Effect of Cyclic Compression on Pore Structure of Battery Materials

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Abstract

Capabilities of an instrument that can measure pore characteristics of battery components as a function of cycles of compression and decompression has been described. Compression cycles with load varying between 15 and 35 psi was used to investigate a commercial battery separator. The influence of cyclic compression of even 1000 cycles was considerable. The largest pore diameter decreased by 44 %. The mean flow pore diameter was not influenced that drastically. The pore distribution shifted to lower pore sizes.

Introduction

Characteristics of the pore structures of components of batteries and fuel cells govern their performance and efficiency. The largest pore diameter, the mean pore diameter, pore distribution, permeability and surface area are some of the important structural parameters of batteries and fuel cells. Battery and fuel cell components experience considerable cyclic stress during the life of the unit due to volume changes associated with charge/discharge cycles. Repeated cyclic stress has the tendency to change the size, shape and distribution of pores, and hence, to alter the structure. The net pore structure under conditions of cyclic stress is relevant for applications. Unfortunately, components are normally characterized under conditions of no stress or static stress [1]. Characterization under true simulated service conditions is, therefore, the appropriate mode of testing.

In this paper a novel technique developed to measure the largest pore size, mean pore size, pore size distribution and permeability of samples as a function of number of cycles of compression and decompression is presented. The effect of cyclic compression on a battery separator is found to be appreciable.

Technique

Principle

The principle of flow porometry (Figure 1) is used to determine pore characteristics [2]. A wetting liquid is allowed to spontaneously fill the pores of the sample and the sample is placed between two porous plates whose pore size is much larger than the pore size of the sample. The sample sandwiched between the rigid plates is loaded in the sample chamber. After subjecting the sample to the required number of compression and decompression cycles, pressure of a non-reacting gas on one side of the sample is increased to remove liquid from pores of the sample and permit gas flow. Pressure of gas and flow rates through wet and dry samples are measured. The following relation is used to compute pore diameter from differential pressure on the sample and the measured parameters are used to compute other pore characteristics.

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

where:
D = pore diameter
γ = surface tension of wetting liquid
θ = contact angle of wetting liquid taken as zero [3]
p = differential pressure on the sample.

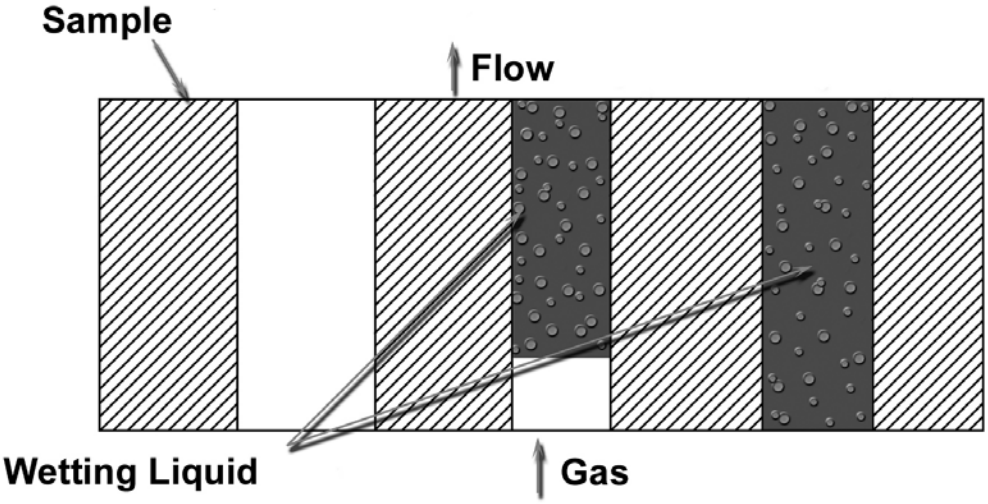

Figure 1. Principle of flow porometry.

Equipment

The PMI Cyclic Compression Porometer was used in this investigation. This instrument had many unique features. Its novel sample chamber design is shown in Figure 2. The instrument is fully automated. It can apply specified compressive stresses between one 15 psi and 3000 psi. The stress may be applied and released at fixed rates. Each cycle takes about ten seconds. However, the number of cycles per minutes (frequency) is adjustable by changing the duration of application of stress on the sample. Typical stress variation in a cycle is shown in Figure 3.

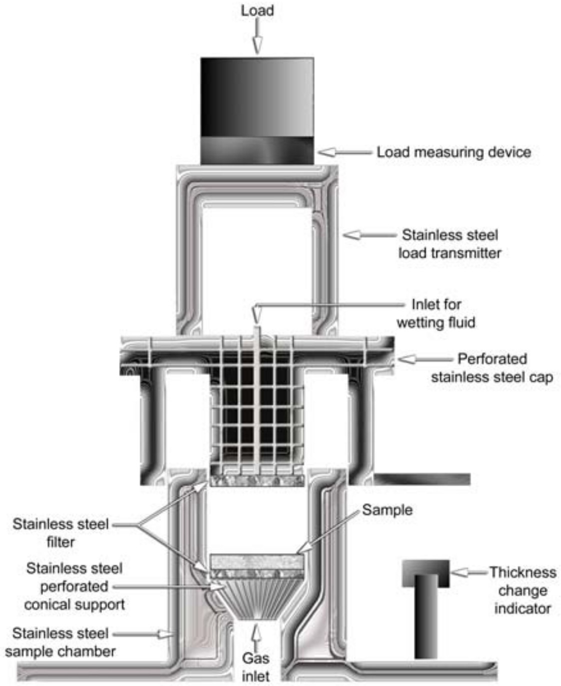

Figure 2 Sketch of the sample chamber of cyclic compression porometer.

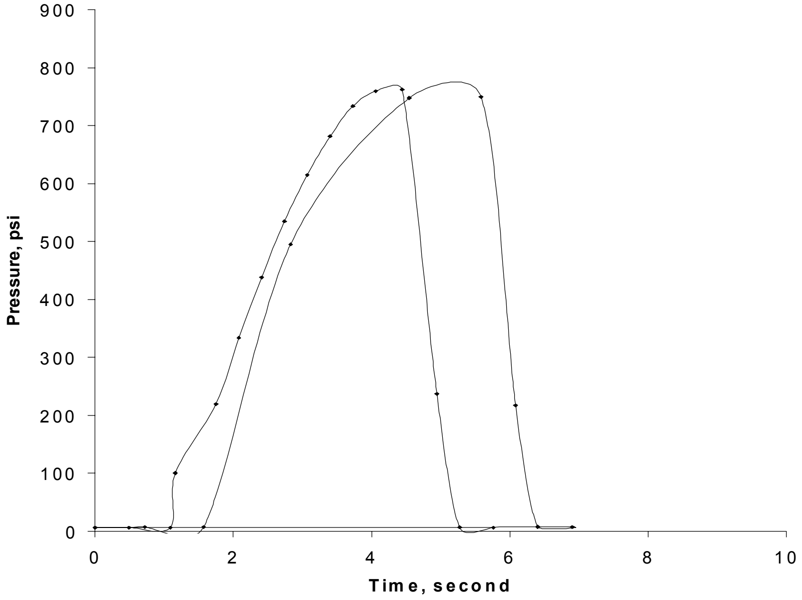

Figure 3. Typical stress variations in two cycles.

The instrument can be programmed to interrupt cyclic compression after specified number cycles, wait for a predetermined length of time, measure characteristics of pores and then continue testing. This can be done up to ten times within a specified range of cycles. The equipment is instrumented to measure thickness changes of the sample. At the completion of a specified number of cycles, the pressure and thickness changes during the previous cycle are recorded.

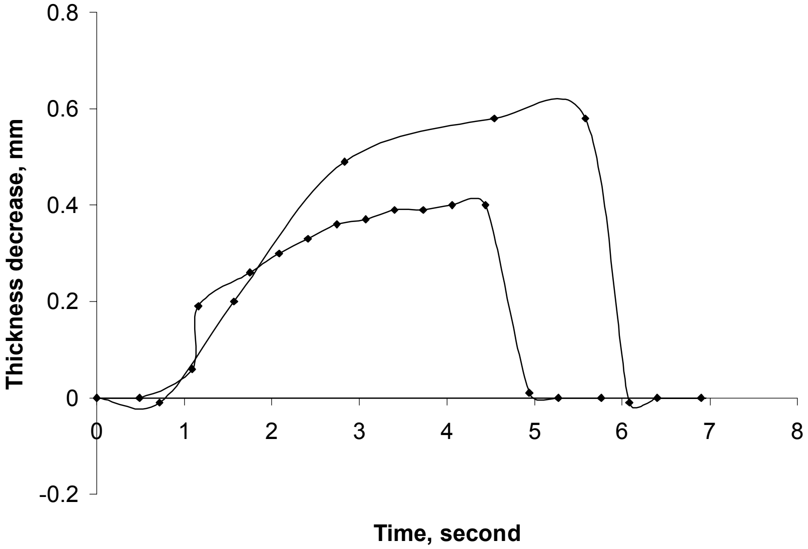

Figure 4. Typical thickness changes detected in a felt during a cycle. The1000 psi maximum stress cycle shows smaller changes than the 100 psi maximum stress cycle.

Results and Discussion

Pore structure without cyclic compression

A commercial battery separator was investigated using PMI Cyclic Compression Porometer. Typical results obtained with a sample of the battery separator without subjecting it to any compressive stress cycle is shown in Figure 5. The dry curve and the wet curve were generated using sample in the dry and wet conditions respectively. The half-dry curve was computed from the dry curve such that at a given differential pressure, half of the flow rate through the dry sample is given by the half-dry curve.

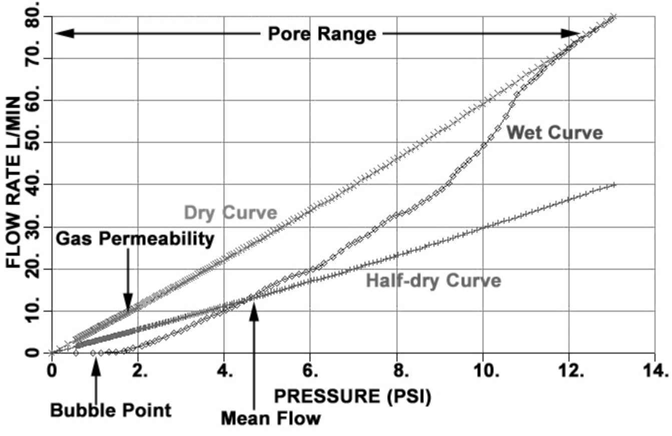

Figure 5. Flow rate and differential pressure measured using a sample without subjecting it to cyclic compression

The pressure at which flow starts through the wet sample gives the largest pore diameter. The largest pore diameter in the sample is 11.600 µm. The pressure corresponding to the intersection of half-dry curve and wet curve yields the mean flow pore diameter. The mean flow pore diameter is 1.474 μm. Pressure at which the wet and dry curves meet gives the minimum detectable pore diameter. The smallest detected pore diameter is 0.508 μm. Ratio of flow rates through wet curve and dry curve yields pore distribution. The dry curve is a measure of gas permeability.

Effect of stress cycles

Pore characteristics of the samples were measured after subjecting the samples to cyclic stress. The maximum stress and the minimum stress in a cycle were 35 and 15 psi respectively. The frequency was six cycles per minute. Tests were performed after 1, 10, 100 and 1000 cycles. The over all effect of cyclic stress can be clearly seen in Figure 6 which contains wet, dry and half-dry curves obtained with samples subjected to no compressive stress cycle and 1000 compressive stress cycles.

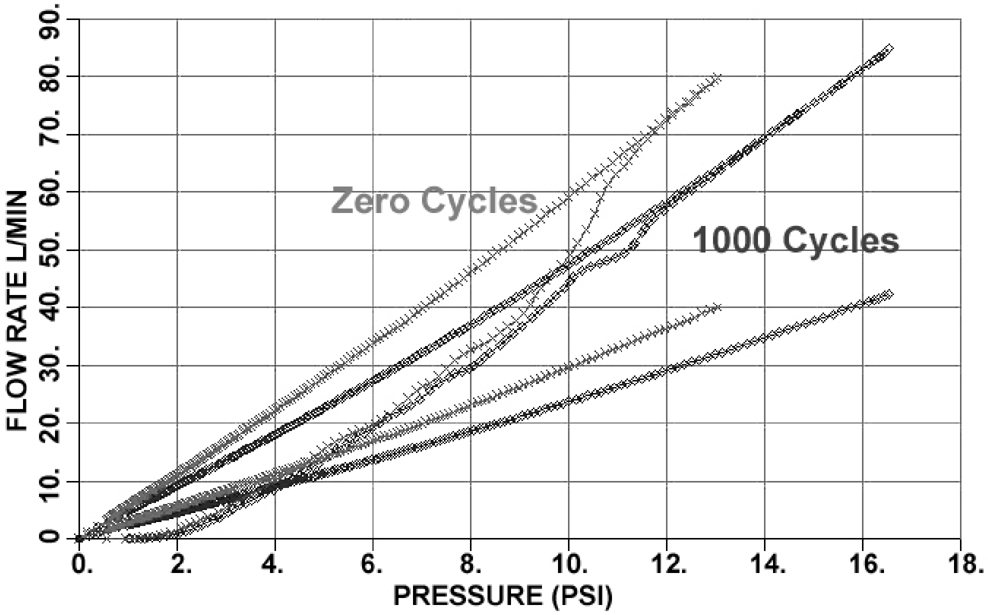

Figure 6. Effect of 1000 stress cycles on pore characteristics.

The largest pore diameter: The percentage change in the largest pore diameter with increase in number of cycles is listed in Table 1. Only one stress cycle is enough to reduce the pore diameter by almost 28 %. After 1000 cycles 44 % reduction in pore diameter is observed. The reduction in the largest pore diameter with increase in number of compression cycles is shown in Figure 7. Initially the diameter gets reduced rapidly. However, with increasing number of stress cycles the diameter gets reduced at a decreasing rate. Such behavior is expected because excess void is removed first and later the reduction becomes less as the material gets compacted.

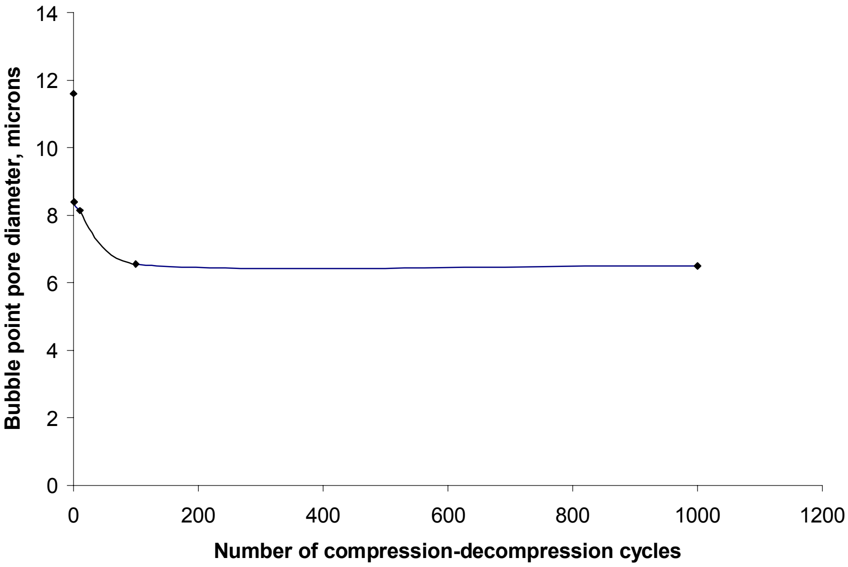

Figure 7. Change of pore diameter with number of stress cycles.

Table 1 Percentage change in the largest pore diameter and the mean flow pore diameter

No. of stress cycles	% change in the largest Pore diameter	% change in the mean flow pore diameter
0	0	0
1	- 27.8	+1.9
10	- 29.9	+4.6
100	-43.6	- 0.2
1000	- 43.9	+ 6.7

The mean flow pore diameter: The mean flow pore diameter is plotted in Figure 8. It shows that the effect of cyclic compression is very small on the mean flow pore size although the effect on the largest pore diameter is large. The percentage change in the mean flow pore diameter listed in Table 1. Although the mean flow pore diameter is increased, the maximum change is only about 7 %. The small change in the mean flow pore diameter compared with the large change in the largest pore diameter suggests that the number of large pores in the sample is small, so that their reduction in size has very small effect on the mean flow pore diameter.

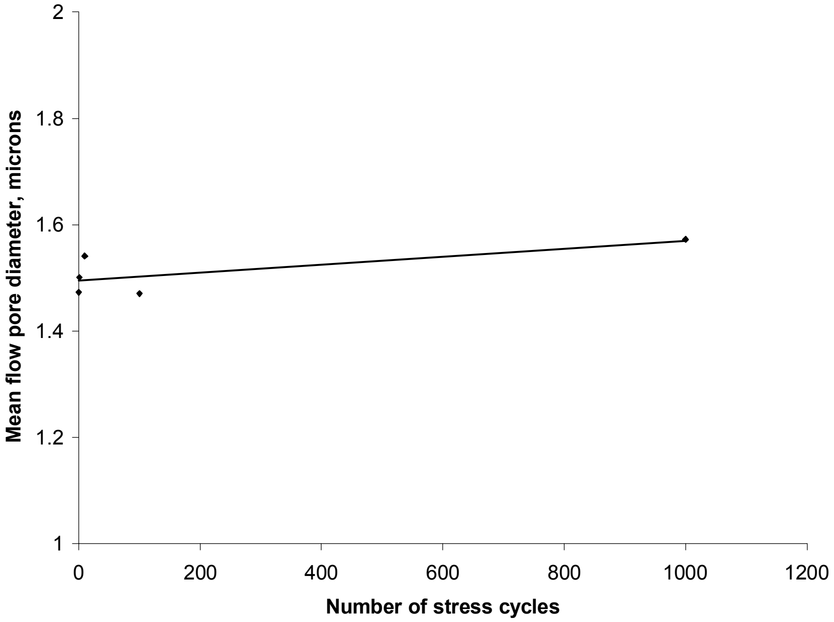

Figure 8. Change of the mean flow pore diameter with increase in the number of stress cycles.

Pore distribution: Figure 9 shows the pore distribution in the sample following zero, ten and one thousand stress cycles. The distributions shift to lower pore size and are consistent with the changes observed in the largest and the mean flow pore diameters. The number of large pores is few and there is considerable reduction in the large pores. However, there is relatively less influence on the small pores. Therefore, the mean flow pore diameter does not change appreciably.

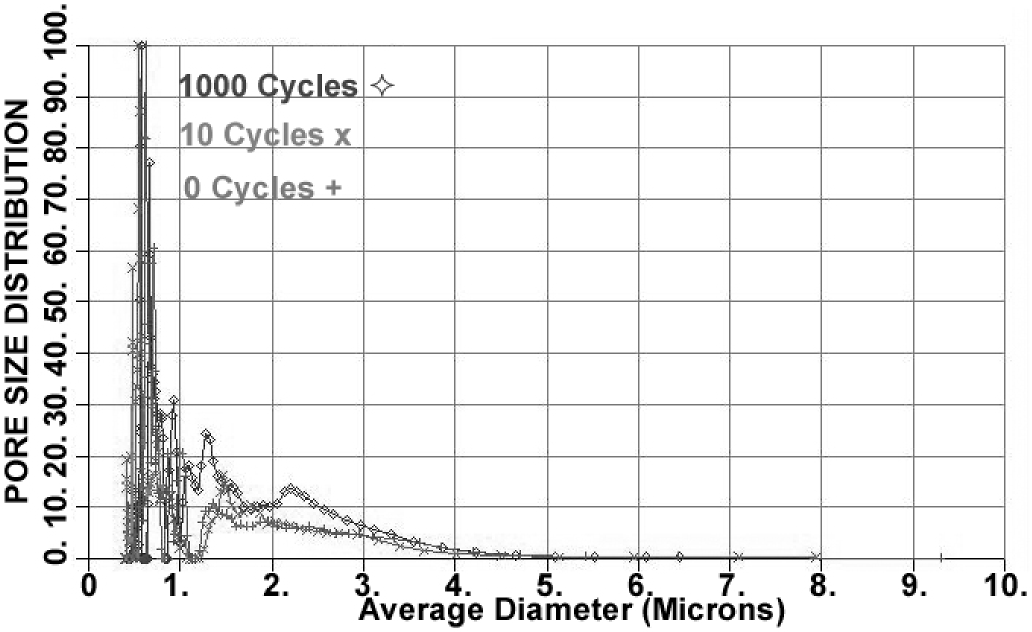

Figure 9. Effect of compression cycles on pore distribution.

Permeability: The gas flow rates through dry samples are presented in Figure 10. It shows that stress cycles have considerable influence on the flow rates. Gas permeability of the separator computed from the flow rates is plotted in Figure 11. The permeability at first decreases rapidly and with increase in number of cycles. With further increase in number of cycles, the gas permeability decreases slowly.

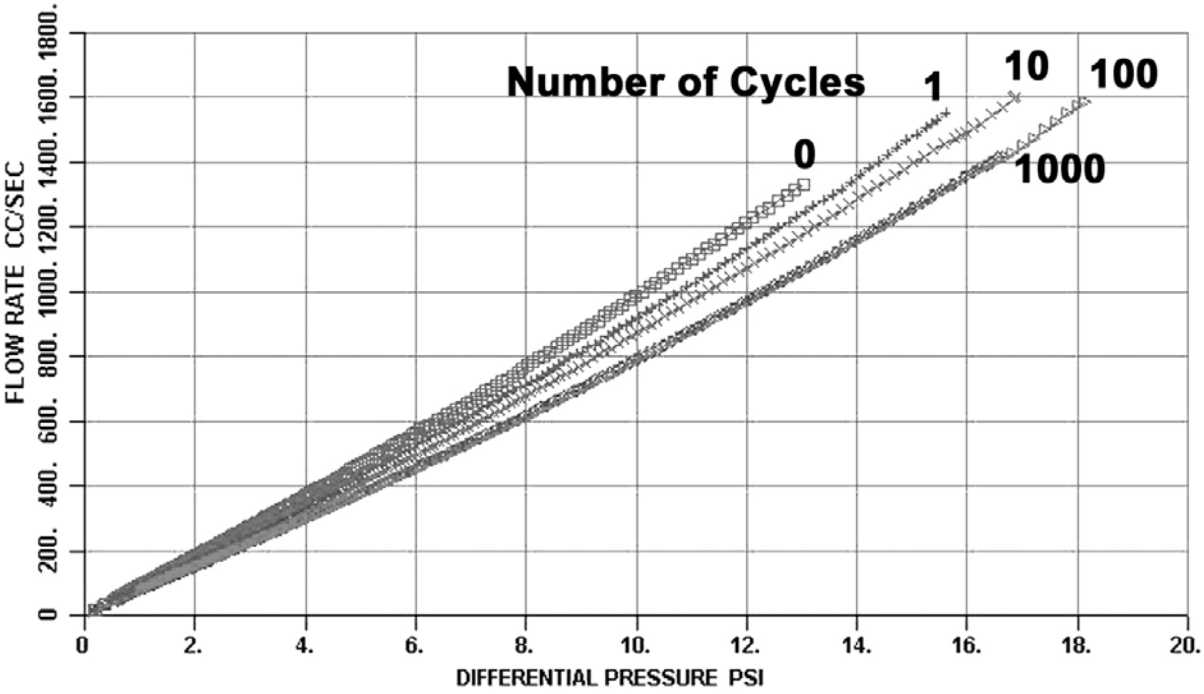

Figure 10. Gas flow rates through dry sample of the separator after subjecting it to stress cycles.

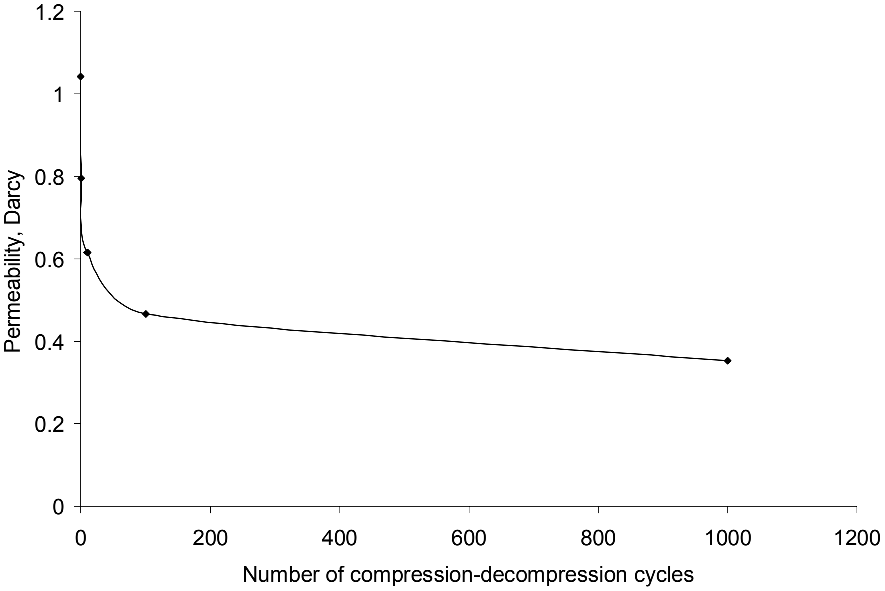

Figure 11. Effect of cyclic compression on permeability.

Thickness changes: The change in the thickness of the sample, due to increase in the number of cycles is shown in Figure 12. As expected the thickness is reduced due to cyclic compression. The magnitude of the reduction is considerable. After 1000 cycles the reduction in thickness is 57.6 %. This is reflected in the observed changes in the properties of the separator.

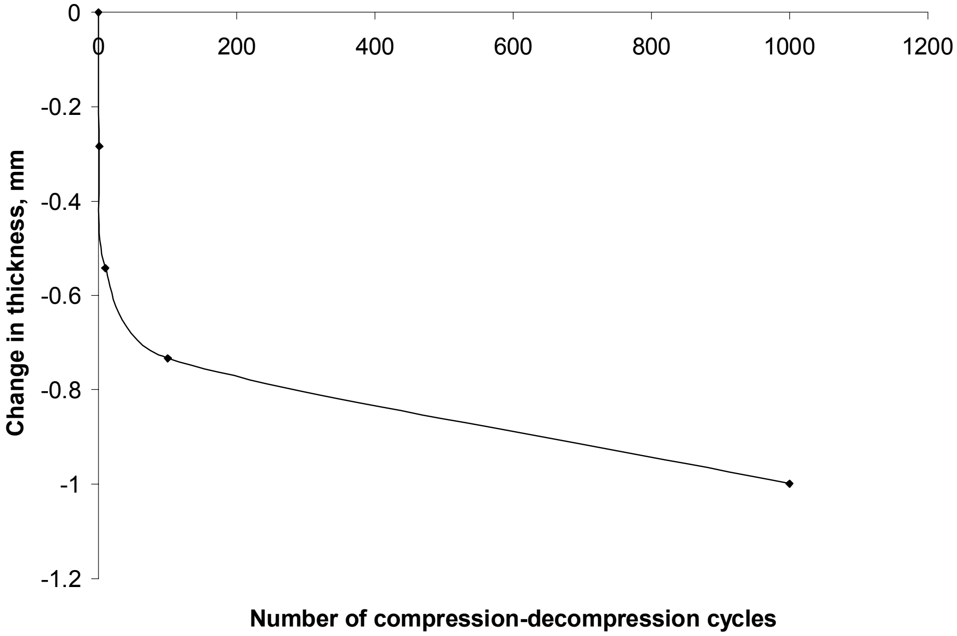

Figure 12. Thickness changes of the separator due to stress cycles.

Summary and Conclusions

(1) An instrument designed to measure pore characteristics of samples subjected to cyclic compression has been described. Its capabilities have been discussed.

(2) A commercial battery separator was investigated using this instrument using stress cycles between 15 and 35 psi..

(3) The largest pore diameter decreased with decreasing rate. The reduction in diameter was 44% due to only 1000 cycles.

(4) The effect of compressive stress cycles on the mean flow pore diameter is considerably less.

(5) The pore distribution showed shift to the lower pore sizes.

(6) Compression cycles had considerable effect on the pore characteristics of the battery separators. It is therefore, more appropriate to test battery components under actual service conditions.

References

1. Akshaya K. Jena and Krishna M. Gupta, Journal of Power Sources, 96, (2001) 214-219.
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3. Vibhor Gupta and A. K. Jena: Advances in Filtration and Separation Technology, 13b, (1999) 833-844.