automatic Speed-up and Continuous Adjustment Logic". This automatic control is driven by the real pore system and allows shorter measuring times with guaranteed equilibrium conditions and detection of all pores within the specification, up to 20,000 measuring points per analysis. Pressure tables are thus

superfluous. Since only two types of dilatometers (sample cells for powder or solids) are sufficient for most measuring tasks,

and furthermore no gases or liquid nitrogen are required, running costs can be kept significantly lower. Other innovations include simplified operation of the BELPORE LP low-pressure porosimeter and employing the ultra-macropore dilatometer an extended measuring range up to pore sizes of 1 millimeter, applicable for thin membranes. Vertical degassing and filling with mercury on the BELPORE LP is not only fast but allows also the degassing pressure to be adjusted. Therefore, it is possible to measure moist samples without changing the material moisture. The 3-D evaluation software PoreXpert is optionally available. With this software, e.g. tortuosity, diffusion, percolation, and much more can be derived from porosimetry data.

An application request from electrode manufacturers was incorporated, namely the compression correction and the bulk modulus value which is calculated from the compression.

BELPORE porosimeters are available in pressure ranges from 0.01 kPa to 450 kPa (and mercury filling), 0.1MPa to 228 MPa or up to 414MPa (Figure 1). High-precision measurements are finished in less than 1 hour, for quality control it can go down to 9 minutes.

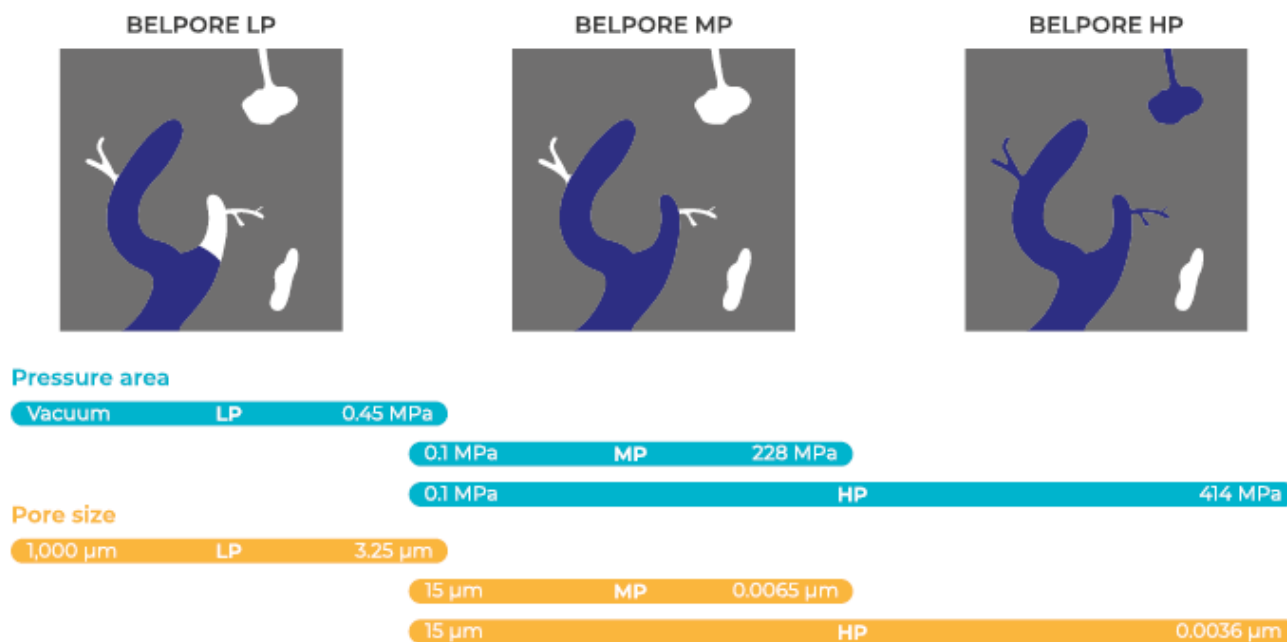


Figure 1. Pressure ranges and accessible pore sizes of the BELPORE porosimeters

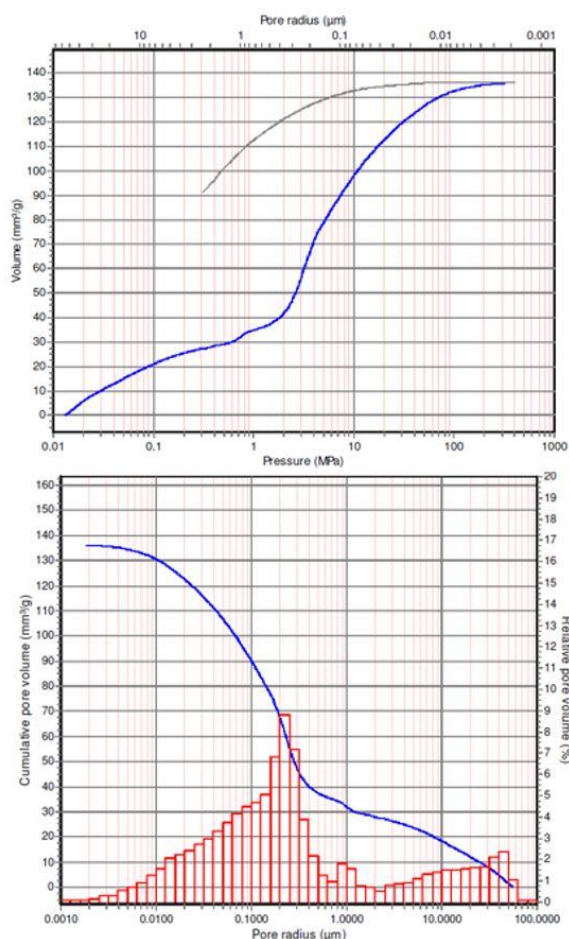
Results

Figure 2 shows two examples of an anode and a cathode. First, the pore volume is different, the anode shows ca. 140mm³/g while the cathode has less volume with ca. 100 mm³/g. In addition, the pore sizes differ with a peak of 200 nm for the anode and 500 nm for the cathode, with a wider pore size distribution of several 10 microns.

The measurement results of two different separators are presented in Figure 3. Again, the entire pore size range from 0.01 to 100 microns is only detectable with mercury intrusion porosimetry.

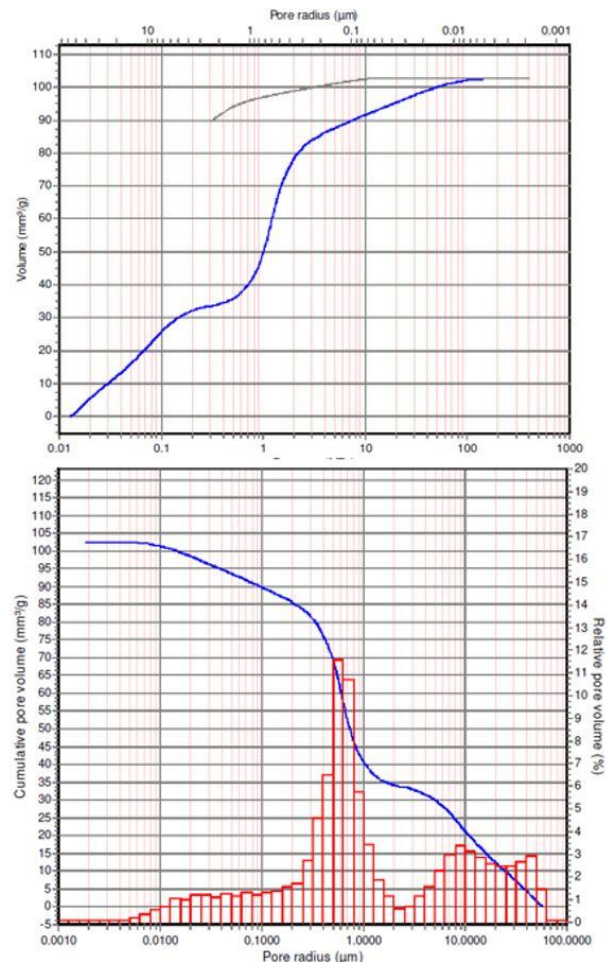
In Figure 3 the pore size distribution is shown as $dV/d \log r$ while also a histogram distribution with variable bar width as in Figure 2 is possible. The latter may be more convenient for quality comparisons.

Anode



Pore Size Max. ca. 200 nm

Cathode



Pore Size Max. ca. 500 nm

Figure 2. Pore size distributions of a battery anode and cathode.

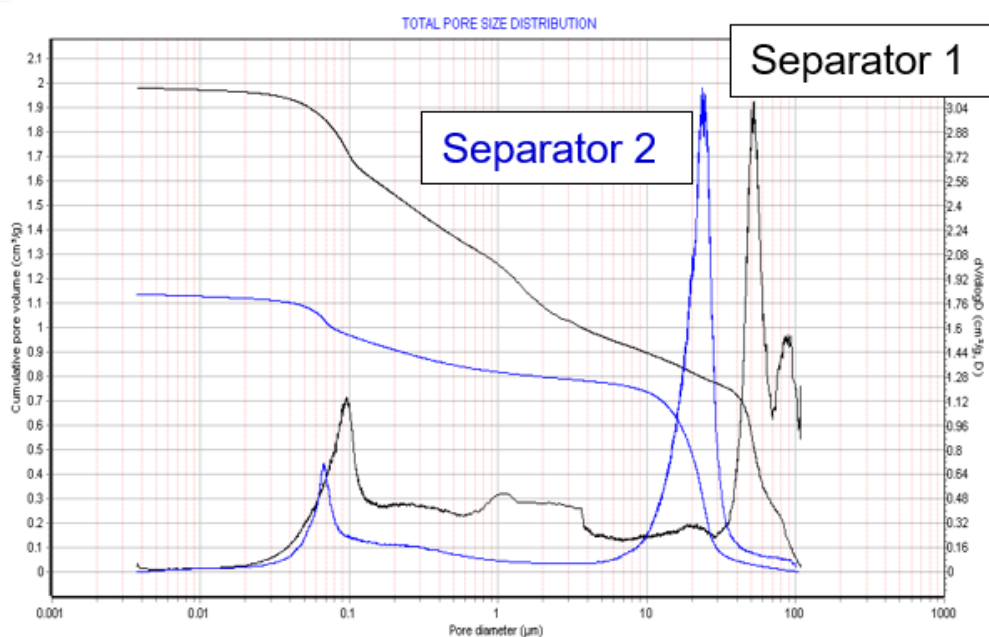


Figure 3. Pore size results of two separators: Separator 1 with pore diameters 0.1, 50 and 90 microns (black). Separator 2 with pore diameters 0.07 and 15 microns (blue).

Conclusion

In conclusion, the use of Mercury Intrusion Porosimetry (MIP) is essential for analyzing the pore structures of battery electrodes and separators.

The BELPORE porosimeters, with their advanced features and wide pressure ranges, provide accurate and comprehensive measurements of pore sizes and volumes. This technology ensures optimal battery performance by enabling precise control over the pore characteristics of the materials used. The results demonstrate significant differences in pore volumes and sizes between anodes and cathodes, as well as between different separators, highlighting the importance of tailored material properties for specific applications.

Overall, the BELPORE porosimeters offer a reliable and efficient solution for battery material analysis, contributing to the development of high-performance batteries.

BELPORE analysis of battery electrodes and separators stands for

- **Mercury Intrusion Porosimetry according to ISO 15901-1**
- **Fast and accurate measurements of pore size and volume.**
- **Safe and easy handling**
- **Small lab space**
- **Advanced results for improving battery performance**