LONG-DURATION DUTY CYCLE REQUIREMENTS: IS THE LEAD ACID BATTERY STILL A VIABLE BACK-UP ENERGY SOURCE?

Wieland Rusch
Research & Development
BAE Batterien GmbH
Berlin Germany

Chris Searles
Director of Business Development
BAE Batteries USA
Somerset WI

INTRODUCTION

Stationary lead-acid batteries remain the economical first choice for standby power batteries with discharge times between 15min and 8h; they have been well proven in practice. The battery can be kept permanently on float in a fully-charged state, as long as both electrodes are in an electrochemical balance[1]. The supply of energy is only required a few times a year and rarely for more than 30 to 50% of DOD. To qualify a battery for this application an Acceptance Test as defined in IEEE 450, or in the case of a Class 1E nuclear application, an accelerated service life test as defined in IEEE 535 is used. In the case of IEEE 535, the test is done with a float charge at 145°F (63°C) and a review of the 2-4h rate discharge at regular intervals is measured and recorded. The failure mode in these cases is mainly the corrosion of the positive grid[2, 3].

Not all stationary stand-by batteries fall within the requirements described above. Many countries in Africa and Asia have daily power outages. Diesel-electric power is expensive, so the battery is discharged daily to about 50% DOD. In developed countries, grid stability becomes an issue, especially if much of the electric power is generated by solar or wind energy. As a result, load levelling in distributed sites has become a new challenge for lead-acid batteries. Therefore, we must ask the question: are there other parameters that should be considered in qualifying a lead acid battery for such applications?

The answer is that we must add the ability to test the endurance in cycles as well as discharge/recharge. With this testing, we find that in addition to the common failure mode of corrosion of the positive grid, we raise the potential for deterioration of the positive mass as well as loss of the internal surface of the negative mass. Therefore, IEC 60 896-2 and IEC 60 896-21 specifies that we must measure the endurance in cycles. This has become an acceptable international standard.

Another application is the installation of special photovoltaic or wind farm systems that are responsible for powering telecommunication sites, various types of lighting and signalling systems, even consumer residences. In these cases the battery can be discharged every day at a rate of approximately 10 to 20% DOD. The stress on the cells comes from cycling at a very low state-of-charge (SOC) in winter or low wind periods, and at a high degree of over-charge in summer or windy periods. And, in sunny areas we normally experience higher temperatures, so the reference temperature needs to be adjusted to higher than 77°F (25°C). Therefore, to qualify the battery for these applications we will use the test procedure of IEC 61 427:2005.

A recent application that is now being introduced is the requirement for battery back-up in nuclear power plants using what is called a “passive plant design”. In this case, the back up power is generally needed for 24-hours up to 72-hours. It is imperative that we see if there are any new failure modes which could occur during these longer discharge periods.

Do we have any experience that would give us confidence that lead acid batteries will perform reliably in service with these long discharge cycles? Fortunately, the answer is yes, we do.

Lead-acid batteries have been used for motive power of diesel-electric submarines with similar profiles, and have been in service for more than 40 years.

For nuclear power plants in the passive plant design 100kW is required over 72h, resulting in a 7.2MWh battery with 2000 cells rated at 3000Ah. Such a large battery weighs about 400 tons and utilizes 600m² of space. This obviously presents several challenges including hydrogen gas and thermal management. Batteries need to be proven safe against thermal run-away and ventilated properly. These testing parameters are defined in IEC 60 896-21.

In this paper we will present testing data from both VLA and VRLA battery models containing a tubular design. These tests have been conducted in both the US and Germany. Interestingly, our testing shows that a tubular design works well with both a lead-selenium/low antimony plate design [VLA] as well as a lead-calcium/aluminum/tin alloy [VRLA]. We believe it is suitable for both standby and cyclical applications.

ENDURANCE IN FLOAT SERVICE OF STATIONARY BATTERIES

In America as well as in Europe the electric power grid demand can be fulfilled reliably by the power generation utilities so that the grid provides electrical power 24/7/365 except in the rare instances of a severe weather event such as a hurricane, tornado or record-setting winter storm as recently experienced in the US. These events usually happen only occasionally, perhaps a few times a year, especially if we count only the outages of more than several seconds or even minutes.

Therefore the stand-by batteries used for telecommunication, uninterruptable power supply, traffic signalling, energy generation, transmission and distribution mainly remain on float service in a fully charged condition with only an occasional discharge.

To qualify stationary batteries for float service, two current methods are commonly used:

1. In Japan, the Japan Institute of Standards (JIS) for stationary batteries stresses the batteries with high overcharge currents over several periods of 30 days. It has become part of the IEC 60 896-11 § 17 – 30 days with 0.2 times I_{10}, followed by a 1h rate capacity test. In § 9.2 a minimum of six periods of overcharge with 1h-capacity tests are required.
2. In North America the IEEE 535:2006 applies an accelerated service life test with normal float voltage but at high temperature of 145°F (63°C). These cells having undergone this accelerated aging are then subjected to seismic qualification at the end of anticipated service life. They are then recharged and discharged one last time to ensure integrity for worst-case condition at end of service life.

In the case of testing for IEEE 535:2006 one year in float service at 77°F (25°C) is equivalent to 20 days when tested at 145°F (63°C). Every 50 days the capacity of the battery is tested with the 2h to 4h rate. The test is stopped when the capacity drops below 80% of the rated capacity. The driving mechanism behind this accelerated service life test is that the prevailing failure mode of a standby battery is the corrosion of the positive grid. This can be understood by overcoming an activation energy, and this process depends on temperature according to the Arrhenius equation:

$$t_1/t_2 = \exp(-E/R/T_2) / \exp(-E/R/T_1)$$, where

E = 15,280cal/mol, R=1.9852cal/mol/°K, T_2=298.2°K, t_2=365days. The equation gives for T_2=336°K (145°F) the test time of 20days. For a test temperature of 313.2°K (104°F) the test time is 106 days which is equivalent to one year at 77°F (25°C).

The results of our testing to IEEE 535 guidelines for the tubular flooded (OPzS), tubular GEL (OPzV) and flat plate batteries (OGi) were presented at INTELEC 2005[3] in detail. We will review only the results of this testing in Table 1.

Table 1. IEEE 535 aging test results

	VLA OPzS	VRLA OPzV	VLA OGi
	Tubular flooded	Tubular GEL	Flat plate flooded
Positive alloy	Lead Selenium	Lead Calcium	Lead Selenium
Float service at 145°F	550 days	450 days	425 days
Float service at 77°F	27.5 years	22.5 years	21.3 years

However, we cannot use this test for qualification of lead acid batteries where the cyclic service is added.
In cyclic service new failure modes can arise.

ENDURANCE IN CYCLES OF STATIONARY BATTERIES

As we pointed out in our introduction, many countries in Africa and Asia suffer from daily outages in the power grid. The total electric energy demand exceeds what the utilities can provide by more than 10%. For this reason the grid can go off-line for 2 hours or more each day. Even when diesel-generators are available as reserve power in telecom base stations, for example, the back-up batteries are used until an end-voltage of about 1.95V is reached in order to save diesel fuel and to get a prolonged overhaul period. As a consequence, the lead acid batteries get daily discharges of up to 50% DOD. What is needed are lead-acid cells with cycle-proof active material.

A design consideration must be given to the tubular batteries in order to increase the endurance in cycles. We know that tubular batteries are used in many cyclic applications, such as fork lift trucks, motors, or diesel starting applications. However, this design consideration takes into account the need for the stand-by float requirement of the stationary cell as well as the cyclic requirement of the new applications described in this paper.

Further we see a growing demand for electric energy storage in the developed world for photovoltaic and wind-farm application. Since the photovoltaic and wind power can't be switched on and off like a gas turbine-generator or coal-fuelled steam generator, pumped-storage hydroelectricity is the most likely economic choice if the geographical conditions are suitable. It costs about $0.05 USD (5 cents) to store and release a single kilowatt/hour (kWh) of power. Lead-acid batteries can be very competitive with that figure. They have a high efficiency of 80 to 85%. The key issue is the endurance in cycles. If we are able to increase the energy through-put of the battery to 3000 - 4000 times that of the rated energy, we are comparable in cost.

To meet this target, we have to optimize the design of the lead acid battery plus insure the operation and charging regime. The final proof will be the test of the endurance in cycles. In IEC 60 896 there are three (3) appropriate cycle regimes:

Table 2. Test standards for endurance in cycles of stationary batteries

	IEC 60 896-11	IEC 60 896-2	IEC 896-21
	VLA	VRLA	VRLA
Discharge	3h with $2*I_{10}$, equivalent to 75% C_4	3h with $2*I_{10}$, equivalent to 75% C_4	2h with $2*I_{10}$, equivalent to 50% C_4
Charge	21h 2.40Vpc, $I_{max} = 2*I_{10}$	21h 2.40Vpc, $I_{max} = 2*I_{10}$	22h float 2.25Vpc, till during discharge the voltage drops below 1.80V, then 168h float, followed by a C_3 capacity test †
Check	Every 50 cycles a C_{10} test	Every 50 cycles a rated C_{rt} test (C_8 or C_{10})	C_3 capacity test
End	$C_{10} < 80\%$	$C_{rt} < 80\%$	$C_3 < 80\%$

† *Before continuing with the cycles the battery gets an equalizing charge, followed by another* C_3 *test.*

The test according to IEC 60 896-21 has not been generally accepted in practice to date because in cycle applications we have to increase the charging voltage to much higher values than the float voltage. We do not have 168 hours or 7-days without a discharge to recover the battery from time to time.

In Fig.1 we see the results of the cycle test per IEC 60 896-11 on 6 cells of our 6 OPzS 420's run from Dec 1994 to Jun 1996.

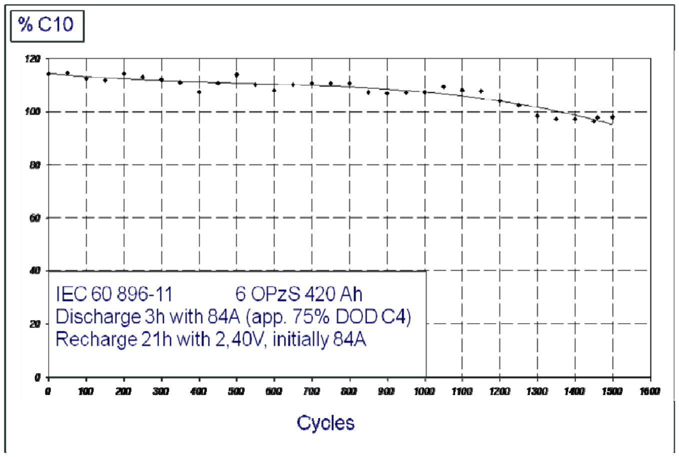

Fig. 1 Endurance in cycles of OPzS cells acc. to IEC 60 896-11

This OPzS is a VLA having tubular plates with a lead selenium alloy in the positive plate. After completing 1,500 cycles (75% C_4) the capacity was 95% at the C_{10} rate. We can estimate 1,700 cycles to 80% at C_{10}

In Fig.2 we see the results of the endurance in cycles test according to IEC 60 896-2 on 6 cells of 6 OPzV- 420's, run from June 1999 to June 2005. This type OPzV is a VRLA type having tubular plates with lead-calcium alloy in the positive plate in a GEL electrolyte. The VRLA type with tubular plates in GEL technique delivers about 1,700 cycles to 75% C_4.

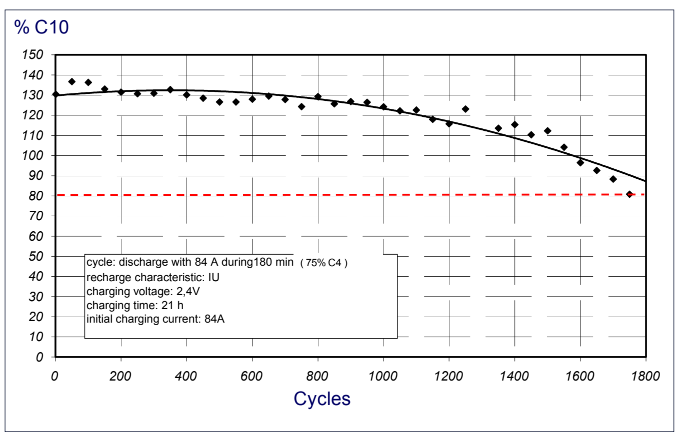

Fig. 2 Endurance in cycles of OPzV cells acc. to IEC 60 896-2

Although the results shown in Fig.1 and Fig. 2 are very satisfactory, we observed an energy through-put of $1700*0.6*C_{10} = 1020 *C_{10}$.

Can we improve the energy through-put? We see that the failure modes for both cycle tests are (1) softening of the positive mass and (2) corrosion of the positive grid. We also discover that softening of the positive mass is increased by discharges below 30% SOC. Additionally, we know that a high voltage charge of 2.40V or greater can deteriorate the cell through corrosion and gas evolution.

Therefore, the answer to the question above is to ensure discharge and charge processes between 30% and 80% SOC, since this gives the best energy through-put. A full charge is required only after 5-10 C_{10} energy through-puts. With these conditions the BEWAG-Battery in Berlin (12 strings of 590 cells OPzS 1000, 14.16 MWh) has reached a through-put of greater than 4000*C10.

This battery was used to regulate the 50Hz frequency in the electrical "island" in West-Berlin from 1987 to 1994.

It is worth discussing this approach with grid engineers to optimize the power in times where a considerable share of renewable energy sources will be allocated according to customer needs in the future.

QUALIFICATION OF STATIONARY BATTERIES FOR SOLAR APPLICATIONS

Stand-alone systems consist of photovoltaic (PV) power sources with a battery as back-up power. As pointed out earlier, they do service along data lines for repeating and improving data; along highways for lighting and 911 telephone centers; along railroads, water canals and lighting for shipping lanes; signalling and communication and along underground pipe lines for cathodic protection. Further, they are in use in villages and personal residences.

The capacity of the battery has to be large enough to give energy in low radiation (e.g. winter) periods. The autonomy time of the battery is mainly 5 to 10 days. The load discharges range from 10 to 20% per day. This seems to be a moderate duty cycle. But in temperate zones the daily radiation is only 20 to 30% in winter as compared to the summer values. Therefore in winter times we cannot always compensate the daily discharge with PV energy as the state of charge (SOC) diminishes. The discharge is restricted by the low voltage cut off. As we see in Fig. 3, cycling is near 10% SOC. In summer the opposite is the case. With the high radiation the battery is full after some hours and in the rest of the sunshine period the battery is being over-charged.

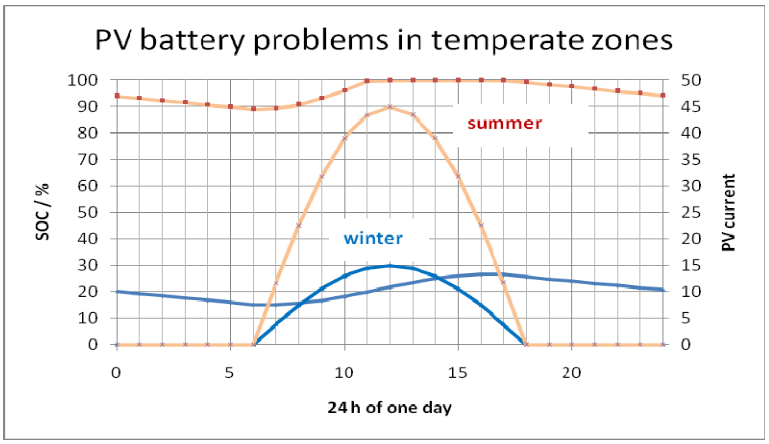

Fig. 3 Radiation and SOC in winter and summer, schematic

IEC 61 427: "Secondary cells and batteries for PV energy systems – General requirements and methods of test" defines endurance in a cycles test with exactly these conditions (see Fig. 4).

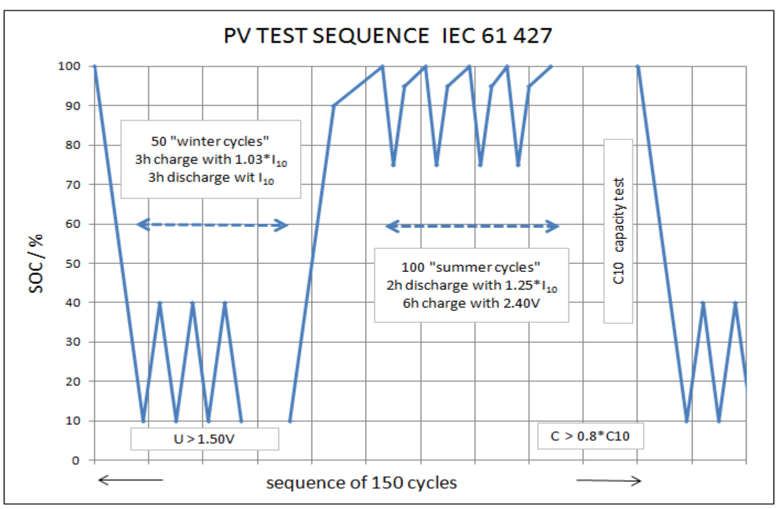

Fig. 4 Cycle endurance test in solar application conditions

The test starts with a 10h rate discharge of 9 hours down to 10% SOC. Then 50 “winter cycles” with 30% charge and 30% discharge are performed. A charging factor of 1.03 is included to compensate for side reactions. After charging to 100% SOC, discharging with 1.25*I10 within 2 hours alternates with 6-hour charging with I10, while the voltage is restricted to 2.40V. After 100 such “summer cycles” a C_{10} capacity test is performed. This test sequence with 150 PV-cycles is repeated, until during “winter cycles” the voltage drops below 1.50Vpc or the actual C_{10} capacity is lower than 0.8*rated C10. The capacity test takes place at reference room temperature, while the cycling takes place at 104°F (40°C).

To find out the endurance in cycles for solar applications according to IEC 61 427 we tested solar VLA batteries in tubular design: lead-selenium (PVS, similar to OPzS); VRLA batteries in tubular design - lead-calcium in a GEL electrolyte (PVV, similar to OPzV). The solar batteries are presented in Table 3. The test started on 01/17/2006 and is still on-going.

Table 3. Test samples for the endurance in cycles for solar application			
			
12V 3 PVV 210	2V 5 PVV 350	12V 3 PVS 210	2V 6 PVS 420
C100 = 210Ah	C100 = 373Ah	C100 = 216 Ah	C100 = 442 Ah
C10 = 169Ah	C10 = 290 Ah	C10 = 154 Ah	C10 = 320 Ah
12V block	6 * 2V cells	12V block	6 * 2V cells

In Fig. 5 we present the voltage response and the temperature during the 16th sequence, i.e. from the PV cycle 2,150 to 2,400. We see the VRLA type on the left-hand side and the VLA type on the right hand side. The test was performed in a water bath kept at104°F (40°C). In both diagrams we see the voltage response during the first 13 days of the winter cycles. The final voltage starts with 1.90V after taking out 90% of the C_{10} rate. During the 50 cycles the final voltage increases to 1.98V for the VRLA type and to 1.93V for the VLA type. It would appear that the applied overcharge factor of 1.03 is slightly too large. By comparing the voltages with the 90% discharge we can calculate the real charging factor for the “winter cycles” (see table 4).

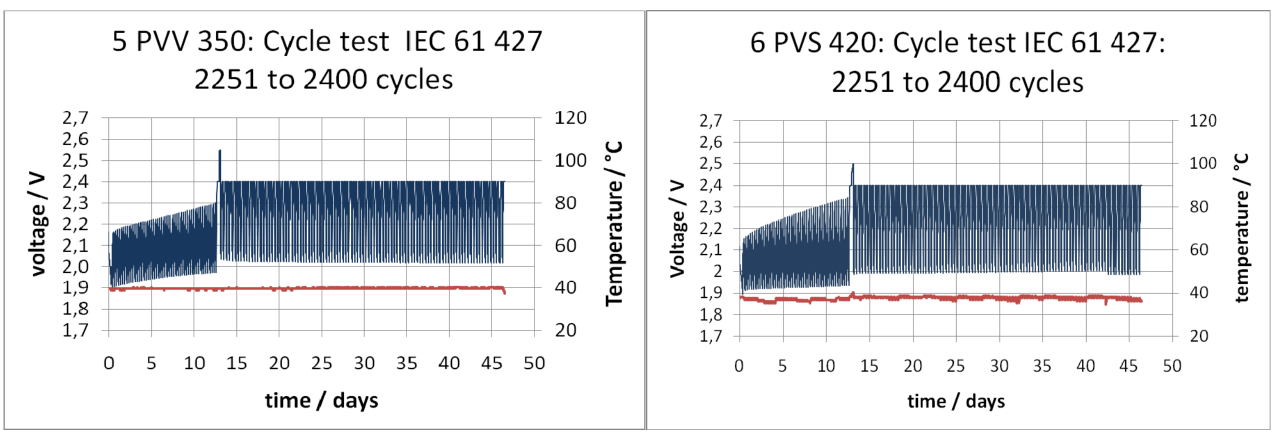

Fig. 5 Voltage and temperature during sequence 16 (2251 to 2400 cycles)

Table 4. Real charging factors from 300 to 2400 cycles			
	300 cycles	1050 cycles	2400 cycles
2V 6 PVS 420 "winter cycles"	1.026	1.028	1.028
2V 5 PVV 350 "winter cycles"	1.023	1.024	1.025
2V 6 PVS 420 "summer cycles"	1.08	1.13	1.21
2V 5 PVV 350 "summer cycles"	1.05	1.14	1.24

The charging factor is lower for the VRLA type, slightly increasing with cycles due to increasing recombination current, while the VLA is slightly increasing due to increased hydrogen development.

During the "summer cycles" the charging factors are higher, because we have an over charge condition with 2.40V at 104°F (40°C). At this temperature we should choose in practice 2.35V. These charging factors are also increasing with cycles, leading to a higher recombination current of the VRLA type and more hydrogen development responsible for the water loss of the VLA type. In Fig. 6 we present the water loss data for the type 6 PVS 420.

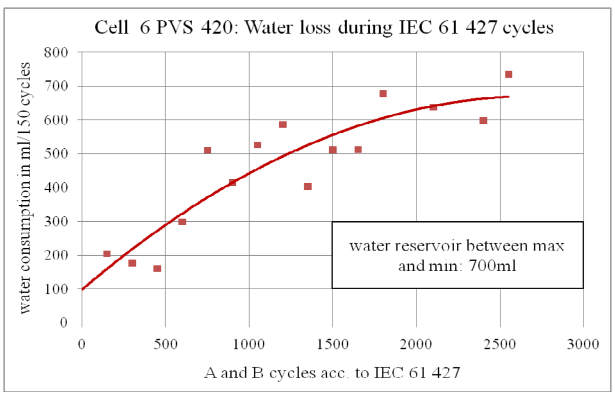

Fig. 6 Water loss of VLA types during PV cycles

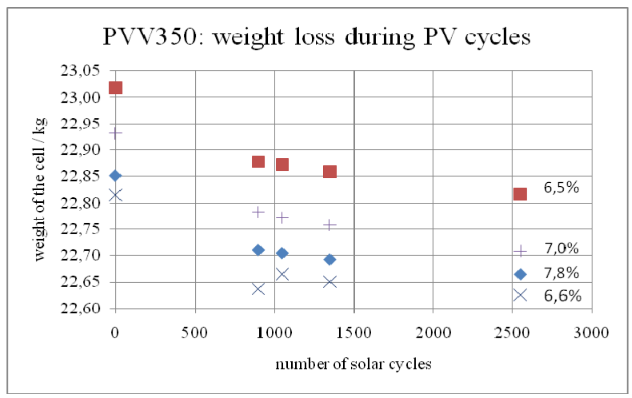

Fig. 7 Weight loss of VRLA types during solar cycles

Although the 6PVS-420 has a water reservoir of 700ml, after 2,550 cycles we see that we use it completely within 150 cycles. Every day one-cycle equates to a water interval of 5 months. By reduction of the charging voltage to 2.35Vpc, the 6-month water interval can be assured. The weight of the VRLA types was checked several times during the test (see Fig. 7). The weight loss is only around 7% of the total water content until 2,550 cycles, and the cells remained stable. Therefore, we don't expect dry-out of the VRLA cells.

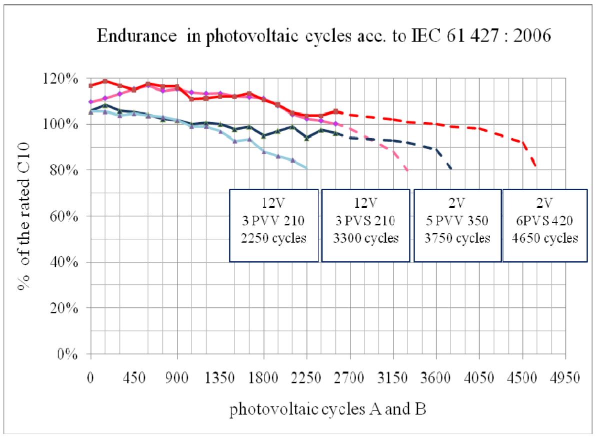

Fig. 8 Endurance in photovoltaic cycles

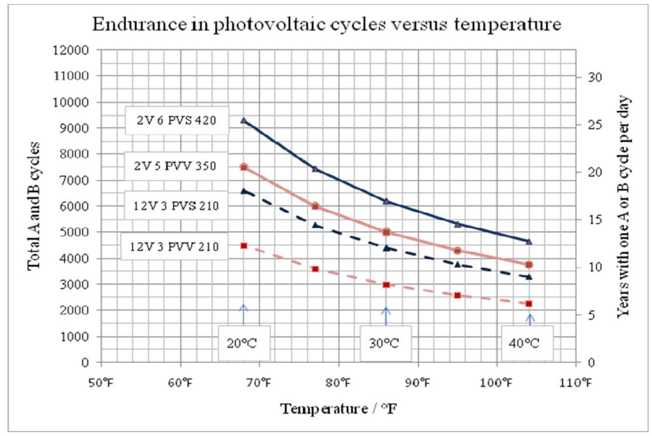

Fig. 9 Endurance in PV cycles versus temperature

In Fig. 8 we present the results of the C_{10} capacity test done in each sequence. Up until now, we have done 17 sequences with 150 cycles each, or a total 2,550 cycles. The capacity values of the three types are still around 100%. Therefore we have made an extrapolation for endurance down to 80% of the rated C_{10} capacity. The sediment space of the 2V 6 PVS 420 is only filled up to 50%. As a result, we expect a maximum value of 4,650 cycles. The "mud space" of the monobloc battery - 12V 3 PVS 210 - is only 2/3 in relative size to those of the single cells. We see that it is nearly filled. Therefore we expect to achieve only 3,300 cycles.

To test the status of the 2V 5 PVV 350 VRLA, we have opened one cell (see Fig. 10). The GEL is in perfect condition as well as the pole bushing. The positive mass is already partly soft, so we have extrapolated a reduced endurance of 3,750 cycles. The monobloc 12V 3 PVV 210 has reached 2,250 cycles. After examination we noticed that several cells of the monobloc were not gas tight, so they were only partly discharged. The condition of the plates showed that they justified a longer endurance in cycles. We present the actual test results here, but we expect higher values in a repeated test with gas tight cells.

In Fig. 9 we show the endurance in cycles in the left coordinate and on the right one the service life in years. The service life in years was calculated by the number of cycles/365 days per year (see Table 5).

To accelerate the cycle test we cycled at 104°F (40°C). The C_{10} capacity tests were made at room temperature. Now the question is: How many cycles can we expect at lower temperatures? The Arrhenius calculation from the endurance in float service is not applicable because it only reflects the positive grid corrosion. We still have to account for the deterioration of the active mass. If we take the temperature correction used for traction batteries in ZVEI notes, Germany: at 104°F factor 1, at 86°F factor 1.33 and at 68°F factor 2.0, then with these factors we can calculate the endurance in cycles and the service life for 86°F and 68°F.

Table 5. Endurance in photovoltaic cycles and service life at different temperatures

	104°F (40°C)		86°F (30°C)		68°F (20°C)	
2V 6 PVS 420	4650 cycles	12.7 years	6200 cycles	17.0 years	9300 cycles	25.5 years
2V 5 PVV 350	3750 cycles	10.3 years	5000 cycles	13.7 years	7500 cycles	20.5 years
12V 3 PVS 210	3300 cycles	9.0 years	4400 cycles	12.1 years	6600 cycles	18.1 years
12V 3 PVV 210	2250 cycles	6.2 years	3000 cycles	8.2 years	4500 cycles	12.3 years

Fig. 10 2V 5 PVV 350 after 2550 cycles, opened

Fig. 11 Water bath and aged cells 2V 6 PVS 420

In Fig. 11 we see the experimental equipment with 6 cells of the 2V 6 PVS 420 in the water tank after 2,550 cycles. Again, the testing started January 17, 2006 and is continuing with the same cells.

Thus, in the present experiment we have proven that for both the VLA and the VRLA cells we have achieved an endurance of 17-cycle sequences that meet IEC 61 427 requirements (2,550 cycles/150 cycles per sequence).

Tests with automotive batteries or derivatives with thicker plates, or other separators including AGM last only several sequences[4].

LONG DURATION DUTY CYCLES FOR FLOAT APPLICATIONS: A NEW CHALLENGE?

If we discharge a large lead acid cell for 72h, we use the active material to a greater extent then if we only discharge one (1) to eight (8) hours. In the actual experiment (see Fig.12) of 24 cells of the 2V 24 OPzS 3000 we convert 55% of the lead dioxide (PbO_2) material to lead sulphate ($PbSO_4$) during discharge and back to lead dioxide during recharging.

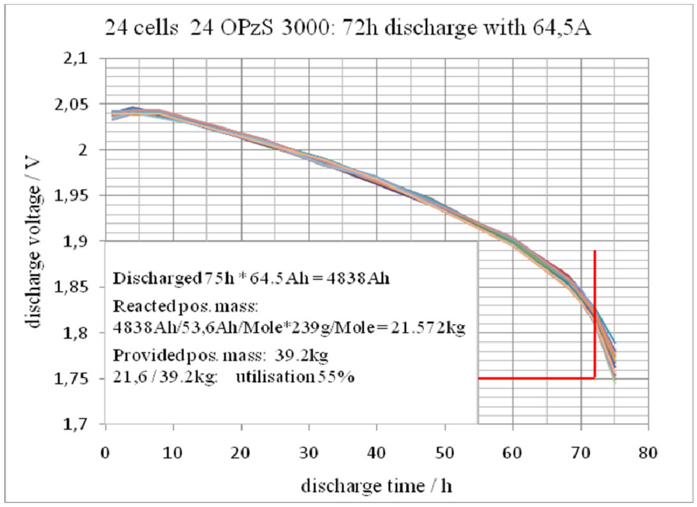

Figure 12 72h discharge with a tubular VLA 48V battery

Every time this is done we see a change in volume:

	Gravity	mole weight	mole volume
β-PbO_2	9.30kg/l	239.2g	$25.7cm^2$
$PbSO_4$	6.29kg/l	303.3g	$48.2cm^3$

Lead sulphate needs 88% (48.2/25.7=1.88) more volume than the lead dioxide it had before. Although the active mass has a porosity of about 50%, this volume change gives an expansion of the positive active mass.

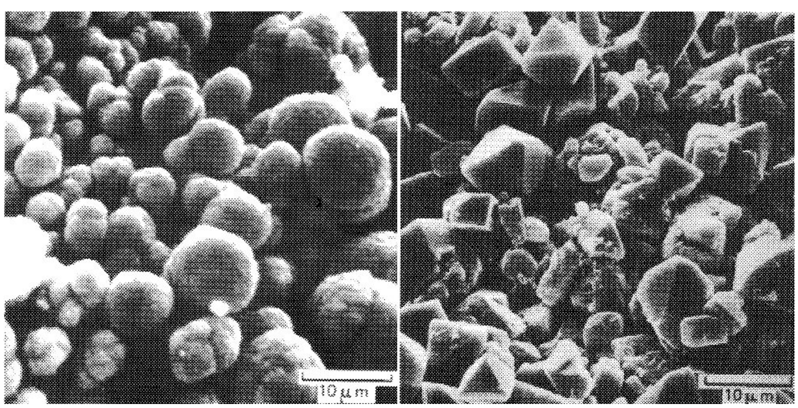

Fig. 13 Positive charged (left) and discharged (right) electrode

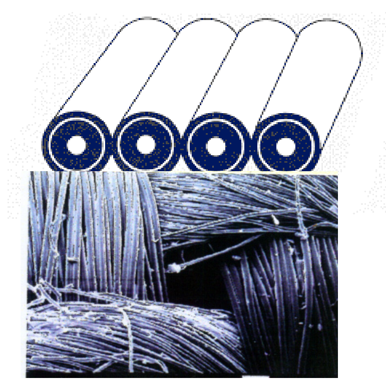

Fig. 14 Woven tubular gauntlet

In all electrochemical processes, the active material needs an electrical contact between the particles and the current collector for exchanging electrons. When the positive active material expands it is likely to lose the electric and mechanic contact between particles (see Fig. 13). The mass becomes soft and the capacity decreases. In the tubular design a gauntlet made of woven polyester (see Fig. 14) presses the active material together and counteracts the expansion. The burst strength of the gauntlet is 40bar before and still 30bar after the oxidation test. So a high stability of the tube is assured over life.

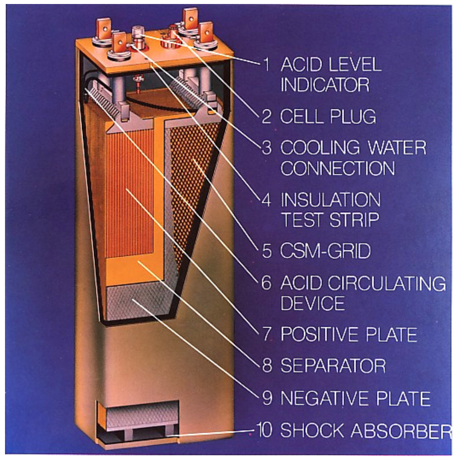

Fig. 15 View of a submarine cell

During long duration duty cycles, we get a higher mass utilisation, hence a larger expansion. Therefore the tubular design with its compression force is beneficial for service life and endurance in cycles. Do we have also practical experience with long duration duty cycles?

We know that batteries used in diesel-electric submarines remain submerged for several days (50 to 120h). During this period the submarine battery is the only energy source. This is a typical long-duration duty cycle and up to 50 such long-duration cycles can be required per year.

VLA batteries (see Fig. 15) with tubular plates of 1,100 mm height and 400mm width have performed this service for about 8-10 years in diesel-electric submarines for the past 40 years. The majority of about 200 diesel-electric submarines world-wide are equipped with tubular batteries. A typical size of a submarine battery is 500 cells each weighing 500kg with 12,000Ah rated capacity at the 100h rate, 12MWh in total.

Interestingly, back-up batteries for nuclear power plants now have a similar long duration duty cycle, currently with up to 72 hours of discharge time with a similar size requirement of 7.2MWh. For such large and compact batteries it is necessary to consider not only the dedicated hydrogen evolution but also the heat management.

In this application it is critical to understand the ventilation requirements of large VRLA batteries. The low hydrogen evolution of VRLA batteries needs only low ventilation. EN 50 272-2 requires 300 m^3/h ventilation for a 12 MWh battery. The heat evolution during float is 2.4A*2.25V*500cells = 2,700W. To transfer this heat out of the room with 300m^3/h air ventilation, the battery temperature has to be 19.8°F (11°C) higher than the temperature of the incoming air! If charge and equalizing processes are present the battery will come to a higher temperature of approximately 113°F (45°C).

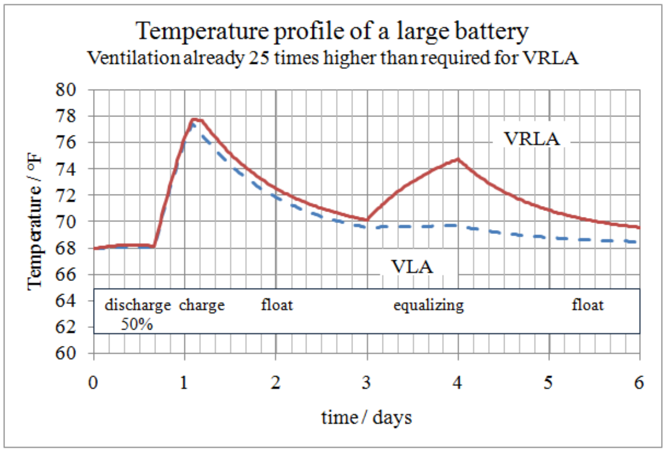

Fig. 16 Temperature profile of a large battery

In Fig. 16 we have used a ventilation of 7,500m³/h, i.e. 25-fold ventilation than what is required for the hydrogen dilution. Still it takes several days to get the heat out of the room after a charging process. We want to emphasize, the thermal management of such large batteries requires a far higher ventilation as we need to dilute the evolved hydrogen of VLA or the VRLA batteries.

CONCLUSION

IEEE 535:2006 defines a well proven accelerated service life test to qualify Stationary Batteries in their stand-by application: 400 days at 145°F correspond to a service life of 20 years at 77°F. Batteries with the tubular design have been qualified according to IEEE 535:2006 with 550 days at 145°F (VLA) and 450 days at 145°F (VRLA) to prove their perfect matching for the stand-by application.

But we do see at present and especially with the more recent applications, that stationary batteries will be required to perform regular cycle service.

The qualification of stationary batteries in cyclic application cannot be done with IEEE 535:2006 as it currently stands. Of course, IEEE 535 can be modified to incorporate the cyclical nature of the new passive design requirements, and such a move may already be underway.

However, the test standards for cyclic applications as given in IEC 60 896-11, IEC 60 896-2 and IEC 60 896-21 could be incorporated as a meaningful qualification method as well.

The special requirements of photovoltaic applications are considered in IEC 61 427.

We have done these tests for endurance in cycles with tubular batteries and have presented the results.
Additionally, discharges with long duration duty cycles of 72h discharge time were performed with tubular batteries.

Properly manufactured stationary batteries of tubular design are an excellent candidate for long-duration duty cycles of two (2) to one-hundred (100) hours of standby application as well as cyclical requirements.

REFERENCES

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