THE EFFECT OF ACTIVE MASS THICKNESS ON THE CYCLE LIFE OF LOW-ANTIMONY LEAD-ALLOY SPINE EMPLOYED IN DEEP-CYCLE BATTERIES

by

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A THESIS

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Declaration

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Abstract

The cycle life of conventional starting-lighting-ignition (SLI) lead-acid batteries with low-antimony lead-alloy grids is reduced when subjected to repetitive deep-discharge cycling. Reduced cycle life is caused by the rich layer of lead sulfate formed in the corrosion layer interface (Barrett et al. 1981; Chang & Valeriote 1985). However, the cycle life of the tubular traction lead-acid batteries containing low-antimony lead-alloy grids is unknown when subjected to identical conditions.

Preliminary forensic analysis of a tubular traction cell subjected to similar conditions at Pacific Marine Batteries (PMB) indicates the reduced cycle life was caused primarily by corrosion of the positive grids which may have caused by stress created by the increased in the corrosion volume produced during cycling. Rogatchev, Papazov and Pavlov (1983) and Garche (1995) demonstrated that with increased in thickness of the active mass in tubular-plate formation of the corrosion product is reduced, hence reduce internal stress. Alternatively, Garche (1995) suggested the stress corrosion may be reduced by the partial compensation of the thickness of the active mass. Likewise, Chang and Valeriote (1985) recommended that low-antimony lead-alloy grids may be more suitable to be used in the design of tubular grids for deep-discharge cycling. They believed easy pathway for the acid to reach the grid surface was the main cause for the rich layer of lead sulfate to form. Therefore, further research is needed to provide insights into, and understanding of, the implication of the preliminary forensic analysis, hence help to extend the cycle life of the batteries.

Cells were assembled with a tubular positive electrode and one flat negative plate. Low-antimony lead alloys spines ~ 2.0 wt.% Sb with a diameter of ~3 mm was used. The independent variable studied was the effect of 1.60 mm, 2.15 mm and 2.80 mm active mass thickness on cycle life of the positive spines subjected to repetitive deep-discharge cycling. Cross-sections of cycled electrodes at different stages during cycling were examined for mode of failure using electron probe micro analysis (EPMA), secondary electron microscopy (SEM) images and iTEM5 image analysis software.
Average cell performance of cycled tubular electrode under 20 h discharge rates for various active mass thicknesses indicated the capacity was not exhibit sign of rapid reduced capacity. Back-scattered electron images and quantitative electron microprobe analysis were used to investigate the elemental distribution of sulfur (S present as sulfate) in the corrosion layer interface have provided no evidence of rich layer of lead sulfate formation in the corrosion layer.

The results from the residual cross-sectional areas indicated that corrosion failure result from stresses was the primary cause of the positive spine of low-antimony lead-alloy tubular-plate traction batteries subjected to repetitive discharge cycling. The effect of the active mass thickness on positive grid corrosion (cycle life) was inconclusive due inconsistent data when subjected to repetitive deep-discharging cycling.
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I hope the results of my thesis would provide some contribution to PMB Defence and to society.
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Nomenclature

%  percentage
µm micro meter
A  ampere
Ah ampere hour
g gram
h hour
kg kilogram
kV kilovolt
ml millilitre
mm millimetre
V volt
α alpha
β beta

Abbreviations

BEVs  battery electrical vehicles
BSE backscattered electron
C/D charge/discharge
CL corrosion layer
DCSL dense corrosion sub-layer
EPMA electron micro-probe analysis
g/cc gram per cubic centimetre
LAB lead-acid battery
MAN mean atomic number
Me metal
NAM negative active mass
PAM positive active mass
PCSL porous corrosion sub-layer
PMB Pacific Marine Batteries
PVC polyethylene vinyl chloride
sat. saturated
SEM scanning electron microscope
sp. gr. specific gravity
tp  polarization time
v/v  volume/volume
WDS  wavelength-dispersive spectroscopy
wt.%  weight percentage
XRD  X-ray diffraction

Chemical abbreviations

Ag  silver
AgCl  silver chloride
Ca  calcium
H+  hydrogen atom
H2  hydrogen gas
H2O  water
H2SO4  sulfuric acid
KCl  potassium chloride
O2  oxygen
Pb  lead
Pb3O4  red lead powder
PbO  lead oxide
PbO2  lead dioxide
PbSO4  lead sulfate
Sb  antimony
Sn  tin