

Porosity Measurements of Positive of Lead-Acid Battery Plates by Mercury Porosimetry

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Abstract:

A mercury porosimeter has been used to measure the intrusion volume of the three types mercury positive lead acid-battery plates. The intrusion volumes were used to calculate the pore diameter, pore volume, pore area, and pore size distribution. The variation of the pore area in positive lead acid-battery plates as well as of the pore volume has the following sequence.

Paste positive > Uncured positive > Cured positive

Key word: porosity measurements, lead-acid battery plates.

Introduction:

The grid make an important part of storage cell which act as supports for the active materials of plates and conduct the electric current developed. It also play an important role in maintaining uniform current distribution throughout the mass of the active material. Grids for both positive and negative plates are frequently of the same design, composition, and weight[1]. The surfaces area of active material depend on curing temperature, as the suitable temperature in curing process is around (56 – 65°C)[2], porous materials are being used as molecular sieve , catalysis – humidity sensors , and contaminant barriers .In particular recent studies propose that the use of micro porous (pores<2nm) and malodorous(pores 250 nm) minerals as adsorbents for pollutants in aqueous systems[3] .

The phase composition and the microstructure of the positive plate active material of the lead-acid battery depend to a large extent on the paste from which the active material has been produced . The paste is obtained by mixing partially oxidized lead powder with a sulphuric acid solution .

It has been established that basic lead sulphates form in these conditions . At room temperature $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ is generated , while at a mixing temperature of 70°C $4\text{PbO}\cdot\text{PbSO}_4$ because of its very interesting structure . The properties of plates obtained form previously synthesized pure $4\text{PbO}\cdot\text{PbSO}_4$ have studied[4]. The porous structure can be characterized by integral or differential curves of porevolume distribution vs. pore radius (porosimetric curves or porograms).

The following methods for measuring porograms are well known: mercury porosimetry - mercury intrusion into a nonwetable porous material , small-angle X-ray scattering ,electronic or optical microscopy; centrifugal porosimetry , displacement of wetting liquids from the porevolume by gas pressure ,capillary condensation. The method of mercury porosimetry (MMP) provides the widest range of measurable pore radii (from 2 to 105 nm). Great disadvantage of this method is the necessity to apply high pressure of mercury (up to thousands of

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atmospheres), which can lead to deformation or even destruction of the samples and to distortion of the porograms. Other drawbacks of this method are: misrepresentation of the results due to amalgamation of most metals, different values of the mercury wetting angle for different materials, complexity of the equipment, toxicity of mercury[5].

A new method of standard porosimetry for investigation for any type of porous materials was also shown to be suitable to determine the effective porosity of cured and formed positive plate lead-acid storage battery[6]. The present work, pore size, pore volume and pore surface area of the positive plate at lead-acid storage battery have been measured by using mercury intrusion porosimeter. No such data are available in the literature.

Material and Methods:

The measurements were made using mercury porosimeter model "pore size 9320", obtained from micromeritics, USA. The mercury porosimeter[7,8] is a device which was capable of generating suitably high pressures and measuring simultaneously both the pressure and volume of the mercury taken up by the pores.

A measurement with gravitas was carried out as follows: on analytical balance the materials of lead battery specimen to be examined was weighted and dried in vacuum oven at (120C^o) for over night. After drying process the specimen was transferred to the low pressure chamber and the measurements proceeded automatically recording the pressure (in psia) and intrusion reading (in PF) (PF = pico farad). The same procedure was employed after the sample was transferred to the high pressure chamber. The duration time of the

experiment lasted about 5 hours. Six types of specimens which have been received directly from ministry of industrial, Babel factory for manufacturing lead acid batteries, Baghdad the sample of the lead battery which have been used in this investigation;

1- Uncured positive plate of the battery. This represented a grid, which was coated with the paste of the positive plate prior to curing stage.

2- Accrued positive plate of step (2).

The samples were ground then sieved and the powder whose the partial size (250 μm) have been used.

Results and Discussion:

The properties of the lead oxide vary markedly with the method of manufacture, compared to ball-mill oxides, Barton oxide, generally have larger particle-size distributions and mean particle diameters.

The porosity measurements enabled the identification of pore volume, pore size, pore area, and the most abundant pores that are present in the mater sales. (table 1) shows typical pore size distribution data form and pore area distribution data form for lead battery. Calculating the pore diameter introduced by mercury at each pressure requires solving the basic equation[9,10]

$$D = -4\gamma \cos \frac{\theta}{P} \dots\dots\dots(1)$$

Where

D = the pore diameter in units of micro meter.

γ = the surface tension of mercury 485 dynes/cm.

θ = the contact angle between mercury and the solid containing the pores and generally varies around 30 degrees.

p = the pressure in pounds per square inch.

Converting intrusion meter readings to pore volumes requires first,

calculate the cumulative changes in capacitance (Initial value taken as zero).

These changes in capacitance multiplied by the conversion factor (pentrometer constant) supplied for the penetrometer (and a units conversion factor) to give the cumulative pore volume. Cumulative pore volumes per gram of sample are obtained by dividing by the weight of the sample. The total pore surface area obtained by assuming that all the pores are cylindrical capillaries. The calculate the pore surface area A for each diameter increment is simply related to incremental pore(V) and the average pore diameter (D) by the equation[11] ;

$$A = \frac{4V}{D} \dots\dots\dots(2)$$

The cumulative surface area for each point is the sum of these for all

points . Table (2) shows the experimental values of pore volume, pore area and median pore diameter on the three samples of lead acid batteries in Baghdad. The value of (D) on the distribution curve corresponding to the maximum value of ΔV/ΔD is termed the media pore diameter. The results of table (3) refer that pore area and pore volume of the three samples of lead acid batteries , follows the sequence as;

Paste positive > Uncured positive > Cured positive

The different pore size distributions were estimated from the plot ΔV/ΔD against D. ΔV and ΔD is obtained from differences cumulative volume and pore diameter points in table (2).

The data obtained are tabulated in table (4) and shown in fig (1-3)

Table (1) Pore volume and pore area for paste positive electrode (Ball Mill Method)

Pressure (pounds/in ²)	Pore Size (μm)	Intrusion Reading (PF)	Cumulative Intrusion (∑ΔPF)	Cumulative pore volume (cc/g)	Average Pressure	Incremental pore volume (cc/g)	Average Pore Size (μm)	Incremental Pore arca (m ² / g)	Cumulative Pore arca (m ² / g)
1,3	139,13.	37,23
2,3	78,739	37,44	.,79	.,100	1,8	.,100	1.,,483	.,.,.117	.,.,.117
3,3	07,071	30,4.	1,83	.,.109	2,70	.,.204	70,77.	.,.,.124	.,.,.1807
3,7	48,883	34,19	2,44	.,.099	3,40	.,.24	02,427	.,.,.183	.,.,.204
4,9	37,912	32,8.	4,43	.,.871	4,3	.,.272	42,072	.,.,.108	.,.,.472
0,7	31,731	32,27	4,97	.,.887	0,3	.,.107	34,127	.,.,.120	.,.,.087
7,7	27,444	31,72	0,01	.,.1084	7,10	.,.107	29,409	.,.,.144	.,.,.731
7,7	23,798	31,28	0,90	.,.1172	7,1	.,.088	20,474	.,.,.119	.,.,.80
8,7	20,789	31,07	7,7	.,.1212	8,10	.,.04	22,192	.,.,.72	.,.,.922
9,7	18,747	3.,88	7,30	.,.1201	9,2	.,.039	2.,.97	.,.,.77	0.00999
1.,9	17,093	3.,79	7,44	.,.1277	1.,3	.,.017	17,07.	.,.,.37	.,.,.1030
11,8	10,327	3.,7.	7,03	.,.1280	11,30	.,.018	10,930	.,.,.40	.,.,.108
12,1	13,807	3.,77	7,07	.,.1293	12,40	.,.008	14,027	.,.,.22	.,.,.1102
12,3	13,099	3.,73	7,7	.,.130.	12,2	.,.007	13,702	.,.,.20	.,.,.1122
12,4	13.,12	3.,71	7,72	.,.1304	12,7	.,.004	13,299	.,.,.12	.,.,.1134
3.,2	.,097	32,10	7,72
488	.,37.	32,72	7,00	.,.1388	390,0	.,.084	.,4073	.,.734	.,.847
882	.,200	32,3.	7,47	.,.1422	780	.,.084	.,274	.,.772	.,.1194
1472	.,123	31,77	8,11	.,.1098	1172	.,.127	.,104	.,3272	.,.0913
2377	.,77	31,.	8,77	.,.1227	1919,0	.,.129	.,.942	.,0477	1.,.8784
389.	.,047	3.,71	9,17	.,.1804	3133,0	.,.077	.,.0377	.,0377	1,2204
0371	.,033	3.,49	9,28	.,.1828	4270,0	.,.024	.,.039.	.,2671	1,8774
770.	.,023	3.,4.	9,27	.,.1847	701,0	.,.018	.,.277	.,2099	2,12704
990.	.,018	3.,34	9,43	.,.1807	880.	.,.011	.,.200	.,2147	2,34114
11200	.,017	3.,24	9,49	.,.1807	1070,0	.,.00.	.,.170	.,.00.	2,44114
12913	.,014	3.,22	9,40	.,.1871	17044	.,.004	.,.149	.,.073	2,44444
13879	.,013	3.,20	9,47	.,.1874	13377	.,.003	.,.130	.,.888	2,03724
14071	.,012	3.,19	9,48	.,.1877	14220	.,.002	.,.122	.,.799	2,10014
10010	.,010	3.,28	9,49	.,.1878	14780,0	.,.002	.,.122	.,.700	2,17074

Table (2) Pore volume and pore area for cured positive electrode(Ball Mill Method)

Pressure (pounds/in ²)	Pore Size (µm)	Intrusion Reading (PF)	Cumulative Intrusion (∑ΔPF)	Cumulative pore volume (cc/g)	Average Pressure	Incremental pore volume (cc/g)	Average Pore Size (µm)	Incremental Pore area (m ² /g)	Cumulative Pore area (m ² /g)
0.7	208,240	37,78
1.7	113,043	37,01	0.17	0.0010	1.10	0.0010	107,278	0.00010	0.00010
2.7	70,322	37,20	0.48	0.0028	2.0	0.0018	90,430	0.00018	0.00028
3.7	07,021	37,30	1.28	0.0083	2.8	0.0000	78,097	0.00038	0.00083
4.7	39,319	30,44	2.24	0.0130	3.9	0.0002	47,376	0.00048	0.00130
7.1	29,700	34,81	2.87	0.0173	0.30	0.0038	33,807	0.00049	0.00179
7.4	24,441	34,04	3.14	0.0189	7.00	0.0017	27,740	0.00028	0.00207
9.0	20,097	34,14	3.04	0.0193	8.2	0.0004	22,007	0.00030	0.00237
10.1	17,007	34,22	3.77	0.0221	9.00	0.0008	18,939	0.00038	0.00275
10.9	17,093	33,90	3.78	0.0228	10.0	0.0007	17,220	0.00037	0.00292
11.8	10,327	33,79	3.89	0.0230	11,30	0.0007	10,930	0.00037	0.00309
12.2	14,704	33,70	3.98	0.0240	12.00	0.0000	10,009	0.00033	0.00302
13.2	13,099	33,72	4.07	0.0240	12.8	0.0000	14,130	0.00014	0.00293
13.4	13,497	33,07	4.11	0.0248	13,30	0.0003	13,048	0.00088	0.00381
13.8	13,107	33,01	4.17	0.0201	13,7	0.0003	13,299	0.00009	0.00390
14.0	12,919	33,41	4.27	0.0208	13.9	0.0007	13,012	0.00010	0.00386
23.0	0,048	31,10	0
40.1	0,001	31,10	4.27	0.0211	39.00	0.0003	0,473	0.00009	0.00397
70.0	0,001	31,03	4.29	0.0210	020,00	0.0004	0,444	0.00010	0.00407
119.8	0,100	30,80	4,07	0.0271	89.9	0.0011	0,201	0.00119	0.00527
20.9	0,087	30,70	4,72	0.0280	33.88	0.0009	0,000	0.00000	0.00527
31.33	0,007	30,47	4,40	0.0290	27.11,0	0.0014	0,779	0.00110	0.00637
41.17	0,043	30,24	0,18	0.0313	36.24,0	0.0014	0,049	0.00148	0.00785
70.19	0,027	30,09	0,33	0.0322	0417,00	0.0009	0,033	0.00099	0.00884
91.77	0,019	30,00	0,42	0.0327	79.42,00	0.0000	0,022	0.00000	0.00884
100.00	0,018	29,97	0,40	0.0329	90.80	0.0002	0,018	0.00044	0.00928

Table (3) Pore volume and pore area for uncured positive electrode(Ball Mill Method)

Pressure (pounds/in ²)	Pore Size (µm)	Intrusion Reading (PF)	Cumulative Intrusion (∑ΔPF)	Cumulative pore volume (cc/g)	Average Pressure	Incremental pore volume (cc/g)	Average Pore Size (µm)	Incremental Pore area (m ² /g)	Cumulative Pore area (m ² /g)
0.8	227,1	38,00
1.0	12,07	38,37	0.14	0.0020	1.10	0.0020	107,27	0.00010	0.00010
2.2	78,07	37,89	0.71	0.0111	1.90	0.0087	90,2	0.00077	0.00087
3.2	07,00	37,20	1.20	0.0218	2,700	0.0107	70,8	0.00070	0.00157
4.4	41,1	37,08	1,92	0.0349	3,80	0.0131	47,7	0.00101	0.00258
0.7	32,2	30,72	2,78	0.0007	0,00	0.0211	32,2	0.00233	0.00491
7.8	27,7	30,22	3,28	0.0097	7,20	0.0091	29,2	0.00120	0.00611
8.3	21,8	37,72	3,78	0.0189	7,000	0.0097	24,0	0.00103	0.00714
9.8	18,0	34,37	4,14	0.0204	9,000	0.0070	20,0	0.00120	0.00834
10.4	17,4	34,20	4,20	0.0270	10,10	0.0021	17,9	0.00047	0.00881
11,2	17,0	33,11	4,29	0.0000	10,80	0.0020	17,7	0.00070	0.00951
12,0	14,0	33,90	4,00	0.0289	11,90	0.0029	10,2	0.00007	0.00958
13,0	13,9	33,87	4,33	0.0444	12,700	0.0010	14,2	0.00042	0.01000
13,0	13,4	33,82	4,78	0.0802	13,200	0.0008	13,7	0.00023	0.01023
13,7	13,2	33,78	4,72	0.0809	13,70	0.0007	13,2	0.00021	0.01044
28.0	0,70	30,79
33.1	0,00	30,07	4,90	0.0901	172,4	0.0042	1,00	0.00170	0.01214
47.7	0,38	30,00	0,01	0.1004	40,40	0.0103	0,40	0.00107	0.01321
77.0	0,22	34,20	7,27	0.1139	72,00	0.0130	0,29	0.00171	0.01492
120.0	0,10	33,37	7,10	0.1301	080,00	0.0127	0,18	0.00100	0.01592
217.0	0,08	32,48	8,03	0.1472	178,00	0.0101	0,11	0.00000	0.01592
431.7	0,04	32,17	8,24	0.1019	323,00	0.0007	0,07	0.00000	0.01592
821.7	0,02	32,02	8,48	0.1044	722,00	0.0020	0,02	0.00000	0.01592
1072.8	0,02	31,97	8,00	0.1008	9422,00	0.0014	0,02	0.00000	0.01592
1108.0	0,01	31,93	8,08	0.1073	11104,00	0.0000	0,02	0.00000	0.01592

Table (4) The porosity parameter for the three different types of positive active method

Type of PbO ₂	pore volume (cc/g)	Pore area (m ² / g)	Median pore diameter : μm
paste positive	0.1868	2.6654	0.15
cured positive	0.0329	0.537626	0.04
uncured positive	0.1563	2.34373	0.15

Table (5) The data of pore size distributions for the three types of positive active method

paste positive		cured positive		uncured positive	
D	ΔV \ ΔD	D	ΔV \ ΔD	D	ΔV \ ΔD
١٠٠,٤٨ ٣	0.0001542	١٥٧,٢٧ ٨	0.0000063	١٥٧, ٣	0.000015 8
٦٥,٧٧٠ 7	0.0005876	٩٠,٤٣٥	0.0000293	٩٥,٢	0.000013 8
٥٢,٤٢٦	0.0017985	٦٤,٥٩٦	0.0002128	٦٥,٨	0.000363 9
٤٢,٠٦٢	0.0026244 6	٤٦,٣٧٦	0.0002854	٤٧,٦	0.000719 7
٣٤,١٢٦	0.0013482	٣٣,٨٠٧	0.0003022 3	٣٦,٢	0.00185
٢٩,٤٠٩	0.0022471 9	٢٦,٧٩٥	0.0002281	٢٩,٢	0.0013
٢٥,٤٧٤	0.0022363	٢٢,٠٥٧	0.0000506 5	٢٤,٠	0.001769
٢٢,١٩٢	0.0012175	١٨,٩٣٩	0.0002565	٢٠,٠	0.001625
٢٠,٠٩٦	0.0018706	١٧,٢٢٥	0.0004084	١٧,٩	0.001
١٧,٥٦٠	0.0006309 1	١٥,٩٣٥	0.0005426	١٦,٧	0.002083
١٥,٩٣٥	0.0011076 9	١٥,٠٠٩	0.0005399	١٥,٢	0.001933
١٤,٥٢٧	0.0056818	١٤,١٣٠	0.0000568 8	١٤,٢	0.0015
١٣,٧٠٢	0.0008484 8	١٣,٥٤٨	0.0005154	١٣,٧	0.004
١٣,٢٩٩	0.0009925 5	١٣,٢٩٩	0.001204	١٣,٣	0.00175
٠,٤٥٧٣	0.01836	١٣,٠١٢	0.002439	١٠,٥	0.004
٠,٢٦٤	0.04345	٠,٤٦٣	0.000647	٠,٤٥	0.017166
٠,١٥٤	0.11454	٠,٣٤٤	0.0036134	٠,٢٩	0.08437
٠,٠٩٤٢	0.21571	٠,٢٠١	0.007692	٠,١٨	0.14727
٠,٠٥٧٧	0.21095	٠,٠٥٥	0.006164	٠,١١	0.14428
٠,٠٣٩٠	0.12834	٠,٠٣٩	-0.1	٠,٠٦	0.114
٠,٠٢٧٧	0.15929	٠,٠٤٩	0.07	٠,٠٣	0.0833
٠,٠٢٠٥	0.15277	٠,٠٣٣	0.05625	٠,٠٢	0.14
٠,٠١٧٠	0.00	٠,٠٢٢	0.04545	٠,٠٢	0.000
٠,٠١٤٩	0.19047	٠,٠١٨	0.05		
٠,٠١٣٥	0.21428				
٠,٠١٢٧	0.25				
٠,٠١٢٢	0.02150				

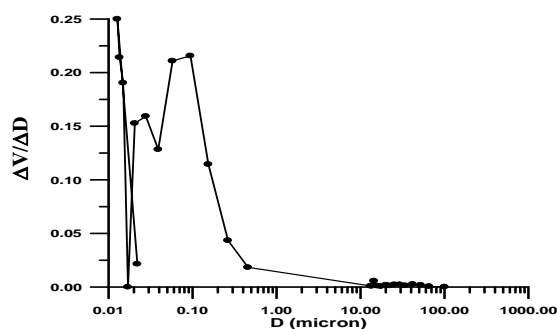


Fig (1) Pore volume distribution over pore diameter for paste positive

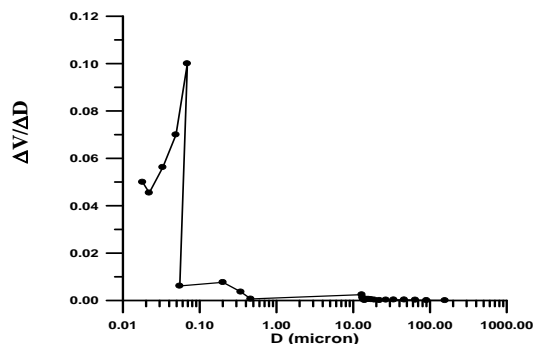


Fig (2) Pore volume distribution over pore diameter for cured positive

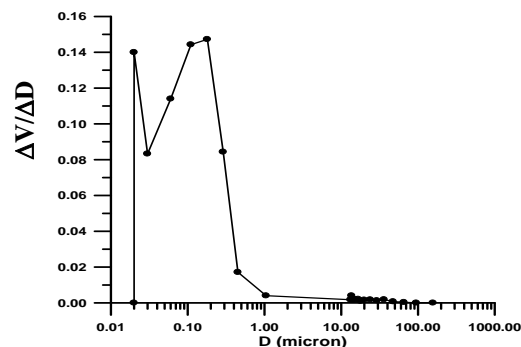


Fig (3) Pore volume distribution over pore diameter for uncured positive

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قياسات المسامية لألواح نضيدة الرصاص الموجبة بطريقة مقياس المسامية الزئبقية

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الخلاصة :

تم استخدام جهاز المسام الزئبقي لقياس حجم الداخلي لثلاثة أنواع ألواح نضيدة الرصاص الحامضية الموجبة ، تم حساب قطر المسام، حجم المسام ، مساحة المسام ، وتوزيع حجم المسام من خلال الحجم الداخلي . أن الاختلاف في مساحة المسام لألواح نضيدة الرصاص الحامضية الموجبة وكذلك حجم المسام تتبع الترتيب الآتي
paste positive > uncured positive > cured positive