

A STUDY OF THE LOW-TEMPERATURE CHARGE ACCEPTANCE OF 500 A h PHOTOVOLTAIC BATTERIES: LABORATORY AND FIELD TESTS

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Summary

Lead/acid cells have been evaluated in both the laboratory and the field as energy-storage media for remote photovoltaic (PV)/battery systems at a low temperature (-40°C). Although the cells could not be fully recharged, they could be cycled between two partially charged states with a very high charging efficiency and, thus, are suitable for the application. Currents, cell and battery voltages, and positive- and negative-plate potentials have been recorded and are discussed. It is determined that the capacity is positive-plate limited. Experimental data also suggested that some compound other than PbO_2 is produced on the positive plates charged at -40°C . This oxidation product is reduced during discharge, and may also be reduced at the negative plate during charging of the cell.

Résumé

L'efficacité en recharge des accumulateurs au plomb a été évaluée en laboratoire à température ambiante et à -40°C . Des accumulateurs couplés à un système photovoltaïque sur un site isolé à Alert, NWT, ont confirmé les données recueillies en laboratoire. Les résultats obtenus ont montré que les accumulateurs ne pouvaient être complètement rechargés à basse température. Toutefois ils pouvaient remonter les exigences demandées en étant cyclés avec une efficacité très élevée entre des états partiellement chargés.

Les données ont montré que les accumulateurs étaient limités en capacité par la performance des plaques positives. L'analyse des courants, des tensions des accumulateurs et des plaques positives et négatives amène à suggérer la formation de composés autre que PbO_2 à la plaque positive lors

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de la recharge à $-40\text{ }^{\circ}\text{C}$. Ces produits d'oxydation seraient réduits lors de la décharge et pourraient éventuellement être réduits à la plaque négative lors de la charge.

Introduction

The high cost of fuel transportation and the need for high reliability make the provision of power to remote sites in the Arctic extremely expensive. In these situations, the application of renewable energy sources (such as solar energy) can become economically attractive. The Canadian Coast Guard, for example, has used a photovoltaic (PV)/battery system to power a set of range lights at Resolute, NWT ($74^{\circ} 43' \text{ N}$). This system, which is used during the shipping season each year, has operated reliably since its installation in 1979.

The absence of solar radiation in the Arctic during the winter months restricts the application of photovoltaics at these latitudes, although several situations arise where the use of photovoltaics does indeed become economically attractive.

In 1984, experiments were initiated to examine the feasibility of employing a PV/battery system to supplement the non-rechargeable batteries that were powering a remote radio repeater site on northern Ellesmere Island in the Canadian Arctic. The goal was to rely upon solar energy for the six-month period from approximately March 15 to September 15 and to revert to the existing zinc/air battery system during the winter months. One of the major concerns with this proposed scheme was the ability of the lead/acid batteries to accept charge during March and early April when the ambient temperatures are at their lowest. At Eureka, NWT, for example, the mean daily temperature in March is $-37\text{ }^{\circ}\text{C}$ with a minimum below $-50\text{ }^{\circ}\text{C}$. It is well known [1, 2] that lead/acid batteries have poor charge acceptance at these low temperatures. The selection of a battery with adequate low-temperature charge acceptance was considered critical for successful operation of the PV/battery system.

In this paper, the results of laboratory tests to measure the charge acceptance of lead/acid cells at $-40\text{ }^{\circ}\text{C}$ are reported, as well as operational data collected from field trials carried out between 1984 and 1987 at Alert, NWT.

Experimental

Laboratory testing

Four, 500 A h cells (Exide DH-5) were evaluated. Each cell contained two positive plates with dimensions 209 mm (height) \times 152 mm (width) \times 24 mm thick, and three negative plates, each of the same height and width as

the positive plates. The thickness of each outside negative plate was 10 mm, and that of the centre one was 24 mm. All grids were made of pure lead. Each cell contained 7.5 kg of 1.31 sp. gr. H_2SO_4 . These cells were found upon delivery to have a capacity of 375 A h when discharged at 6.4 A to 1.9 V, according to the rating conditions at room temperature. They were then subjected to five additional cycles, at the end of which their capacities had declined slightly to 355 A h. Three of these cells were placed in a cold chamber at -40°C . The fourth cell was cycled at room temperature ($20 \pm 2^\circ\text{C}$). The cycling test conditions for these cells were as follows. All were discharged at 1 A for 12 h, rested for 5 min, and then charged for 8 h. One of the cold cells was charged at 2.65, one at 2.70, and one at 2.75 V. The room-temperature cell was charged at 2.40 V. The maximum charging current was 4 A. The cells were then rested for 5 min before they were discharged again. The testing routine was executed by a computer-based battery testing system. The potentials of both positive and negative plates were measured against an $\text{Hg}/\text{Hg}_2\text{SO}_4$ (1.30 sp. gr. H_2SO_4) reference electrode.

Field testing

80 W/500 A h PV/battery system

In June 1984 an 80 W(peak)/500 A h PV/battery system was installed at Alert, at the northern tip of Ellesmere Island (82.5°N). The system consisted of two, 40 W Solarex SX120 solar panels, a Solarex CCG014-80 shunt regulator, and a 14 V, 500 A h battery bank consisting of a string of seven Exide DH-5 cells. The battery was housed in an insulated wooden battery box and was fully charged prior to installation. The specific gravity and voltage of the cells were 1.30 and 2.15 V, respectively. The regulator was adjusted to give a charging voltage of 16.8 V at 25°C and was temperature compensated with a nominal temperature coefficient of $-0.0378\text{ V}/^\circ\text{C}$. This corresponded to a charging voltage of 2.75 V per cell at -40°C . The battery was discharged into a $30.94\ \Omega$ resistive load during the period from March 15 to September 15 and was essentially on open-circuit stand during the winter period from September 15 to March 15, although the timing circuitry resulted in a small (13 mA) drain. The following parameters were continuously measured from June 1984 to June 1987: temperatures of the ambient, batteries and PV array; wind speed; solar radiation intensity; voltages of the batteries and PV array; current and power taken from the PV array and put into the batteries. Data were collected at 5-min intervals. In addition, three site visits were made to measure the specific gravities, electrolyte levels and voltages of the cells.

400 W/2000 A h PV/battery system

In June 1985, a 400 W 2000 A h PV/battery system was installed next to the 80 W installation (Fig. 1). This system consisted of ten, 40 W Solarex SX120 solar panels, a Solarex SHO-12-500 AF shunt regulator, and a 14 V, 2000 A h battery bank consisting of four parallel strings of seven Exide DH-5 cells. The cells were fully charged and placed in uninsulated wooden



Fig. 1. 80 W/500 A h and 400 W/2000 A h photovoltaic/battery systems installed at Alert (82.5° N), NWT, Canada, and one of the authors (C.L.G.)

battery boxes. A timer was installed to connect the battery to a nominal 9.8Ω load during the daylight period from March 15 to September 15. The tests of the system reported in this paper cover the period from June 4, 1985 to July 31, 1986.

Results of laboratory tests

Charge acceptance

The currents at the end of the charging period in each cycle for all the test cells are recorded in Fig. 2. It can be seen that the end-of-charge current for the cell at room temperature was about 0.2 A at the first cycle and decreased to 0.05 A at the 40th cycle. By contrast, the end-of-charge current for the cells at -40°C increased from 0.3 A to 1 A around the 20th cycle and remained at this level to the end of the 40th cycle. Figure 3 shows the corresponding charge return for the test cells in the cycling test. The charge return for the cell at room temperature was about 105% over the first few cycles; then it stabilized at about 102% to the end of the test. The situation was very different with cells cycled at -40°C . For the first two cycles, the charge return was less than 50%. However, it increased rather quickly with cycling to 80% at about the 10th cycle. Then, it increased gradually to about 95% at the 22nd cycle and, in general, remained between 95% and 102%

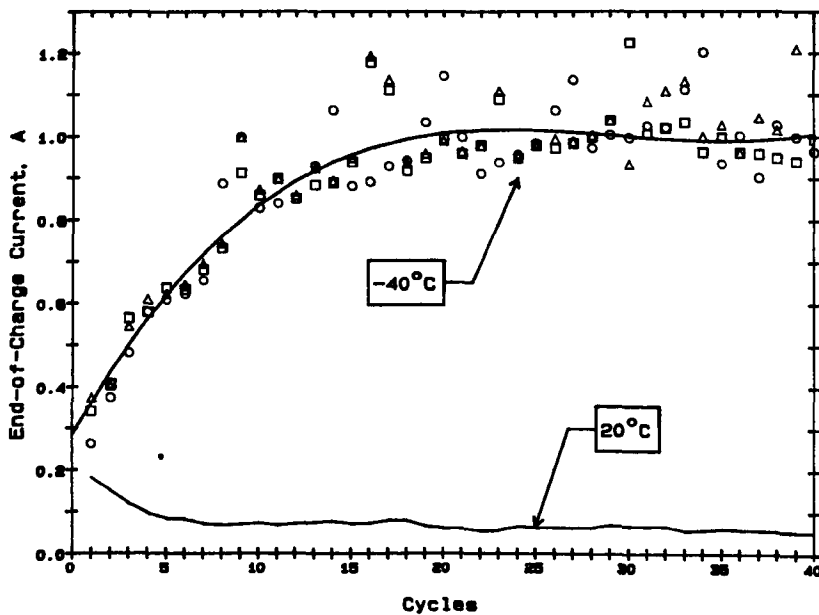


Fig. 2. Current at the end of charging of Exide DH-5 cells. Charging voltages at -40°C : (\circ) 2.65 V; (\square) 2.70 V; (\triangle) 2.75 V. (---) Least-squares fit for all experimental points at -40°C . (—) 20°C , 2.40 V.

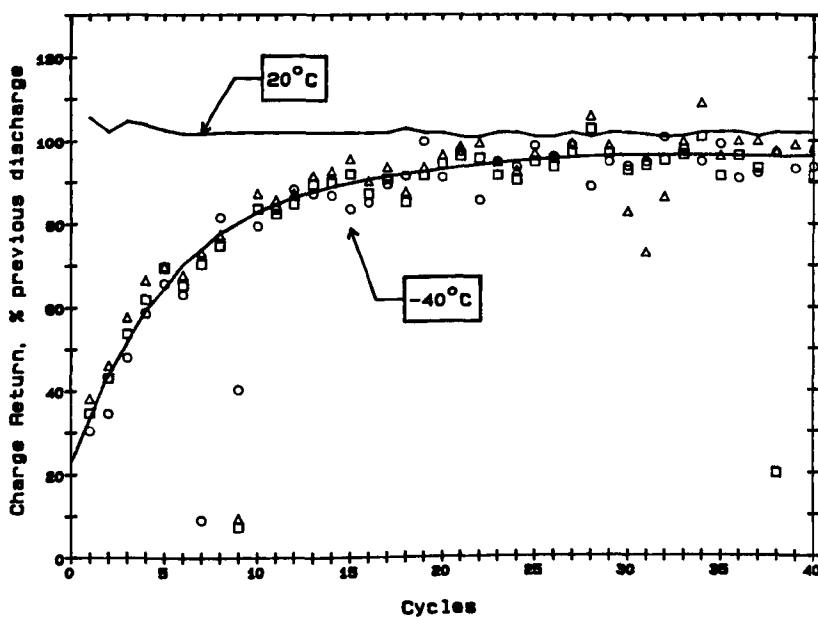


Fig. 3. Charge returns for Exide DH-5 cells. Charging voltage at -40°C : (\circ) 2.65 V; (\square) 2.70 V; (\triangle) 2.75 V. (---) Least-squares fit for all experimental points at -40°C . (—) 20°C , 2.40 V.

until the 40th cycle. Correspondingly, the measured specific gravity of the acid showed the following changes. In the cell at room temperature, it decreased from 1.31 to 1.30 at the 12th cycle, and then remained unchanged to the end of test. For the cells at -40°C , it declined to about 1.285 at about the 15th cycle and remained constant thereafter.

To determine the state-of-charge (SOC) at the end of the test, all cells were charged according to the experimental conditions after the last (40th) discharge, and then allowed to warm up to room temperature. Without any further charging all cells were discharged at 6.4 A to 1.9 V. It was found that the cell tested at room temperature had been fully charged. For the cells charged at 2.65, 2.70 and 2.75 V at -40°C the SOC's were 65.3, 67.5 and 66.3%, respectively. Thus, raising the charging voltage from 2.65 to 2.75 V did not appreciably enhance the SOC of the cells at -40°C . At the end of this discharge test, the positive and the negative-plate potentials of all the cells were 0.99 V and -0.91 V, respectively. For the fully charged cell at room temperature, the open-circuit potential for the positive was 1.206 V, and for the negative, -0.969 V. Therefore, at the end of discharge, the positive was about 200 mV and the negative about 60 mV below the open-circuit potential. The discharge-potential curves showed that, at the cut-off voltage, the positive potential of each cell had passed the knee of the discharge-potential curve, whereas the negative potential had not. Therefore, the discharge capacities of all the test cells at the end of the 40-cycle test were determined by those of the positive plates.

Positive and negative plate potentials

Typical variations of potential and current, represented by those at about the 25th cycle, are plotted in Figs. 4 and 5 for the cells at room temperature and -40°C , respectively. There were no substantial differences among cells being charged at different voltages in the range 2.65 - 2.75 V.

Cell at room temperature

Charging period. In the initial 2.5 h of charging at room temperature, the cell accepted 4 A as the cell voltage approached its 2.40 V limit (Fig. 4). The rate dropped rapidly thereafter. In the last 4 h of charging, the current was below 100 mA. As soon as the charging started, the positive-plate potential climbed rapidly from 1.18 to 1.3 V in about 0.5 h. It increased at a much lower rate thereafter. By contrast, the negative-plate potential rose rather slowly from -0.96 to -1.0 V at the end of the first 2 h of charging; at that time about 70% of the ampere-hours taken out in the previous discharge had been returned. Then, the negative potential rapidly increased until the cell charging voltage limit of 2.40 V was reached. From that point on, the negative-plate potential increased at the expense of the positive-plate potential. After 4 h of charging, about 95% of the previous discharge was returned. From then to the end of the charging period the negative-plate potential increased very slowly to -1.17 V, accompanied by a slow decrease of the positive-plate potential to 1.23 V. Thus, at the end of charging, the

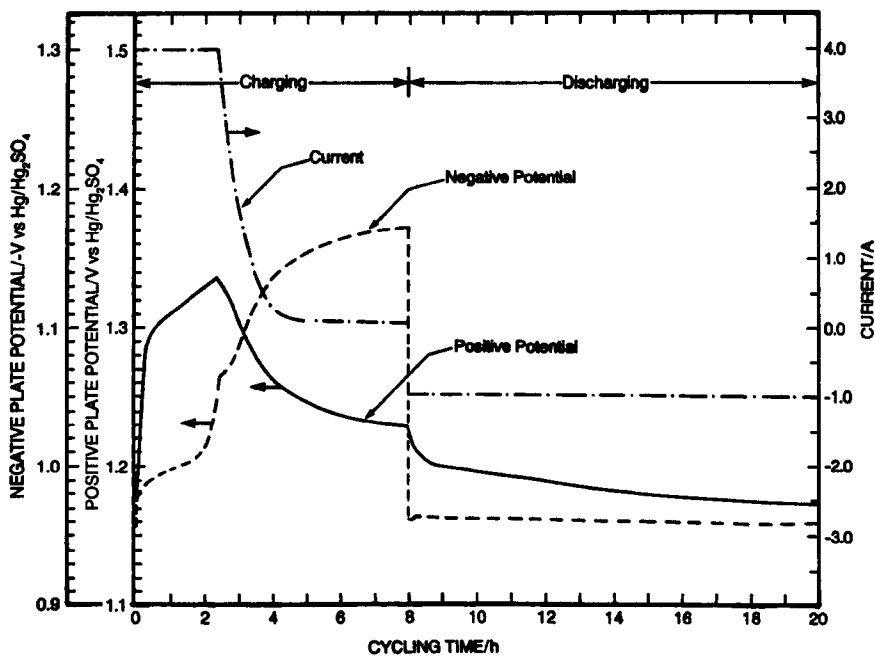


Fig. 4. Potentials of positive (—) and negative (---) plates, and current (- · -) during typical charge-discharge cycle of Exide DH-5 cell at room temperature and charged at constant voltage of 2.40 V with maximum current of 4 A.

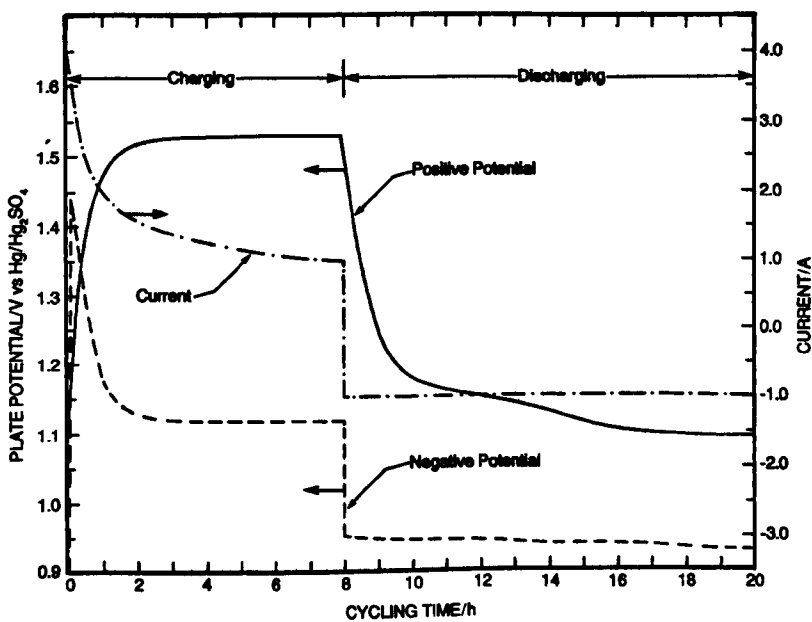


Fig. 5. Potentials of positive (—) and negative (---) plates, and current (- · -) during typical charge-discharge cycle of Exide DH-5 cell at -40 °C and charged at 2.65 V. Note, potentials for negative plate should be read with a negative (-) sign.

overpotential for the positive plate was only 20 - 30 mV, compared with 200 mV for the negative. It is known that the charging efficiency for the positive plate is lower than that for the negative [1]. Therefore, an incompletely charged cell is, most likely, due to undercharged positive plates. The experimental data showed, however, that the cell was fully recharged. The high charging efficiency for the positive might be due to the very shallow discharge and the low (2.40 V) charging voltage.

Discharging period. At the end of the discharge, as shown in Fig. 4, the positive potential was about 30 mV and the negative potential was about 10 mV below the respective open-circuit value; this showed that more polarization occurred at the positive plates than at the negative plates.

Cells at -40°C

Charging period. At room temperature, the negative-plate potential rose only after the charge was substantially (70%) returned. By contrast, at -40°C , as shown in Fig. 5, the potential jumped to -1.4 V or greater, almost immediately after the charging current started flowing. The rate of increase in positive-plate potential was, however, about the same as that at room temperature. After 15 min it reached 1.3 V or higher, and was still increasing. Since the charging voltage for the cells was limited, further increase was made at the expense of the negative-plate potential. With decreasing negative potential, the current was reduced at a high rate. After 2 h of charging, the positive-plate potential reached a plateau at about 1.52 V; the negative-plate potential decreased correspondingly and also reached a plateau, the level of which depended on the charging voltage. At that point, the number of ampere-hours returned to the cell was about, or less than, 45% of that taken out in the previous discharge. At the end of the charging period, the positive-plate potential was 1.53 V, regardless of the charging voltage. The corresponding potentials for the negative plates were -1.114 , -1.165 and -1.214 V in the cells that were charged at 2.65, 2.70 and 2.75 V, respectively. In other words, the additional charging voltage only raised the negative potential. The current at the end of the charging period was about 1 A regardless of charging voltage.

Discharging period. The negative potential dropped instantaneously below the open-circuit potential when the discharge was started and then declined to about -0.920 V at the end of discharge. At -40°C , when the cells were fully charged, the open-circuit potential for the positive was 1.207 V, and for the negative, -0.958 V versus Hg/Hg₂SO₄ (-40°C). Thus, the negative end-of-discharge potential was about 40 mV below the open-circuit value. By contrast, it took about 1.5 h for the positive-plate potential to decrease to its open-circuit value. At the end of discharge, the potential dropped to about 1.08 V, which was 120 mV below the open-circuit value, much lower than the corresponding value for the negative plates.

Results of field tests

80 W PV/battery system

The system operated successfully for the three-year period from June 1984 until June 1987, when the tests were terminated. During that period, the system was on a nominal 7.5 W load from March 15 to September 15 each year. Figure 6 shows battery voltages and load powers measured. An estimate of the charge efficiency of the battery was obtained from the measurement of current put into the battery and current taken from the battery to power the load during the three-year period. Based on these data, a charge efficiency of 96% was estimated. Assuming an initial capacity of 500 A h and a charge efficiency of 96%, the SOC for the system as a function of time is shown in Fig. 7. At the beginning of the operating season (March), the SOC of the battery declined, because the power generated by

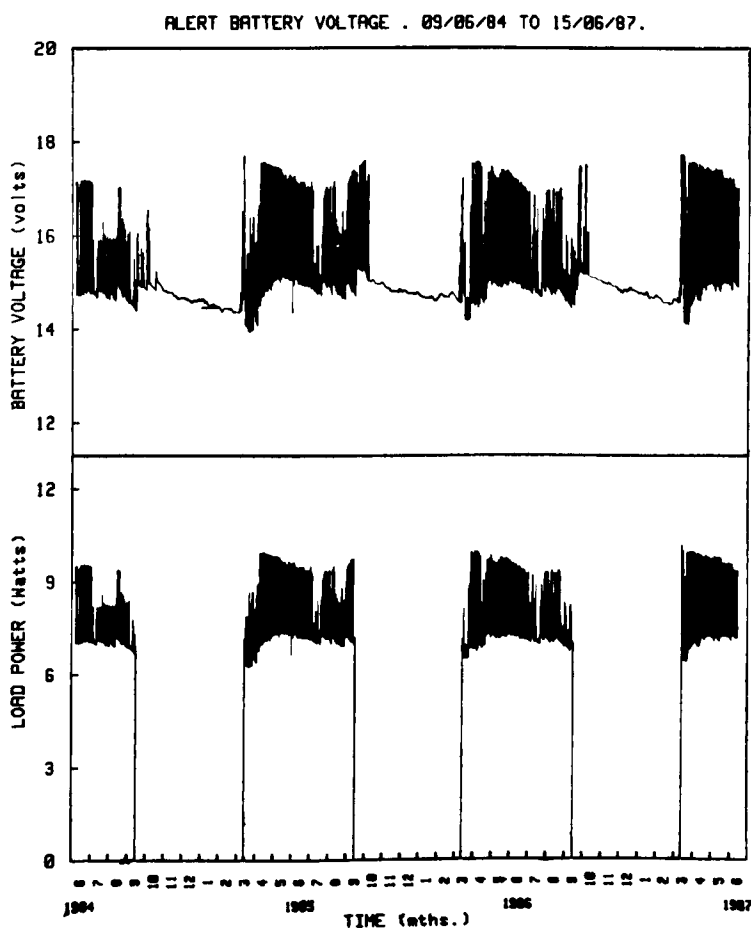


Fig. 6. Battery voltage and power load for 80 W/500 A h photovoltaic/battery system (containing seven Exide DH-5 cells in series) installed at Alert, Canada.

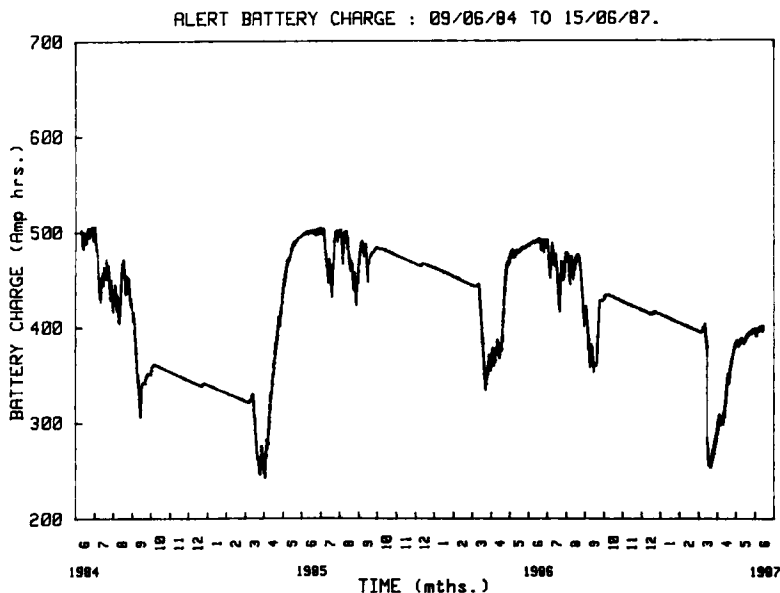


Fig. 7. Calculated SOC for battery in 80 W/500 A h photovoltaic/battery system, assuming initial capacity of 500 A h and charging efficiency of 96%.

the PV system was less than the battery load. From April to August, the battery was charged up and appeared to be fully charged, because the input was usually larger than the load. Several troughs in the curve were caused by local weather conditions. In September, the input usually was again smaller than the load, so that the SOC declined. From September 15 to March 15, the battery was on open circuit. However, the maintenance of timing circuitry caused a small drain on the battery.

Water loss was negligible and no addition was made to the electrolyte during the three-year period. Specific gravity measurements indicated a considerable degree of electrolyte stratification. For example, in June 1985, the specific gravity at the top of the cells was 1.280. This rose to 1.300 after agitation of the electrolyte.

400 W PV/battery system

The system operated in the test period generally as expected. The results were similar to those of the 80 W system. Some operational problems were encountered. There was a loss of load from July 27, 1985 to September 9, 1985. In addition, the voltage regulator did not function properly until June 1986. During that period, the battery was connected directly to the solar panels, and the uncontrolled battery charging voltage was usually higher than the designed limit. These problems resulted in considerable overcharging of the battery during the period from installation until June 1986, when the voltage regulator was repaired. A calculation showed that, due to these problems, an excess charge of almost 3000 A h was put into the battery.

Discussion

Laboratory tests (Figs. 2 and 3) showed that, during the first 10 cycles at -40°C , the number of ampere-hours returned was much less than that taken out from the cells and the SOC's were progressively decreased. The average amounts returned to the cells charged at 2.65, 2.70 and 2.75 V were 51, 57 and 60%, respectively, for the first 10 cycles. The capacities thus lost were more than 40% of the total loss after 40 cycles. In other words, a substantial proportion of capacity loss was incurred during the first 10 cycles. As the SOC's decreased, however, the charge acceptance increased. The measurements of cell voltage and acid specific gravity indicated that after about 20 cycles, the loss of capacity with cycling was probably very small. After 40 cycles at -40°C , the loss of capacity was only one-third of the original measured capacity. The overall coulombic charge efficiency for the three cells throughout the 40 test cycles at -40°C was found to be 89%. This implies that the charging efficiency in the last 20 cycles was substantially higher than 90%. All the experimental results suggest that after 20 cycles the cells were essentially being cycled between two partially charged states, and they would withstand much more than 40 cycles under the experimental conditions.

The overall charge efficiency of the 500 A h battery connected to the 80 W array was estimated to be about 96% during the three-year period that the system was in service.

Figure 5 shows that at the beginning of a discharging period at -40°C , the positive potential of a cell in the laboratory stayed above the open-circuit potential for more than 1.5 h, indicating that a compound other than PbO_2 was being discharged. Thus, the facts suggest that during the charging period some positively charged soluble species were produced [1 - 3], which could be reduced at the negative plate during charge, and be reduced at either plate during discharge. It has been shown [3] that when acid concentration is increased, charge acceptance is decreased and the production of oxidation compounds other than PbO_2 is correspondingly increased. At the beginning of the cycling test at -40°C , the acid concentration was high, at 1.31 sp.gr., which may be one of the reasons for the low charge acceptance. This insufficient recharge caused reduction of the acid concentration which, in turn, caused the charge acceptance to increase. After the SOC of the batteries was reduced, and the acid specific gravity decreased to about 1.28, the charging efficiency rose to higher than 90%, as shown by the experimental data. Thus, after 20 cycles, the decrease in capacity was at a very low rate. These facts appear to suggest that it may be beneficial to fill batteries with 1.28 sp.gr. H_2SO_4 for -40°C cycling. It should be noted, however, that a lowering of the acid concentration will raise the freezing point of the electrolyte. This might be a serious problem, especially when the battery has to be deeply discharged. Moreover, in this experiment the increase in charge efficiency with cycling is accompanied by a decrease in

the SOC of the batteries. A lower SOC of the active material in the battery might also be a major factor for the increased charge efficiency.

At the beginning of a charging period at $-40\text{ }^{\circ}\text{C}$, the negative plates exhibited an overpotential of about 500 mV. This was a very high polarization, considering that the current density was less than 3.2 mA cm^{-2} . A similar phenomenon at $-18\text{ }^{\circ}\text{C}$ was reported by Sharpe and Conell [4]. The high polarization of the negative plates did not persist, however, because of the rapid increase in the overpotential of the positive plates. With constant-voltage charging, as the potential of the positive increased, the current decreased, and with it, the negative potential. Near the end of the charging period, all the positive plates exhibited a high overpotential of 320 mV, which increased by only about 5 mV when the cell voltage was raised by 100 mV. Obviously, some electrochemical processes were preventing the positive plates from being effectively charged. The increase of cell voltage from 2.65 to 2.75 V raised the negative charging potential from -1.11 to -1.21 V, corresponding to overpotential of 160 and 260 mV, respectively. This might have improved the charging of the negatives and/or increased some parasitic reaction. However, since the discharge capacity at the low rate used was limited by the positives, raising the charging voltage from 2.65 to 2.75 V appeared to give no appreciable benefit.

Conclusions

The lead/acid cells evaluated in this study can be satisfactorily employed for energy storage in remote photovoltaic/battery systems operating at a very low temperature ($-40\text{ }^{\circ}\text{C}$). Although the cells could not be fully recharged under the conditions examined, they could operate by cycling between two partially charged states with a very high charging efficiency.

Both positive and negative plates showed high overpotentials during charging at $-40\text{ }^{\circ}\text{C}$. The capacity of the cells was limited, however, by the recharging of the positive plates at $-40\text{ }^{\circ}\text{C}$. The experimental data suggest that some compound other than PbO_2 was produced at the positive plates during charging at $-40\text{ }^{\circ}\text{C}$. During discharging, this compound (or, possibly, more than one) discharged and contributed to the discharge capacity of the cell. There was some indication that this compound was soluble and could migrate to the negative plates and be reduced during charging.

Acid concentration is one (but not the only) factor affecting the charging efficiency of lead/acid batteries at $-40\text{ }^{\circ}\text{C}$. A reduction of acid concentration, for instance, from 1.31 to 1.28 sp.gr. might be beneficial if the freezing point of the electrolyte at the end of discharge is still sufficiently low for the particular application.

Acknowledgements

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