LEAD/ACID BATTERIES IN ARCTIC PHOTOVOLTAIC SYSTEMS

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Introduction

At present, photovoltaic power systems are widely used to provide electricity in remote areas of sunny countries [1]. In addition, there are important Arctic applications, mainly in the field of navigation and telecommunications. In such applications, the energy storage is of primary importance: the dark season lasts several months and the temperature can fall to −50 °C in the most demanding locations. In these systems, the batteries must tolerate long excursions to a low state-of-charge and electrolyte freezing has to be avoided. The discharge current is low, typically at the rate of several hundreds of hours. This, in turn, requires that the low-rate capacities at low temperatures and their effects on freezing must be known. The batteries have to be fully recharged during the summertime with the available small charging power.

There is little information on battery recovery from long-term deep discharges and on low-rate capacities at low temperatures. The active interest of photovoltaic users encouraged research on these properties. The preliminary work reported here proved to be interesting because observations have been made contrasting traditional points of view on lead/acid technology. Initially, it was expected that non-antimonial, sealed lead/acid batteries would exhibit the greatest problems as a result of long-term deep undercharging. Therefore, particular attention was focussed on this type of battery and tests were conducted on units stored in a deep-discharged state for up to one year. In addition, investigations were carried out on freezing and low-rate capacities of customized, flooded lead/acid batteries at room temperature and at −40 °C.

Effect of long-term deep-discharge on the performance of non-antimonial lead/acid batteries

The aim of these investigations was to simulate long-term seasonal storage in photovoltaic systems. The tests were performed at room temperature, which was assumed to represent the worst case. It was expected that

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irreversible sulphatation would occur if a lead/acid battery was stored for long periods of time in a low state-of-charge [2]. Under such conditions, the $PbSO_4$ crystals that are formed initially in the active masses during battery discharge gradually recrystallize into larger crystals. Owing to the smaller surface area of the latter crystals, recharging of the battery should be hindered. Several types of non-antimonial and low-antimonial batteries were examined in order to characterize the expected sulphatation phenomenon. The results are reported here for a valve-regulated lead/acid battery 'Support TS' manufactured by Neste Battery Ltd. [3]. The battery is of the absorptive glass mat (acid-starved) design and has calcium–tin grids and thin plates.

The batteries were first subjected to conditioning cycles in order to reach a stable initial $C/10$ capacity. After this procedure, the batteries were stored at room temperature in a discharged state for different periods of time. Two depths-of-discharge were used: either 100% $C/10$ by using the 10 h current or 120% $C/10$ by using the 100 h current. The storage times ranged from 1.5 months to one year. After storage, the batteries were recharged under a constant-current/constant-voltage schedule (IU) with a current limit of the 50 h rate and a voltage limit of 2.40 V/cell; these are typical values for PV systems. The remaining capacity was then measured.

Figure 1 gives the remaining capacity as a function of the storage time. It can be seen that full capacity is recovered, even after storage times for as long as one year at 120% $C/10$ depth-of-discharge. This is an astonishing result because it shows that sulphatation does not cause a reduction in capacity. Other types of batteries tested yielded, qualitatively, the same results. For example, a tubular, flooded, stationary battery of the GRL-type (manufactured by Neste Battery Ltd. with Snastag-alloy) showed no loss of $C/10$ capacity, even after storage for 18 weeks at 168% nominal $C/10$ depth-of-discharge. In the latter tests, longer storage times were not used. The
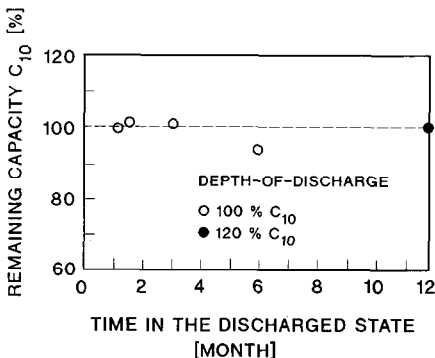

Fig. 1. Recovered $C/10$ capacity of sealed lead/acid battery 'Support TS' by Neste Battery Ltd. as a function of storage time in the discharged state. Two discharge levels have been used for the storage period: either 100% $C/10$ discharged at the 10 h rate or 120% $C/10$ discharged at the 100 h rate. Each symbol corresponds to one test performed with 6 cells. It demonstrates that capacity loss does not result, even after the battery has been stored for one year at 120% $C/10$ discharged.
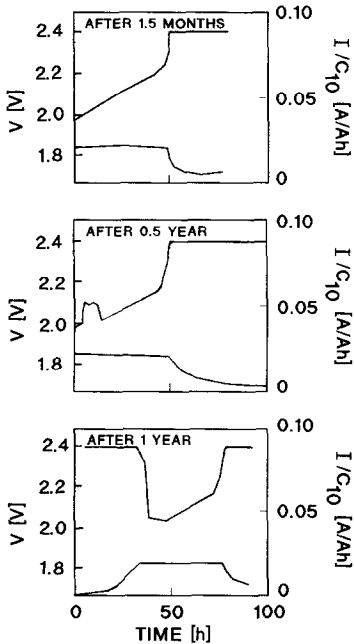
Fig. 2. Charging curves of sealed lead/acid battery 'Support TS' by Neste Battery Ltd. after storage times of 1.5 months (uppermost figure), 6 months (middle figure) and 1 year (bottom figure). 100% $C/10$ (top and middle figures) and 120% $C/10$ (bottom figure) have been discharged for the storage. The charging limits were selected according to the photovoltaic systems: the maximum current was the 50 h rate and the maximum voltage was 2.40 V/cell. Increased internal resistance manifests itself as a bump in the voltage curve of the middle figure. In the bottom figure the voltage rises to the voltage limit and the increased internal resistance initially limits the charging current. In this case IU-charging is modified to UIU. In spite of this anomaly the battery was fully chargeable.

charging regime for the flooded batteries after long storage was similar to that for the sealed batteries but with voltage limit set at 2.47 V/cell.

The above observations do not imply that long undercharging does not exert any effect. Indeed, long undercharging was seen to modify charging, as illlustrated in Fig. 2. The three curves represent the charging curves for a sealed lead/acid battery, 'Support TS', after storage times of 1.5, 6 and 12 months, respectively, in a discharged state. After 1.5 months, the battery is still normally rechargeable. After 6 months, a peak in the charging voltage is observed during the galvanostatic charging period. This peak is fully developed in the final set of curves that correspond to charging the battery after storage for one year in a discharged state. In this case, the battery did not accept charge with the specified voltage limit. After a certain time (in this case 24 h), the battery started to recover, and thereafter an almost normal charging behaviour was observed. In other words the long undercharging had changed the charging profile from IU to UIU.

A general qualitative observation was made: the longer the undercharging the longer the required charging time. For example, after 1.5 months the charging of the 'Support TS' battery required approximately 70 h (according to the above conditions), and after 1 year approximately 160 h. These values were determined from the stabilization of the charging current during the potentiostatic charging stage. A quantitative determination of the charging time was not made because the tests would have been too time-consuming. For the same reason, the charging efficiency was not quantitatively determined as a function of storage time. It appears, however, that the charging efficiency is reduced due to long undercharging. A rough estimation showed the A h-charging efficiency of the 'Support TS' battery after 1 year at a low state-of-charge to be 75% when using the above system.

In order to characterize the observed phenomena conclusively, it would be necessary to measure the positive and negative electrode potentials separately and investigate the crystal structures of the active masses. Such a study has not, as yet, been completed. In the bottom set of curves in Fig 2, part of the lead sulphate may have recrystallized to large crystals, thereby resulting in a smaller specific surface area and increasing internal resistance. In the worst case, therefore, only a small current will be accepted initially with the applied voltage limitation. The dissolution of large sulphate crystals commences with charging and is assisted by the fact that the solubility of lead sulphate is increased in dilute acid. It appears that the charging of overdischarge batteries somewhat resembles traditional 'water charging' to recover a heavily sulphated cell.

Effect of very low temperatures on the performance of lead/acid batteries

Traditionally, nickel/cadmium batteries are preferred to lead/acid batteries in Arctic applications because the electrolyte of the former does not become diluted during the discharge process and therefore is more resistant to freezing. Nickel/cadmium batteries are, however, much more expensive than their lead/acid counterparts and this limits their application. The work presented below argues that a tailor-made lead/acid battery is an attractive alternative, even in Arctic applications.

Two aspects have to be considered in designing a battery for service in the Arctic:

● What are the low-rate capacities at low temperatures?

● What are the freezing points corresponding to the discharge capacity?

Figure 3 gives the dischargeable capacities of a tailor-made, flooded, tubular lead/acid battery at room temperature and at $-40\,^{\circ}C$.* The data show that the very-low-rate capacity of a battery with a large reservoir of concentrated

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*Arctic photovoltaic equipment and batteries are marketed by Neste Advanced Power Systems, Rälssitie, SF-01510 Vantaa, Finland.
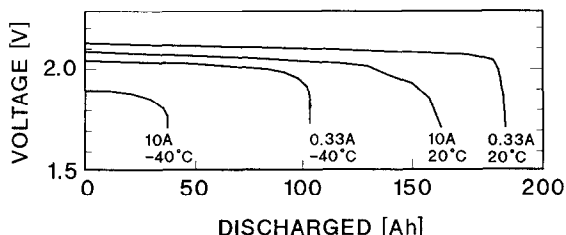
Fig. 3. Discharge curves of a tubular lead/acid battery which has been customized to Arctic applications by using an extra reservoir of 1.31 g cm^{-3} of acid. In the normal layout, one would obtain approximately 100 A h from the same plates at the 10 h rate at room temperature. This battery yields approximately 100 A h at the 300 h rate at −40 °C.

acid at −40 °C is comparable with the room-temperature $C/10$ value of the corresponding plates in the batteries with a normal amount of electrolyte. It is noteworthy that large, low-rate energy densities are obtained at low temperatures because low rates allow sufficient time for the slowed reactions to take place. Freezing was not observed in these tests. The dischargeable capacity depends more on the discharge current at low temperatures than at higher temperatures; this finding is also valid for other types of batteries.

The freezing point depends solely on the density of the electrolyte. For example, the density is 1.23 and 1.12 g cm^{-3} at −40 and −10 °C, respectively. The density of the electrolyte at the end of discharge depends both on the active-mass balance of the battery and on the dischargeable capacity at a given rate. The freezing point can be lowered by increasing the amount of acid compared with the amount of positive and negative active material. On the other hand, the freezing point shifts to higher temperatures if the capacity test is performed with lower current down to a fixed end-of-discharge voltage. For example, a generic sealed battery may not freeze, even at −40 °C, if the capacity test is performed at a sufficiently high current because only a small capacity can be discharged at that rate. At the very low rates relevant to Arctic photovoltaic systems, however, even the slowed reactions allow high capacity to be discharged, leading to the possible danger of freezing. Therefore, it is advisable to be very specific in defining the conditions under which freezing must not occur.

In summary, two general conclusions can be drawn about the effect of very low temperatures on the performance of lead/acid batteries. First, sealed batteries are likely to freeze at very low temperatures and low-rate discharges (for example, the 300 h rate), therefore they are not acceptable in all Arctic applications. Frozen sealed batteries do not supply electricity, but their containers will not fracture and cause damage to the surrounding instrumentation. Second, two kinds of flooded batteries can be operated at low temperatures: the difference in category depending on the amount of acid. If this is sufficiently high, the battery will not freeze at any temperature and depth-of-discharge. On the other hand, if the volume of acid is small, then the battery will freeze unless the depth-of-discharge is limited.
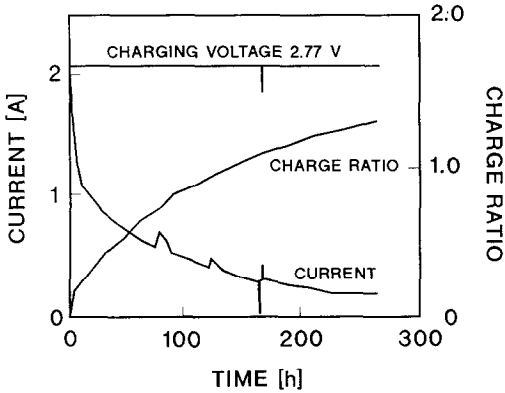
Fig. 4. Low-temperature charging curves of a tubular lead/acid battery described in Fig. 3. Temperature: −40 °C; charging voltage: 2.77 V/cell. Prior to this charge, 103 A h had been discharged. This curve clearly shows that the battery accepts charge even at extremely low temperatures and that the battery is not frozen.

In the latter case, freezing of the battery might result in fracture of the container.

The tailor-made, flooded, Arctic battery of Fig. 3 did not freeze according to visual inspection. It was also electrically serviceable because it could even be charged at low temperature, as illustrated in Fig. 4. In Arctic applications, it is important for the charging to be started during the cold period to ensure that the batteries will be fully charged by the end of the summer. A corresponding sealed test battery did not accept charge after discharge at the nominal $C/10$ current down to a voltage limit of 1.75 V/cell and was therefore taken to be frozen.

Although the Arctic environmental conditions are harsh, they protect batteries in two ways. First, the seasonal deep-discharge takes place during the cold period and therefore excessively deep discharges are prevented in normal use. Second, although the higher density of electrolyte increases the corrosion rate of the positive electrode in these applications, corrosion is slowed by the low temperature and lower acid density during seasonal storage.

Conclusions

There are specific aspects to be considered when lead/acid batteries are used for energy storage in the Arctic. For example: how do the batteries recover from long-term undercharging, how does temperature affect the low-rate capacity, what are the corresponding freezing points, etc.? This paper has described investigations where such behaviour is examined on a qualitative basis.

It has been found that some non-antimonial batteries recover remarkably well from long-term deep discharges. The period in the discharged state was from a few weeks to one year. The depth-of-discharge was more than 100% $C/10$. The full capacity was recovered. The charging characteristics were modified. In particular, charging time was increased, probably because of plate sulphatation.

At the very low temperatures of $-40\,°C$, a customized, flooded battery with a large reservoir of concentrated acid gave a capacity at the 300-h rate that was similar to that achieved from a corresponding normal battery at the 10-h rate at room temperature. Freezing can be avoided, as demonstrated by charge acceptance tests at $-40\,°C$. The freezing point depends on the acid volume and dischargeable capacity; the latter depends greatly on the current at low temperatures.

Acknowledgement

References

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