

Characterization of Pore Structure of Fuel Cell Components Containing Hydrophobic and Hydrophilic Pores

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Abstract: The hydrophobic and hydrophilic pores in a mixture of such pores constituting a fuel cell component have been characterized using water intrusion porosimetry, mercury intrusion porosimetry and capillary flow porometry. The hydrophilic pores constitute 75 % of pore volume and 91 % pore surface area. Hydrophobic pores are partly through and partly blind and their mean pore diameter is 1.57 μm . The hydrophilic pores consist of large through pores with wide mouths and $> 3.88 \mu\text{m}$ mean diameter, and fine pores of very low volume and high surface area.

Keywords: pore structure; hydrophobic pores; hydrophilic pores; characterization;

Introduction

Porous components of advanced fuel cells such as electrodes contain hydrophobic as well as hydrophilic pores in order to overcome problems related to water management. Pore diameter, pore shape, pore volume and pore distribution of hydrophobic and hydrophilic pores are critical characteristics that control performance of components. There is no suitable technique available for characterization of such complex pore structures. In this investigation, it has been demonstrated that use of multiple techniques can be used to characterize such complex structures.

Techniques

Three pore structure characterization techniques, Capillary Flow Porometry, Water Intrusion Porosimetry and Mercury Intrusion Porosimetry were used in this study.

Water Intrusion Porosimetry: 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 is 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 after Equation 1 [1].

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

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 was used in this investigation.

Mercury Intrusion Porosimetry: Mercury does not wet hydrophilic and hydrophobic pores, and cannot enter these pores spontaneously. Application of pressure on mercury can force it in to pores. In mercury intrusion porosimetry, mercury surrounds the sample and application of differential pressure on mercury forces it in to pores. The measured intrusion volume is equal to the pore volume and the differential intrusion pressure is related to pore diameter after Equation 1 using γ and θ as the surface tension and contact angle respectively of mercury. The PMI Mercury Intrusion Porosimeter was used in this investigation.

Extrusion Flow Porometry: In this technique, a wetting liquid, galwick was used to fill the hydrophilic and the hydrophobic pores of the sample. The inert gas, dry air was used to remove the liquid from pores and permit gas flow. The airflow rate and differential air pressures were measured using dry and wet samples. The differential pressure yielded pore diameter after Equation 2 [2].

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

Where D is pore diameter, γ and θ are surface tension and contact angle respectively of the wetting liquid and p is the differential pressure. These measurements are used to compute pore diameter, the largest pore diameter, the mean flow pore diameter and flow distribution. Figure 1 illustrates the principle and some of the measurable characteristics [1,3]. The PMI Capillary Flow Porometer was used in this investigation.

Results

All techniques measure pore diameter. However, pore cross-sections normally change in an irregular manner along pore length. Therefore, the pore size of a pore changes along pore length. Pore diameter, which is a measure of pore size is not defined. The pore diameter, D measured in all of these techniques is defined in the same way as given below [1].

$$\begin{aligned} (dS/dV)_{\text{pore}} &= (dS/dV)_{\text{circular opening of diameter D}} \\ &= 4/D \end{aligned} \quad (3)$$

where dS is the small increase in surface area corresponding to the small increase in volume dV. Each through and blind pore is associated with many pore diameters as illustrated in Figure 2.

The pore diameters and intrusion volumes measured in the water intrusion porosimeter (Aquapore) are shown in

Figure 3. Because water under pressure enters both hydrophobic through and blind pores, the measured pore diameters and pore volumes are those of hydrophobic through and blind pores.

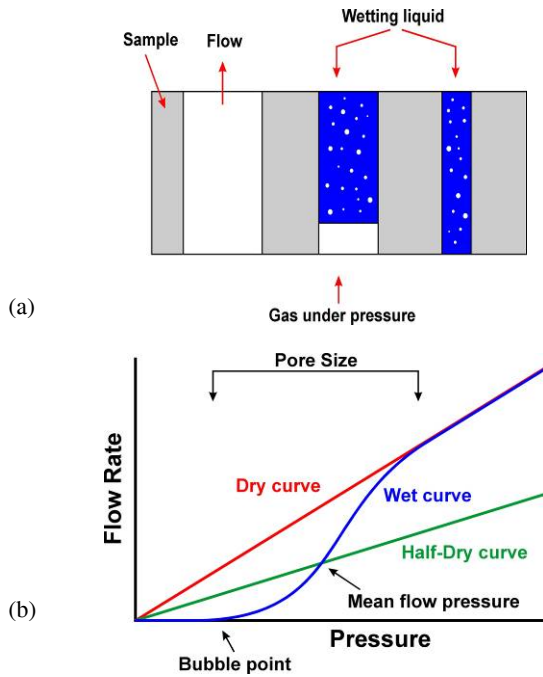


Figure 1. (a) Principle. (b) Measurable Characteristics

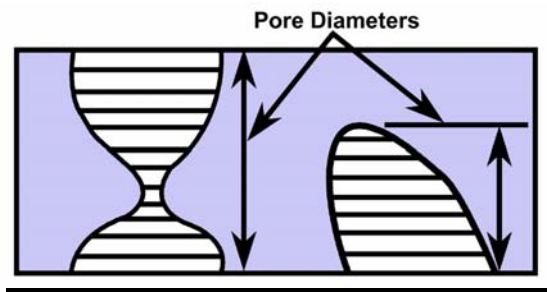


Figure 2. Pore diameters

Mercury is nonwetting for both hydrophobic and hydrophilic pores. Therefore, mercury under pressure can enter hydrophobic and hydrophilic through and blind pores and the pore volume and pore diameters measured by this technique are those of hydrophobic and hydrophilic through and blind pores. The pore volume and pore diameters measured in the mercury intrusion porosimeter are shown in Figure 4.

The gas flow rates and differential pressures measured by capillary flow porometry are shown in Figure 5. The wet and dry curves in Figure 5 are generated using wet and dry samples. The half-dry curve is computed from dry curve to yield half of the flow rate through the sample at a given differential pressure. The differential pressure yields pore diameter after Equation 2. In this test, galwick was used to spontaneously fill all the hydrophobic and hydrophilic pores and air pressure was used to push out the liquid from pores and allow gas flow. Therefore, pore diameters

and flow rates of hydrophobic and hydrophilic through pores are

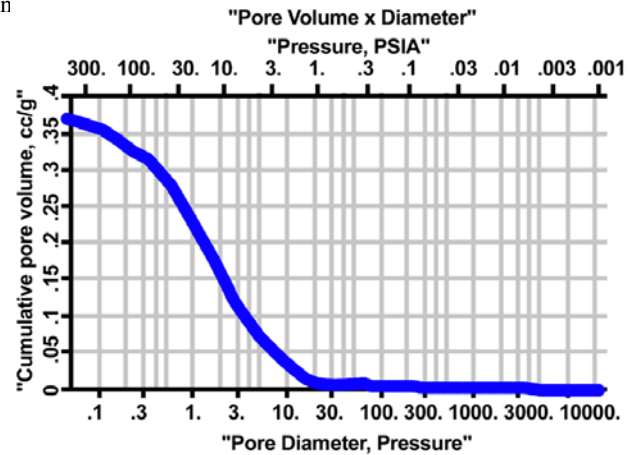


Figure 3. Pore volume and pore diameter of Hydrophobic through and blind pores detected by aquapore (water intrusion porosimetry)

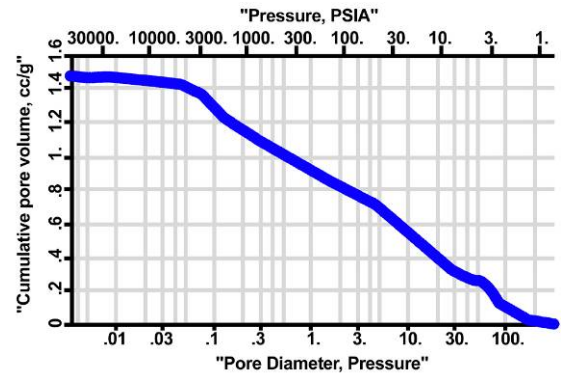


Figure 4. Pore volume and diameters of hydrophobic and hydrophilic through and blind pores measured by mercury intrusion porosimetry.

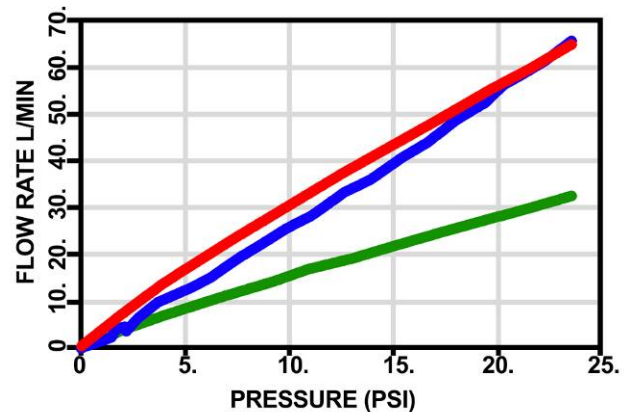


Figure 5. Differential pressures and flow rates measured by capillary flow porometry

Discussion

Pore Diameter: The three techniques measure different pore diameters [3]. In the water and mercury intrusion methods, the nonwetting liquids first enter the widest

accessible part of the both through and blind pores followed by the narrower parts. Thus, each small increase in pressure measures the volume of liquid that intrudes in to the pore space of diameter given by the applied pressure. Water intrusion porosimetry and mercury intrusion porosimetry measure all diameters of each pore along its length (Figure 2). The pore diameters are listed in Table 1.

The capillary flow porometer senses the presence of a pore by detecting increase in gas flow due to that pore. When gas pressure is sufficient to remove liquid from the entire pore, flow rate increases due to gas flow through the open pore, the presence of the pore is detected and the applied pressure yields the diameter of the pore. Gas can remove liquid from the entire pore only when gas pressure is sufficient to displace liquid at the most constricted part of the pore. Therefore, the differential pressure at which gas flow starts gives the pore diameter at the most constricted part of the pore (pore throat). Capillary flow porometry measures only one pore diameter per through pore and it is the through pore throat diameter (Figure 2).

Through pore throat diameter; the largest, the mean and the range: The pressure at which gas flow through the wet sample is initiated yields the largest pore diameter (Figure 5). The pressure at which wet and half-dry curves intersect gives the mean flow pore diameter (Figure 5). The smallest detectable pore diameter is obtained from the pressure at which wet curve meets the dry curve (Figure 5). The largest and the smallest detected pores give the pore size range. The pore diameters are listed in Table 1.

Pore surface area: Integration of Equation 3 shows that:

$$dS = \int 4 D^{-1} dV \quad (4)$$

Using this relation, surface area is computed from measured pore volume and pore diameter and listed in Table 1.

Pore volume distribution: Pore volume distribution can be derived from the pore volumes measured by water intrusion porosimetry and mercury intrusion porosimetry. The distribution is given in terms of the distribution function, Fv.

$$Fv = - [dV/d \log D] \quad (5)$$

Where V is cumulative pore volume and D is pore diameter. The pore volume distributions are shown in Figures 6 and 7 as histograms. The distribution function is such that the area under the distribution function in any pore diameter range is the volume of pores of diameter in that range. The hydrophobic pores have significant volume in the range 0.2- 10 μm (Figure 6). The hydrophobic and hydrophilic pores are appreciable in the range 0.1-100 μm

(Figure 7). The gas flow distribution over pore diameter is given in terms of the distribution function, f.

$$f = - d[\{Fw/Fd\} \times 100] / dD \quad (5)$$

where Fw and Fd are gas flow rates through wet and dry samples at the same differential pressure respectively. The equation shows that the area under the distribution function in any pore diameter range is the percentage gas flow through pores of diameter in that range. The flow distribution is shown in Figure 8 as a histogram. The pores with appreciable flow are in the range 0.3-10 μm .

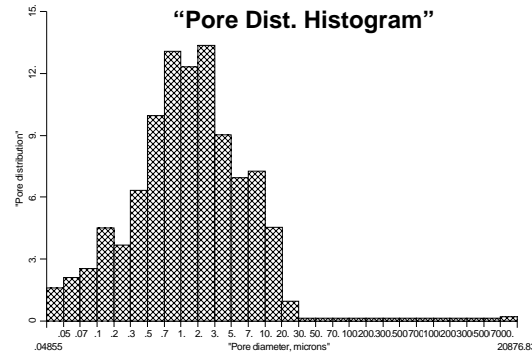


Figure 6. Pore volume distribution of hydrophobic through and blind pores detected by aquapore (water intrusion porosimetry)

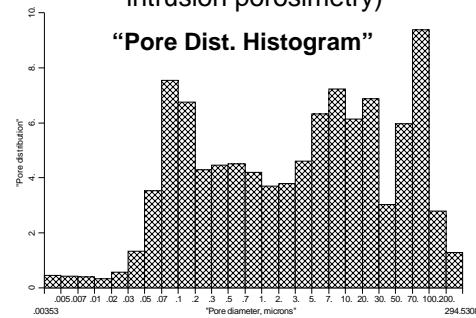


Figure 7. Pore volume distribution of hydrophobic and hydrophilic through and blind pores measured by mercury intrusion porosimetry

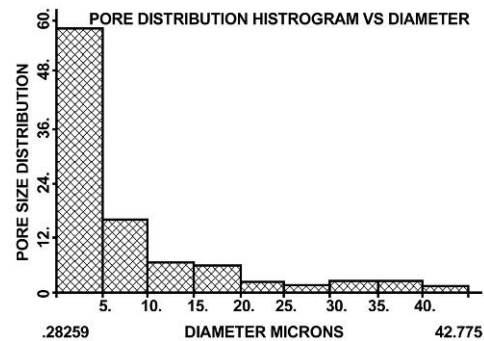


Figure 8. Gas flow distribution over pore diameter obtained from the results of capillary flow porometry

Table 1. Pore structure characteristics

Characteristics	Hydrophobic & hydrophilic pores		Hydrophobic pores
	Through Pores	Through & Blind Pores	Through & Blind Pores
Throat Diameter, μm			
Largest	42.78	--	--
Mean	4.16	--	--
Pores with appreciable flow	$\approx 0.3 - 10$	--	--
All Diameters, μm			
Mean	--	3.88	1.57
Pores with significant volume	--	$\approx 0.1 - 100$	$\approx 0.2-10$
Volume			
Total, cm^3/g	--	1.48	0.37
Percentage		100 %	25 %
Surface Area, m^2/g	--	30.93	2.7

Interpretation of results: The pore volume of hydrophobic through and blind pores is $0.37 \text{ cm}^3/\text{g}$ and that of hydrophobic and hydrophilic through and blind pore mixture is $1.48 \text{ cm}^3/\text{g}$. Hence, the hydrophobic pores constitute only 25 % of the pore volume and the hydrophilic pores constitute 75 % of the pore volume.

Hydrophobic pores are appreciable in the diameter range, $0.2 - 10 \mu\text{m}$ and the volume average mean pore diameter is $1.57 \mu\text{m}$ compared with much larger diameter range of $0.1 - 100 \mu\text{m}$ and mean pore diameter of $3.88 \mu\text{m}$ for the mixture of hydrophilic and hydrophobic pores. Thus, mean pore diameter of hydrophilic pores must be $> 3.88 \mu\text{m}$ and some of these pores must have much wider parts as well as much narrower parts. The pore throat diameter of through and blind pores is $4.16 \mu\text{m}$ ($0.3- 10 \mu\text{m}$ range) compared with the mean pore diameters of $>3.88 \mu\text{m}$ for the hydrophilic pore and the mean pore diameters of $1.57 \mu\text{m}$ for the hydrophobic pore. Therefore, one might expect that the large hydrophilic pores are primarily through pores with wide parts and the narrow hydrophilic pores are blind pores. The hydrophobic pores could be partly through and partly blind.

The pore surface area is 9 % for the hydrophobic pores and 91 % for the hydrophilic pores. The volume of hydrophilic pores is three times that of hydrophobic pores, but the surface area is almost ten times. Consequently, the hydrophilic pores must contain many small pores such that their contribution to pore volume is small but their contribution to surface area is large.

The characteristics of the two kinds of pores in the mixture are summarized in Table 2.

Conclusions

A partially hydrophobic and partially hydrophilic fuel cell component was characterized by capillary flow porosimetry,

Table 2. Characteristics of hydrophobic and hydrophilic pores in the pore mixture in the fuel cell component

Characteristics	Hydrophobic	Hydrophilic
Volume, cm^3/g	0.37	1.11
	25 %	75 %
Mean diameter, μm	1.57	> 3.88
Pores having significant volume, μm	0.2-10	0.1-100
Surface area, m^2/g	2.7	28.2
	9 %	91 %

mercury intrusion porosimetry and aquapore (water intrusion porosimetry). The analysis of results obtained using multiple techniques showed that the pores are expected to be primarily symmetrical through pores with constrictions and wide mouths. The volume of hydrophobic pores was only 25 %. These pores also had very small pore diameters compared with the hydrophilic pores.

References

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