



VALVE-REGULATED LEAD-ACID BATTERIES

D. A. J. Rand

Valve-regulated Lead–Acid Batteries

This Page Intentionally Left Blank

Valve-regulated Lead–Acid Batteries

Editors

D.A.J. Rand

CSIRO Energy Technology
Victoria, Australia

P.T. Moseley

International Lead Zinc Research Organisation Inc.
North Carolina, USA

J. Garche

Ulm, Germany

C.D. Parker

North Carolina, USA



2004

ELSEVIER

Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

ELSEVIER B.V.
Sara Burgerhartstraat 25
P.O. Box 211
1000 AE Amsterdam
The Netherlands

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego
CA 92101-4495
USA

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington,
Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London
WC1X 8RR
UK

© 2004 Elsevier B.V. All rights reserved.

This work is protected under copyright by Elsevier B.V., and the following terms and conditions apply to its use:

Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: permissions@elsevier.com. Requests may also be completed on-line via the Elsevier homepage (<http://www.elsevier.com/locate/permissions>).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2004

Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

British Library Cataloguing in Publication Data

Valve-regulated lead-acid batteries

1. Lead-acid batteries

I. Rand, D. A. J. (David Anthony James), 1942-
621.3'1242

ISBN: 0-444-50746-9

Ⓢ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).
Printed in The Netherlands.

Preface

For over a hundred years from its conception, the lead–acid cell was normally operated with unrestricted access between the surface of its electrolyte and the external atmosphere so that, during periods of overcharge, hydrogen and oxygen were lost from the cell via electrolysis. As a result, periodic additions of distilled water were necessary. Since about 1970, an alternative to the traditional ‘flooded’ cell has been available — one that avoids the need for water maintenance. Moreover, acid is immobilized in the new design and this endows the cell with the additional advantages of being ‘spill-proof’ and able to operate in any orientation (upright, on its side, or even upside down).

The change to the so-called ‘valve-regulated lead–acid’ (VRLA) technology has not, however, been accomplished without some difficulty. Experience has demonstrated forcibly the fundamental differences between the two systems, and the lead–acid battery manufacturing industry has faced major challenges in investing the VRLA version with a performance to match that of its flooded predecessor. Nevertheless, research into understanding the electrochemistry, producing improved cell components and optimizing charge strategies has resulted in VRLA batteries becoming well-established and reliable devices. Operators now take advantage of the particular properties of these batteries for the storage of electrical energy in a wide variety of stationary applications.

Much of the recent advancement of VRLA technology has been achieved through a co-operative research effort under the auspices of the Advanced Lead-Acid Battery Consortium (ALABC). The main effort has been directed towards the development of VRLA battery systems for new-generation road transportation — electric and hybrid electric vehicles — that will reduce fuel consumption and lower emissions. The progress gained in this endeavour will ultimately also benefit the enormously important markets in telecommunications and remote-area power supplies.

This volume presents a detailed account of recent advances in the science and technology of VRLA batteries. The expert contributors are from organizations which have either been members of, or contractors to, the ALABC. In editing the contributions, we have aimed to unify the style of the volume as far as possible, but have allowed a little overlap between those chapters where there is a natural interaction between topics. It is hoped that this work will constitute a sound exposition of the present status of VRLA batteries, and will provide a resource that will enable technologists to deliver products with performances that surpass the requirements of the major markets.

We wish to express our special appreciation of the dedication and expert skills of Ms. Rita Spiteri (CSIRO) for producing the complete text for publication and redrafting most of the illustrations.

D.A.J. Rand	J. Garche
P.T. Moseley	C.D. Parker

This Page Intentionally Left Blank

List of Contributors

W. Böhnstedt
Daramic, Inc.
Erlengang 31
D-22844 Norderstedt, Germany
E-mail: WBohnstedt@Daramic.com

C.J. Boreiko
International Lead Zinc Research
Organization, Inc.
PO Box 12036
Research Triangle Park
NC 27709-2036, USA
E-mail: cboreiko@ilzro.org

R.D. Brost
Ford Motor Company
Sustainable Mobility Technologies
15050 Commerce Drive North
Dearborn, MI 48120, USA
E-mail: rbrost@ford.com

K.R. Bullock
980 Clover Court
Blue Bell, PA 19422, USA
E-mail: coolohm@earthlink.net

A. Cooper
Lead Development Association
International
42 Weymouth Street
London, W1G 6NP, UK
E-mail: ACatCorfe@aol.com

T.C. Dayton
Wilson Greatbatch Technologies, Inc.
10,000 Wehrle Drive
Clarence, NY 14031, USA
E-mail: tdayton@greatbatch.com

J. Garche
Center for Solar Energy
and Hydrogen Research (ZSW)
Electrochemical Energy Storage
and Energy Conversion Division
Baden-Württemberg
Helmholtzstr. 8
D-89081 Ulm, Germany
E-mail: Jugarche@aol.com
juergen.garche@zsw-bw.de

K. Ihmels
Daramic, Inc.
Erlengang 31
D-22844 Norderstedt, Germany
E-mail: KIhmels@Daramic.com

A. Jossen
Center for Solar Energy
and Hydrogen Research (ZSW)
Electrochemical Energy Storage
and Energy Conversion Division
Baden-Württemberg
Helmholtzstr. 8
D-89081 Ulm, Germany
E-mail: andreas.jossen@zsw-bw.de

L.T. Lam
CSIRO Energy Technology
Novel Battery Technologies Group
Bayview Avenue
Clayton South
Victoria 3169, Australia
E-mail: Lan.Lam@csiro.au

E. Meissner
VARTA Automotive
Am Leineufer 51
30419 Hannover, Germany
E-mail: eberhard.meissner@jci.com

P.T. Moseley
International Lead Zinc
Research Organization, Inc.
2525 Meridian Parkway
Suite 100
Durham, NC 27713, USA
E-mail: pmoseley@ilzro.org

R.F. Nelson
Recombination Technologies
909 Santa Fe Drive
Denver, CO 80204, USA
E-mail: Nelson909SantaFe@aol.com

R.H. Newnham
CSIRO Energy Technology
Novel Battery Technologies Group
Bayview Avenue
Clayton South
Victoria 3169, Australia
E-mail: Russell.Newnham@csiro.au

C.D. Parker
International Lead Zinc Research
Organization, Inc.
PO Box 12036
Research Triangle Park
NC 27709-2036, USA
E-mail: cparker@ilzro.org

D. Pavlov
Central Laboratory of Electrochemical
Power Sources
Bulgarian Academy of Sciences
Acad. G. Bonchev Str., Bl. 10
Sofia 1113, Bulgaria
E-mail: dpavlov@mbox.cit.bg

K. Peters
Battery Design & Manufacturing Services
Glen Bank
Broadoak Park
Worsley
Manchester M28 2GG, UK
E-mail: PetersGlenbank@aol.com

R.D. Prengaman
RSR Technologies, Inc.
2777 Stemmons Freeway
Suite 1800
Dallas, TX 75207, USA
E-mail: rdprengaman@rsrtechnologies.com

D.A.J. Rand
CSIRO Energy Technology
Bayview Avenue
Clayton South
Victoria 3169, Australia
E-mail: David.Rand@csiro.au

G. Richter
VARTA Automotive
Am Leineufer 51
30419 Hannover, Germany
E-mail: gerolf.richter@jci.com

M.W. Stevenson
Pasminco
Level 7, Royal Domain Centre
380 St. Kilda Road
Melbourne
Victoria 3001, Australia
E-mail: StevensM@Pasminco.com.au

R. Wagner
EXIDE Technologies
Network Power R&D Centre
D-63654 Büdingen, Germany
E-mail: rainer.wagner@exide.de

M.J. Weighall
12 Low Stobhill
Morpeth
Northumberland, NE61 2SG, UK
E-mail: mjweighall@battery1.demon.co.uk

B. Wilson
International Lead Management
Center, Inc.
P.O. Box 14189
Research Triangle Park
NC 27709-4189, USA
E-mail: bwilson@ilmc.org

Contents

Preface	v
List of Contributors	vii
Abbreviations, Symbols and Units used Repeatedly in text	xix

Chapter 1

The Valve-regulated Battery — A Paradigm Shift in Lead–Acid Technology	1
1.1. Lead–Acid Batteries — A Key Technology for Energy Sustainability	1
1.2. The Lead–Acid Battery	2
1.3. The Valve-regulated Battery	7
1.4. Heat Management in Lead–Acid Batteries	10
1.4.1. Heat generation	10
1.4.2. Heat dissipation	11
1.5. The Challenges Ahead	12
References	14

Chapter 2

Lead Alloys for Valve-regulated Lead–Acid Batteries	15
2.1. Antimony-free Grid Alloys	15
2.2. Pure-lead Positive Grids	15
2.3. Lead–Calcium Alloys	16
2.3.1. Hardening mechanism in lead–calcium alloys	17
2.4. Tin Additions to Pure Lead and Lead–Calcium Alloys	20
2.5. Lead–Calcium–Tin Alloys	21
2.5.1. Grain structure	21
2.5.2. Mechanical properties of cast lead–calcium–tin alloys	22
2.5.3. Aluminium addition	24
2.5.4. Corrosion of lead–calcium–tin alloys	24
2.5.5. Tin effects on conductivity of battery grids	25
2.5.6. Silver additions to lead–calcium–tin alloys	28
2.6. Lead–Antimony–Cadmium Alloys	32
References	32

Chapter 3

Formation of Lead–Acid Batteries and Structure of Positive and Negative Active Masses	37
3.1. Introduction	37
3.1.1. Manufacture of lead–acid battery plates	37
3.1.2. Survey of soaking and formation phenomena	40
3.2. Soaking of Plates	42
3.2.1. Filling VRLA cells with H ₂ SO ₄ solution	42

3.2.2.	Chemical zonal processes during soaking	44
3.2.3.	Soaking of 3BS-cured pastes	46
3.2.4.	Soaking of 4BS-cured pastes	52
3.3.	Formation of Positive Plates	54
3.3.1.	Thermodynamics of formation processes	54
3.3.2.	Reactions during formation of PAM from 3BS-cured pastes	55
3.3.3.	Zonal processes during formation of PAM from 3BS-cured pastes	59
3.3.4.	β -PbO ₂ : α -PbO ₂ ratio and its effect on capacity of positive plates	62
3.3.5.	Structure of PAM	64
3.3.6.	Gel-crystal forms of PbO ₂ particles	66
3.3.7.	Mechanism of formation of PbO ₂ particles	70
3.3.8.	Formation of pore system in PAM and its functions	71
3.3.9.	Influence of basic lead sulfates on cycle-life of positive plates	76
3.3.10.	Formation of plates prepared with 4BS-cured pastes	79
3.3.11.	Influence of current-collector surface on formation of PbSO ₄ crystals at grid-PAM interface	83
3.4.	Formation of Negative Plates	85
3.4.1.	Thermodynamics of formation processes	85
3.4.2.	Reactions during formation of negative plate	86
3.4.3.	Zonal processes	88
3.4.4.	Structure of negative active mass	91
3.4.5.	Evolution of pore structure of plate during formation	94
3.4.6.	Effect of expanders on NAM	96
3.4.7.	Effect of expander structure on battery performance	99
3.5.	Technology of Formation	100
3.5.1.	Technological parameters of formation process	100
3.5.2.	Stages of formation of positive and negative plates	100
3.5.3.	General current (voltage) algorithm for formation of positive plates	103
3.6.	Conclusions	106
	References	107

Chapter 4

Positive-Plate Additives to Enhance Formation and Battery Performance		109
4.1.	Introduction	109
4.2.	Modelling the Effects of Additives	109
4.3.	Non-conductive Additives	111
4.3.1.	Hollow glass microspheres	111
4.3.2.	Carboxymethyl cellulose	112
4.3.3.	Silica gel	113
4.3.4.	Designer additives	113

4.4.	Conductive Additives	114
4.4.1.	Barium plumbate	115
4.4.2.	Titanium oxide	118
4.4.3.	Conductive polymers	119
4.4.4.	SnO ₂	120
4.4.5.	Iron boride	120
4.4.6.	Lead-coated glass wire	120
4.4.7.	Carbon	121
4.4.8.	Lead dioxide	123
4.5.	Chemically Active Additives	124
4.5.1.	Sulfate salts	124
4.5.2.	Phosphates	127
4.5.3.	Bismuth	130
4.5.4.	Polyvinylsulfonic acid and its salts	131
4.6.	Conclusions	131
	References	132

Chapter 5

Negative Plates in Valve-regulated Lead–Acid Batteries 135

5.1.	Introduction	135
5.2.	Basic Electrochemical Characteristics	136
5.3.	Negative-plate Additives	142
5.3.1.	Carbon	144
5.3.2.	Barium sulfate	146
5.3.3.	Organic additives	147
5.4.	Charging Influences	154
5.5.	Use of Internal Catalysts	157
5.6.	Summary	159
	References	160

Chapter 6

The Function of the Separator in the Valve-regulated Lead–Acid Battery 163

6.1.	Introduction	163
6.2.	Characteristics of Absorptive Glass Mat (AGM)	164
6.2.1.	Wetting behaviour of AGM materials	164
6.2.2.	Physical properties of AGM materials	171
6.3.	Gel Batteries	173
6.4.	Separator Properties and Function	174
6.4.1.	Compression characteristics	174
6.4.2.	Oxygen cycle and recombination efficiency	176
6.4.3.	Stratification and drainage	178
6.5.	Future Developments	179
	References	180

Chapter 7

Separator Materials for Valve-regulated Lead–Acid Batteries	183
7.1. Introduction	183
7.2. State-of-the-art Separators	183
7.2.1. Absorptive glass mat (AGM) separators	183
7.2.2. Separators for gel batteries	185
7.3. Development Trends for VRLA Battery Separators	186
7.4. Separator Developments	187
7.4.1. Modified AGM	187
7.4.1.1. AGM — high surface-area	187
7.4.1.2. AGM — high/low surface-area composite	190
7.4.1.3. AGM — membrane sandwich	191
7.4.1.4. AGM — with organic fibres	191
7.4.1.5. Silica-loaded glass mat (SLGM)	193
7.4.1.6. Other AGM modifications	194
7.4.2. Alternative separators	195
7.4.2.1. Synthetic wood-pulp separators (SWP)	195
7.4.2.2. Polymeric microfibre mat	197
7.4.2.3. Staflex	197
7.4.2.4. Acid jellying separator	199
7.4.2.5. Ceramic separator	201
7.4.2.6. Granular silica	203
7.5. Conclusions	203
References	204

Chapter 8

Battery Management	207
8.1. Introduction	207
8.2. Tasks of Battery Management Systems	208
8.3. Designs of Battery Management System	209
8.4. Battery Data Acquisition	210
8.5. Determination of Battery State	212
8.5.1. Battery state-of-charge	213
8.5.2. Battery state-of-health	225
8.6. Electrical Management of Batteries	229
8.6.1. Control of charge	229
8.6.2. Control of discharge	229
8.6.3. Multiple battery systems	231
8.7. Thermal Management of Batteries	233
8.7.1. Air systems	233
8.7.2. Liquid systems	234
8.7.3. Electrical systems	235
8.7.4. Passive cooling systems and isolation	236
8.7.5. Phase-change materials	237

8.7.6.	Other systems	237
8.8.	Storage of Historical Battery Data	237
8.9.	Safety Management of Batteries	238
8.10.	System Communications	238
8.11.	Conclusions	239
	References	239

Chapter 9

Charging Techniques for VRLA Batteries **241**

9.1.	Introduction	241
9.1.1.	Basic charging — chemistry/secondary reactions	242
9.1.2.	Traditional charging methods	245
9.1.2.1.	Constant-voltage charging	245
9.1.2.2.	Constant-current charging	247
9.1.2.3.	Constant voltage–constant current combinations	249
9.1.2.4.	Taper-current charging	251
9.1.2.5.	Pulsed-current charging	253
9.2.	Charging of VRLA Products	254
9.2.1.	The oxygen cycle and saturation effects	254
9.2.2.	Gas transport and oxygen cycle	257
9.2.3.	Overcharge processes	259
9.3.	Existing Charging Methods Applied to VRLA Products	262
9.3.1.	Float charging	262
9.3.2.	Cyclic charging	267
9.3.3.	Fast charging	271
9.3.4.	Charge-termination strategies	272
9.3.5.	Failure modes attributable to charging	274
9.4.	Evolving and Optimized Charging Methods	276
9.4.1.	Optimized approaches to float charging	276
9.4.2.	Optimized approaches to cyclic charging	279
9.4.3.	Partial-state-of-charge cycling — an evolving algorithm	285
9.5.	Summary and Conclusions	288
	References	291

Chapter 10

Battery Energy-Storage Systems for Power-Supply Networks **295**

10.1.	Introduction	295
10.2.	A Historical Perspective	295
10.3.	Energy-Storage Technologies	297
10.3.1.	Lead–acid (and advanced) batteries	301
10.3.2.	Supercapacitors	301
10.3.3.	Flywheels	302
10.3.4.	Superconducting magnetic energy storage	302
10.4.	Energy-storage Applications	302

10.4.1.	Rapid reserve (generation)	304
10.4.2.	Area control and frequency responsive reserve (generation)	304
10.4.3.	Commodity storage (generation)	305
10.4.4.	Transmission system stability (T&D)	305
10.4.5.	Transmission voltage regulation (T&D)	305
10.4.6.	Transmission facility deferral (T&D)	305
10.4.7.	Distribution facility deferral (T&D)	305
10.4.8.	Renewable energy management (customer service)	306
10.4.9.	Customer energy management (customer service)	306
10.4.10.	Power quality and reliability (customer service)	306
10.5.	Battery Energy-storage Systems	306
10.5.1.	Elektrizitätswerk Hammermuehle, Germany	306
10.5.2.	BEWAG AG, Berlin, Germany	308
10.5.3.	Hagen Batterie AG, Soest, Germany	309
10.5.4.	Crescent Electric Membership Corporation, Statesville, NC, USA	309
10.5.5.	Southern California Edison, Chino, CA, USA	310
10.5.6.	Johnson Controls, Inc., Milwaukee, WI, USA	311
10.5.7.	Puerto Rico Electric Power Authority	312
10.5.8.	GNB Technologies, Vernon, CA, USA	313
10.5.9.	Metlakatla, AK, USA	314
10.5.10.	Herne and Bochold, Germany	315
10.5.11.	PQ2000	316
10.6.	Power Conversion	317
10.6.1.	Basic concepts	318
10.6.2.	Switch considerations	321
10.6.3.	Performance issues	321
10.7.	Cost Considerations	322
10.8.	Concluding Remarks	323
	References	325

Chapter 11

Valve-regulated Lead–Acid Batteries in Automotive Applications — A Vehicle Manufacturer’s Perspective		327
11.1.	Introduction	327
11.1.1.	Battery selection process	328
11.1.2.	Sub-system description	334
11.1.3.	Initial design phase	334
11.1.4.	Failure modes and effects analysis	337
11.1.5.	Design validation plan	337
11.1.6.	Future electric loads	337
11.1.7.	Environmental	342
11.1.8.	Cost	343

11.1.9.	Reliability	344
11.1.10.	Safety	346
11.1.11.	Maintenance-free	346
11.1.12.	Weight savings	347
11.2.	VRLA in Automotive Applications	347
11.2.1.	VRLA features of interest to the automotive industry	348
11.2.2.	Continuum of electric drive	351
11.3.	Automotive Applications	353
11.3.1.	12-V automotive	353
	11.3.1.1. Performance requirements	356
	11.3.1.2. Controls and diagnostics for 12-V automotive batteries	360
	11.3.1.3. VRLA as a 12-V automotive battery	361
11.3.2.	42-V automotive	363
	11.3.2.1. General requirements	365
	11.3.2.2. Controls and diagnostics for 42-V automotive batteries	367
	11.3.2.3. VRLA as 42-V automotive battery	368
11.3.3.	Soft hybrids	369
	11.3.3.1. General requirements	370
	11.3.3.2. Controls and diagnostics for soft hybrid batteries	375
	11.3.3.3. VRLA as a soft hybrid battery	376
	11.3.3.4. Low initial cost of VRLA	378
11.3.4.	Parallel-series hybrids	378
	11.3.4.1. General requirements	380
	11.3.4.2. Controls and diagnostics for parallel-series hybrid vehicles	382
	11.3.4.3. VRLA as a parallel-series hybrid battery	383
11.3.5.	Electric vehicles	385
	11.3.5.1. Performance requirements	388
	11.3.5.2. Controls and diagnostics for EVs	391
	11.3.5.3. VRLA as an EV battery	394
11.4.	Conclusions	396
	References	396

Chapter 12

Valve-regulated Lead-Acid Batteries in Automotive Applications — A Battery Manufacturer’s Perspective		397
12.1.	Introduction	397
12.2.	History of Automotive Batteries and Vehicle Electrical Systems	401
12.2.1.	The beginning	401
12.2.2.	Development of vehicle electrical power systems and automotive batteries in 20th century	401

12.2.3.	Expected changes in vehicle electrical systems in next decade and corresponding demands on automotive batteries	407
12.3.	Design, Components, Manufacturing of Automotive Batteries	409
12.3.1.	Components	409
12.3.2.	Special designs/special applications	409
12.3.3.	Plate arrangement — plate stacking and spiral winding	410
12.3.4.	AGM and gel technology in vehicles	413
12.3.5.	VRLA automotive 12-V batteries for standard vehicle electrical systems	414
12.3.6.	36-V VRLA automotive batteries for 42-V PowerNets	415
12.4.	The VRLA Battery in Automotive Applications and its Interaction with the Vehicle	417
12.4.1.	VRLA batteries in present vehicle electric systems	417
12.4.2.	VRLA batteries in vehicles with new components and new operating strategies	420
12.4.3.	State-detection and management of VRLA batteries	426
12.5.	Performance Data	427
12.6.	Outlook	427
	References	430

Chapter 13

Valve-regulated Lead–Acid Batteries for Telecommunications and UPS Applications		435
13.1.	Introduction	435
13.2.	Features of VRLA Technology	436
13.2.1.	Positive-grid corrosion	436
13.2.2.	Improvement of service-life	440
13.3.	Gel Batteries	446
13.4.	AGM Batteries	451
13.5.	Large Batteries for Stationary Applications	455
13.6.	Future Trends in Stand-by Batteries	459
13.6.1.	Continuous plate-processing	459
13.6.2.	Spiral technology	461
13.6.3.	Advanced separators	462
13.7.	Conclusions	462
	References	463

Chapter 14

Remote-area Power-supply (RAPS) Systems and the Valve-regulated Lead-Acid Battery		467
14.1.	The Need for Remote-area Power-supply Systems	467
14.2.	RAPS System Components	467

14.2.1.	Battery bank	468
14.2.2.	Diesel generator	469
14.2.3.	Photovoltaic array	469
14.2.4.	Wind generator	470
14.2.5.	Hydro-generator	470
14.2.6.	Inverter	471
14.2.7.	Control system	472
14.3.	RAPS System Design	472
14.3.1.	Direct-current RAPS systems	473
14.3.2.	Alternating-current RAPS systems	474
14.4.	VRLA Batteries for RAPS Systems	476
14.4.1.	Advantages	476
14.4.2.	Disadvantages	477
14.4.3.	Failure modes	478
	14.4.3.1. Overcharging	479
	14.4.3.2. Undercharging	480
	14.4.3.3. Temperature extremes	481
	14.4.3.4. Deep-cycle operation	482
14.4.4.	Preferred design features	482
	14.4.4.1. Purpose-built batteries	482
	14.4.4.2. Lower-cost batteries	483
14.4.5.	Recent developments	484
14.4.6.	Advanced operating strategies	484
	References	489

Chapter 15

Recovery and Recycling of Lead–Acid Batteries		491
15.1.	Introduction	491
15.2.	Battery Collection and Processing	492
	15.2.1. Battery collection	492
	15.2.2. Battery processing	493
15.3.	Recovery and Refining	496
	15.3.1. Pyrometallurgical methods	496
	15.3.2. Hydrometallurgical methods	503
	15.3.3. Refining and alloying of lead	503
	15.3.3.1. Fine refining	504
	15.3.3.2. Electrolytic refining	507
15.4.	Challenges Facing the Secondary Lead Industry	508
	15.4.1. Processing and recovery	508
	15.4.2. Refining	509
	15.4.3. Silver	509
	15.4.4. Antimony	510
	15.4.5. Catalyst elements	510
	15.4.6. Other elements	511
	References	511

Chapter 16

Environmental Aspects of Recycling Valve-regulated Lead–Acid Batteries	513
16.1. Introduction	513
16.2. Justification for Recycling	514
16.3. Recycling Rates	515
16.4. Collection of Used VRLA Batteries	515
16.5. Transport of Used VRLA Batteries	517
16.6. Recycling Process	519
16.7. Recycling Options	522
16.8. Monitoring and Controlling Emissions	526
16.9. Engineering Control in the Workplace	527
16.10. Process Emission Controls	528
16.11. Emission Testing and Analysis	529
16.12. Biological Monitoring	532
16.13. Respiratory Protection	534
16.14. Employees' Amenities	537
16.14.1. Location	537
16.14.2. Segregation	538
16.14.3. Containment	538
16.15. Effluent Control	539
16.16. International Conventions and Protocols	543
16.16.1. Basel Convention	543
References	547

Chapter 17

The Next Great Challenge for Valve-regulated Lead–Acid Batteries: High-rate Partial-state-of-charge Duty in New-generation Road Vehicles	549
17.1. Future Automobile Electrical Systems	549
17.2. The Challenge of High-rate Partial-state-of-charge (HRPSoC) Duty	550
17.3. Mechanism of Lead Sulfate Accumulation During HRPSoC Duty	554
17.4. Controlling Secondary Reactions During High-rate Charge	559
17.4.1. Trace element control	559
17.4.2. Separator design	559
17.4.3. Carbon inventory	559
17.5. Grid Design for HRPSoC Duty	560
17.6. The Role of Plate Thickness	562
17.7. Concluding Remarks	564
References	565

Subject Index	567
----------------------	------------

ABBREVIATIONS, SYMBOLS AND UNITS USED REPEATEDLY IN TEXT

Abbreviations

a.c.	alternating current
AGM	absorptive glass mat
AGV	automatically guided vehicle
AJS	acid jellying separator
ALABC	Advanced Lead-Acid Battery Consortium
AM	active mass
AMCL	active-mass collecting layer
ANN	artificial neural network
BCI	Battery Council International
BESS	battery energy-storage system
BET	Brunauer, Emmett, Teller method of measuring surface area (<i>J. Am. Chem. Soc.</i> , 60 , (1938) 309)
BJT	bipolar junction transistor
BMM	battery management module
BMS	battery management system
BoP	balance-of-plant
1BS	monobasic lead sulfate, $\text{PbO} \cdot \text{PbSO}_4$
3BS	tribasic lead sulfate, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$
4BS	tetrabasic lead sulfate, $4\text{PbO} \cdot \text{PbSO}_4$
CAES	compressed-air energy storage
CAFE	corporate average fuel economy
CAN	controller area network
CBEMA	Computer and Business Equipment Manufacturers' Association
CC	constant current
CCA	cold-cranking amps
CFMEA	Concept Failure Modes and Effects Analysis
CI	current interrupt
CMC	carboxymethyl cellulose
CoP	Conference of the Parties
COS	cast-on-strap
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSM	copper-stretch-metal
CV	constant voltage

d.c.	direct current
DFMEA	Design Failure Modes and Effects Analysis
DLC	double layer capacitor
DoD	depth-of-discharge
DST	dynamic stress test
DVP	design verification plan — plan to verify component/system design to functional intent
DVPR	design verification plan and report — program/product oriented structured system to determine verification test requirements for a new or modified part, component, or system
ECE	Economic Commission for Europe
ECU	engine control unit
EDI	electronic data interchange — a protocol for the electronic exchange of data and documents
EDS	electrical distribution system
EMC	Electric Membership Corporation
EMI	electromagnetic interference
EN	European Norm. (a standard)
EPA	Environmental Protection Authority
EPRI	Electric Power Research Institute
EOL	end-of-life
EV	electric vehicle
FM	failure mechanism
FMEA	failure modes and effects analysis
FUDS	Federal Urban Drive Schedule
GE	General Electric Company
GTO	gate-turn-off (thyristor)
HEPA	high efficiency particulate air
HEV	hybrid electric vehicle
HMW	high molecular weight
HRPSoC	high-rate partial-state-of-charge
HVAC	high-voltage alternating current
HVDC	high-voltage direct current
HWFET	Highway Fuel Economy Test
IC	intermittent charging
ICE	internal-combustion engine
IEC	International Electrotechnical Commission
IGBT	insulated gate bipolar transistor
IPTV	incidents per thousand vehicles
ISA	integrated starter alternator
ISG	integrated starter generator
ISO	International Standards Organization
IU	current-limited constant voltage (charging)

IUI	current-limited constant voltage (charging) with constant-current finishing step
JIS	Japanese Industrial Standard
JEVs	Japan Electric Vehicle Society
KST	Kochis Stress Test
LMT	Lead Metal Technologies (Mexico)
LMW	low average molecular weight
MCE	mixed cellulose ester
MP&L	Metlakatla Power and Light
MOSFET	metal-oxide-semiconductor field effect transistor
MSDS	material safety data sheet
NAM	negative active mass
NERC	National Energy Reliability Council
NVH	noise, vibration, and harshness — the acoustic and tactile stimuli generated by the vehicle that are perceived by the customer as indicators of product quality
OCV	open-circuit voltage
OCSM	CSM (copper-stretch-metal)-technology battery
OEM	original equipment manufacturer
OSHA	Occupational Safety & Health Administration
PAM	positive active mass
PCL	premature capacity loss
PCM	phase-change material
PCS	power-conditioning system
PFMEA	process failure modes and effects analysis
PG&E	Pacific Gas & Electric
POB	power-optimized battery
PowerNet	vehicle electrical system
PREPA	Puerto Rico Electric Power Authority
PSoC	partial-state-of-charge
PSoR	partial-state-of-recharge
PTFE	polytetrafluoroethene
PV	photovoltaic <i>also:</i> process validation — production validation (PV) — program of engineering tests and evaluations conducted to assure that initial production parts meet the design intent
PVC	polyvinyl chloride
PWM	pulse-width modulation
RAPS	remote-area power supply
RBSM	recombinant-battery separator mat (same as AGM)
RC	reserve capacity
rel. dens	relative density

RFI	radio frequency interference
RFQ	request for quotation
RFV	resistance-free voltage
RIMU	relaxable insufficient mass utilization
RMS	root mean square
rpm	revolutions per minute
SAE	Society of Automotive Engineers
SCE	Southern California Edison
SCR	silicon controlled rectifier
SDG&E	San Diego Gas & Electric
SDS	system design specification
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SLGM	silica-loaded glass mat
SLI	starting, lighting and ignition
SMES	superconducting magnetic energy storage
SNL	Sandia National Laboratory
SoC	state-of-charge
SoH	state-of-health
SPC	statistical process control — the process which uses statistical techniques such as control charts to analyze a process output
SGTP	strap-grid tubular plate
SWP	synthetic wood pulp
T&D	transmission and distribution
TC	taper current
TCLP	toxic characteristic leaching procedure
TGR	things gone right
TGW	things gone wrong
ToCV	top-of-charge voltage
UL	Underwriters Laboratory
ULAB	used lead–acid batteries
UPS	uninterruptible power supply
USDOE	US Department of Energy
VAR	volt-ampere reactive
VC	vehicle controller
VPC	volts per cell
VRLA	valve-regulated lead–acid (battery)
VS-A	Vanisperse A (negative-plate expander)
XRD	X-ray diffraction

Symbols and units — Roman letters

<i>a</i>	activity of species which is usually specified as a subscript (e.g., HSO_4^-)
----------	---

A	ampere
Ah	ampere hour (= 3600 coulombs)
°C	degree Celsius
C	capacity (symbol also used for capacitance)
C_b	heat capacity of materials in battery
$C_p(i)$	heat capacity of component i
C_X/t	discharge rate (current) of a battery, where C is the rated capacity; X is the hour rate; t is the specified discharge time, usually in hours
cm	centimeter
d	interplanar spacing in crystal
D_{H_2}	diffusion constant for hydrogen
D_{O_2}	diffusion constant for oxygen
ΔG	Gibbs free energy of reaction
e^-	electron
E	electrode potential under load
E_a	activation energy
E_M	mixed potential
E^0	standard electrode potential
E_r	reversible electrode potential
F	faraday (96,485 coulombs per mole) <i>also:</i> farad (1 coulomb per volt)
g	gram
GW	gigawatt
h	hour
H	henry (1 volt second per ampere)
ΔH	enthalpy of reaction
Hz	hertz (= 1 cycle per second)
i	current density
I	current
I_{ch}	current on charge
I_{corr}	grid corrosion current
I_d	current on discharge
I_{float}	float current
I_{H_2}	hydrogen evolution current
I_{O_2}	oxygen evolution current
I_{O_2-red}	oxygen reduction current
in	inch
J	joule
kg	kilogram
kJ	kilojoule (= 238.85 calories)
km	kilometer

kPa	kilopascal
kW	kilowatt
kWh	kilowatt hour
l	litre
m	metre
$m(i)$	mass of component i
M	molar
mA	milliampere
mAh	milliampere hour
min	minute
mm	millimeter
MPa	megapascal
mol	mole
mV	millivolt
MV	megavolt
mW	milliwatt
MW	megawatt
mWh	milliwatt hour
MWh	megawatt hour
μm	micrometer
pH	negative value of logarithm of hydrogen ion concentration
Q_g	heat generated
Q_d	heat dissipated
r	Sn:Ca ratio in lead alloys
R	gas constant (8.3145 joules per degree per mole)
s	second
ΔS	entropy of reaction
t	time
T	temperature
U	voltage (see also V)
UTS	ultimate tensile strength
V	volt
ΔV	shift in voltage
V_p	total pore volume
$V_{\mu\text{p}}$	volume of micropores
W	watt
Wh	watt hour
wt. %	percentage by weight
x	distance variable
YS	yield strength

Symbols and units — Greek letters

ε	Stefan-Boltzmann constant
η	overpotential (symbol also used for viscosity)
λ	thermal conductivity
θ	phase angle
ρ	density
σ	emissivity (with respect to an ideal emitter)
Ω	ohm

This Page Intentionally Left Blank

—CHAPTER 1—

THE VALVE-REGULATED BATTERY — A PARADIGM SHIFT IN LEAD-ACID TECHNOLOGY

P.T. Moseley and D.A.J. Rand

1.1. Lead-Acid Batteries — A Key Technology for Energy Sustainability

A ready and affordable supply of energy is essential for maintaining the standard-of-living of the developed world and for markedly improving that of the less-developed countries. Coal, mineral oil, and natural gas (the ‘fossil fuels’), together with uranium (‘nuclear energy’), have long been exploited as major sources of primary energy. The most important, versatile, and useful means of distributing such energy to where it is needed is through conversion to electricity. Unfortunately, the cumulative environmental effects of burning fossil fuels, the profligate consumption of these fuels, and concerns over the safety of nuclear power and radioactive wastes, have placed Planet Earth in jeopardy.

One strategy for safeguarding the future is to move away from the traditional fuels towards so-called ‘renewable’ sources of energy which are of a non-polluting nature and are sustainable. The harnessing of renewable energies — hydro, solar, wind, geothermal, wave, tidal, biomass — presents, however, a further set of technical and economic problems. Unlike fossil and nuclear fuels, which are concentrated sources of energy that can be easily stored and transported, renewable forms of energy are, for the most part, highly dilute and diffuse. Moreover, their supply can be extremely intermittent and unreliable. It is therefore not surprising that, except for hydro-electric power, renewable energy sources have made little contribution to world electricity supplies. In 1999, for example, renewables provided only 1.6% of the energy required for world electricity generation; the remainder came from: coal, 38.1%; hydroelectric power, 17.5%; nuclear power, 17.2%; natural gas, 17.1%; oil, 8.5% [1].

Irrespective of the source, an effective storage system is critical for the efficient use of the energy, and for the good stewardship of its supply. The development of effective and affordable means to store electrical energy for an ever-increasing number of applications of great variety continues to present a major challenge to scientists, technologists, and engineers.

The scale of energy-storage systems ranges from minuscule elements on integrated circuits to pumped hydroelectric reservoirs that store the equivalent of giga watt-hours of electrical energy. The needs of small electrical appliances can be supplied by primary (single-use and discard) batteries, or by a rapidly developing range of

rechargeable types which are principally based on the use of lithium or nickel. To date, however, batteries based on these two metals have failed to become economically viable for larger energy-storage applications. Examples of this category include systems designed to cope with diurnal fluctuations in electricity demand. In small communities remote from a grid supply, electricity generated during the day by photovoltaic ('solar') installations must be stored for use during the hours of darkness. In electricity utility systems, there is often a need to store surplus energy generated during the night for use at peak periods on the following day. When electric power is used for transport, it is often necessary for a vehicle to move free from the source of power and for the electricity to be stored 'in a box'. In most medium- and large-scale energy-storage functions, lead-acid batteries, in one form or another, have been the technology of choice.

Lead-acid batteries are employed in a wide variety of different tasks, each with its own distinctive duty cycle. In internal-combustion engined vehicles, the battery provides a quick pulse of high current for starting and a lower, sustained current for other purposes; the battery remains at a high state-of-charge for most of the time. The same is true of batteries used for back-up power in telecommunications and in other uninterruptible power supplies, although in such service (so-called 'float duty') the battery should seldom be called upon to discharge. Electric vehicle (EV) batteries, on the other hand, are expected to undergo deep discharges and recharges over periods of a few hours repeatedly (so-called 'deep-discharge duty'). In between the extreme cases of float duty and deep discharge, the batteries in hybrid electric vehicles (HEVs) and in storage units for remote-area power supply (RAPS) systems spend most of the time cycling about an intermediate state-of-charge, often near 50% (so-called 'partial-state-of-discharge duty').

In all cases, the battery must be able to provide adequate power for the task in hand. This may be a more severe requirement for batteries in EVs and HEVs than for batteries in solar-based RAPS systems. For mobile applications, the energy-storage capability should be provided with a minimum weight penalty. In essence, the battery should have a high 'specific energy', i.e., a high energy output per unit weight, Wh kg^{-1} . Generally, a high coulombic efficiency (charge out : charge in) is also an asset as this preserves primary energy.

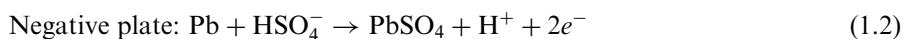
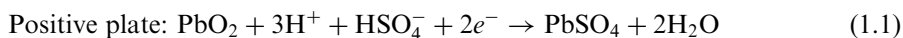
Finally, a *sine qua non* is acceptable cost. The factors to be considered are the initial price of the battery, the operational life of the battery, and the associated maintenance costs. Lead-acid batteries are eminently suitable for medium- and large-scale energy-storage operations because they offer an acceptable combination of performance parameters at a cost which is substantially below that of alternative systems.

1.2. The Lead-Acid Battery

The fundamental elements of the lead-acid battery were set in place over 100 years ago. Gaston Planté [2] was the first to report that a useful discharge current could be drawn from a pair of lead plates that had been immersed in sulfuric acid and subjected to a charging current. Later, Camille Fauré [3] proposed the concept of

the pasted plate. In the subsequent hundred years or so, the principal elements of the battery have not undergone any further radical change. The most commonly employed design has ‘flat plates’. These are prepared by coating pastes of lead oxides and sulfuric acid on to conductive lead or lead-alloy ‘grids’, which act as current-collectors. The plates are then ‘formed’ electrolytically into ‘active’ materials. One alternative cell design uses positive plates in which the active material is contained in tubes, each fitted with a coaxial current-collector. Such ‘tubular plates’ serve to prevent shedding of the material during battery service (*v.i.*). A more recent cell design, aimed at high-power applications, has a single pair of positive and negative plates which are interleaved with microfibre-glass mat separators and wound together in a cylindrical can (the ‘spirally wound’ or ‘jellyroll’ design). Ironically, this arrangement mimics that invented originally by Planté. Schematics of the various plate types are given in Fig. 1.1.

The discharge reactions of the lead–acid cell are as follows:



In both cases, a solid conductor of electrons (semi-conducting lead dioxide, PbO_2 , in the positive plate; metallic lead, Pb , in the negative) reacts with sulfuric acid to form a non-conductive, solid product of lead sulfate, PbSO_4 . Both discharge reactions are accompanied by an increase in volume of the solid phase. The volume increase for the transformation of PbO_2 to PbSO_4 (shown in Fig. 1.2) is 92%, while that for Pb to PbSO_4 is 164%.

The key technical challenge to be met in maximizing battery performance involves facilitating continuity of supply, contact and interaction of reactants. In principal, this requires an adequate supply of acid, solid reactants of high surface-area, maintenance of good contact between the particles of the active material (particularly in positive plates that show a tendency to expand during charge–discharge service, *v.i.*), and minimization of the insulating effects of PbSO_4 .

After each discharge, the above set of optimum conditions is to be restored by charge reactions, which are the reverse of those expressed by eqns. (1.1) and (1.2). In the ideal case, the discharge capacity would be constant during cycling of the cell (or during time on float). For even the most advanced design of commercial battery, however, the practical utilization of the active materials is generally limited to considerably less than 50% when discharge is performed at a rate of five hours, or less. As cycling (or life) proceeds, a number of processes (‘failure mechanisms’) can degrade further this limited performance. Conventional batteries (*i.e.*, those with free electrolyte, so-called ‘flooded’ designs) commonly suffer from one or more of the following five failure mechanisms.

FM1. Positive-plate expansion. This can occur both in the plane of the plate (if the grid is stretched by a growing corrosion layer) and in the direction normal to the plate (through expansion of the active material itself). Repetitive discharge and

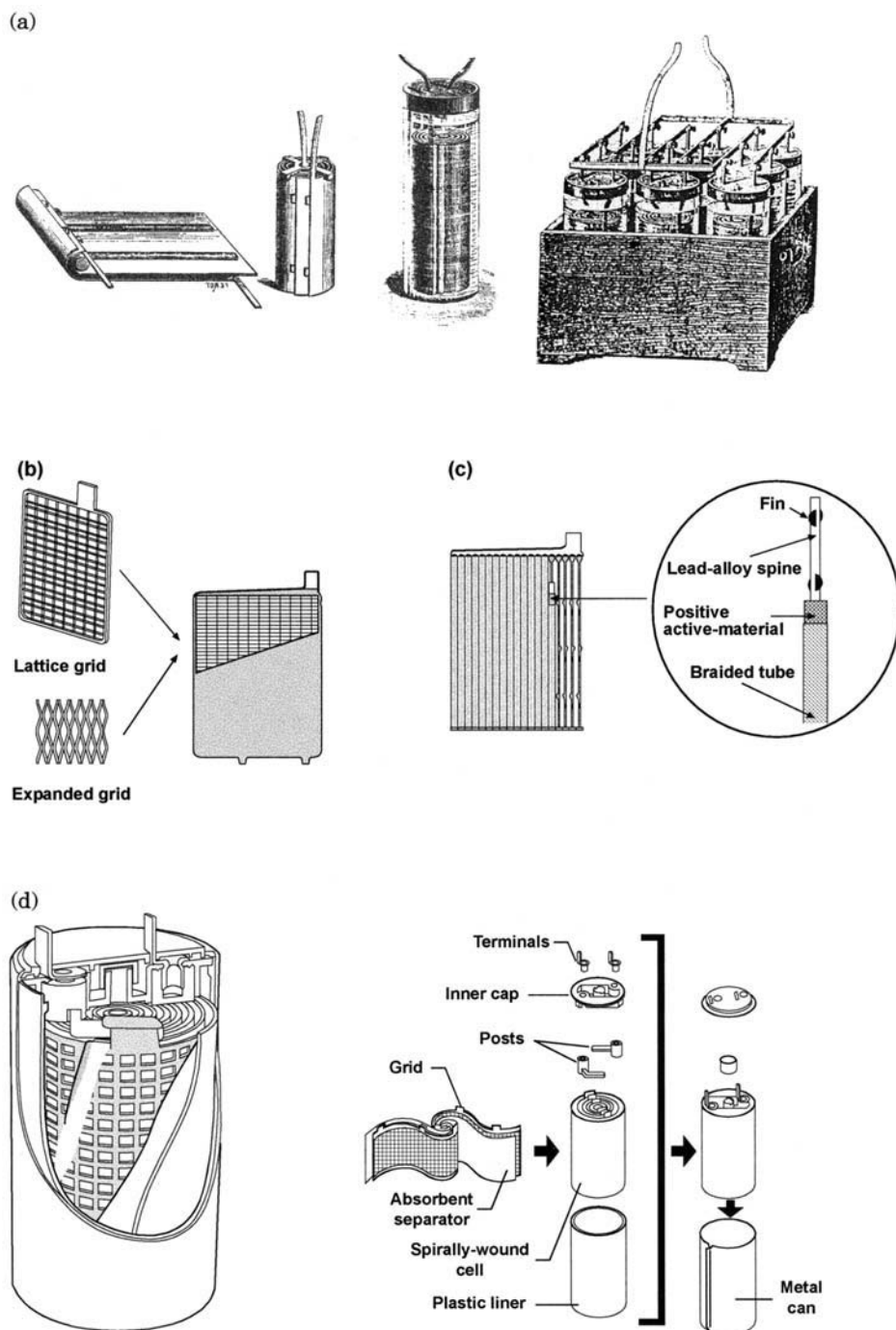


Fig. 1.1. (a) Gaston Planté's cell and battery; (b) flat plate; (c) tubular positive plate; (d) spiral-wound cell.