



Gelled electrolytes for use in absorptive glass mat valve-regulated lead-acid (AGM VRLA) batteries working under 100% depth of discharge conditions

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ABSTRACT

Gelled electrolytes prepared from fumed silica for use in absorptive glass mat valve-regulated lead-acid (AGM VRLA) batteries and the effect of veratraldehyde addition on the electrochemical behavior and performance of AGM VRLA batteries are investigated. Cyclic voltammetry is used to investigate differences in the electrochemical behaviors of nongelled and gelled electrolytes and between gelled electrolytes with and without veratraldehyde. Battery performance is tested under 100% depth of discharge (100% DoD) conditions at both low- (0.1 C) and high- (1 C) rate discharges. The addition of silica or veratraldehyde does not affect the main reaction of the lead-acid batteries but tends to suppress the hydrogen evolution reaction. AGM VRLA batteries with gelled electrolytes have a higher discharge capacity and longer cycle life than the conventional nongel AGM VRLA batteries. The addition of 0.005% (w/v) veratraldehyde further improves battery performance, but higher (0.01%, w/v) veratraldehyde concentrations reduce it and correlate with the enhanced growth of lead sulfate crystals. The AGM VRLA battery prepared from a gelled electrolyte containing 0.005% (w/v) veratraldehyde provides the best battery performance in every operating temperature studied (0–60 °C).

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1. Introduction

Although lead-acid batteries were invented more than a century ago, they remain the most widely used type of rechargeable battery and are used in many applications such as automotive, traction and stationary applications, uninterruptible power supplies (UPS), solar traffic lights, telecommunications and energy storage devices for renewable energy. Valve-regulated lead-acid (VRLA) batteries, which use an immobilized electrolyte, were developed to extend the service life and to minimize maintenance compared with conventional flooded lead-acid batteries. With the immobilized electrolyte, the oxygen generated during the charge is captured and recombined in the battery, in the so-called “oxygen recombination cycle”, and gases are allowed to escape only if the internal pressure exceeds a certain level by means of pressure-release valves so that water loss during battery operation is minimized.

There are two distinctly different types of technologies for immobilizing the electrolyte in VRLA batteries. One is the absorptive glass mat (AGM) technology, in which the sulfuric acid

electrolyte is captured in an absorptive glass mat separator. The other is gel technology, in which the sulfuric acid solution is mixed with a gelling agent to form a gelled electrolyte. Overall, gel VRLA batteries possess several advantages over AGM VRLA batteries, including a longer service life, higher reliability under depth of discharge cycles, lower electrolyte stratification, less or even no leakage of acid electrolyte, less corrosion, higher resistance to thermal runaway [1,2] and the flexibility of installation in any orientation. Consequentially, gel VRLA batteries have increased in proportional market share, leading to further research effort on improving the performance of gel VRLA batteries in the last two decades [1–11].

In this work, a combination of two VRLA battery technologies, called the “gel AGM VRLA battery”, was studied. The electrochemical behavior and performance of gel AGM VRLA batteries with various gelled electrolyte compositions were investigated and compared with a nongel AGM VRLA battery. The gelled electrolytes were prepared from different concentrations of fumed silica, with and without different levels of veratraldehyde. The choice of veratraldehyde, a derivative of benzaldehyde, as a model additive was based on previous studies reporting that several additives [1,12–16] can inhibit hydrogen evolution in liquid sulfuric acid electrolytes, with potential applications in lead-acid batteries. We preliminarily investigated the effect of fumed silica concentration and the presence of veratraldehyde on gel formation, which

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Table 1
Cyclic test algorithms used in the battery tests under 100% depth of discharge.

Step	100% DoD		
	Low-rate discharge (0.1 C)	High-rate discharge (1 C)	Cycle life test (1 C) ^b
1	Charge (0.8 A/14.1 V/7 h)	Charge (1 A/14.1 V/9 h)	Charge (2 A/14.1 V/9 h)
2	Rest (5 h)	Rest (5 h)	Rest (5 h)
3	Discharge (0.4 A/10.5 V)	Discharge (4 A/9.6 V)	Discharge (7 A/9.6 V)
4	Charge (0.8 A/14.1 V/11 h)	Charge (1 A/14.1 V/9 h)	Charge (2 A/14.1 V/9 h)
5	Repeat steps 3 and 4 14 times ^a	Repeat steps 3 and 4 29 times	Repeat steps 3 and 4 199 times

^a For temperature test: repeat three times.

^b 12 V/7 Ah batteries.

directly affect gel properties, the electrolyte filling or manufacturing process and the performance of the gel AGM VRLA batteries. Only gel formulations that had suitable gel properties were then selected for further study. The electrochemical behaviors of the electrolytes were investigated by cyclic voltammetry. To evaluate the performance of the AGM VRLA batteries, electrolytes of different formulations were filled into 12 V/4 Ah or 12 V/7 Ah batteries and tested under 100% depth of discharge conditions (100% DoD). After the tests, the negative electrodes were examined by scanning electron microscopy (SEM). The performance of AGM VRLA batteries operating at different temperatures (0–60 °C) was also studied.

2. Experimental

2.1. Electrolyte preparation

All electrolytes were prepared with fixed concentrations of sulfuric acid (1.325 g cm⁻³) and sodium sulfate (0.013 g cm⁻³); the latter was added to the sulfuric acid solution to replenish sulfate ions depleted during discharge [17] and to improve battery rechargeability at a low state of charge [10]. To prepare the gelled electrolytes, various amounts of commercial fumed silica and veraldehyde, hereafter referred to as SiO₂ and AL, respectively, were added to obtain the desired concentrations (0–5%, w/v, for SiO₂ and 0–0.01%, w/v, for AL). The electrolyte was then mixed at 2000 rpm for 10 min and was then filled into the 12 V/4 Ah or 12 V/7 Ah AGM batteries under a vacuum condition.

The gelled electrolyte formulations were screen-tested based on the gelling time and the gel characteristics during and after the electrolyte filling process. The gelling times of the electrolyte formulations were determined by measuring the penetration of lead balls that were dropped onto the gel at different times. Gelled electrolyte formulations that maintained a liquid state until they were completely distributed throughout the battery cells were selected for subsequent examination of their electrochemical behavior and battery performance. The preliminary results (data not shown) indicated that the electrolytes with SiO₂ concentrations of 2% (w/v) or less took several days to gel or did not form a completely stable gel. Increasing the SiO₂ concentration above 2% (w/v) led to a shorter gelling time and to a firmer gelled electrolyte, but too much SiO₂ (>5%, w/v) hindered the filling process and created inaccessible spaces in the battery cells, leading to a poor battery performance. Thus, SiO₂ concentrations of 3–5% (w/v) were selected for further study. Note that the addition of sodium sulfate was found to have no substantial effect on the gelling process. In contrast, the addition of AL was found to affect the gelling process and shorten the gelling time, even when only a very small amount (0.005%, w/v) was present. Therefore, the concentration of AL in the gelled electrolyte formulations was limited to a maximum of 0.01% (w/v).

2.2. Electrochemical testing

Cyclic voltammetry experiments were performed to investigate the electrochemical behavior of the different gel formulations, which were allowed to stand for five days after preparation to assure complete gel formation. The experiments were conducted using an Autolab PGSTAT 10 potentiostat (Eco Chemie) with a classical three-electrode system. A 1-cm² planar lead electrode polished with sequentially finer grades of SiC abrasive paper (800, 1500 and 2000) was used as the working electrode. A platinum gauze was used as the counter electrode, and Ag/AgCl was used as the reference electrode. Cyclic voltammetry was performed between –2.5 and 3.0 V vs. Ag/AgCl at a 50 mV s⁻¹ scan rate. All electrochemical experiments were conducted at room temperature (30 °C).

2.3. Battery testing

Different gel formulations were filled under vacuum conditions into 12 V/4 Ah AGM VRLA batteries, a size that is commonly used for standby applications such as UPS, emergency lights and solar traffic lights. Conventional nongel AGM VRLA batteries were also tested for comparison. The batteries were tested under 100% DoD conditions, based on the Japanese industrial standard (JIS) [18], at the low- (0.1 C) and high- (1 C) rate discharges using Ultimate Battery Analyzer (UBA4) instrumentation (Vencon Technologies) and a battery charge/discharge and data processing control system (Huizhou Xinkehua Industry), respectively. The life cycle tests were performed on 12 V/7 Ah AGM VRLA batteries with selected gelled electrolyte formulations under a 100% DoD at the high-rate discharge (1 C). The cyclic testing algorithms for the battery tests are shown in Table 1. Unless otherwise stated, all experiments were performed at room temperature (30 ± 3 °C). After the tests, the batteries were carefully disassembled to investigate the physical structures of the negative plates using SEM (JEOL JSM-6400). X-ray diffraction analysis (Bruker D8-Discovery) was used to examine the phase compositions of the negative plates.

To investigate battery performance at different temperatures, the 12 V/4 Ah AGM batteries filled with various electrolytes were tested under a 100% DoD at the low-rate discharge (0.1 C) and the desired temperatures (0–60 °C at 10 °C intervals), with the temperature controlled by a water bath (Mettler) during the discharge periods. Lead-acid batteries, however, are generally not ready for use immediately after filling, particularly when they are operated under conditions considerably deviating from their normal operating condition (i.e., room temperature); premature operation can lead to a loss of rechargeability and eventual battery failure. Therefore, to avoid this problem, prior to the temperature tests, each newly prepared battery underwent a conditioning process by being charged and discharged at high current for a few cycles at room temperature to activate and prepare the battery for use at different temperatures.

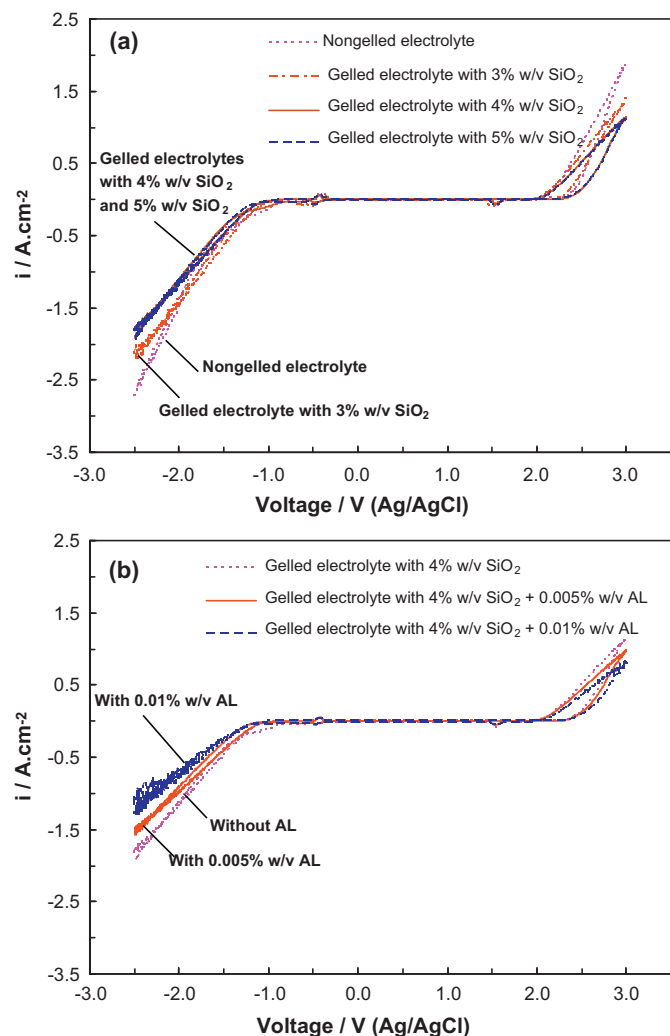


Fig. 1. Cyclic voltammograms of lead working electrodes in different electrolytes at 50 mV s^{-1} : (a) nongelled electrolyte vs. gelled electrolytes prepared with different SiO_2 concentrations and (b) gelled electrolytes prepared from 4% (w/v) SiO_2 with different AL concentrations.

3. Results and discussion

3.1. Electrochemical studies

Cyclic voltammetry curves for the lead electrodes in various electrolytes are shown in Fig. 1. The addition of SiO_2 to the gelled electrolyte in the range of 3–5% (w/v) does not result in the appearance of additional peaks in the voltammograms; as with the nongelled electrolyte, only peaks at -0.5 V and 1.5 V are seen (Fig. 1a), corresponding to the Pb/PbSO_4 and $\text{PbO}_2/\text{PbSO}_4$ reactions [16,19], respectively. This result indicates that there is no secondary redox reaction due to the added SiO_2 in the potential range studied and that the SiO_2 is stable under the operating conditions of the lead-acid battery. The gelled electrolytes shows no noticeable shift of hydrogen and oxygen overpotentials but has a much lower intensity for both hydrogen and oxygen evolution than the nongelled electrolyte; increasing the SiO_2 concentration from 3% to 4 or 5% (w/v) lowers the rates of the hydrogen and oxygen reactions. This observation indicates that the electrolyte gel formed by the SiO_2 network significantly diminishes the hydrogen and oxygen evolution reactions, which could result in lower water loss, a longer service life and a lower self-discharge rate in batteries with gelled electrolytes compared with the nongelled formulations.

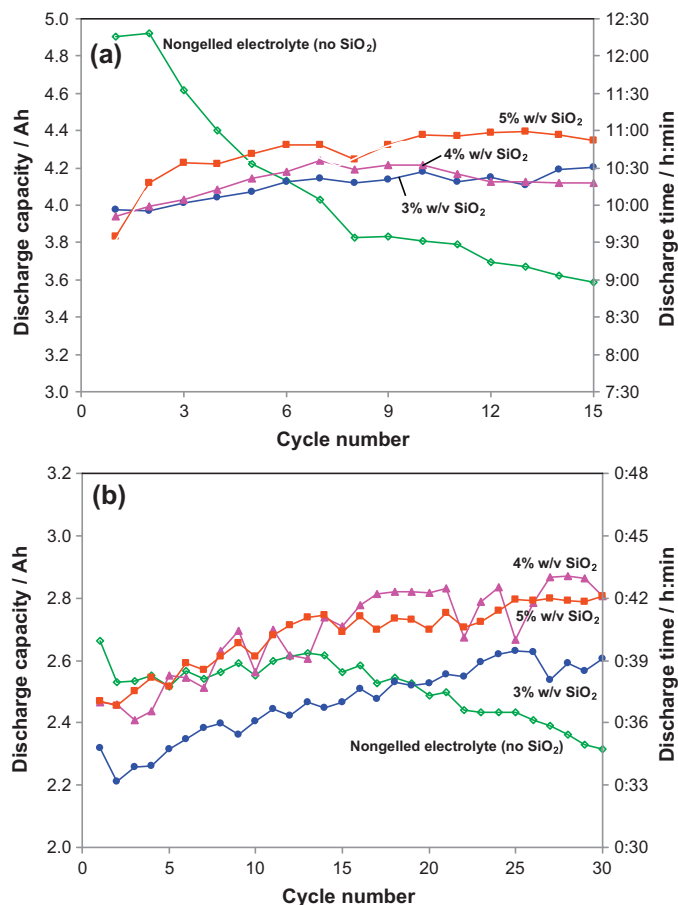


Fig. 2. Discharge capacities and discharge times of 12V/4 Ah gel AGM VRLA batteries prepared with different SiO_2 concentrations during 100% DoD tests at (a) the low- (0.1 C) and (b) high- (1 C) rate discharges.

The diminution of hydrogen and oxygen evolution in the gelled electrolyte may be due to the adsorption of hydrogen ions and sulfate ions by SiO_2 , reducing their activities [7,10], or due to the three-dimensional network structure of the gel, which obstructs ion diffusion.

The addition of AL to the 4% (w/v) SiO_2 gelled electrolyte suppresses the hydrogen and oxygen evolution reactions to an even greater degree than that with 4% (w/v) SiO_2 alone, with a higher level of suppression observed at higher AL concentrations, whereas the other peaks remain unchanged (Fig. 1b). This result indicates that AL likely further reduces the water loss during the battery operation while having no influence on the main reaction. Thus, AL can potentially be used as an electrolyte additive in lead-acid batteries.

3.2. Battery tests

3.2.1. Gelled electrolyte with no additive

The discharge capacities and discharge times of the gel AGM VRLA batteries prepared with different SiO_2 percentages are compared with the nongel AGM VRLA batteries, as shown in Fig. 2. The nongel AGM VRLA batteries have a higher initial discharge capacity (i.e., after one cycle) than all the gel AGM VRLA batteries, particularly at a low-rate discharge (Fig. 2a). As the charge/discharge process continues, the discharge capacity of the nongel AGM VRLA battery, however, decreases fairly sharply from the third to the eighth charge/discharge cycle, inclusively, and then decrease gradually thereafter. For the high-rate discharge, a gradual drop in the discharge capacity is observed after 16–19 charge/discharge cycles (Fig. 2b). The decrease in the discharge capacities of the nongel

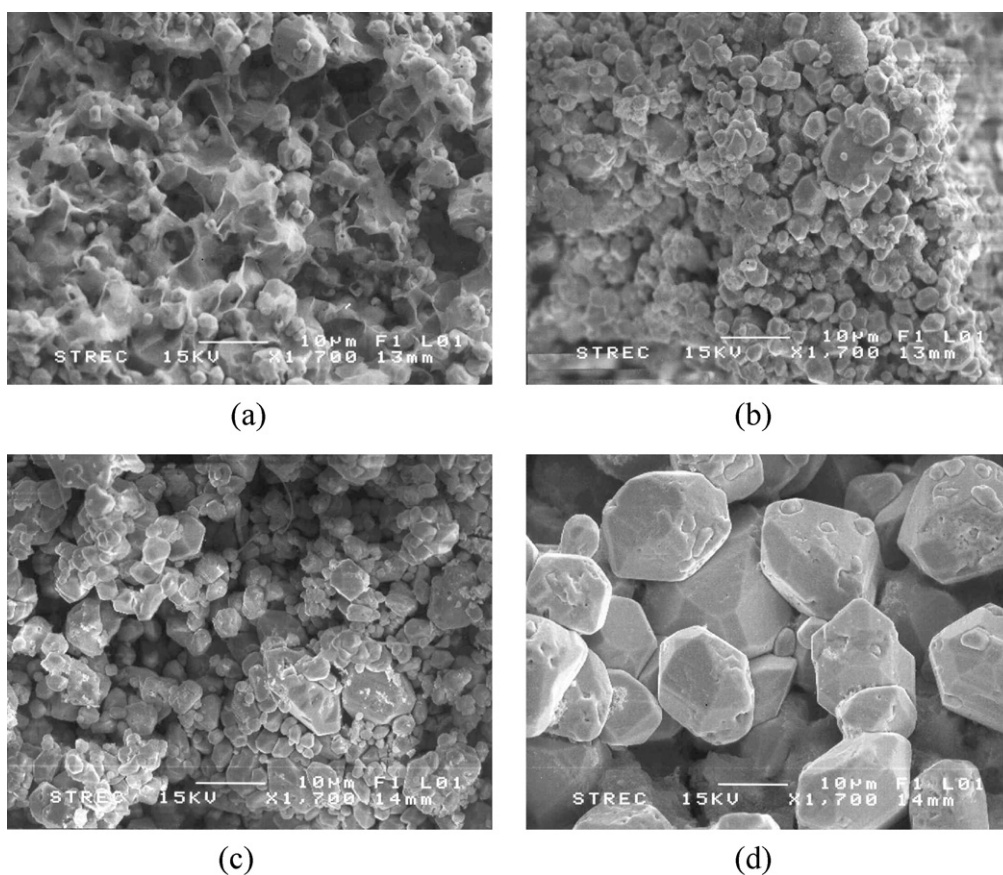


Fig. 3. SEM images (all at 1700 \times magnification) of negative plates from 12 V/4 Ah AGM VRLA batteries with different electrolytes: (a) nongelled electrolyte, (b) gelled electrolyte with 4% (w/v) SiO₂, (c) gelled electrolyte with 4% (w/v) SiO₂ and 0.005% (w/v) AL and (d) gelled electrolyte with 4% (w/v) SiO₂ and 0.01% (w/v) AL, after 100% DoD tests at the low-rate discharge (0.1 C).

AGM VRLA batteries may be due to water loss and electrode corrosion, which are expected to be more severe for the electrolyte in the liquid state. In contrast, the gel AGM VRLA batteries exhibit an opposite trend in that, despite their lower initial discharge capacities, the discharge capacities of all the gel AGM VRLA batteries gradually increase and remain stable throughout the test period of 15 (low rate) or 30 (high rate) charge/discharge cycles. The performance of all the gel AGM VRLA batteries eventually surpass that of the nongel AGM VRLA batteries after six cycles for the low-rate discharge and after 19 cycles for the high-rate discharge. The performance differences between the two types of electrolyte used for AGM VRLA batteries, therefore, become even more pronounced as the charge/discharge process continues.

The gradually increasing discharge capacities of the gel AGM VRLA batteries may be attributed to the thixotropic properties of the gelled electrolyte. Thixotropic properties allow materials to soften or to become less viscous under an applied force [1]. The charge/discharge of the gel batteries is analogous to applying an external force on the gelled electrolytes, such that during the rapidly repeated charge/discharge cycles, the gelled electrolyte becomes less viscous and is more fluid, allowing the electrolytes to gain easier access to every part of the battery cells and to become more homogeneous throughout the battery cell. As the number of trapped air zones is reduced, the ionic transfer between electrodes is improved. In addition, the newly filled gel AGM VRLA batteries may need time during the initial stage to develop the microcrack network required for oxygen diffusion in the oxygen recombination cycle [1,2,4,20]. As a result, the discharge capacities of the gel AGM VRLA batteries gradually increase in the initial charge/discharge cycles. In the same manner, a higher rate discharge is comparable

to applying a greater force on the gelled electrolyte, which tends to make the gelled electrolyte become more fluid or softer. Thus, the differences in the initial discharge capacities between the gel and the nongel AGM VRLA batteries are diminished at the high-rate discharge (Fig. 2b).

Comparing the gel AGM VRLA batteries with different SiO₂ concentrations, the gel AGM VRLA batteries with 3 and 4% (w/v) SiO₂ have relatively similar discharge capacities (but less than those of the 5%, w/v, SiO₂) at the low-rate discharge (0.1 C), whereas those with 4 and 5% (w/v) SiO₂ have relatively similar discharge capacities (but higher than that with 3%, w/v SiO₂) at the high-rate discharge (1 C). Overall, the gel AGM VRLA battery with 5% (w/v) SiO₂ yields the best performance at both low- and high-rate discharges.

The SEM images of the negative plates of the AGM VRLA batteries after 100% DoD tests at the low- and high-rate discharges are shown in Figs. 3 and 4, respectively. The micrographs reveal polyhedral crystals of lead sulfate distributed on the electrodes, except that in the nongel AGM VRLA battery after the low-rate discharge (Fig. 3a); this negative plate instead shows a porous and poorly defined grain structure. The negative plate of the nongel AGM VRLA battery after the 100% DoD test at the high-rate discharge, in contrast, does not show a porous structure (Fig. 4a) and, although the discharge capacity of the nongel AGM VRLA batteries also decreases at the high-rate discharge (Fig. 2b), it decreases less sharply than at the low-rate discharge. These results show that, if the porous structure indicates corrosion of the electrode, the electrode corrosion in the nongel AGM VRLA battery occurring during the low-rate discharge can be attributed to the severe drop in its discharge capacity after two charge/discharge cycles (Fig. 2a). This also implies that the nongel AGM VRLA battery is not suitable for

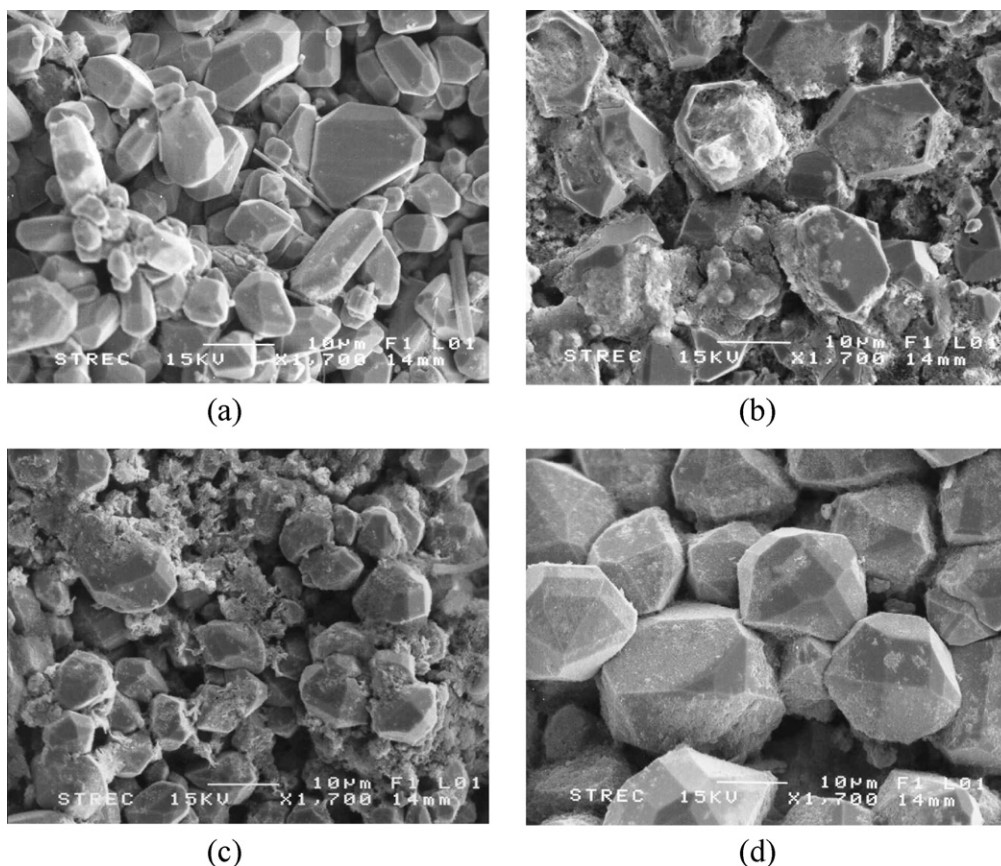


Fig. 4. SEM images (all at 1700 \times magnification) of negative plates from 12 V/4 Ah AGM VRLA batteries with different electrolytes: (a) nongelled electrolyte, (b) gelled electrolyte with 4% (w/v) SiO₂, (c) gelled electrolyte with 4% (w/v) SiO₂ and 0.005% (w/v) AL and (d) gelled electrolyte with 4% (w/v) SiO₂ and 0.01% (w/v) AL, after 100% DoD tests at the high-rate discharge (1 C).

applications under low-rate depth of discharge conditions. Overall, the negative plates of the AGM VRLA batteries tend to form bigger sulfate crystals at the high-rate discharge (Fig. 4) than at the low-rate discharge (Fig. 3).

3.2.2. Gelled electrolyte with veratraldehyde

To study the effect of this additive, AL was added to the gelled electrolytes containing 4% (w/v) SiO₂ to final concentrations of 0.005 and 0.01% (w/v). The maximum concentrations of SiO₂ and AL were limited to 4% and 0.01% (w/v), respectively, because the preliminary study of gel formation found that the addition of AL substantially shortened the gel formation process and influenced gel properties. The 100% DoD discharge capacities and discharge times of the gel AGM VRLA batteries prepared from 4% (w/v) SiO₂ with 0.005 and 0.01% (w/v) AL are shown in Fig. 5. The discharge capacities of the gel AGM VRLA batteries prepared from 4 and 5% (w/v) SiO₂ without the additive are included in the figures for comparison.

As shown in Fig. 5, the performance of the gel AGM VRLA batteries prepared from 4% (w/v) SiO₂ are enhanced by the addition of 0.005% (w/v) AL but decrease as more AL (0.01%, w/v) is added. At the low-rate discharge, the performance of the gel AGM VRLA battery prepared from 4% (w/v) SiO₂ plus 0.005% (w/v) AL rises to the same level as that prepared from 5% (w/v) SiO₂ with no additive (Fig. 5a). When a higher amount of AL is added, the performance of the gel AGM VRLA battery decreases to a significantly lower level than that with the 4% (w/v) SiO₂ gelled electrolyte without additive, and significantly drops after nine charge/discharge cycles, whereas those of the other two gel AGM VRLA batteries are relatively stable until the end of the test. At the high-rate discharge, the higher

AL addition (0.01%, w/v) also lowers the performance of the gel AGM VRLA battery (Fig. 5b), but not as dramatically as at the low-rate discharge, because the discharge capacity of the 4% (w/v) SiO₂ gelled electrolyte with 0.01% (w/v) AL still increases throughout the course of the test. After 16 charge/discharge cycles, the discharge capacity is at roughly the same level as that seen with the 4% (w/v) SiO₂ gelled electrolyte without AL and is slightly higher than that with the 5% (w/v) SiO₂ gelled electrolyte.

Generally, as shown by the cyclic voltammograms (Fig. 1), the addition of AL should reduce hydrogen evolution during the charging period, which is one possible reason for the improved battery performance with the electrolytes formulated with 0.005% (w/v) AL, as shown in Fig. 5. Although a higher amount of AL was expected to further suppress the hydrogen evolution rate, it is found that too much AL deteriorates battery performance. It is possible that AL present in the electrolyte may adsorb onto the negative plates and modify the properties of the electrodes during the charge/discharge process. The SEM images show that the addition of 0.005% (w/v) AL to the gelled electrolyte has a subtle effect on the morphology of the electrode in the gel AGM VRLA battery in the low-rate discharge test (Fig. 3b vs. c) and a slightly more significant effect, where smaller crystals are obtained, in the high-rate discharge test (Fig. 4b vs. c). The inclusion of 0.01% (w/v) AL into the gelled electrolytes, however, leads to much larger crystals, especially at the low-rate discharge, than those formed on the electrodes of the gel AGM VRLA batteries prepared with no or 0.005% (w/v) AL. In addition, the XRD results, shown in Fig. 6, reveal the presence of lead hydroxycarbonate crystals (i.e., Pb₃(CO₃)₂(OH)₂), in addition to lead sulfate crystals, on the negative plate of the gel AGM VRLA battery with AL. These indicate that the addition of AL may modify

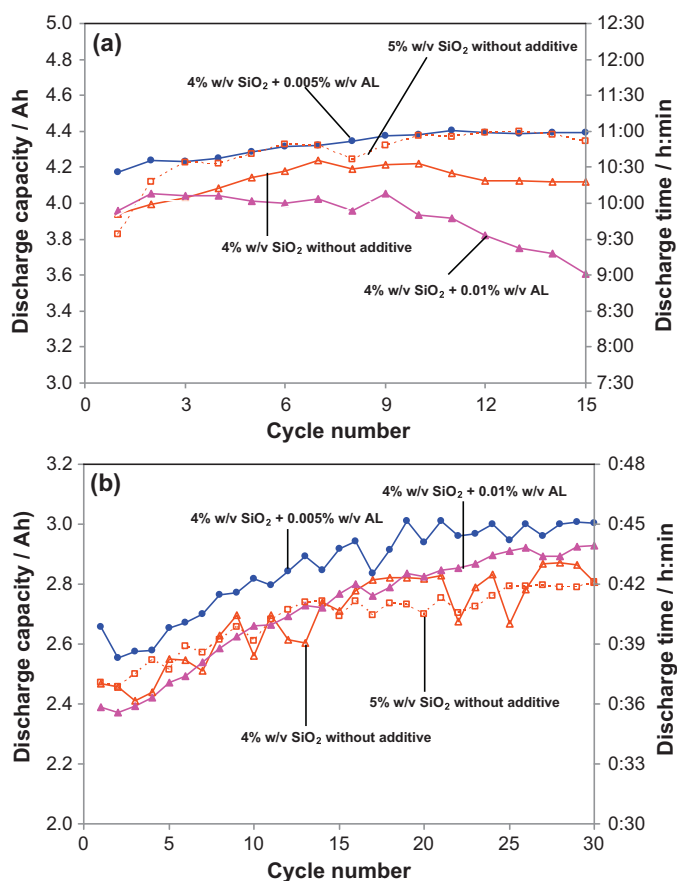


Fig. 5. Discharge capacities and discharge times of 12 V/4 Ah gel AGM VRLA batteries prepared from 4% (w/v) SiO₂ and different AL concentrations during 100% DoD tests at (a) the low- (0.1 C) and (b) high- (1 C) rate discharges.

the physical and chemical properties of the negative plate. Thus, the addition of a small amount AL (0.005%, w/v) can improve the negative plate material, leading to improved battery performance in gel AGM VRLA batteries, whereas an excess amount enhances the recrystallization of lead compounds and the sulfation process, leading to a decreased discharge capacity. The cyclic voltammetry results imply that the addition of AL may reduce hydrogen

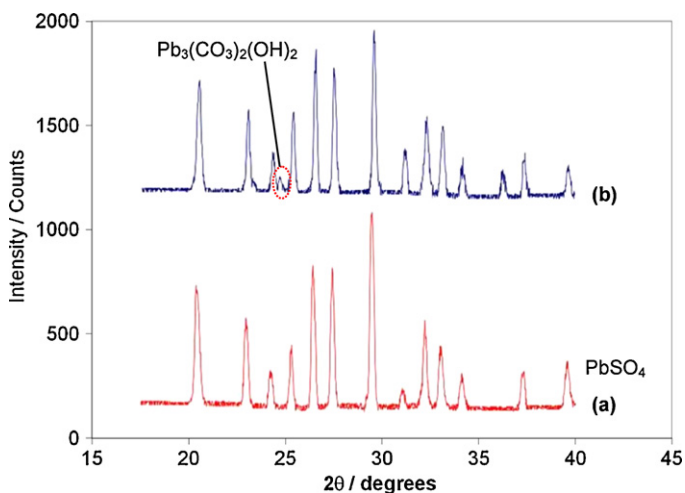


Fig. 6. XRD patterns of negative plates from 12 V/4 Ah AGM VRLA batteries with (a) gelled electrolyte prepared from 4% (w/v) SiO₂ and (b) gelled electrolyte prepared from 4% (w/v) SiO₂ and 0.005% (w/v) AL after 100% DoD tests at the low-rate discharge (0.1 C).

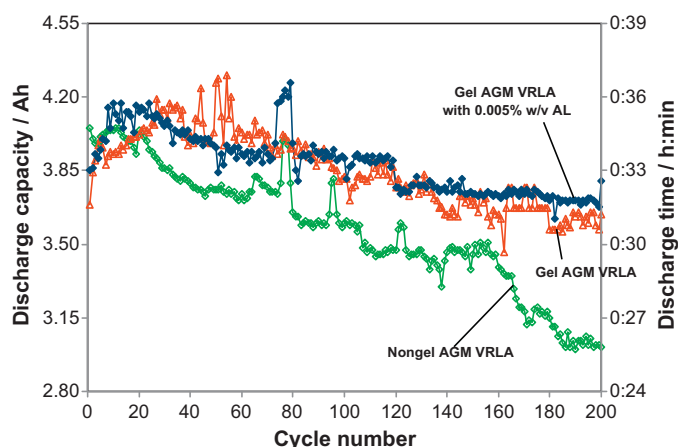


Fig. 7. Discharge capacities and discharge times of 12 V/7 Ah AGM VRLA batteries with different electrolytes during 200 cycle life tests performed under 100% DoD at the high-rate discharge (1 C).

evolution, but this should be confirmed by the measurement of hydrogen evolution during battery testing. Even so, this inhibition of hydrogen formation may not be the sole reason for the observed performance differences. There is also evidence that the influence of AL on the negative active material during the charge/discharge process may play the major role in modifying the properties of the negative plate, leading to improved or worsened battery performance. It is difficult at this stage to explicitly identify the actual cause of the improvement in battery performance with the addition of the suitable amount of AL in the gelled electrolyte.

It is also possible that, as mentioned previously, the higher AL concentration in the electrolyte shortens the gelling time so that the electrolyte may form a gel before the battery cells are thoroughly filled. This may create voids in the battery that lower battery performance. In addition, due to the thixotropic properties of the gelled electrolyte, the gelled electrolyte can reform itself more effectively at the high-rate discharge than at the low-rate discharge to form an electrolyte with fewer or no void regions. Thus, the difference between the discharge capacities of the gel AGM VRLA battery prepared with 0.01% (w/v) AL and that prepared without AL or with 0.005% (w/v) AL is less pronounced at the high-rate discharge than at the low-rate discharge.

Overall, the gel AGM VRLA battery prepared with 4% (w/v) SiO₂ and 0.005% (w/v) AL provides the highest discharge capacity and the best battery performance. At the low-rate discharge, it achieves the same level of performance as the battery with a 5% (w/v) SiO₂ gelled electrolyte without the AL additive, whereas at the high-rate discharge it yields a substantially higher performance than all the rest. Thus, the gel AGM VRLA battery prepared with 4% (w/v) SiO₂ and 0.005% (w/v) AL was selected for further study.

3.2.3. Cycle life tests

To investigate the long-term performance of the AGM VRLA batteries, cycle life tests of AGM VRLA batteries with different forms of electrolyte were performed using 12 V/7 Ah batteries under a 100% DoD at the high-rate discharge (1 C) for 200 cycles, following the cyclic test algorithm shown in Table 1. The cyclic performance data, including the 100% DoD discharge capacities and discharge times, of the gel AGM VRLA batteries prepared from 4% (w/v) SiO₂ without AL and with 0.005% (w/v) AL are shown in Fig. 7 along with that of the nongel AGM VRLA battery.

Similar to the 4 Ah batteries (Fig. 5b), the discharge capacity of the nongel AGM VRLA battery is initially higher than those of gel AGM VRLA batteries but steadily decreases with each charge/discharge cycle, whereas the discharge capacities of both

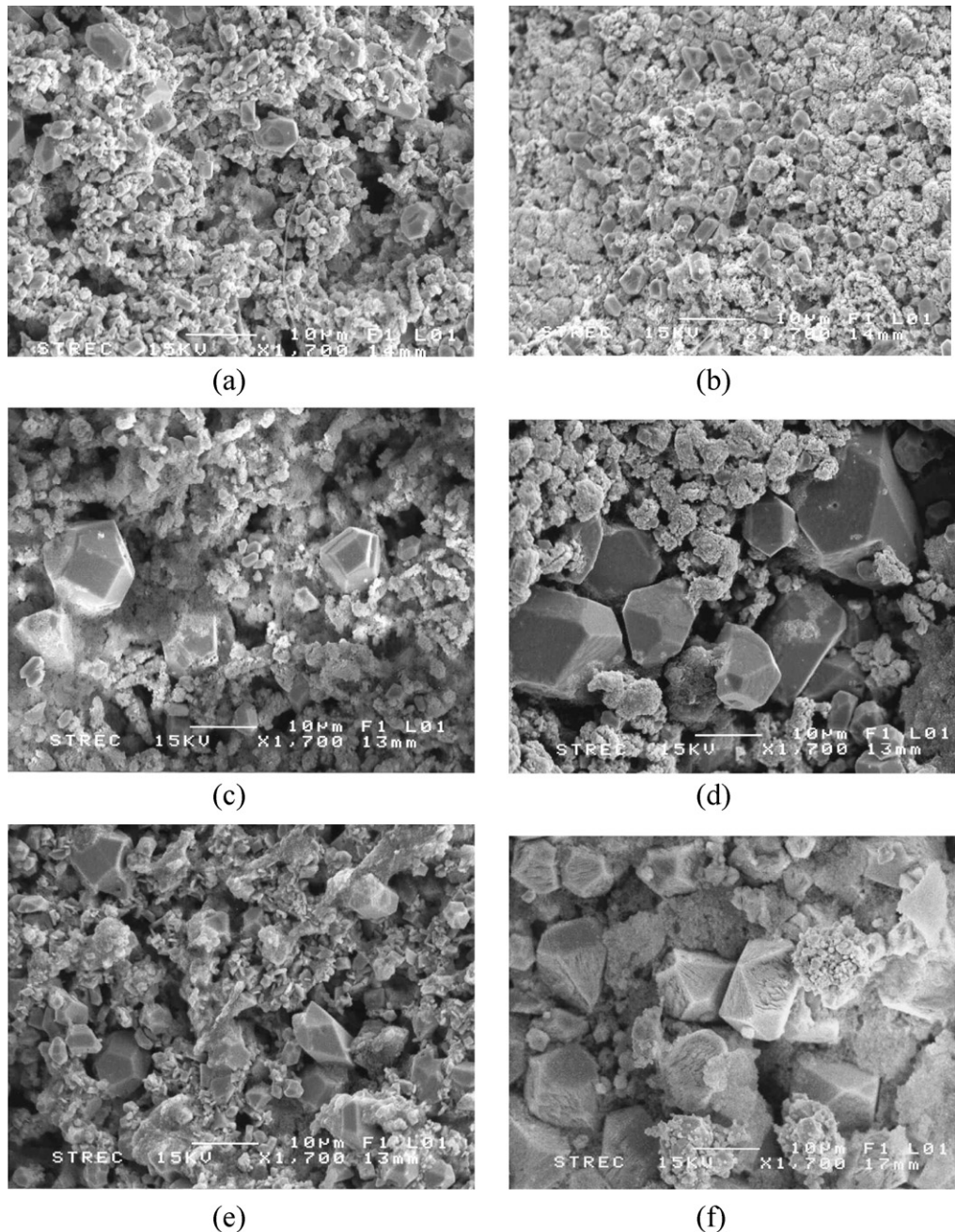


Fig. 8. SEM images of negative plates from 12 V/7 Ah AGM VRLA batteries with different electrolytes: (a and b) nongelled electrolyte, (c and d) gelled electrolyte with 4% (w/v) SiO_2 and (e and f) gelled electrolyte with 4% (w/v) SiO_2 and 0.005% (w/v) AL, after (a, c and e) 10 cycles and (b, d and f) 200 cycles under 100% DoD tests at the low-rate discharge (0.1 C).

gel AGM VRLA batteries gradually increase and exceed that of the nongel AGM VRLA battery after approximately 20 charge/discharge cycles (Fig. 7). The two AGM VRLA batteries with different gel compositions display generally similar cyclic performance, where the discharge capacities remain high, with only a slight overall decrease over the 200 charge/discharge cycles. As the number of test cycles increases, the differences in the discharge capacities between the gel AGM VRLA batteries (with and without AL) and the nongel AGM VRLA battery become more pronounced. The steep decline in the battery performance of the nongel AGM VRLA battery towards the end of the test, which implies a shorter cycle life, may be due to electrolyte stratification, a condition often found in nongelled electrolyte batteries operating under depth of discharge conditions that leads to intense corrosion in the lower regions of the electrodes

(i.e., grids and active materials), causing premature capacity loss and accelerating battery failure [1]. The much slower decline in the discharge capacities seen in the AGM VRLA batteries with gelled electrolytes indicates promising results for these batteries because, despite their many advantages, nongel AGM VRLA batteries have been previously reported to show low performance under depth of discharge conditions [1]. Both gel AGM VRLA batteries retain a discharge capacity above 3.25 Ah or have a discharge time longer than 27 min, which is higher than the JIS specification [18], even after 200 cycles at 100% DoD. The discharge capacity of the gelled electrolyte with 0.005% (w/v) AL is still slightly higher than that of the gelled electrolyte without AL.

SEM images of the negative plates removed from the AGM VRLA batteries with different electrolytes after cycle life tests (200 cycles)

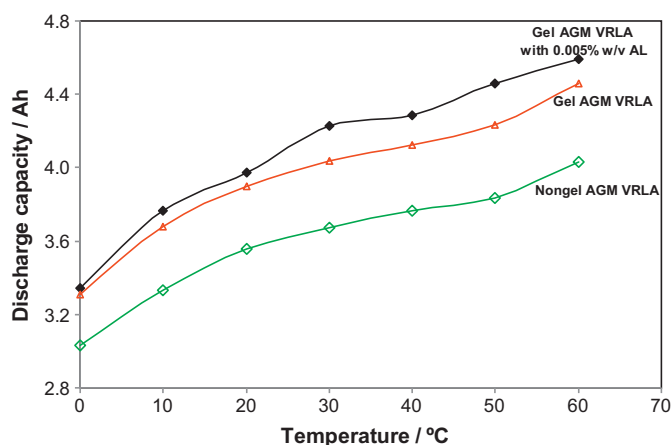


Fig. 9. Discharge capacities of 12 V/4 Ah AGM VRLA batteries with different electrolytes after 4 cycles under 100% DoD tests at the low-rate discharge (0.1 C) at different temperatures, as indicated.

are shown in Fig. 8, along with those obtained after 10 cycles for comparison. The structures of the electrodes from the nongel AGM VRLA batteries are clearly different from those from the gel AGM VRLA batteries with or without AL. After 10 charge/discharge cycles, the electrode from the nongel AGM VRLA battery displays a mixture of areas with a poorly defined grained structure and those with a small grained, relatively porous structure (Fig. 8a); after 200 cycles, the plate develops a denser and smoother surface (Fig. 8b). It is possible that the porous structure may allow electrolytes to gain easy access to the interior of the electrode, leading to a higher discharge capacity in the initial state. After a large number of charge/discharge cycles, the small sulfate grains grow and fill the pores, making the electrode surface denser and resulting in the obstruction of electrolyte access into the inside of the electrode. This obstruction could be one reason for the significant drop in the discharge capacity towards the end of the cycle life test.

Unlike the electrode structure in the nongel AGM VRLA battery, the electrodes of the two types of gel AGM VRLA batteries consist of irregularly shaped grains with the presence of large sulfate crystals (Fig. 8c–f). The amount and size of these polyhedral crystals increases with increasing numbers of charge/discharge cycles, and this increase correlates with the decreased battery performance compared to the initial stage. Although the electrodes of the two types of gel AGM VRLA batteries have significantly larger polyhedral grains than those of the nongel AGM VRLA battery, the performance of the gel AGM VRLA batteries are still substantially higher than that of the nongel AGM VRLA battery at the end of the 200-charge/discharge-cycle test.

3.2.4. Temperature tests

To evaluate battery performance at different temperatures, the three 12 V/4 Ah AGM VRLA battery types, i.e., the one with the nongelled electrolyte and those with the 4% (w/v) SiO₂ gelled electrolyte with and without the inclusion of 0.005 (w/v) AL, were tested at 100% DoD at the low-rate discharge (0.1 C) for 4 cycles, under controlled temperatures from 0 to 60 °C in 10 °C intervals. The discharge capacities of the tested AGM VRLA batteries at the end of 4 charge/discharge cycles are shown in Fig. 9. The reason that the discharge capacity of the nongel AGM battery at 30 °C that is shown here is substantially lower than that shown in Fig. 2a after 4 charge/discharge cycles is that every battery used in the temperature test had undergone a conditioning process before starting the temperature test. Thus, the discharge capacity after 4 cycles in the temperature test at 30 °C (Fig. 9) should be compared to that measured after approximately 8 cycles, as shown in Fig. 2a, because

the conditioning process should be taken into account for the first several cycles.

Overall, the discharge capacities at the end of 4 charge/discharge cycles increase with temperature for all three batteries. Like the results obtained under normal test conditions, the discharge capacities of the AGM VRLA batteries with the gelled electrolytes are substantially higher than those for the nongelled electrolyte battery at all temperatures tested. Comparing the two gelled electrolytes, the one with 0.005% (w/v) AL displays a superior performance than the one without AL over the whole range of temperatures studied. These results are promising, suggesting that gel AGM VRLA batteries can be used outdoors, where temperatures can vary widely year-round, for applications such as traffic lights and solar lights because the nongel AGM VRLA batteries have been reported to be very sensitive to operating temperatures [1].

4. Conclusions

The preparation of gel AGM VRLA batteries is studied and their performance is compared with conventional nongel AGM VRLA batteries. The addition of fumed silica and veratraldehyde to gelled electrolyte formulations has no substantial effects on the main reactions during battery operation but suppresses hydrogen evolution, which can reduce water loss from the batteries. Under 100% DoD conditions, the nongel AGM VRLA batteries have a higher initial discharge capacity than the gel AGM VRLA batteries but show a greater decline in performance with increasing numbers of charge/discharge cycles, falling to an inferior level. Despite having lower initial discharge capacities, the gel AGM VRLA batteries gradually improve their discharge capacities with increasing numbers of charge/discharge cycles and surpass those of the nongel AGM VRLA batteries. Gel AGM VRLA batteries have a much longer cycle life and outperform the nongel AGM VRLA battery at every operating temperature studied (0–60 °C). The addition of 0.005% (w/v) veratraldehyde improves the overall performance of the gel AGM VRLA battery, which may be due to the inhibition of hydrogen evolution and/or the improved negative electrode. Despite its potential to inhibit hydrogen evolution, higher levels of veratraldehyde, however, deteriorate battery performance because it enhances the irreversible sulfation process, thus, decreasing the discharge capacity.

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