Short communication

Investigations on self-discharge of gel valve-regulated lead–acid batteries

Yonglang Guo[*], Junmei Hu, Mingxiang Huang

College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, 350002 PR China

Available online 7 February 2006

Abstract

The performance of the self-discharged gel cell has been studied in this work. Although the gel valve-regulated lead–acid (VRLA) batteries were shelved for nearly 3 years, the active mass structure of the positive plate, its resistance and the corrosion layer of the grid are not much affected. On the negative plate, the potential of hydrogen evolution in gel cell is more negative than that in AGM cell. So its self-discharge rate is slower. However, there is still slight accumulation of big $PbSO_4$ crystals. It makes the resistance and overpotential of the self-discharged negative plate increase. But it is not enough to limit the capacity of the gel batteries, which is susceptible to the electrolyte amount. And the capacity of the long self-discharged gel cell can be completely restored by recharging.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Gel valve-regulated lead–acid batteries; Negative plate; Self-discharge; Sulfation

1. Introduction

In practice, two different battery technologies with the immobile electrolyte have been widely used. One is the valve-regulated lead–acid (VRLA) battery with the AGM (absorptive glass mat) separator and the starved electrolyte [1–3]. The other is the VRLA battery with the gelled electrolyte, which is prepared by mixing the H_2SO_4 solution and micron diameter silicon dioxide [4–6]. The gel VRLA batteries have many advantages such as high reliability, low self-discharge rate, no electrolyte stratification, good charge stability (resistant to thermal runaway), long service life, etc. Although, up to now, much work has been done on the AGM VRLA batteries, less research is reported on the gel VRLA batteries. It is significant to further understand the effects of the gel electrolyte on the performance of the battery and its mechanism.

The VRLA batteries used for the telecommunication are required to have high reliability and long service life. Accordingly, the design of tubular positive plates and gelled electrolyte is very suitable for the telecom application [7–10]. In the gelled electrolyte, the corrosion rate of the positive grids is lower, compared with the AGM-technology [11]. And its overpotential of hydrogen evolution on the negative plate is also higher [12–13]. It is mainly because of these two characteristics of the gelled electrolyte that the VRLA batteries have high performance. In the cyclic application, the VRLA batteries with the gel-technology have also a very long cycle life [14–18]. Furthermore, there is no electrolyte stratification in the gel VRLA batteries, which greatly contributes to the resistance against the sulfation of the active mass [19–20].

The aim of this work is to study the characteristics of the gel VRLA batteries, to further understand the advantageous effects of the gel electrolyte and its mechanism.

2. Experimental

The test plates were those of the commercial electric bicycle battery and had 1.25 and 1.5 Ah capacity at 2 and 10 h discharge rates, respectively. The cell consisting of eight positive and nine negative plates had 10 Ah capacity (2 h rate). The analytical reagent and redistilled water were used. The H_2SO_4 solution (1.30 *sp gr*) and 5% fumed silica were mixed to prepare the gel electrolyte. In order to increase the amount of the gel electrolyte, the container with larger specific volume was made and the performance of the cell with one positive and one or two negative plates were measured. The Arbin BT2000 instrumentation and HP34970A data Acquisition/Switch Units were used in the experiments. The electrode potential reported was against the $Hg/Hg_2SO_4/H_2SO_4$ (1.300 $g\,cm^{-3}$) reference electrode, which was separated from the plate stack by a Nafion film.

The potential of the hydrogen evolution was measured at constant current controlled by a potentiostat (CHI1140). The

phase composition of the active mass was analyzed by the X-ray diffraction (X'Pert-MPD) and its appearance was observed by the scanning electron microscopy (JSM-35CF).

3. Results and discussion

3.1. Capacity before and after self-discharge

Since the gel VRLA cell used is the same as the container of the commercial 12V10Ah (C_2) AGM VRLA batteries in this experiment, its volume is relatively small for the gel VRLA cell, which normally needs the larger volume, compared with the AGM VRLA cell. To study the self-discharge performance, the gel VRLA cell was shelved for 33 months at room temperature after its performances were measured. Table 1 shows the discharge capacity of the gel VRLA cell before and after the self-discharge. It can be seen that the capacity is low at different discharge rates before the cell shelving. This is due to the smallness of the container, which limits the amount of the gel electrolyte. So the capacity of the cell is controlled by the amount of the gel electrolyte. After 33 months of shelving, the voltage of the gel VRLA cell on open circuit is 2.028 V and its state of charge (SOC) without recharging still keeps 35.9% at 10 h discharge rate. The capacity restoration reaches about 90–95% after the recharge at constant voltage of 2.5 V while the full charge can be obtained after charging at constant current. It means that the self-discharge rate of the gel cell is very slow and its capacity can be completely restored by the constant current charge although it has been shelved for nearly 3 years and the sulfation of the active mass is inevitable. It is quite difficult for the AGM batteries to have such low self-discharge rate and to completely restore the capacity of the battery.

3.2. Overpotential of positive and negative plates

Since the electrode potentials of the positive and negative plates mainly depend on the H_2SO_4 concentration which changes during discharging, the equilibrium potentials and voltage were measured after 10 h rest for each SOC of the gel and AGM cells. Table 2 shows the dependence of the equilibrium potential and voltage of the gel and AGM cells on the discharge capacity. It can be seen from the R^2 value that they have good straight-line relationship between the equilibrium potential or

Table 2
The dependence of the equilibrium potentials and voltage of the gel and AGM VRLA cells on the discharge capacity

Cell type	Plates/cell	Equilibrium potentials (V)	R^2
Gel cell	Positive plate	$E_+ = 1.2178 - 0.0149C$	0.9938
	Negative plate	$E_- = 0.0075C - 0.9851$	0.9979
	Cell	$E = 2.2030 - 0.0224C$	0.9955
AGM cell	Positive plate	$E_+ = 1.2508 - 0.0186C$	0.9961
	Negative plate	$E_- = 0.0070C - 0.09789$	0.9903
	Cell	$E = 2.2315 - 0.0257C$	0.9995

C denotes the discharge capacity of the gel cell.

voltage and the discharge capacity of the cells. So the overpotential can be obtained by the difference between the equilibrium potential and the potential measured during discharging. Fig. 1 shows the changes of the overpotential on the positive and negative plates of the gel cell after it was shelved for 33 months. To compare, the data of a new AGM VRLA cell are also shown in Fig. 1. The low capacity in the gel cell is due to the limited amount of the electrolyte. It is found that the overpotential of the negative plate in the gel cell increases significantly while that of the positive plate hardly changes after nearly 3 years of shelving. Since the overpotential of the positive plate in the new AGM cell rises sharply at the end of the discharge and that of the negative plate remains unchanged, its capacity depends on the positive plate. It is interesting to note that the overpotential of the positive plate in the AGM cell decreases slowly before about 70% depth of discharge (DOD). However, all results reported in the literatures show that the potential of the positive plate drops continually with discharging. It seems that the polarization becomes higher and higher. In practice, the H_2SO_4 concentration decreases during discharging, which leads to the falling of the equilibrium potential of the positive plate. The results above reveal that the falling rate of the equilibrium potential is faster than that of the polarization potential. This may be due to the decrease of the specific resistance of the H_2SO_4 solution. When the cell is discharged to 60–70% SOC, and the specific gravity of H_2SO_4 solution whose specific resistance is minimum, reaches about 1.22. So before this time, the polarization of IR drop in the electrolyte becomes smaller and smaller. It also means that the polarization of the electrolyte is dominant during discharging before 60–70% SOC. In gel cell, the long-shelved negative plate has also affected its capacity. This is because its self-discharge

Table 1
The discharge performance of gel VRLA cell before and after 33 months of the shelf

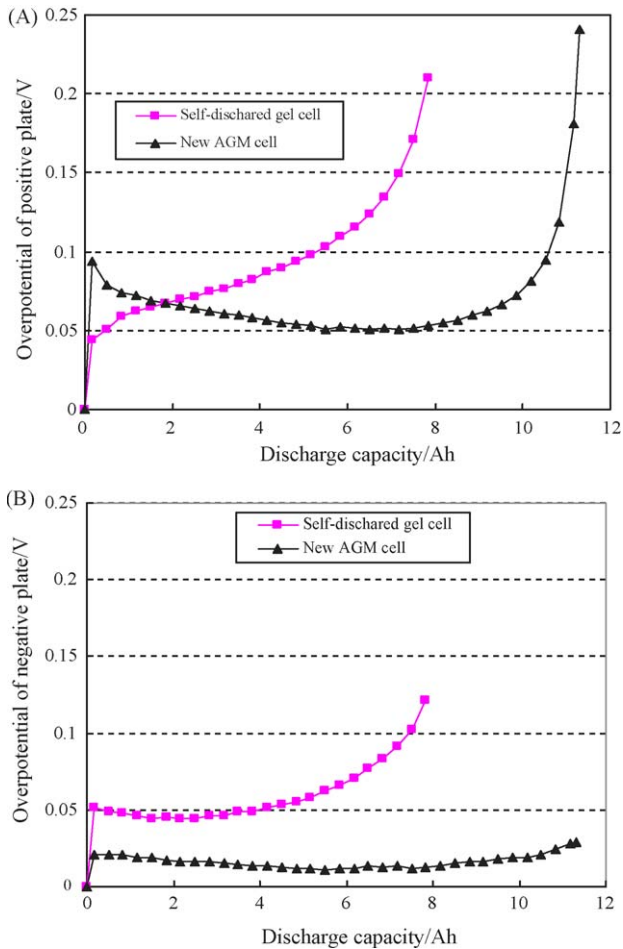| Cycle No.	Self-discharge	Charge methods	Discharge rates	Capacity (Ah)	State of charge (%)
1	Before shelving	Constant voltage	10 h	10.80	
2			2 h	8.21	
3			3 C	5.10	
1	After shelving	Without charge	10 h	3.88	35.9
2		Constant voltage	10 h	10.24	94.8
3			2 h	7.33	89.3
5		Constant current	2 h	8.17	99.5
6			10 h	10.90	100.9

Fig. 1. The evolution of the overpotential on (A) positive and (B) negative plates after the new AGM and self-discharged gel cells were discharged at 5 A (2 h rate).
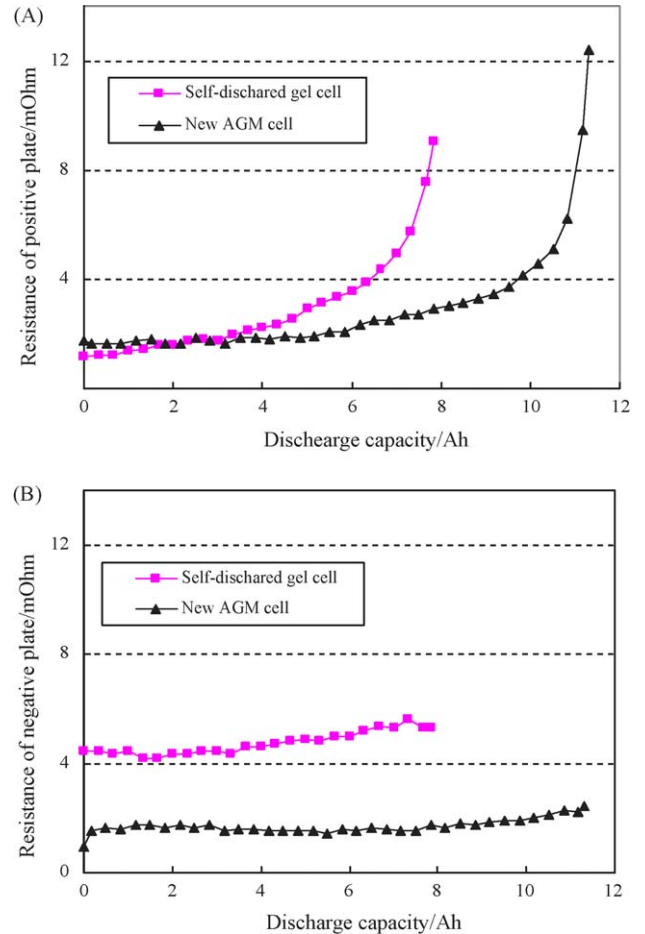

Fig. 2. The evolution of the resistance on (A) positive and (B) negative plates when the new AGM and self-discharged gel cells were discharged at 5 A (2 h rate).

is unavoidable during its shelving and slight sulfation may occur on the negative plate.

3.3. Resistance of positive and negative plates

To investigate the behavior of active mass in the self-discharging cell, the very short current pulse with 5 A and 1 ms was exerted on the cell. So the resistance of the positive and negative plates can be measured according to the response of the potentials. It is clear that it includes all polarization resistance except the concentration difference. This is because the concentration difference is believed to change little within 1 ms. Therefore, the evolution of the resistance mainly shows the change of active mass structure. Fig. 2 indicates the changes of the resistance on the positive and negative plates when the cell is discharged at 5 A. It is found that at the end of the discharge, great changes take place in the resistance of the positive plate while that of the negative plate is almost unchanged. It means that the positive plate determines the cell capacity either for the AGM or for self-discharged gel cell. However, the 3 years of self-discharge has hardly affected the resistance of the positive plate in the gel cell, while it has an impact on that of the negative plate. Its resistance is 1.7 and 4.3 mΩ, respectively.

3.4. Appearance observation

It is shown from the results above that the discharge rate of the gel cell is very low during its long shelf. In order to understand the sulfation of the negative plate, the appearances of its active mass have been observed. Fig. 3 shows the SEM of the active mass on the negative plate after the gel cell was shelved for 33 months (Fig. 3A and B). To compare, the SEM of the active mass on the formed and serious sulfated negative plates has also been shown in Fig. 3C and D, respectively. The active mass in Fig. 3C has the structure of the dendrite metallic lead. It is found from Fig. 3A that the active mass of the negative plate has two structures. One is the sponge structure of dendritic metallic lead. The other is the structure of big intact $PbSO_4$ crystals shown by an arrow in Fig. 3A. And during the self-discharge only a few big $PbSO_4$ crystals are formed. These crystals are very similar to those seriously sulfated ones in Fig. 3D, but they are smaller. It is also found that most of the active mass of the negative plate has the porous sponge structure as well (see Fig. 3B). However, the seriously sulfated active mass in Fig. 3D has dense and intact crystal structure. And there are fewer micropores. It indicates from Fig. 3A that the accumulation of the big $PbSO_4$ crystals or sulfation only occurs slightly on the negative plate. Since the
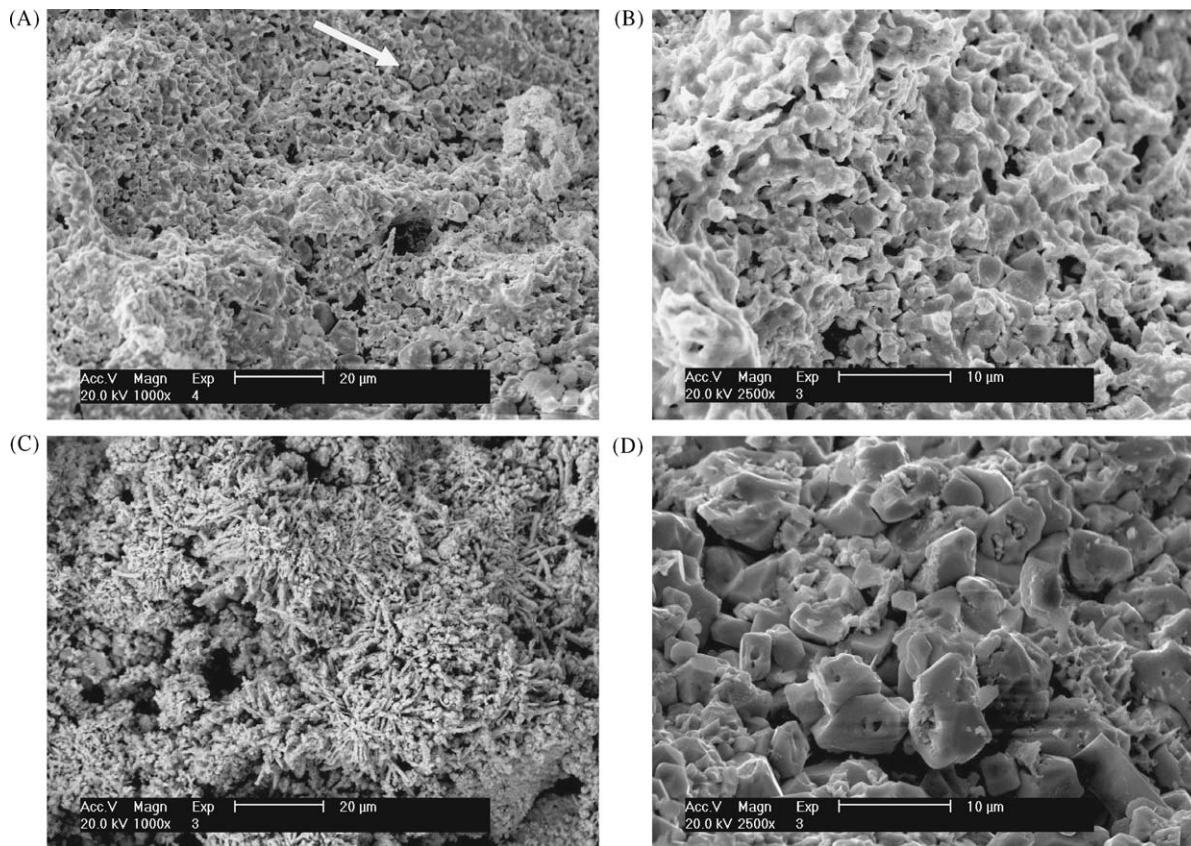
Fig. 3. SEM of active mass on the negative plate. Shelved gel cell: (A) ×1000; (B) ×2500; formed negative plate: (C) ×1000; negative plate with serious sulfation: (D) ×2500.

capacity of the VRLA batteries does not depend on the negative plate, a few big $PbSO_4$ crystals formed cannot affect the capacity of the gel cell.

Fig. 4 shows the appearance of the corrosion layer on the positive grid after the gel VRLA cell was self-discharged for nearly 3 years. Fig. 4A is the SEM of the cross-section of the corroded grid. Fig. 4B and C are the transition layer between the grid and corrosion film and the outside surface of the corrosion layer, respectively. It is observed from Fig. 4A that a corrosion layer with about 60 μm thickness is very clear and shown by the arrow. Its structure mainly consists of fine crystals. There are no large $PbSO_4$ crystals, which are intact. In the transition layer of Fig. 4B, there are many large particles, which may be the corroded substrate alloy particles rather than $PbSO_4$ crystals. If many big $PbSO_4$ crystals exist in the interior of the corrosion layer, it can lead to premature capacity loss (PCL) of the batteries. Since the capacity of the shelved gel cell can be completely restored by recharging, the accumulated big $PbSO_4$ crystals do not occur in the corrosion layer. In Fig. 4C, the corrosion products of the outer surface of the grid show an aggregate structure, which consists of the hydrated and incomplete PbO_2 crystals. It is similar to the structure of the normal positive active mass. Therefore, the corrosion layer of the positive grid in the self-discharged gel cell has good structure and good adhesion to the grid surface.

It is not easy for the gel cell to produce the phenomenon of PCL-1.

3.5. X-ray diffraction

In order to further understand the self-discharge and sulfation of the gel cell, the full charged cell was torn off and its active mass was analyzed by X-ray diffraction (XRD). Fig. 5 shows the XRD patterns of the active mass on the positive and negative plates of the self-discharged gel cell. It is found from Fig. 5A that almost all the active mass on the positive plate is made up of β-PbO_2, so the diffraction peaks of α-PbO_2 and $PbSO_4$ are hardly observed. This is because α-PbO_2 can be transformed slowly into β-PbO_2 during the long shelving and no sulfation appears on the positive plate. However, on the negative plate, the self-discharge is inevitable and the hydrogen evolution leads to the discharge of its active mass. Since the discharge rate is very slow, the $PbSO_4$ crystals grow very large. And it is very difficult for these crystals to be reduced during recharging, which results in the sulfation of the negative plate. Fig. 5B also indicates that there are many $PbSO_4$ crystals on the negative plate, except for the metallic lead. But even so, the capacity of the self-discharged gel cell can be completely restored by recharging. It is clear that only slight sulfation occurs on the negative plate as shown by the arrow in Fig. 3A. And the design of
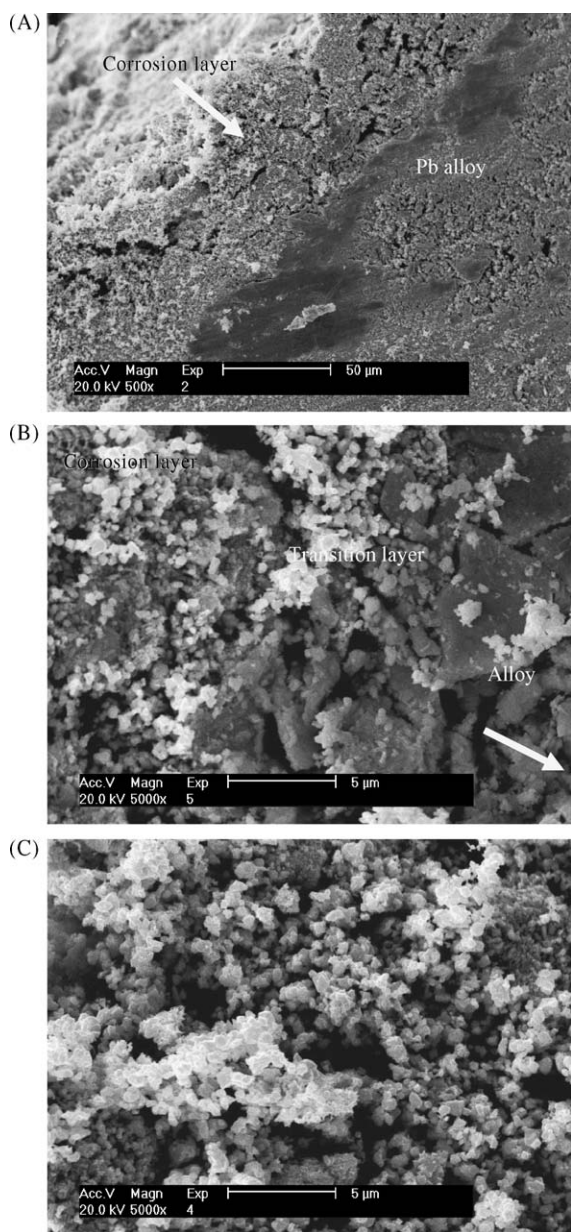
Fig. 4. SEM of the positive grid of the shelved gel cell. (A) Cross-section of corroded grid (×500); (B) transition layer between the grid and corrosion film (×5000); (C) outer surface of corroded grid (×5000).

surplus capacity for the negative plat is enough to compensate the sulfation.

3.6. Overpotential of hydrogen evolution

During the shelving of the battery, the discharge of the negative plate accompanies the hydrogen evolution and the large $PbSO_4$ crystals are formed in the active mass, which can lead to the passivation of the negative plate. And in the discharge, its rate depends on the overpotential of hydrogen evolution. In order to understand the effects of the gel on the self-discharge rate, the AGM and gel VRLA cells with one positive and one negative plates were overcharged and then the hydrogen polarization was measured at the constant current. Fig. 6 shows the
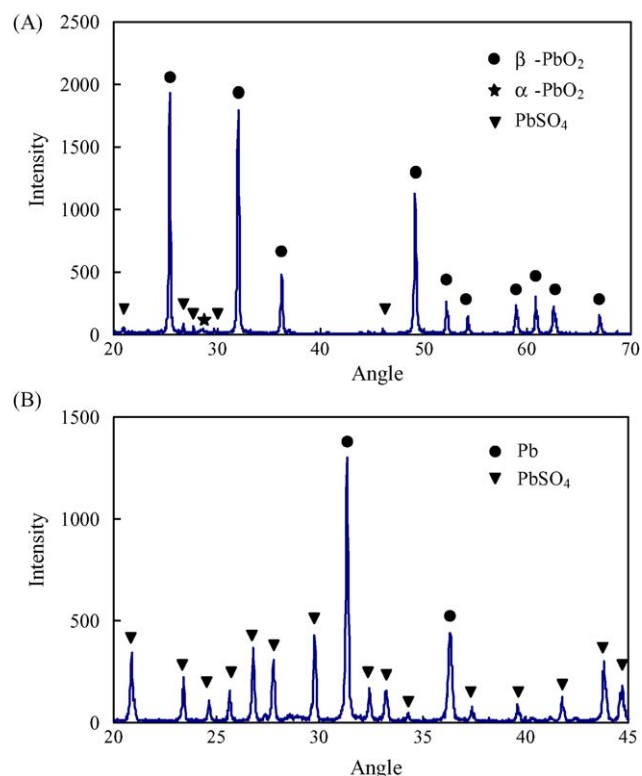

Fig. 5. XRD patterns of active mass on (A) positive and (B) negative plates of the self-discharged gel cell.

potential of hydrogen evolution in the AGM and gel VRLA cells at different saturations. It is found that its potential in the gel cell is more negative than that in the AGM cell. And the lower the saturation, the higher the hydrogen polarization becomes. On the negative plate, in practice, a mixed potential appears. They are the reactions of both $PbSO_4$ reduction and hydrogen evolution. Although the cells are thoroughly overcharged, the polarization depends on the $Pb/PbSO_4$ electrode rather than the H_2 evolution reaction at very low charge current because of much higher exchange current density of the $Pb/PbSO_4$ electrode, compared with that of the H_2/H^+ electrode. With overcharging and the
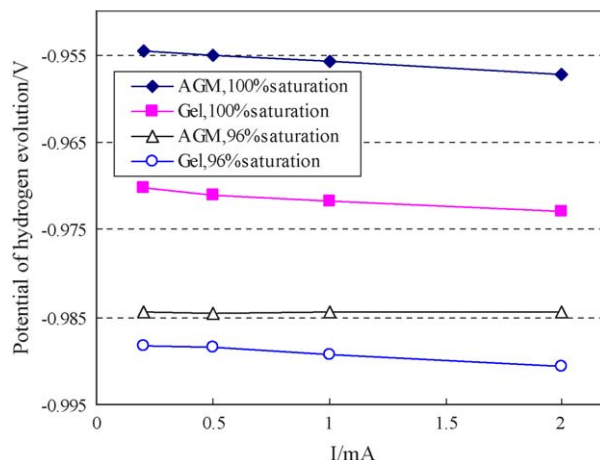

Fig. 6. The potential of hydrogen evolution in the AGM and gel VRLA cells at different saturations.

Table 3
The discharge performance of the gel cell with excessive electrolyte

Cell type	Discharge rates	Capacity (Ah)
1 positive + 1 negative plate	2 h	1.69
	3 C	0.68
1 positive + 2 negative plates	2 h	1.59
	3 C	0.73

decrease of the saturation, water loss occurs in the cells, which condenses the H_2SO_4 solution. So the potential of the negative plate shifts in the negative direction at low saturation. In the gel electrolyte, the fumed silica is inert. Though the same H_2SO_4 solution as shown in the AGM cell was used to prepare the gel electrolyte, Fig. 6 indicates that the potential of hydrogen evolution in the gel cell is more negative than that in the AGM cell. Therefore, the self-discharge rate of the gel cell is very small, which significantly improves the performance of the battery, but the function of the gel is still unclear.

3.7. Capacity of gel cell with more electrolyte

The gel cell normally needs more electrolyte than the AGM cell. When the electrolyte is not enough, Fig. 1 indicates that the capacity of the gel cell is relatively low. Table 3 shows the capacity of the gel cell with the excessive electrolyte when the cell consists of one positive and one or two negative plates. Although the capacity of each plate for the 12 Ah cell is 1.5 Ah at 10 h discharge rate, its capacity is conversely high at 2 h discharge rate in the excessive electrolyte. And for the gel cell with one positive and one negative plate, the real current density is doubled, compared with the cell with two negative plates. It is the same case at a high discharge rate. The results indicate that the electrolyte amount plays an important role in the capacity of the gel VRLA batteries.

4. Conclusions

For the same container and plate stack, the capacity of the gel VRLA batteries is smaller than that of the AGM VRLA batteries, which is limited by the electrolyte amount. Therefore, the gel battery should be designed to have larger container and more electrolyte.

In the shelved gel VRLA batteries, there is not only no stratification of the electrolyte, but also no sulfation occurs on the positive plate. The positive grid has also a good corrosion layer structure. So the active mass structure of the positive plate and its polarization resistance are not much affected during the long shelving.

On the negative plate, the potential of hydrogen evolution of the gel VRLA batteries is a little more negative than that of AGM VRLA batteries. Its self-discharge rate is also slower. For a long-shelved gel battery, most of the active mass on the negative plate has a good sponge structure, but some big $PbSO_4$ crystals also accumulate on the negative plate, which makes its resistance and overpotential increase. But it is not enough to limit the capacity of the gel batteries, which can be completely restored by recharging.

Acknowledgement

References

[1] P.T. Moseley, J. Power Sources 88 (2000) 71.
[2] K. Peters, J. Power Sources 59 (1996) 9.
[3] G. Papazov, D. Pavlov, B. Monahov, J. Power Sources 113 (2003) 335.
[4] G.J. May, P. Lenain, J. Power Sources 40 (1992) 187.
[5] D.W.H. Lambert, P.H.J. Greenwood, M.C. Reed, J. Power Sources 107 (2002) 173.
[6] J. Strebe, B. Reichman, B. Mahato, K.R. Bullock, J. Power Sources 31 (1990) 43.
[7] D. Kölbel, International Telecommunications Energy Conference (Proceedings), 1998, pp. 156–160.
[8] F. Kramm, International Telecommunications Energy Conference (Proceedings), 1998, pp. 161–165.
[9] G.J. May, J. Power Sources 42 (1993) 147.
[10] G.J. May, J. Power Sources 59 (1996) 147.
[11] S.K. Martha, B. Hariprakash, S.A. Gaffoor, A.K. Shukla, Bull. Mater. Sci. 26 (2003) 465.
[12] M.P. Vinod, K. Vijayamohanan, J. Appl. Electrochem. 24 (1994) 44.
[13] M.P. Vinod, A.B. Mandle, S.R. Sainkar, K. Vijayamohanan, J. Appl. Electrochem. 27 (1997) 462.
[14] R.H. Newnham, W.G.A. Baldsing, J. Power Sources 59 (1996) 137.
[15] R.H. Newnham, W.G.A. Baldsing, J. Power Sources 66 (1997) 27.
[16] M. Shiomi, K. Takahashi, M. Tsubota, J. Power Sources 42 (1993) 173.
[17] G. Poesch, J. Power Sources 33 (1991) 127.
[18] H. Tuphorn, J. Power Sources 40 (1992) 47.
[19] F. Alavyoon, A. Eklund, F.H. Bark, R.I. Karlsson, D. Simonsson, Electrochim. Acta 36 (1991) 2153.
[20] F. Mattera, D. Desmettre, J.L. Martin, Ph. Malbranche, J. Power Sources 113 (2003) 400.