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

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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^{o}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 $3PbO.PbSO_4.H_2O$ is generated , while at a mixing temperature of 70^{o}C $4PbO.PbSO_4$ because of its very interesting structure . The properties of plates obtained form previously synthesized pure $4PbO.PbSO_4$ 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 nonwettable 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 usingmercury 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 token 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 lager 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]

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

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] ;

$$A = \frac{4V}{D} \qquad \text{.................(2)}$$

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	139.130	37.23	0	0	0	0	0	0	0
2.3	78.639	36.44	0.79	0.0155	1.8	0.0155	100.483	0.000617	0.000617
3.2	56.521	35.40	1.83	0.0359	2.75	0.0204	65.770	0.00124	0.001857
3.7	48.883	34.19	3.04	0.0599	3.45	0.024	52.426	0.000183	0.00204
4.9	36.912	32.80	4.43	0.0871	4.3	0.0272	42.062	0.00158	0.00462
5.7	31.731	32.26	4.97	0.0787	5.3	0.0107	34.126	0.00125	0.00587
6.6	27.404	31.72	5.51	0.1084	6.15	0.0106	29.409	0.00144	0.00731
7.6	23.798	31.28	5.95	0.1172	7.1	0.0088	25.474	0.00119	0.0085
8.7	20.789	31.07	6.16	0.1212	8.15	0.004	22.192	0.00072	0.00922
9.7	18.646	30.88	6.35	0.1251	9.2	0.0039	20.096	0.00077	0.00999
10.9	16.593	30.79	6.44	0.1267	10.3	0.0016	17.560	0.00036	0.01035
11.8	15.327	30.70	6.53	0.1285	11.35	0.0018	15.935	0.00045	0.0108
13.1	13.806	30.66	6.57	0.1293	12.45	0.0008	14.527	0.00022	0.01102
13.3	13.599	30.63	6.6	0.1300	13.2	0.0007	13.702	0.00020	0.01122
13.9	13.012	30.61	6.62	0.1304	13.6	0.0004	13.299	0.00012	0.01134
303	0.596	33.15	6.62	0	0	0	0	0	0
488	0.370	32.72	7.05	0.1388	395.5	0.0084	0.4573	0.0734	0.0847
882	0.205	32.30	7.47	0.1472	685	0.0084	0.264	0.1272	0.21194
1462	0.123	31.66	8.11	0.1598	1172	0.0126	0.154	0.3272	0.53913
2377	0.76	31.0	8.77	0.1727	1919.5	0.0129	0.0942	0.5477	1.08684
3890	0.046	30.61	9.16	0.1804	3133.5	0.0077	0.0577	0.5337	1.62054
5371	0.033	30.49	9.28	0.1828	4630.5	0.0024	0.0390	0.2461	1.86664
7650	0.023	30.40	9.37	0.1846	6510.5	0.0018	0.0277	0.2599	2.12654
9950	0.018	30.34	9.43	0.1857	8800	0.0011	0.0205	0.2146	2.34114
11255	0.016	30.34	9.49	0.1857	10602.5	0.000	0.0170	0.000	2.34114
12913	0.014	30.32	9.45	0.1861	12084	0.0004	0.0149	0.1073	2.44844
13879	0.013	30.30	9.47	0.1864	13396	0.0003	0.0135	0.0888	2.53724
14561	0.0124	30.29	9.48	0.1866	14220	0.0002	0.0127	0.0629	2.60014
15010	0.0120	30.28	9.49	0.1868	14785.5	0.0002	0.022	0.0655	2.66564

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 arca (m^2 / g)	Cumulative Pore arca (m^2 / g)
0.7	258.385	37.68	0	0	0	0	0	0	0
1.6	113.043	37.51	0.17	0.0010	1.15	0.001	157.278	0.000025	0.000025
2.4	75.362	37.20	0.48	0.0028	2.0	0.0018	90.435	0.000079	0.000104
3.2	56.521	36.30	1.38	0.0083	2.8	0.0055	64.596	0.000340	0.000444
4.6	39.319	35.44	2.24	0.0135	3.9	0.0052	46.376	0.000448	0.000892
6.1	29.650	34.81	2.87	0.0173	5.35	0.0038	33.807	0.000449	0.001347
7.4	24.441	34.54	3.14	0.0189	6.75	0.0016	26.795	0.000238	0.001579
9.0	20.096	34.14	3.54	0.0213	8.2	0.0024	22.057	0.000435	0.002014
10.1	17.907	34.02	3.66	0.0221	9.55	0.0008	18.939	0.000168	0.002182
10.9	16.593	33.90	3.78	0.0228	10.5	0.0007	17.225	0.000162	0.002344
11.8	15.327	33.79	3.89	0.0235	11.35	0.0007	15.935	0.000175	0.002519
12.3	14.704	33.70	3.98	0.0240	12.05	0.0005	15.009	0.000133	0.002652
13.3	13.599	33.62	4.06	0.0245	12.8	0.0005	14.130	0.000141	0.002793
13.4	13.497	33.57	4.11	0.0248	13.35	0.0003	13.548	0.000088	0.002881
13.8	13.106	33.51	4.17	0.0251	13.6	0.0003	13.299	0.000090	0.002971
14.0	12.919	33.41	4.27	0.0258	13.9	0.0007	13.012	0.000215	0.003186
330	0.548	31.15	0	0	0	0	0	0	0
451	0.401	31.10	4.32	0.0261	390.5	0.0003	0.463	0.00259	0.005776
600	0.301	31.03	4.39	0.0265	525.5	0.0004	0.344	0.00465	0.010426
1198	0.150	30.85	4.57	0.0276	899	0.0011	0.201	0.02189	0.032316
2090	0.086	30.70	4.72	0.0285	3288	0.0009	0.055	0.06545	0.097766
3133	0.057	30.47	4.95	0.0299	2611.5	0.0014	0.069	0.08115	0.178916
4116	0.043	30.24	5.18	0.0313	3634.5	0.0014	0.049	0.11428	0.293196
6719	0.026	30.09	5.33	0.0322	5417.5	0.0009	0.033	0.10909	0.402286
9166	0.019	30.00	5.42	0.0327	7942.5	0.0005	0.022	0.09090	0.493186
10005	0.018	29.97	5.45	0.0329	9585	0.0002	0.018	0.04444	0.537626

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 arca (m^2 / g)	Cumulative Pore arca (m^2 / g)
0.8	226.1	38.50	0	0	0	0	0	0	0
1.5	120.6	38.36	0.14	0.0025	1.15	0.0025	157.3	0.00006	0.00006
2.3	78.6	37.89	0.61	0.0111	1.90	0.0086	95.2	0.00036	0.00042
3.2	56.5	37.30	1.20	0.0218	2.75	0.0107	65.8	0.00065	0.00107
4.4	41.1	36.58	1.92	0.0349	3.80	0.0131	47.6	0.00101	0.00208
5.6	32.3	35.72	2.78	0.0506	5.00	0.0211	36.2	0.00233	0.00441
6.8	26.6	35.22	3.28	0.0597	6.20	0.0091	29.2	0.00125	0.00566
8.3	21.8	36.72	3.78	0.0689	7.55	0.0092	24.0	0.00153	0.00719
9.8	18.5	34.36	4.14	0.0754	9.05	0.0065	20.0	0.00130	0.00849
10.4	17.4	34.25	4.25	0.0775	10.10	0.0021	17.9	0.00047	0.00896
11.3	16.0	33.11	4.39	0.0800	10.85	0.0025	16.7	0.00060	0.00956
12.5	14.5	33.95	4.55	0.0829	11.90	0.0029	15.2	0.00076	0.01032
13.0	13.9	33.87	4.63	0.0844	12.75	0.0015	14.2	0.00042	0.01074
13.5	13.4	33.82	4.68	0.0852	13.25	0.0008	13.7	0.00023	0.01097
13.7	13.2	33.78	4.72	0.0859	13.60	0.0007	13.3	0.00021	0.01118
280	0.65	35.79	0	0	0	0	0	0	0
331	0.55	35.56	4.95	0.0901	172.4	0.0042	1.05	0.01600	0.02718
477	0.38	35.00	5.51	0.1004	404.0	0.0103	0.45	0.09156	0.11874
770	0.23	34.25	6.26	0.1139	623.5	0.0135	0.29	0.18621	0.30495
1200	0.15	33.36	7.15	0.1301	585.0	0.0162	0.18	0.36000	0.66495
2160	0.08	32.48	8.03	0.1462	1680.0	0.0101	0.11	0.58545	1.25040
4312	0.04	32.17	8.34	0.1519	3236.0	0.0057	0.06	0.38000	1.63040
8217	0.02	32.3	8.48	0.1544	6264.5	0.0025	0.03	0.33333	1.96373
10628	0.02	31.96	8.55	0.1558	9422.5	0.0014	0.02	0.28000	2.24373
11580	0.01	31.93	8.58	0.1563	11104.0	0.0005	0.02	0.10000	2.34373

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
100.483	0.0001542	157.278	0.0000063	157.3	0.0000158
65.770	0.00058767	90.435	0.0000293	95.2	0.0000138
52.426	0.0017985	64.596	0.0002128	65.8	0.0003639
42.062	0.00262446	46.376	0.0002854	47.6	0.0007197
34.126	0.0013482	33.807	0.00030223	36.2	0.00185
29.409	0.00224719	26.795	0.0002281	29.2	0.0013
25.474	0.0022363	22.057	0.00005065	24.0	0.001769
22.192	0.0012175	18.939	0.0002565	20.0	0.001625
20.096	0.0018706	17.225	0.0004084	17.9	0.001
17.560	0.00063091	15.935	0.0005426	16.7	0.002083
15.935	0.00110769	15.009	0.0005399	15.2	0.001933
14.527	0.0056818	14.130	0.00005688	14.2	0.0015
13.702	0.00084848	13.548	0.0005154	13.7	0.004
13.299	0.00099255	13.299	0.001204	13.3	0.00175
0.4573	0.01836	13.012	0.002439	1.05	0.004
0.264	0.04345	0.463	0.000647	0.45	0.017166
0.154	0.11454	0.344	0.0036134	0.29	0.08437
0.0942	0.21571	0.201	0.007692	0.18	0.14727
0.0577	0.21095	0.055	0.006164	0.11	0.14428
0.0390	0.12834	0.069	-0.1	0.06	0.114
0.0277	0.15929	0.049	0.07	0.03	0.0833
0.0205	0.15277	0.033	0.05625	0.02	0.14
0.0170	000	0.022	0.04545	0.02	0.000
0.0149	0.19047	0.018	0.05		
0.0135	0.21428				
0.0127	0.25				
0.022	0.02150				

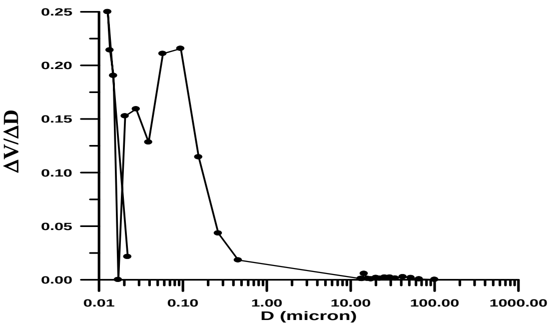

Fig (1) Pore volume distribution over pore diameter for paste positive

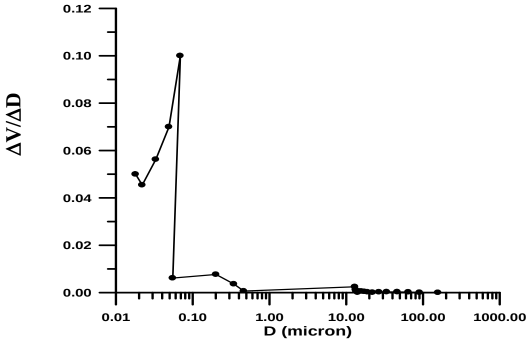

Fig (2) Pore volume distribution over pore diameter for cured positive

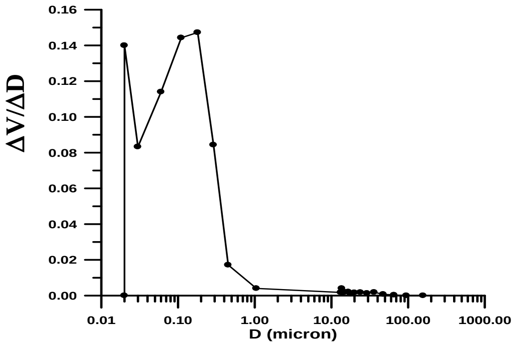

Fig (3) Pore volume distribution over pore diameter for uncured positive

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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 الحجوم الداخلة . أن الاختلاف في مساحة المسام لألواح نضيدة الرصاص الحامضية الموجبة وكذلك حجم المسام تتبع الترتيب الأتي

paste positive > uncured positive > cured positive