A Novel Technique for Surface Area and Particle Size Determination of Components of Fuel Cells and Batteries

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Abstract
In this contribution, the measurement of surface area, particle size, and fiber diameter by a novel technique has been reported. The technique is based on gas permeametry. The through-pore surface area measured in an instrument based on this principle is in excellent agreement with that measured by the gas adsorption technique. The gas flow technique has a number of advantages over the gas adsorption technique

Introduction
Many critical components of fuel cells and batteries such as electrodes, separators, and inorganic chemical powders are porous. The electrodes themselves may contain the powders. In a number of designs, the gaseous fuel passes through porous electrodes and reacts with other components of the electrolyte at the surface of electrodes. The surface area determines the reaction rate. The blind pores contribute to surface area, where as the through pores contribute to both surface area and the flow rate of the electrolyte. Surface area is an important parameter that controls the performance of various components. For quality control, rapid determination of surface area and average particle size or fiber diameter are required. The traditional nitrogen adsorption BET technique is not sufficiently accurate for measurement of the low surface areas associated with these components. Also the BET technique is time consuming. In this presentation, the application of the recently developed novel equipment, ESA for the rapid determination of surface area and average particle size has been described.

Background
It has been shown that [1] the flow of gases through porous media may be expressed by the following equation.

$$(dn/dt) = [a\, p\, P^3\, \underline{p}] / [l\, k\, (1-P)^2\, S^2\, \mu\, R\, T] + [a\, p\, z\, P^2\, \pi] / [\, l\, (1-P)\, S\, (2\, \pi\, M\, R\, T)^{1/2}\,] \qquad (1)$$

where: (dn/dt) = flow rate in moles/sec, a = cross-sectional area of the porous medium, p = pressure drop across the porous medium, P = porosity (pore volume / total volume), $\underline{p}$ = mean pressure in the porous medium, l = thickness of the porous medium, k = a constant determined by the geometry of the pore structure of the porous medium, S = through-pore (pores through which gases flow) surface area per unit volume of solid, μ = viscosity of the gas, R = the gas constant, T = test temperature in K, z = a constant, and M = molecular weight of the gas**.**
Equation 1 can be written in the following more convenient form containing Q, the volume flow rate at the average pressure [2].

$$[\, Q\, l / p\, a\,] = \{P^3 / [\, k\, (1-P)^2\, S^2\, \mu\,]\} + [\, z\, P^2\, \pi\,] / [(1-P)\, S\, (\, 2\, \pi\, \rho\, \underline{p})^{1/2}] \qquad (2)$$

where ρ is the density of the gas at the average pressure. The constant, k, is known to have a value close to 5 for random pored media and z has been shown to be (48 / 13 π) [1]. Porosity, P, is obtained from the bulk and true densities of the porous medium. Density of the gas at the average pressure is calculated from that at the standard temperature and pressure. The rest of the quantities in Equation 2 required for calculating surface area, S, are directly measured in the experiment.

Equipment

The Envelope Surface Area Analyzer (ESA) designed to measure surface area by flow permeametry is shown in Figure 1. It incorporates state-of-the-art gauges, meters, valves, and a number of innovative designs. Operation of the instrument, execution of the test, data acquisition, and data reduction are fully automated. Consequently, the Envelope Surface Area Analyzer is capable of yielding highly reliable and reproducible data [2,3]. The instrument is also easy to use because of deployment of thirty-two bit windows-based software.

Figure 1. The Envelope Surface Area Analyzer (ESA).

Surface area of the powder was also measured by the traditional gas adsorption technique for comparison. The PMI Sorptometer was used for these measurements. This is a sophisticated and fully automated instrument capable of generating highly reliable data.

Results and Discussion

ESA surface area

The lead monoxide powders from a commercial electrode, and a commercial battery separator were investigated using the Envelope Surface Area Analyzer. The tests in the ESA were performed at room temperature using air. The integrated software calculated the envelope surface area from the measured flow rates, pressures, sample dimensions, sample weight and porosity. Bulk and true densities required for the calculation of porosity, were measured using the PMI Pycnometer capable of yielding highly accurate and reproducible data. Figure 2 shows a typical set of data obtained with the lead monoxide powder. Because the computer performed the test and executed all the calculations, it took only a few minutes to get the result. Surface area of the battery separator was also measured in the ESA. The results are listed in Table 1.

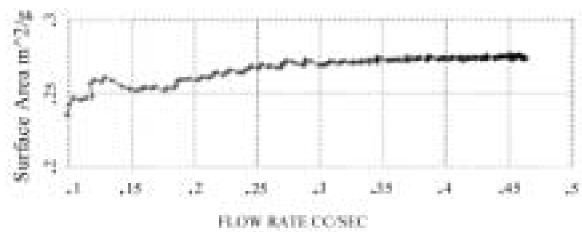

Figure 2. Surface area shown as a function of flow rate for lead monoxide powder.

Comparison with BET surface area

The gas adsorption technique (BET) was also used to measure the surface areas. For maximum accuracy krypton gas was used for the adsorption experiment at liquid nitrogen temperature. The surface areas of the two materials measured using the BET gas adsorption technique are listed in Table 1.

Table 1. Surface area

Material	Surface area by ESA, m^2/g	Surface area by BET, m^2/g
Lead Monoxide powder	0.25	0.11
Battery separator	0.56	0.52

The surface area of a porous medium is due to the pore surfaces of three different kinds of pores that exist in the material. The through pores extend from one end to the other, the blind pores end inside the material, and the closed pores are not accessible (Figure 3). Only the through pores permit the gases to flow. Therefore, the flow technique (ESA) measures the surface areas of through pores. The gas adsorption technique measures the surface areas of through pores and blind pores. If the sample contains appreciable quantity of blind pores, the gas adsorption technique would give a value of the surface area larger than that measured by ESA. However, the surface area measured in the BET is lower than that measured in ESA (Table 1). The measured surface areas are very small. Small surface area is normally associated with large pore diameters and large flow (Flow rate is proportional to the fourth power of diameter). Hence, the flow rate can be more accurately measured. The amount of gas adsorbed on a small surface is very small. Therefore, error in the measurement of surface area by BET is large. This is the most probable reason for the lower value of surface area obtained from the BET. Thus, for characterization of battery and fuel cell components, which generally have small surface areas, flow technique appears to be a better choice.

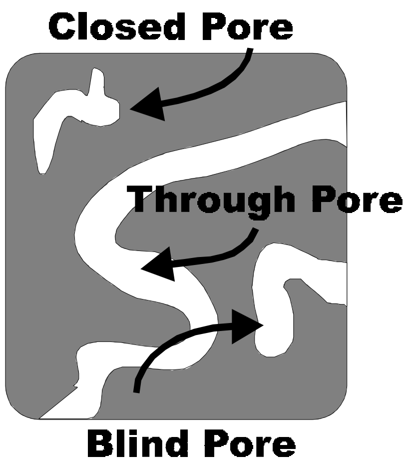

Figure 3. Three types of pores.

Average particle diameter

The average particle size can be estimated by assuming all the particles to have the same spherical shape and size. The average particle diameter, D, is given by:

$$D = 6 / (S_{sp} \rho_a) \tag{4}$$

where S_{sp} is the specific surface area per unit mass of the sample and ρ_a is the true density. ρ_a for lead monoxide is 9.53 g/cc. Hence, the average particle size of the powder is 2.52 microns. Average fiber diameter can also be calculated using additional available software.

Operational advantages of ESA

(1) Tests are performed at room temperature. Liquid N_2 temperature is not required.
(2) The test takes only a few minutes rather than hours required by the gas adsorption test. Rapid data generation is suitable for quality control applications.
(3) The test is easy to perform as the instrument is fully automated.
(4) Special requirements such as prolong evacuation and high purity gases are not needed.
(5) Real time graphical display of data is possible.
(6) The equipment is environment friendly.

Conclusion

(1) A fully automated instrument, ESA has been designed to measure envelope surface area accurately.
(2) Surface areas of commercial lead monoxide powder and a battery separator were measured using PMI Envelope Surface Area Analyzer (ESA) and BET.
(3) The average particle size was calculated.
(4) Components having small surface area are more reliably characterized by ESA
(5) ESA has a number of major operational advantages over BET. It saves a lot of operation time and is suitable for quality control applications.

References

1. Gerard Kraus, John W. Ross, L. A.Girifalco, Phys. Chem., Vol. 57, (1953) 330.
2. Howard Sanders, Presented in Chem. Show, New York, (1999).
3. Vibhor Gupta, A. K. Jena, Filtration News, Vol. 17, (1999) 40.