

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**Towards
a Comprehensive Model for
the Positive Electrode System of
a Lead-Acid Traction Cell**

A thesis presented
in partial fulfilment of the requirements
for the degree of
Doctor of Philosophy
in Production Technology at
Massey University

Ross Richard Nilson

1989



Massey University Library

Thesis Copyright Form

Title of thesis: Towards a Comprehensive Model for the
Positive Electrode System of a Lead-Acid Traction Cell.

(1) (a) I give permission for my thesis to be made available to readers in the Massey University Library under conditions determined by the Librarian.

(b) I do not wish my thesis to be made available to readers without my written consent for _____ months.

(2) (a) I agree that my thesis, or a copy, may be sent to another institution under conditions determined by the Librarian.

(b) I do not wish my thesis, or a copy, to be sent to another institution without my written consent for _____ months.

(3) (a) I agree that my thesis may be copied for Library use.

(b) I do not wish my thesis to be copied for Library use for _____ months.

Signed R. Nilsson

Date 19/12/89

The copyright of this thesis belongs to the author. Readers must sign their name in the space below to show that they recognise this. They are asked to add their permanent address.

NAME AND ADDRESS

DATE

Massey University Library

Thesis Copyright Form

Title of thesis: Towards a Comprehensive Model for the
Positive Electrode System of a Lead-Acid Traction Cell.

(1) (a) I give permission for my thesis to be made available to readers in the Massey University Library under conditions determined by the Librarian.

(b) I do not wish my thesis to be made available to readers without my written consent for _____ months.

(2) (a) I agree that my thesis, or a copy, may be sent to another institution under conditions determined by the Librarian.

(b) I do not wish my thesis, or a copy, to be sent to another institution without my written consent for _____ months.

(3) (a) I agree that my thesis may be copied for Library use.

(b) I do not wish my thesis to be copied for Library use for _____ months.

Signed R Nilsson

Date 19/12/89

The copyright of this thesis belongs to the author. Readers must sign their name in the space below to show that they recognise this. They are asked to add their permanent address.

NAME AND ADDRESS

DATE

Abstract

This thesis develops a detailed model for the positive electrode system of an industrial lead-acid traction cell. This is referred to as the VIAM model since it relates the positive electrode voltage (V) and cell current (I) to internal distributions of current, potential, acid concentration and active mass (AM). The model can simulate both discharge and charge for a wide range of practical currents. The model takes account of microstructure, macrostructure and non-reactive structure in the positive active mass (AM). It also takes account of other cell components that affect the supply of acid to the positive electrode. The model has direct application to fundamental cell design (for example AM development) and cell systems design (for example cell charger design).

The model is based on established experimental studies, theories of electrochemical interface reactions and theories of ionic transport in electrolyte solution. From this base, three elemental models and an aggregate model are developed. The elemental models represent details of the microstructure of the positive electrode AM. The aggregate model represents the electrolyte mass (acid) and charge transport system within the positive electrode and other cell components. The combination of the elemental and aggregate models make up the VIAM model. The performance of the VIAM model (and underlying models) is assessed by comparing model results with findings from experimental studies in the literature. In addition, experiments undertaken as part of this work are used to test the model. The model and experimental results are in close agreement.

Acknowledgements

I would like to thank Dr R. I. Chaplin, Professor W. Monteith and Professor R. M. Hodgson for the encouragement and constructive criticism they have offered throughout the course of this work.

Neville Manson, Technical Manager of Chloride Batteries New Zealand Limited, kindly provided technical details for the cell used in experiments performed in this work.

My thanks also to my wife, Mary, who not only managed two very active children, Jonathan and Elissa, without help for many evenings during the preparation of this thesis, but also had enough energy left to proof-read the text.

Contents

Abstract	ii
Acknowledgments	iii
Contents	iv
List of Figures	xi
List of Tables	xv
Units and Symbols	xvi
Chapter 1: Introduction	1
Chapter 2: Lead-acid Traction Cells and Systems	5
2.1 Lead-acid Traction Cells	6
2.2 Cell Service Life	8
2.2.1 The Influence of the Vehicle	9
2.2.2 The Influence of the Charger Unit	10
2.2.3 Life Reducing Processes in Perspective	13
2.3 Cell Centred Approaches to Improving Service Life	14
2.3.1 Fundamental Studies	14
2.3.2 Technological Improvements	18
2.3.3 Expectations from Cell Centred Work	19
2.4 A Complementary Approach to Improving Cell Life	19
2.5 Developing a Cell Life Prolonging Charger	21
2.6 A Model for the Positive Electrode System	23

Chapter 3: Foundations for a Positive Electrode Model	25
3.1 The Charge and Discharge Mechanism	26
3.1.1 A Description of the Charge and Discharge Mechanism	26
3.1.2 Conclusions Regarding the Charge and Discharge Mechanism	29
3.2 The Mechanical Structure of the AM	30
3.2.1 A Description of the Mechanical Structure of the AM	30
3.2.2 Conclusions Regarding the AM Mechanical Structure	35
3.3 The Electrochemical Reaction	36
3.3.1 The Equilibrium Potential	37
3.3.2 The Current/Low Overpotential Characteristic	38
3.3.3 The Current/High Overpotential Characteristic	40
3.3.4 Conclusions Regarding the Electrochemical Reaction	45
3.4 Transport in Solution	46
3.4.1 Mass Flux Density	47
3.4.2 Electroneutrality	48
3.4.3 Charge Flux Density	49
3.4.4 An Alternative Form for Mass Flux Equations	50
3.4.5 Concentration Changes with Time	51
3.4.6 Conclusions Regarding Transport in Solution	52
3.5 Gas Evolution in the Electrode and Cell	52
3.5.1 Current and the Gas Evolving Reaction	53
3.5.2 Electrolyte Mass Transport and Gas Evolution	54
3.5.3 Electrolyte Resistivity and Gas Evolution	54
3.5.4 Surface Masking and Gas Evolution	55
3.5.5 Conclusions Regarding Gas Evolution	55

3.6 Common Models for Porous Electrodes	56
3.6.1 The Single Pore Model	56
3.6.2 The Macrohomogeneous Model	58
3.6.3 Other Models of Interest	62
3.6.4 Conclusions Regarding Porous Electrode Models	62
3.7 Voltage, Current and AM Experimental Data	63
3.7.1 Electrode Voltage and Current	64
3.7.2 Electrode AM Distribution	68
3.7.3 Conclusions Regarding Experimental Data	70
3.8 Development Areas for a Positive Electrode Model	71
Chapter 4: Three Elemental Models for the Positive Electrode	73
4.1 An Elemental Discharge Capacity Model	75
4.1.1 The Microstructure: A Discharge Limiting Factor	75
4.1.2 Local Discharge Capacity Formulations	76
4.1.3 Charge State Formulations	78
4.2 An Elemental Discharge Surface Area Model	79
4.2.1 A Qualitative Description of the Discharge	79
4.2.2 Discharge Surface Area Formulations	81
4.3 An Elemental Charge Surface Area Model	82
4.3.1 A Qualitative Description of the Charge	84
4.3.2 A Simple Geometric Model at Full Discharge	85
4.3.3 PbSO_4 Surface Area Formulations	87
4.3.4 Actual PbO_2 Surface Area Formulations	88
4.3.5 Effective PbO_2 Surface Area Formulations	96
4.3.6 The Elemental Charge Surface Area Model: A Practical Approach	98

Chapter 5: An Aggregate Model for the Positive Electrode	106
5.1 The Aggregate Model	107
5.1.1 Transport System Parts	108
5.1.2 A Minimum Representation of the Acid Transport System	110
5.1.3 An Aggregate Model for the Acid Transport System	110
5.2 Physical Dimensions of the Aggregate Model	113
5.2.1 The m-channel Dimensions	113
5.2.2 The μ -channel Dimensions	114
5.2.3 The h-channel Dimensions	118
5.2.4 The s-channel Dimensions	119
5.2.5 The n-channel Dimensions	120
5.2.6 The r-channel Dimensions	121
5.3 Aggregate Model Electrical Formulations	123
5.3.1 The h-channel Equivalent Circuit	125
5.3.2 The m-channel Equivalent Circuit	127
5.3.3 The μ -channel Equivalent Circuit	128
5.3.4 The Complete Equivalent Circuit	132
5.3.5 Supplementary Formulations for the s-channel and n-channel	133
5.4 Aggregate model Acid Transport Formulations	135
5.4.1 The General Transport, Boundary Condition and Initial Condition Equations	135
5.4.2 Acid Transport in the μ -channels	137
5.4.3 Acid Transport in the m-channel	140
5.4.4 Acid Transport in the h-channel	141
5.4.5 Acid Transport in the r-channel	142
5.4.6 Acid Transport in the n-channel	144
5.4.7 Acid Transport in the s-channel	145

5.5 Operating the Aggregate Model: A Practical Approach	147
5.5.1 Discrete Representations for Time and Space	148
5.5.2 A Practical Equation Set and Solution Procedure	148
5.5.3 Discrete Electrical Equations	150
5.5.4 Computing the Electrical Parameter Values	152
5.5.5 Discrete Acid Transport Equations	155
5.5.6 Computing the Concentration Values from the Transport Equations	165
5.5.7 Discrete Equations for Structural Change	168
5.5.8 Computing the Structural Parameter Values	169
5.5.9 The Over-all Computational Procedure	170
Chapter 6: Industrial Traction Cell Experiments	171
6.1 The Experimental Equipment	172
6.1.1 Equipment Overview	172
6.1.2 The Data Acquisition System	174
6.1.3 The Purpose Built Hardware	177
6.2 The Cell Under Test	182
6.2.1 General Specification	182
6.2.2 Physical Construction Details	182
6.2.3 Grid and Paste Composition Details	184
6.3 Experimental Procedure and Schedule	187
6.3.1 Discharge/Charge Cycle Procedures	187
6.3.2 The Experimental Schedule	188
Chapter 7: Results and Discussion	189
7.1 The Elemental Models	190
7.1.1 The Discharge Capacity Model Results	190
7.1.2 The Discharge Capacity Model: a Discussion	192
7.1.3 The Discharge Surface Area Model Results	194
7.1.4 The Discharge Surface Model: a Discussion	195
7.1.5 The Charge Surface Area Model Results	196
7.1.6 The Charge Surface Area Model: a Discussion	206

7.2 The Aggregate Model	210
7.2.1 Aggregate Model Dimensions	210
7.2.2 Aggregate Model Dimensions: a Discussion	213
7.2.3 Functions for the Aggregate Model	214
7.3 The VIAM Model	215
7.3.1 VIAM Model Results for a Standard Case	216
7.3.2 Other VIAM Model Results	225
7.3.3 The VIAM Model μ -channel Component	241
7.3.4 The VIAM Model: a Discussion	241
7.4 Experimental Results	249
7.4.1 Calculations Performed on the Raw Data	249
7.4.2 Presentation of the Experimental Results	255
7.4.3 Experimental Results for a Standard Case	256
7.4.4 Other Experimental Results	259
7.4.5 Experimental Results: a Discussion	266
7.5 Comparing VIAM Model and Experimental Results	268
7.5.1 Acid Diffusion and Exchange Currents for for the VIAM Model	268
7.5.2 The VIAM Model and Experimental Results	269
Chapter 8: Conclusion	277
8.1 The Contribution of this Work	277
8.1.1 A New Positive Electrode Model	277
8.1.2 Model Performance	278
8.1.3 Model Application	280
8.2 Extensions to the Model	281
8.2.1 Exchange Reaction Representation	281
8.2.2 Cell Gassing	281
8.2.3 A Two Dimensional Plate	282
8.2.4 Cell Temperature	282

Appendix 1: The Elemental Charge Surface Area Model	
Program Listing	283
Appendix 2: The Aggregate Model Program Listing	288
Appendix 3: Functions for Various Models	304
A3.1 Effective Charge Surface Area Functions	304
A3.2 The Lead Dioxide Electrode Equilibrium Potential	304
A3.3 The Electrolyte Resistivity	305
A3.4 The Acid Diffusion Coefficient	305
A3.5 The Lead Dioxide Electrode Exchange Current	306
References	308

List of Figures

Figure

1.1 The VIAM Model and Underlying Models . . .	3
2.1 Cell Energy and Replacement Cost per Charge Cycle	8
2.2 Traction Cell Cycle Life and Discharge Depth .	9
2.3 Positive Grid Corrosion and Polarisation Effects	16
2.4 Development of a Life Prolonging Charger . . .	21
3.1 Pore Volume and Surface Area Distribution . . .	31
3.2 Micrographs of Positive Active Mass	32
3.3 Pore Volume Distribution and Charge State . . .	33
3.4 Experimental Surface Area and Charge State . . .	34
3.5 Cathodic Tafel Plots for Two Lead Dioxide Electrodes	44
3.6 Dissociation of Sulphuric Acid	46
3.7 The Single Pore Model Equivalent Circuit . . .	56
3.8 Macrohomogeneous Model Discharge Voltage Predictions	61
3.9 Experimental Cell Polarisation Components . . .	65
3.10 Experimental Charge Voltage and Discharge Rate	66
3.11 Experimental Charge Voltage and Discharge Depth	67
3.12 Experimental AM Distribution in Positive Plate	69
4.1 A Representation of the Discharge Process . . .	81
4.2 The Discharge Surface Area Model	82
4.3 A Representation of the Charge Process	84
4.4 A Geometric Model of the Discharged AM	85
4.5 A Rectangular System for Lead Dioxide Growth . . .	89
4.6 An Elemental Volume for the Pb^{2+} Mass Balance . . .	90
4.7 The Lead Dioxide Lobe Surface Area	92
4.8 Calculation of Charge Surface Area	105

Figure

5.1	Components of the Acid Transport System	109
5.2	The Aggregate Model Components	112
5.3	μ -Channel Arrangement Around the m-Channel	116
5.4	The m-Channel Equivalent Circuit	127
5.5	The μ -Channel Equivalent Circuit	129
5.6	The Aggregate Model Equivalent Circuit	133
5.7	Calculation of Electrical Parameters	154
5.8	Boundary between Channels on Same Axis	158
5.9	The m-Channel/ μ -Channel Boundary	161
5.10	Calculation of Transport Parameters	168
5.11	Over-all Calculation Procedure	169
6.1	Block Diagram of Experimental Equipment	173
6.2	Discharge/Charge Cycle Algorithm	174
6.3	Programmable Voltage Source Schematic	177
6.4	Measurement Interface Circuits	178
6.5	Temperature Controller Schematic	180
6.6	The Purpose Built Hardware	181
6.7	Cell Grid and Separator Components	183
7.1	Possible Distribution of Discharge AM in Plate	191
7.2	The Discharge Surface Area Model Approximation	195
7.3	Charge Surface Area Development	198
7.4	Lobe Profiles at Various Charge States	198
7.5	Charge Surface Area for Various Currents	201
7.6	Lobe Profiles for Various Currents	201
7.7	Charge Surface Area for Various Acid Concentrations	202
7.8	Lobe Profiles for Various Acid Concentrations	202
7.9	Charge Surface Area for Various Geometric Constants	204
7.10	Lobe Profiles for Various Geometric Constants	204
7.11	Model and Fitted Effective PbO_2 Charge Surface Area	206
7.12	Model and Experimental Charge Surface Area	209
7.13	Discharge Voltage for 20 Ampere Full Discharge	218

Figure

7.14 Rest and Charge Voltage for 20 Ampere Full Discharge	218
7.15 Discharged Plate AM for 20 Ampere Full Discharge	219
7.16 Plate Acid for 20 Ampere Full Discharge	219
7.17 Plate Current for 20 Ampere Full Discharge	220
7.18 Plate Solution Potential for 20 Ampere Full Discharge	220
7.19 Adjacent Acid for 20 Ampere Full Discharge	221
7.20 Reservoir Acid for 20 Ampere Full Discharge	221
7.21 Discharge Voltage for 3.5 Ampere Full Discharge	226
7.22 Rest and Charge Voltage for 3.5 Ampere Full Discharge	226
7.23 Discharged Plate AM for 3.5 Ampere Full Discharge	227
7.24 Plate Acid for 3.5 Ampere Full Discharge	227
7.25 Discharge Voltage for 140 Ampere Full Discharge	230
7.26 Rest and Charge Voltage for 140 Ampere Full Discharge	230
7.27 Discharged Plate AM for 140 Ampere Full Discharge	231
7.28 Plate Acid for 140 Ampere Full Discharge	231
7.29 Discharge Voltage for More Tortuous AM	233
7.30 Rest and Charge Voltage for More Tortuous AM	233
7.31 Discharged Plate AM for More Tortuous AM	234
7.32 Plate Acid for More Tortuous AM	234
7.33 Discharge Voltage with Non-participating AM	236
7.34 Rest and Charge Voltage with Non-participating AM	236
7.35 Discharged Plate AM with Non-participating AM	237
7.36 Plate Acid with Non-participating AM	237
7.37 Discharge Voltage for Increased Exchange Current	239
7.38 Rest and Charge Voltage for Increased Exchange Current	239
7.39 Discharged Plate AM for Increased Exchange Current	240
7.40 Plate Acid for Increased Exchange Current	240
7.41 Experimental and Model Discharge Voltage	244
7.42 Experimental and Model Charge Voltage	245
7.43 Experimental and Model Discharged Plate AM	247

Figure

7.44	Experimental and Model Cell Life	248
7.45	Potential Differences in Cell Under Test	250
7.46	AD100R20 Cell Voltage	257
7.47	AD100R20 Electrode Voltage Estimate	257
7.48	AD100R20 Reservoir Acid Concentration	258
7.49	AD100R10-R20 Cell Discharge Voltage	260
7.50	AD100R10-R20 Electrode Discharge Voltage	260
7.51	AD050R05-R40 Cell Discharge Voltage	261
7.52	AD050R05-R40 Electrode Discharge Voltage	261
7.53	AD010R05-R40 Cell Discharge Voltage	262
7.54	AD010R05-R40 Electrode Discharge Voltage	262
7.55	AD100R10-R20 Cell Rest and Charge Voltage	263
7.56	AD100R10-R20 Electrode Rest and Charge Voltage	263
7.57	AD050R05-R40 Cell Rest and Charge Voltage	264
7.58	AD050R05-R40 Electrode Rest and Charge Voltage	264
7.59	AD010R05-R40 Cell Rest and Charge Voltage	265
7.60	AD010R05-R40 Electrode Rest and Charge Voltage	265
7.61	VIAM model and AD100R20 Electrode Voltage	270
7.62	VIAM model and AD100R10 Electrode Voltage	270
7.63	VIAM model and AD050R40 Electrode Voltage	271
7.64	VIAM model and AD050R20 Electrode Voltage	271
7.65	VIAM model and AD050R10 Electrode Voltage	272
7.66	VIAM model and AD050R05 Electrode Voltage	272
7.67	VIAM model and AD010R40 Electrode Voltage	273
7.68	VIAM model and AD010R20 Electrode Voltage	273
7.69	VIAM model and AD010R10 Electrode Voltage	274
7.70	VIAM model and AD010R05 Electrode Voltage	274

List of Tables

Table

2.1 Some Features of Traction and SLI Cells	7
2.2 Effect of Charge on SLI Cell Life	20
3.1 Experimental Current/Overpotential Parameters	43
6.1 Cell Dimensions	184
6.2 Comparison of AM Production Processes	186
6.3 Experimental Schedule	188
7.1 Some Aggregate model Parameters	210
7.2 Remaining Aggregate Model Parameters	212
7.3 Aggregate Model Dimensions	212

Units and Symbols

a) Units.

Normal SI units (Chiswell and Grigg (1971)) are used throughout this text with the following additions.

i) Hour(s) (abbreviated to hr(s)) is used as a measure of time (3600 s).

ii) Ampere hour(s) (abbreviated to Ahr(s)) is used as a measure of electrical charge (3600 A.s).

iii) Watt hour(s) (abbreviated to Whr(s)) is used as a measure of energy (3600 W.s).

iv) The gram (abbreviated to g) is used as a measure of mass (1×10^{-3} kg).

These additions are consistent with common practices in the battery industry.

b) Symbols for units.

Normal SI unit symbols (Chiswell and Grigg (1971)) are used throughout this text with the following additions.

i) Hr(s) for hour(s).

ii) Ahr(s) for Ampere hour(s).

iii) Whr(s) for watt hour(s).

iv) g for the gram.

v) v for the volt.

c) Symbols for variables.

Symbols for variables are fully defined in the body of text where they are first used.

d) Symbols for experiment designations.

An example designation for the experiments performed in this work is AD100R20. This should be interpreted as follows.

i) The first character (A) is the cell label that defines the cell involved (here cell A).

ii) The following four characters (D100) define the depth of discharge (here 100 Ahrs).

iii) The last three characters (R20) define the rate of discharge (here 20 A).