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

by

VAN HAO NGUYEN

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF ENGINEERING SCIENCE

School of Chemical Engineering
The Faculty of Engineering, Computer and Mathematical Science (EMCS)

THE UNIVERSITY OF ADELAIDE
South Australia

January 2015

Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

I give my consent for this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

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.

Acknowledgement

This thesis would not have eventuated without the help and support from a number of people, including the company for which I currently work who have contributed significantly to this research and I would like to express my gratitude to all.

PMB Defence for their encouragement and for providing the opportunity and support to further improve my study and knowledge which may be helpful for the company and my own achievement.

Associate Professor Brian O'Neill, School of Chemical Engineering, University of Adelaide, my principal supervisor, for his precious time to support, guide and assist my thesis writing.

Mr. Peter Chaplin, PMB Defence Engineer, my ex-manager and external supervisor, who has encouraged me to complete my Master Degree, and for his ideas and support to build test equipment to conduct this research.

Mr. Brenton Swansson, my current manager, who allowed me to conduct this research in the Laboratory and during work hours.

Ms. Rosalie Louey, PMB Defence Engineer, my current work colleague at PMB and Mr. Rocky Caruso, Exide Technologies, my ex-work colleague at Exide for their technical review of my thesis.

I would like to dedicate this thesis to my parents, wife (Jasmine) and sons (Jamie & Jordan) for their endless love and support.

I hope the results of my thesis would provide some contribution to PMB Defence and to society.

Table of Contents

List of Figures

List of Tables

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
H_2	hydrogen gas
H_2O	water
H_2SO_4	sulfuric acid
KCl	potassium chloride
O_2	oxygen
Pb	lead
Pb_3O_4	red lead powder
PbO	lead oxide
PbO_2	lead dioxide
$PbSO_4$	lead sulfate
Sb	antimony
Sn	tin