



A Study of Lead Acid Battery Self-discharge Characteristics

Effects of shelf life on Lead Acid batteries

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Lead Acid batteries, regardless of construction chemistry all exhibit a self-discharge characteristic that varies by storage temperature, state of health and state of charge of the subject battery. This Paper will explain the phenomenon and give the various self-discharge values for each of the popular lead acid battery chemistries.

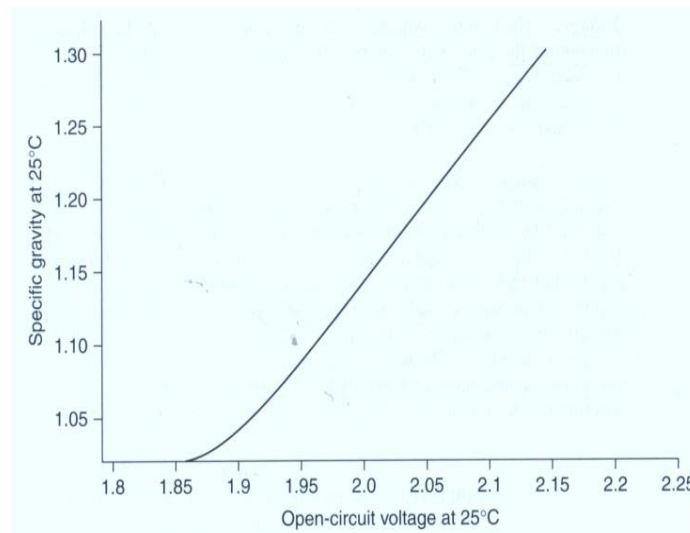
Abstract:

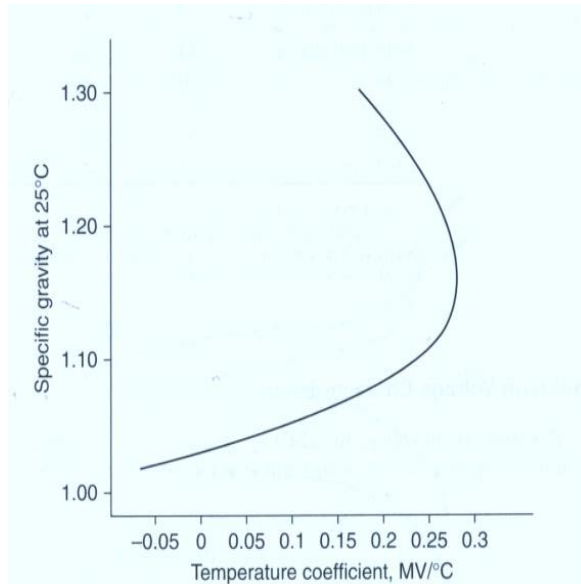
Lead Acid batteries, regardless of construction chemistry all exhibit a self-discharge characteristic that varies by storage temperature, state of health and state of charge of the subject battery. This Paper will explain the phenomenon and give the various self-discharge values for each of the popular lead acid battery chemistries.

Introduction:

The open circuit voltage for a battery system is a function of temperature and electrolyte concentration as expressed in the Nernst equation for the lead acid cell. Since the concentration of the electrolyte varies, the relative activities of H_2SO_4 and H_2O in the Nernst equation change. The open circuit voltage (OCV) is also affected by temperature. Most lead acid batteries operate above 2 Molar H_2SO_4 – 1.120 specific gravity and have a thermal coefficient of about $+0.2 \text{ mV}/^\circ\text{C}$.

The Chart below demonstrates the effect of temperature on specific gravity concentration and OCV at 25.0°C





This chart shows the temperature coefficient, $\text{mV}/^{\circ}\text{C}$. The reversible potential of the system increases with increasing temperature.

Self-Discharge Explanation:

Polarisation and Resistive Losses;

When a battery is being discharged, the voltage under load (current draw) is lower than the open circuit voltage at the same concentrations of H_2SO_4 and H_2O in the electrolyte and Pb or PbO_2 and PbSO_4 in the plates. The thermodynamically stable state for lead acid batteries is the *discharged state*. Charging must be done to cause the equilibria of the electrochemical reactions to change in both plates, thus the voltage of the power source for charging the lead acid battery must be higher than the Nernst voltage of the battery on open circuit. Storage of lead acid batteries will therefore lead to a level of

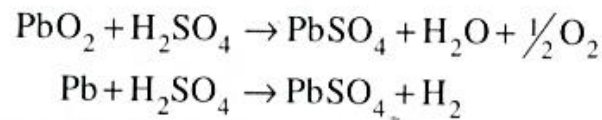
self-discharge in direct relationship to the battery chemistry employed and the storage temperatures involved over the duration of the storage cycle.

The deviations from the OCV during charge and discharge are due, in part, to resistive losses internally in the battery (*hence reason for Validation of the new battery I_R*) and, in part, to Polarisation. Polarisation voltages stabilize at some value when the plates are recharged and are gassing freely.

Self- Discharge;

The equilibria of the electrode reactions are normally in the discharge direction since, thermodynamically, the discharged state is more stable. The rate of self-discharge (loss of capacity [charge] when no external load is applied) of the lead acid cell is fairly rapid, but it can be reduced significantly by incorporating certain design features.

The rate of self-discharge depends on several factors. Lead and lead dioxide are thermodynamically unstable in sulphuric acid solutions, and on open circuit they react with the electrolyte. Oxygen is evolved at the positive electrode and hydrogen at the negative, at a rate dependent on temperature and acid concentration – the gassing rate increases with increasing acid concentration as follows;



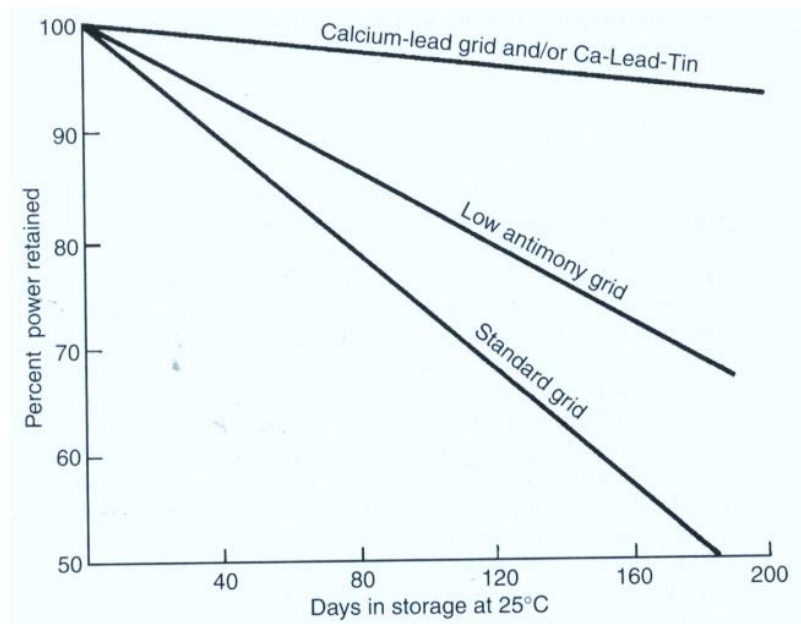
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For most positives the formation of PbSO_4 by self-discharge is slow, typically much less than 0.5% per day at 25°C . The self-discharge of the negative is generally more rapid, especially if the cell is contaminated with various catalytic metallic ions.

Club Assist recently had a first-hand experience of this contamination with the premature degradation of OCV due to contaminated metallic ions in a series of imported batteries.

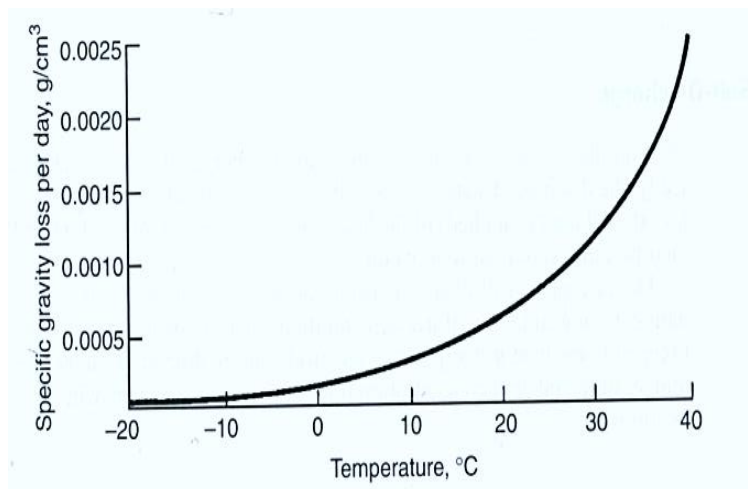
For example, antimony (Sb) lost from the positive grids by corrosion can diffuse to the negative grid, where it is deposited, (*visible as a discoloration of the inter-cell straps – termed Antimonial poisoning*) resulting in a “local action” discharge cell which converts some lead acid active material to PbSO_4 . New batteries with lead-antimony grids lose about 1% of charge per day at 25°C , but the charge loss increases by a factor of 2 to 5 as the battery ages.

Batteries with non-antimonial or high Ca content grids lose less than 0.5% of charge per day **REGARDLESS** of age. This characteristic is illustrated in the following chart.



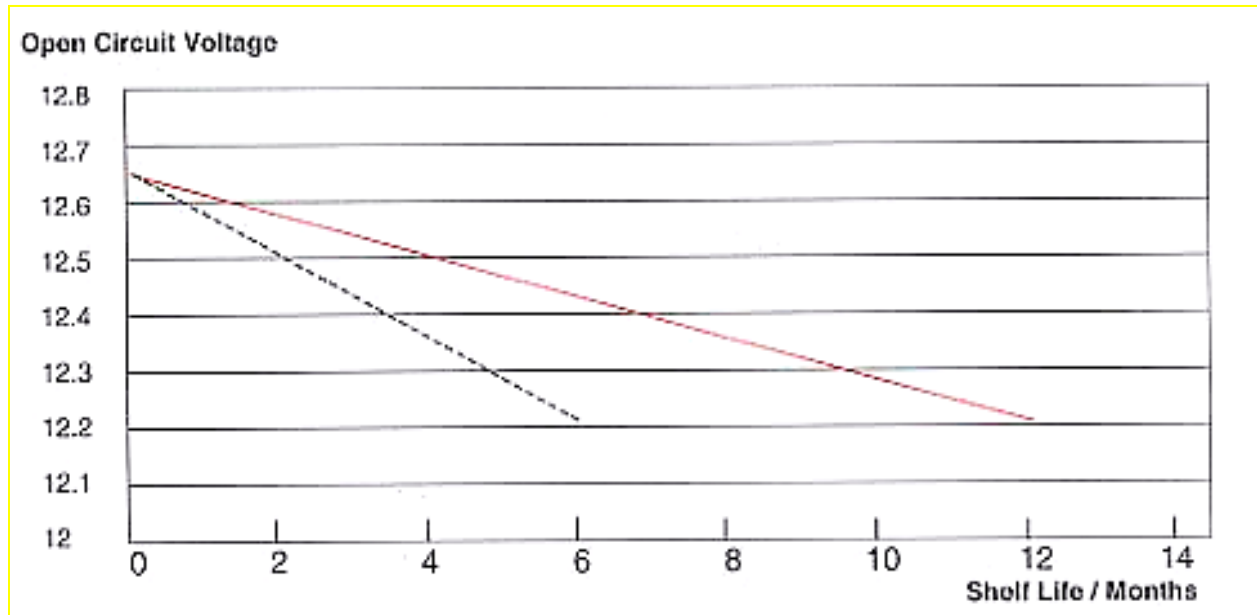
Maintenance –free and charge-retention-type batteries, where the self-discharge rate must be minimised, use low antimony or antimony free alloy (such as calcium lead nil or minimal Sb) grids. This grid metallurgy is common in deep cycle non SLI battery types. However, because of other beneficial effects of antimony (Sb), its complete elimination may not be desirable and low antimony – lead alloys are a useful compromise. This chemistry and metallurgy for grids is as we see in the current range of batteries imported by Club Assist and its affiliates in all Regions.

Self-discharge is temperature dependent, as shown in the illustration chart below.



The graph shows the fall in specific gravity per day of a new fully charged battery with 6% antimonial lead grids. Self-discharge can thus be minimised by storing batteries at temperatures between 5 and 15⁰C.

Detailed in the following graph is a typical comparative chart that demonstrates the deterioration of antimonial (Sb) in regard to self-discharge when compared with Ca contained in the grid alloys.



Calcium based batteries have roughly double the shelf life of an Antimonial based battery before the OCV falls below 12.2 volts. Due to the phenomenon of self-discharge, the lead antimony battery will lose up to 30% of surface charge in 30 days, even when not in use, and still sitting on the shelf.

Calcium constructed batteries with their specially refined lead do not exhibit the same aggressive levels of self-discharge, thus allowing longer periods of “just sitting idle”.

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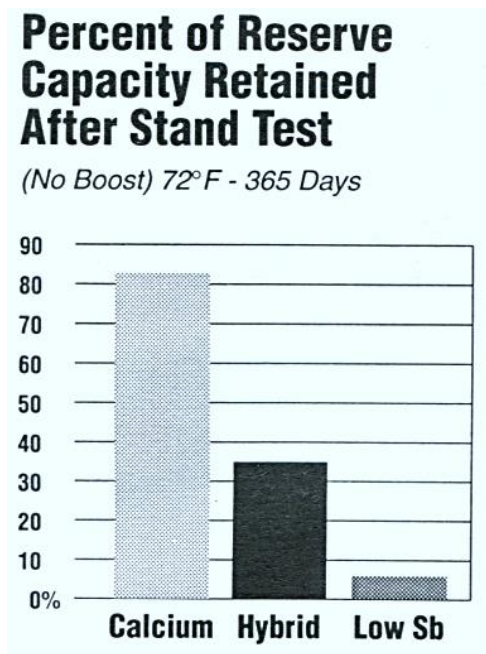
The table shown below indicates the values of Sb and Ca in a typical maintenance free high heat operation SLI battery grid. It can be seen from the table that the actual content of Calcium is around 0.07-0.09% by weight.

Grid Metallurgy:		
% Ca	0.07~0.09	Target 0.05%-1.1% calcium
% Sb	0.02	Target 1.0%-9.0% antimonial chemistry only – far less in Ca/Ca grids alloy mix
% Sn	1.2 ± 0.1	Target 0.5%-2.5% tin in PbCaSn & CaSnAl, 0.05%-3.5% PbSb
% Al	Minimal	Target 0.15%-0.025% aluminium in PbCaSnAl
% As	0.002 ↓	Target 0.05%-0.23% arsenic – all chemistries
% Se	Minimal	Target 0.015%-0.035% selenium – all chemistries
% Cu	0.005 ↓	Target 0.02%-0.04% copper – all chemistries
% S	Minimal	Target 0.005%-0.02% sulphur – all chemistries
% Ag	Minimal	Target 0.01%-0.02% silver PbCaSn & PbCaSnAl in positives for added cycle life.
% C	0.2	Target 0.5%-2.5% carbon as an expander in Neg grids, to enhance formation and capacity - Ah

Self-Discharge – Reserve Capacity:

The chart below compares the percent of reserve capacity retained while the battery is on the shelf in stock, without recharging. Note the rate of decline of the Hybrid vs.

Calcium constructed grids after 12 months.



While the Ca chemistry retains most of its capacity, the Hybrid *loses* more than 65% and the low antimony *loses* 95% of its reserve capacity. After 12 months without charging, low antimony and many Hybrid batteries will not hold a charge, while Calcium content batteries recharge easily with no capacity loss.

Conclusion:

This Paper has explored the effect on open circuit voltage, specific gravity and reserve capacity when the battery is stored on a shelf or display rack. There are very distinct advantages of the calcium addition to the metallurgy in the grids, which result in many days of retained acceptable OCV when compared to other Hybrid and low antimonial alloys in grids.

The effect of temperature on the OCV is also outlined, thus allowing a decision to be made in regard to how to store batteries, how long to store and when to start re-charge regimes from a display rack charger.

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