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CHARACTERISATION OF SAMPLES OF SILICA FOR USE IN GEL-TYPE MAINTENANCE FREE LEAD ACID BATTERIES

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Silica based gel electrolyte has been used as one of the routes in the development of maintenance free lead acid batteries. Both precipitated silica samples and pyrogenic silica have been characterised in terms of their properties, namely, apparent density, particle size and size distribution, surface area, acid absorption etc. The samples show a wide variation in apparent density values, the pyrogenic samples having the lowest value. The particle size distribution of the pyrogenic sample is not as expected, probably because of the difference in the particle shape and formation of agglomerates. Acid absorption values also show a regular increase with the fineness of the silica sample. It is also found that the pyrogenic sample forms a gel suitable for battery electrolyte with sulphuric acid alone while the other samples require a gelling agent for repelling the silica particles and for catalysing the cross linking of siloxane groups. The finer the sample, the better the conductivity as well as the performance of the battery using the gel electrolyte. Temperature is also having an influence in the formation of the gel, high temperature accelerating the gel formation and low temperatures retarding the same. The keeping quality of the gel is also found to be good. Test results of a few small capacity batteries with gel electrolyte are presented and compared with those with pure sulphuric acid.

Key words: Maintenance free lead acid batteries, gel electrolyte, thixotropy, silica

INTRODUCTION

The manganese-zinc system used in portable appliances is not able to meet heavy duty requirements due to its high internal resistance. Though Ni- Cd cells are a better substitute, their high cost is a prohibitive factor. Even though the lead acid battery system dominates the secondary battery field, it has not been proved to be suitable for portable applications because of the necessity of troublesome maintenance required very often as well as extreme care required during handling.

Concept of the maintenance free battery received greater importance and attention from the beginning of the space age. While maintenance free battery is more suitable for terrestrial and underwater application, it is an essential requirement for spacecrafts. Gelled electrolyte as well as sealed lead acid batteries have recently been developed and is used in consumer applications such as portable tools, portable TV, trans-receivers etc. The gelled batteries were introduced by Globe Union Inc. , in 1965. Since no water or electrolyte need be added, the battery may be considered sealed and maintenance free. When the internal pressure increases beyond a particular limit during charging, a one way relief valve releases the excess pressure and automatically recloses. But gel cells may again have the disadvantage of possible leak when turned upside down.

Materials such as albumen, starch, burnt clay, pumice, cellulose, soap, fatty acid, plaster of Paris, asbestos, sand, water glass, fullers earth etc. , have been used earlier to make the battery electrolyte viscous [1] so that spilling is eliminated and the necessity for constant topping up is avoided. Of these silica has been found to be most suitable. A gel may be considered as a partially coagulated colloidal system behaving as a solid of relatively low elasticity. A suitable gel electrolyte should meet the following requirements. Internal resistance, cycling characteristics and capacity should be comparable with those of liquid electrolyte. It should not shrink as a result of syneresis, thereby breaking contact with the active mass. The fine cracks formed may cause self- discharge due to the easy accessibility of oxygen. The gel electrolyte should be thixotropic and should have an initial low viscosity, so that during filling, the plates are completly wetted. A porous retainer for absorbing some excess liquid might be placed on top of the gelled electrolyte for greater safety.

Silica gels can be prepared by different methods, either using silica alone along with an acid, or using silica and acid together with an addition agent which prevents the complete coagulation of the silica solution. When sodium silicate is used, the reaction with silicate and sulphuric acid may be represented by the following equation

$$Na_2SiO_3 + xH_2O + H_2SO_4 \longrightarrow SiO_2\ (x+1)H_2O + Na_2SO_4$$

Both acid and water glass should be pure and chlorides are found to be very harmful. The time of setting and the stiffness of gel formed are controlled by the proportion of acid and water glass. When silica alone is used, it forms about 10% of the total weight of the gel.

Batteries containing gel electrolyte are having poor electrical properties compared to ordinary electrolyte. Internal resistance is found to be high, capacity low and life short.

The authors have tried different samples of silica for preparing gel electrolyte and have optimised conditions for preparing the same. In the present paper, the characteristics of the different silica samples and the gel electrolyte prepared from them and the performance of the test cells using the gel electrolyte are given.

EXPERIMENTAL

Both precipitated and pyrogenic silica samples have been characterised. Three samples of precipitated silica and two samples of pyrogenic silica — one indigenous and the other imported — have been investigated. Precipitated silica is produced by acidifying aqueous sodium silicate solution, washing out the anions of the acid used and dehydrating the resultant gel. Colloidal silica is prepared by decomposition of volatile compounds.

True densities of the samples were determined using sp.gr. bottle and apparent densities using a one cc cube cup. Particle size and size distribution analysis were carried out using the Malvern Laser Diffraction particle sizer, Model 3600 E system. Specific surface area for the samples were determined with Quantasorb QS-14 using the single point BET method as well as with Rigdon's apparatus using the air permeability method. SEM pictures were taken at two different magnifications. For determination of acid absorption, sulphuric acid of specific gravity 1.26 was used. Gel electrolyte was prepared using the optimum conditions arrived at in our laboratory. Viscosity of the gel electrolyte was determined using the rotating paddle viscometer (Stormer Krebs Type). Specific conductivities were determined using the Toshniwal digital conductivity bridge. Effect of temperature on gel formation and the keeping quality of the gel were examined. 2V/ 2Ah, 2V/6Ah, 6V/12Ah and 2V/30Ah cells were assembled and tested using the gel electrolyte.

RESULTS AND DISCUSSION

Apparent density for the different samples are given in Table I. It is found that the different samples of precipitated silica are having different apparent density values depending upon the conditions of their preparation. The pyrogenic silica is having a very low apparent density.

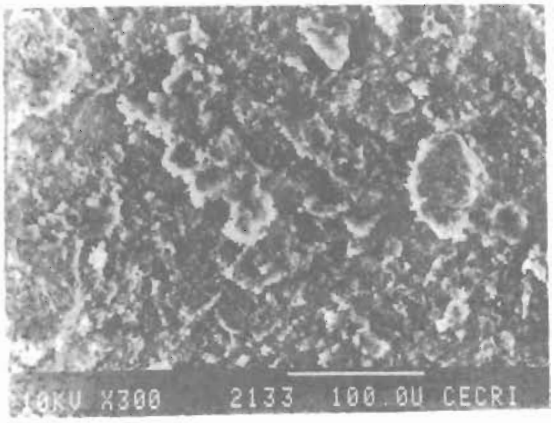
Particle size analyses data are given in Tables II to V for the different samples. It is found that the apparent density and particle size analysis data do not correlate, probably because of the difference in shape of the particles. Sample C and pyrogenic silica are plate-like in shape while the other samples are round or irregular. This is found more evidently from the SEM pictures.

Acid absorption values for different samples are given in Table I. It is found that as the apparent density decreases, the acid absorption value increases. It is inferred that for the best gel, silica of the lowest apparent density and having the highest acid absorption is most suitable.

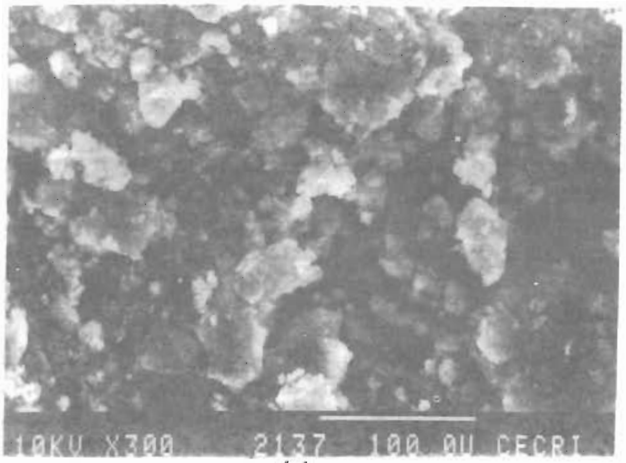
SEM pictures (Fig. 1) for the samples were taken at two different magnifications. These clearly show that sample C and especially the pyrogenic sample is plate-like in shape. This explains the anomaly noticed in the particle size distribution when compared with the respective apparent densities. This shape also accounts for the high acid absorption values found with the sample.

Specific surface area of the samples as determined using Quantasorb are given in Table I. The specific surface area is found to

(a)



(b)



(c)

Fig. 1: SEM pictures of the different silica samples
*(a) Precipitated silica, Sample **A** (b) Precipitated silica, Sample **C** (c) Pyrogenic silica*

TABLE-I: Physical properties of the different samples of silica

Sample	True density g/cc	Apparent density g/cc	Acid absorption cc/gm	Surface area m^2/gm
Precipitated silica				
Sample 'A'	2.03	0.344	1.233	15.99
Sample 'B'	2.07	0.133	1.830	40.21
Sample 'C'	2.10	0.103	2.180	62.22
Pyrogenic silica				
Imported	2.11	0.0228	3.66	238.08
Indigenous	2.11	0.0231	3.58	235.8

TABLE-II: Particle size distribution of silica sample 'A'

Size	Percentage		Size	Percentage	
microns	Under	In band	microns	Under	In band
118.4	100	0.5	11.1	11.5	5.0
102.1	99.5	1.5	9.6	6.5	2.0
88.1	98.0	2.2	8.3	4.5	1.2
76.0	95.8	2.7	7.2	3.3	0.9
65.6	93.2	2.9	6.2	2.4	0.5
56.6	90.2	3.0	5.3	1.8	0.4
48.8	87.2	3.3	4.6	1.5	0.3
42.1	83.9	4.0	4.0	1.1	0.4
36.3	79.9	5.1	3.4	0.8	0.2
31.3	74.8	6.0	3.0	0.6	0.0
27.0	68.7	6.3	2.6	0.6	0.1
23.3	62.5	6.0	2.2	0.5	0.1
20.1	56.4	5.8	1.9	0.4	0.3
17.4	50.6	18.5	1.9	0.2	0.1
15.0	32.1	12.4	1.4	0.1	0.1
12.9	19.7	8.2	1.2	0.0	0.0

be larger with samples of lower apparent density as is generally the case. Silica gel with large surface area will have a high acid absorption and hence will have a good conductivity and better thixotropic properties.

Characteristics of the gel

A number of patents on the preparation of gel electrolyte are available in literature [25]. The gellant used is a special type of a silica produced by the hydrolysis of silicon tetrachloride. In our experiments pyrogenic silica as well as precipitated silica samples have been used for preparing the gel. In the case of pyrogenic silica, it forms a gel with sulphuric acid alone, while such gel formation with the precipitated silica is very difficult. This is probably because the pyrogenic sample is having enough hydroxyl groups on their surfaces, so that they do not coagulate but interact with most liquids and with each other by hydrogen bonding. Thus the sample forms gel on treatment with sulphuric acid. To prepare a gel with the precipitated sample, some addition agents were used so that the silica particles are kept in solution without precipitation but form a gel on adding sulphuric acid. It has been found that indigenous silica of the precipitated variety can also be used in preparing a gel electrolyte having comparable properties with that prepared using pyrogenic silica which is costlier.

The gel prepared is having good thixotropic properties, one of the main requirements for an immobilized electrolyte. It changes to liquid form on applying a mechanical shear. This sets again into a gel as soon as the force is released. Near the end of charge, the gas produced at the electrodes forces the liquid electrolyte out of the pores of the plates and the gel absorbs this free electrolyte.

TABLE-III: Particle size distribution of silica sample 'B'

Size	Percentage		Size	Percentage	
microns	Under	In band	microns	Under	In band
118.4	100.0	5.2	11.1	22.2	0.1
102.1	94.8	12.4	9.6	22.0	0.0
88.1	82.4	14.9	8.3	22.0	11.0
76.0	67.6	12.6	7.2	11.0	7.6
65.6	55.0	5.8	6.2	3.4	0.0
56.6	49.2	0.4	5.3	3.4	1.4
48.8	48.8	0.4	4.6	1.9	2.0
42.1	48.3	0.3	4.0	0.0	0.2
36.3	48.0	0.1	3.4	0.0	0.0
31.3	47.9	0.0	3.0	0.0	...
27.0	47.9	0.0	2.6	0.0	...
23.3	47.9	0.0	2.2	0.0	...
20.1	47.9	0.5	1.9	0.0	...
17.4	47.4	17.8	1.6	...	...
15.0	29.5	7.4	1.4	...	...
12.9	22.2	0.0	1.2	...	...

TABLE-IV: Particle size distribution of silica sample 'C'

Size	Percentage		Size	Percentage	
microns	Under	In band	microns	Under	In band
118.4	100.0	3.2	11.1	24.4	2.4
102.1	96.8	7.7	9.6	22.0	3.3
88.1	89.0	9.4	8.3	18.6	7.3
76.0	79.6	8.1	7.2	11.4	7.1
65.6	71.5	4.1	6.2	4.2	3.2
56.6	67.4	1.0	5.3	1.1	0.9
48.8	66.4	1.0	4.6	0.1	0.2
42.1	65.4	0.8	4.0	Nil	Nil
36.3	64.6	0.3	3.4	...	...
31.3	64.3	0.0	3.0	...	...
27.0	64.3	0.0	2.6	...	...
23.3	64.3	0.1	2.2	...	...
20.1	64.2	0.9	1.9	...	...
17.4	63.3	23.7	1.6	...	...
15.0	39.7	11.6	1.4	...	...
12.9	28.1	3.7	1.2	...	...

Moreover, the gas bubbles exert a small mechanical shear on the gel, causing liquefaction of the gel which sets again as soon as the gas bubbles escape. This helps in improving the quality of the gel from any adverse effects due to ageing.

The conductivity of the different gel electrolytes prepared using the various samples of silica was measured using the Toshniwal digital conductivity bridge and the data are given in Table VI. It is found that the conductivity is not very much varied for the different samples. Characteristics of the gel electrolyte prepared from the two samples of pyrogenic silica are almost the same. Gel prepared with silica and acid alone shows a comparatively lower conductivity due to the higher silica to acid ratio required to produce a gel with suitable thixotropic properties. The gel prepared using an addition agent exhibits a better conductivity due to the silica to acid ratio being lower.

Viscosity of the gel samples prepared is about 86 Kerb units

TABLE-V: Particle size distribution of silica sample pyrogenic

Size	Percentage		Size	Percentage	
microns	Under	In band	microns	Under	In band
118.4	100.0	1.9	11.1	3.2	1.2
102.1	98.1	5.2	9.6	2.0	0.9
88.1	92.8	7.7	8.3	1.1	0.5
76.0	85.1	9.4	7.2	0.6	0.3
65.6	75.7	10.3	6.2	0.3	0.2
56.6	65.4	10.4	5.3	0.2	0.0
48.8	55.0	9.5	4.6	0.1	0.1
42.1	45.5	7.8	4.0	0.1	Nil
36.3	37.7	5.9	3.4	0.0	...
31.3	31.8	5.9	3.0	Nil	...
27.0	25.9	4.6	2.6	...	...
23.3	21.3	2.6	2.2	...	...
20.1	18.7	3.1	1.9	...	...
17.4	15.6	5.3	1.6	...	...
15.0	10.3	4.7	1.4	...	...
12.9	5.6	2.3	1.2	...	...

TABLE-VI: Specific conductivity of the gel electrolyte samples

Sample prepared from	Specific conductivity at 300 K mohs x 10^3
Precipitated silica	
Sample 'A'	674
Sample 'B'	676
Sample 'C'	692
Pyrogenic silica	
Silica alone	460
Silica with addition agent	698
Sulphuric acid sp.gr. 1.260	726

equivalent to 9.6 poise and does not differ much from sample to sample.

It is found that temperature is having an effect on the time of gellation. Lower temperature slows down the gellation while higher temperatures have an accelerating effect.

Keeping quality of the gel at room temperature was examined. It was found that the gel prepared under the conditions standardized, was having excellent keeping quality even after one year and no syneresis was observed.

Performance of the gel electrolyte

A few 2V/6Ah, 6V/12 Ah and 2V/30Ah cells were assembled, filled with gel electrolyte and charge-discharge studies were carried out. The performance of the cells is given in (Fig. 2) which shows the capacity obtained with the number of cycles. It is found that the capacity obtained at 20 hr rate is about 85% of the theoretical capacity, and the capacity does not vary much upto 50 cycles over a period of six months. The performance of the gel is found to be satisfactory. No cracks were observed in the gel and there was no syneresis also. The gel also maintained its thixotropic properties.

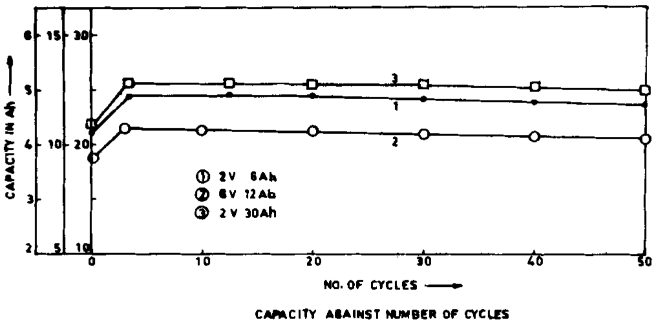


Fig. 2: Capacity against number of cycles

Improved versions of batteries using lead-antimony-cadmium alloy grids and with absorbent separators along with the gel electrolyte are being assembled and tested and their performance will be reported in a later communication.

CONCLUSION

A silica -based immobilized electrolyte for use in maintenance free lead acid batteries has been developed and the conditions of its preparation standardized. Performance of the gel in test cells was found to be satisfactory without any deterioration in its required properties. Even indigenous silica of the precipitated variety is suitable for preparing the gel electrolyte but the pyrogenic silica is found to be the best. Characteristics of the silica powder and the gel electrolyte prepared from it are almost the same both in the case of indigenous and imported samples.

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