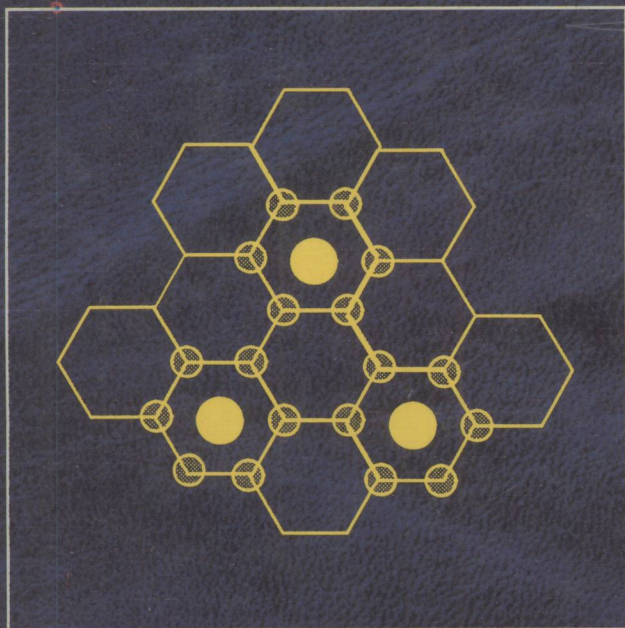


Industrial Chemistry Library, Volume 5

Lithium Batteries

New Materials, Developments and Perspectives

G. Pistoia (Editor)



Elsevier

TM911
L776
E.2

9660012

Industrial Chemistry Library, Volume 5

Lithium Batteries

New Materials, Developments and Perspectives



Edited by

G. Pistoia

*Centro di Studio per la Elettrochimica e la Chimica Fisica delle Interfasi
Consiglio Nazionale delle Ricerche, Rome, Italy*



ELSEVIER **Amsterdam — London — New York — Tokyo** **1994**

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

First printing 1994
Second edition 1995

ISBN: 0-444-89957-X

© 1994 Elsevier Science B.V. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science B.V., Copyright & Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.

Special regulations for readers in the USA - This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the copyright owner, Elsevier Science B.V., unless otherwise specified.

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.

This book is printed on acid-free paper.

Printed in The Netherlands

Industrial Chemistry Library, Volume 5

Lithium Batteries

New Materials, Developments and Perspectives

Industrial Chemistry Library

Advisory Editor: S.T. Sie, *Faculty of Chemical Technology and Materials Science
Delft University of Technology, Delft, The Netherlands*

- Volume 1 Progress in C1 Chemistry in Japan
 (Edited by the Research Association for C1 Chemistry)
- Volume 2 Calcium Magnesium Acetate. An Emerging Bulk Chemical for
 Environmental Applications
 (Edited by D.L. Wise, Y.A. Levendis and M. Metghalchi)
- Volume 3 Advances in Organobromine Chemistry I
 (Edited by J.-R. Desmurs and B. Gérard)
- Volume 4 Technology of Corn Wet Milling and Associated Processes
 (by P.H. Blanchard)
- Volume 5 Lithium Batteries. New Materials, Developments and Perspectives
 (Edited by G. Pistoia)

Preface

In 1958, an american student, W. Harris, published a thesis mainly based on the study of propylene carbonate and its electrolyte solutions. This investigation may be considered as the first milestone marking the road of an entirely new research trend on batteries.

The interest in these new power sources grew so rapidly that as early as 1973 the first lithium battery was commercialized by SAFT. The 70's and 80's have been eventful decades both for commercialization of other batteries and for development of theoretical approaches providing the bases to the experimental evidences.

During this time, the scientific community has organized regular meetings and symposia to update the advancements in the field. The International Meetings on Li Batteries, the Symposia held in the framework of the Electrochemical Society Meetings, the International Power Sources Symposia (New Jersey) and the International Seminars on Battery Technology and Applications (Florida) are the most important ones.

The related proceeding volumes often provide a quick updating of the state-of-art. However, as obvious, the information of these sources is fragmentary and, sometimes, of a very preliminary nature.

It is certainly surprising that, by comparison with these proceedings volumes, the number of books devoted to the field of lithium batteries is quite low. It can be sufficient to mention that the last two books reviewing the field with selected chapters on the main areas were published in 1983 ("Lithium Batteries", J.P. Gabano editor, Academic Press) and in 1984 ("Lithium Battery Technology", H.V. Venkatesetty editor, J. Wiley).

The need of having, at regular intervals, an organized survey of the main advancements is rather obvious, as articles in journals and in proceedings cannot fulfil this requirement. This book has been conceived with this aim in mind. On the other hand, recently some revolutionary concepts have been put forward (i.e. the Li-ion battery concept) which deserve a careful review.

When organizing the book contents, it was decided to privilege the space devoted to the applications. Indeed, the book is application-oriented and,

whenever theoretical aspects are dealt with, they underlie the corresponding practical aspects.

As the book could not be exhaustive, some areas which have not recently manifested important advancements (e.g. batteries working above room temperature) have been excluded. Instead, the new developments have been stressed and, to make the updating more timely, the publication in the camera-ready format has been chosen. A minor loss in style is more than compensated by the freshness of the information.

Gianfranco Pistoia

List of Contributors

- K.M. ABRAHAM, *EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062, U.S.A.*
- M. ALAMGIR, *EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062, U.S.A.*
- N. BAFFIER, *Laboratoire de Chimie Appliquee de l'Etat Solide, CNRS URA 1466, ENSCP, 11 rue P. et M. Curie, Paris, France*
- P. CHENEBAULT, *SAFT, Rue Georges Leclanche', BP 1039, 86060 Poitiers, France*
- J.R. DAHN, *Department of Physics, Simon Fraser University, Burnaby, B.C. V5A1S6, Canada*
- C. DELMAS, *Laboratoire de Chimie du Solide, CNRS, 351 cours de la Libération, 33405 Talence, France*
- L. A. DOMINEY, *Covalent Associates, Inc., 10 State Street, Woburn, MA 01801-6820, U.S.A.*
- HANG SHI, *Department of Physics, Simon Fraser University, Burnaby, B.C. V5A1S6, Canada*
- C.F. HOLMES, *Technology Division, Wilson Greatbatch Ltd., Clarence, N. Y. 14031, U.S.A.*
- C. JULIEN, *Laboratoire de Physique des Solides, associe' au CNRS, Universite' P. et M. Curie, 4 Place Jussieu, Paris, France*
- K. NISHIO, *Functional Materials Research Center, Sanyo Electric Co., Ltd., 1-18-13, Hashiridani, Hirakata-shi, Osaka 573, Japan*
- T. NOHMA, *Functional Materials Research Center, Sanyo Electric Co., Ltd., 1-18-13, Hashiridani, Hirakata-shi, Osaka 573, Japan*
- T. OHZUKU, *Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan*
- J.P. PEREIRA-RAMOS, *Laboratoire d'Electrochimie Catalyse et Synthese Organique, CNRS UM 28, 2 Henry Dunant, 94320 Thiais, France*
- G. PISTOIA, *Centro di Studio per la Elettrochimica e la Chimica Fisica delle Interfasi, CNR, Via Castro Laurenziano 7, Rome, Italy*

- J.N. REIMERS, *Moli Energy (1990) Ltd., 20000 Stewart Cresc., Maple Ridge, B.C., Canada*
- T. SAITO, *Functional Materials Research Center, Sanyo Electric Co., Ltd, 1-18-13, Hashiridani, Hirakatashi, Osaka 573, Japan*
- A.K. SLEIGH, *Moli Energy (1990) Ltd., 20000 Stewart Cresc., Maple Ridge, B.C., Canada*
- U. von SACKEN, *Moli Energy (1990) Ltd., 20000 Stewart Cresc., Maple Ridge, B.C., Canada*
- B.M. WAY, *Department of Physics, Simon Fraser University, Burnaby, B.C. V5A1S6, Canada*
- K. WEST, *Department of Physical Chemistry, The Technical University of Denmark, DK-2800 Lingby, Denmark*
- W.J. WEYDANZ, *Department of Physics, Simon Fraser University, Burnaby, B.C. V5A1S6, Canada*
- R. YAZAMI, *Laboratoire d'Ionique et d'Electrochimie de Solides de Grenoble, URA CNRS 1213, E.N.S.E.E.G., Institut Nationale Polytechnique de Grenoble, 38042 Saint Martin d'Heres, France*
- S. YOSHIMURA, *Functional Materials Research Center, Sanyo Electric Co., Ltd, 1-18-13, Hashiridani, Hirakata-shi, Osaka 573, Japan*
- Q. ZHONG, *Moli Energy (1990) Ltd., 20000 Stewart Cresc., Maple Ridge, B.C., Canada*

Table of contents

| | |
|---|------|
| Preface | v |
| List of Contributors | viii |
| Chapter 1. Carbons and Graphites as Substitutes for the Lithium Anode 1 J. R. Dahn, A.K. Sleight, Hang Shi, B.M. Way, W.J. Weydanz, J.N. Reimers, Q. Zhong and U. von Sacken | |
| Chapter 2. Electrode Materials Based on Carbon and Graphite Intercalation Compounds in Liquid and Polymeric Electrolytes R. Yazami | 49 |
| Chapter 3. Room Temperature Polymer Electrolytes M. Alamgir and K.M. Abraham | 93 |
| Chapter 4. Current State of the Art on Lithium Battery Electrolytes ... L.A. Dominey | 137 |
| Chapter 5. Thin Film Technology and Microbatteries C. Julien | 167 |
| Chapter 6. Four-Volt Cathodes for Lithium Accumulators and the Li- Ion Battery Concept T. Ohzuku | 239 |
| Chapter 7. Cathode Materials Synthesized by Low Temperature Techniques J.P. Pereira-Ramos, N. Baffier and G. Pistoia | 281 |
| Chapter 8. Solid-State Sodium Batteries K. West | 323 |
| Chapter 9. Comparison of High-Power Ambient Temperature Cells .. P. Chenebault | 347 |
| Chapter 10. Implantable Lithium Power Sources C.F. Holmes | 377 |
| Chapter 11. Commercial Cells Based on MnO₂ and MnO₂-related Cathodes T. Nohma, S. Yoshimura, K. Nishio and T. Saito | 417 |

| | |
|--|-----|
| Chapter 12. Intercalation in Layered and Three-Dimensional Oxides . . | 457 |
| C. Delmas | |
| Subject Index | 479 |

Chapter 1

Carbons and Graphites as Substitutes for the Lithium Anode

J.R. Dahn^a, A.K. Sleight^b, Hang Shi^a, B.M. Way^a, W.J. Weydanz^a,
J.N. Reimers^b, Q. Zhong^b and U. von Sacken^b

^a Department of Physics, Simon Fraser University, Burnaby, B.C., V5A1S6, CANADA

^b Moli Energy (1990) Ltd., 20000 Stewart Cresc., Maple Ridge, B.C., CANADA

1 Introduction

Lithium-ion cells currently represent the state-of-the-art in small rechargeable batteries. These cells deliver almost 4 volts, they have specific energies near 120Whr/kg and they have long shelf life at room temperature. The technology is based on the use of suitably chosen lithium intercalation compounds for the electrodes. Usually a lithium transition metal oxide is used for the cathode and a carbonaceous material for the anode. Our goal in this chapter is to explain the physics and chemistry of the carbon anode and its application as an intercalation electrode in Li-Ion cells.

First we will review the motivation for the use of electrochemical cells based on lithium and some historical developments in section 2. Early rechargeable cells (and some still being developed today) used metallic Li as the anode. The switch to a carbon-based anode leads to some tradeoffs, but the advantages of the carbon anode over metallic lithium, especially in cost, cycle-life and safety far outweigh its disadvantages (if any). We consider these tradeoffs carefully in section 3.

Selecting the best carbon for use in Li-ion cells is a work in progress. This is because hundreds of carbons are commercially available. These include cokes, fibers, mesocarbons, synthetic and natural graphites. Furthermore, special carbons with selected additives, dopants or substituents can also be prepared and show promise in this application. The carbon crystal structure influences the intercalation of Li within it, both in how much can be intercalated and at what voltage. Therefore, to understand the behavior of different

carbons, it is necessary to have a good understanding of carbon structures ranging from the most disordered (usually made at low temperature) carbons to the most ordered or graphitic ones. We give a review of carbon structures in section 4.

The vapor-phase intercalation of lithium in graphite has been extensively studied by the physics community and is relevant to our understanding of electrochemical intercalation of lithium in graphite. This is reviewed in section 5. In section 6, we consider the electrochemical intercalation of lithium in graphite and explain the reversible (good) and irreversible (bad) behavior of lithium/graphite test cells. We discuss methods for reducing the irreversible capacity of these electrodes. Section 7 considers the intercalation of Li in petroleum coke, which differs greatly from that which occurs in graphite.

Heat-treating carbonaceous materials increases their crystallinity. In section 8 we show how heat-treating disordered carbons affects their structure and their ability to intercalate lithium. We also discuss which carbons are most suitable for anodes in Li-ion cells.

Most carbons heated to temperatures above 1300°C are relatively pure and contain little impurities at all. However, carbons made at lower temperatures can be prepared with a wide variety of additives. For example, phosphorus, nitrogen and boron can be incorporated. Boron atoms substitute directly for carbon atoms in the carbon sites of B_zC_{1-z} materials prepared by chemical vapor deposition. In section 9, the effect of boron and nitrogen in carbon will be discussed. Finally, section 10 contains a summary and suggestions for further research.

Throughout this chapter we will draw most heavily from examples taken from our own work. However, reference to other workers in the field will be made when appropriate. Many research groups have contributed to the understanding and application of carbons as electrodes in Li-ion cells and all deserve credit.

2 Historical Overview

In the early 1970's it was discovered that intercalation compounds could be used as electrodes in secondary Li batteries. An intercalation 'host' is a solid which can reversibly incorporate 'guest' atoms or molecules within its crystal lattice with only small structural changes. The electrode reactions which occur in a $\text{Li}/\text{Li}_x(\text{HOST})$ cell, where HOST is an intercalation cathode, are:

$\delta x \text{ Li} \rightarrow \delta x \text{ Li}^+ + \delta x e^-$ at the Li metal anode and

$\delta x \text{ Li}^+ + \delta x e^- + \text{Li}_x(\text{HOST}) \rightarrow \text{Li}_{x+\delta x}(\text{HOST})$ at the cathode

leading to an overall cell reaction of

$\delta x \text{ Li} + \text{Li}_x(\text{HOST}) \rightarrow \text{Li}_{x+\delta x}(\text{HOST})$.

Simple prototype cells built using this principle showed the promise of very high energy density, moderate cycle life and higher voltage than conventional aqueous technologies. Many organizations in Japan, the United States, Europe, and Canada started ambitious programs to develop products based on these ideas.

During the 1970's and 80's almost all work on secondary Li battery electrodes centered on the use of intercalation compounds as the positive electrode and metallic Li or Li-Alloys for the anode. Of these, the rechargeable Li/MnO₂ 'Molicel²' AA-size cell built by Moli Energy Ltd. (British Columbia, Canada) in the late 80's was probably the most sophisticated product. Apart from a few small-size secondary coin cell products, these chemistries have not generally survived into the 1990's. AA-size and larger cells have proven very difficult to make safe and there have been incidents of fires in equipment powered by secondary Li/MoS₂ cells, which led to a product recall (1,2). To understand why this is so, we must consider the difficulties associated with the use of such metal anodes.

When Li is electroplated onto a metallic Li anode during the recharge of an intercalation cell, it forms a deposit more porous than the original metal. This causes the electrode to swell (3). In a cylindrical 'jelly roll' cell design, this swelling pushes the electrodes against the interior walls of the cell can, generating 'stack pressure' once the jelly roll tightly fills the can. The growth of the Li anode with cycle number becomes small after about 15 atmospheres of stack pressure have been generated (3). Very high figures of merit (> 50) have been achieved under high stack pressure conditions (3). The figure of merit is the number of times a Li atom can be transferred between the electrodes before it is lost to another process. In cells with Li metal anodes, lithium is lost predominantly at the anode/electrolyte interface which is thermodynamically unstable and remains kinetically stable only through the presence of a passivating film of reaction products (4). Apparently, the high stack pressure limits the growth of electrode surface area and hence the consumption of Li, resulting in high figures of merit. In coin cells with thin walled cases it is not possible to generate such large stack pressures, so alloy anodes are used. The advantages of the alloy appear to be that the electrode growth per cycle is smaller than metallic Li under low stack pressure conditions. It is unclear whether this advantage exists once the stack pressure is high.

The poor safety of secondary Li cells with metallic Li anodes can be understood now that we are aware that the surface area of the negative electrode, and hence the area of contact between the lithium and the electrolyte, gets larger and larger as the cells are cycled. Since this interface is not thermodynamically stable, the cells become increasingly sensitive to thermal, mechanical and electrical abuse. Only if the electrolyte and Li did not react at all would this situation be acceptable. Alternatively, if the surface area of the negative electrode could be kept small and constant, it is likely that acceptable cell safety could be achieved.

In the Li-ion approach, two intercalation electrodes, each highly reversible, are used as electrodes. In practical cells, the surface area of the powders used to make up the

electrodes is normally in the $1\text{m}^2/\text{g}$ range and apparently does not increase with cycle number (5). This suggests that the safety of such cells should be independent of cycle number and easily quantified. We return to this point in the next section.

The choice of materials to use for the anode in Li-ion cells is restricted to those with a potential reasonably close to that of Li metal. Although some exotic materials like WO_2 have been proposed as anodes, carbonaceous materials are clearly the most suitable candidates. The cost, availability, performance and potential versus Li metal of carbon-based materials are all acceptable for practical cells. One piece of evidence for this is that LiCoO_2 /carbon cells are now commercially available (6).

In view of the difficulties associated with the lithium metal anode, a careful examination of the relative merits of carbon and metallic lithium is worthwhile.

3 Advantages of using Carbon Anodes

3.1 Specific Capacity, Manufacturability and Recharge Rate

The specific capacity of Li is 3.86 Ahr/g and its density is 0.51g/cc . The maximum amount of Li that can be intercalated into graphite is 1 Li per 6 carbons, yielding a specific capacity of 0.372 Ahr/g . The density of graphite is 2.2g/cc , but practical powder electrodes normally are the order of 50% bulk density, so an 'electrode density' for carbon of about 1g/cc is reasonable. At first glance, it appears that the substitution of carbon for Li will lead to a large penalty in energy density. However, this is not the case as we show next.

The figure of merit for metallic Li anodes is between 50 and 100 in the best case. This means that about 1% of the Li anode is consumed on each cycle of the cell. Therefore, to attain a cycle life of 500 cycles, cells with metallic Li anodes require a five or six-fold stoichiometric excess of Li compared to that needed to fully intercalate the cathode. By contrast, the cycling efficiency of the carbon electrode is nearly 100%, and no excess anode is included in Li-ion cells, even for those which attain 1200 cycles (6). The 'practical specific capacity' of metallic Li is obtained from the theoretical one by dividing by a factor of five or six, which gives about 0.75 Ahr/g and 0.37 Ahr/cc for metallic Li. The corresponding numbers for graphite in a practical anode configuration are about 0.230 Ahr/g (taking the current collector and binder into account) and about 0.330 Ahr/cc . For small cells, where the volume is constrained, the switch to carbon anodes incurs almost no capacity penalty, with a small weight penalty. Experience with prototype AA cells confirms these arguments. For example, the AA-size Li/MnO_2 'Molicel²' had a capacity of about 600 mAh, which is equal to that of graphite/ LiCoO_2 prototypes made by Sanyo (7,8).

The excess Li in cells with metallic Li anodes can cause other problems if the cells

are allowed to discharge to low voltages outside their normal operating range. Many intercalation cathodes decompose (eg. to form Li_2S or Li_2O) if allowed to react with excess Li (9). The cells are then only poorly rechargeable because of irreversible chemical and structural changes in the cathode. In addition, the reactions which occur at low voltage can often totally consume the Li anode, making charging difficult. By contrast, Li-ion cells have no excess Li and are hence anode limited. In one recent report (5), we showed that coke/LiNiO₂ cells could be repeatedly cycled to zero volts without damage.

Practical cells with metallic Li anodes use both optimum electrolytes and stack pressures of about 15 atmospheres to attain figures of merit between 50 and 100. Special separators which can withstand high uniaxial pressure and which have a pore size smaller than the diameter of typical Li dendrites must be used in these cells. These separators, generally polypropylene or polyethylene microporous films, are very expensive and contribute significantly to the cost of a spiral wound cell. Furthermore, as long as metallic Li is used, the stack pressure requirement precludes the construction of flat or prismatic cells with thin-walled cases. By contrast, there is no significant swelling of, or stack pressure generation by, the carbon electrode on prolonged cycling. There is no dendrite formation. Therefore, more flexibility is allowed in the choice of separators and cell configurations.

Secondary cells with Li metal anodes typically use recharge currents which correspond to $C/10$ (10 hours for full recharge) rates (10). This is because the risk of dendrite penetration of the separators increases as the recharge current is increased and because the Li cycling efficiency is improved when the current density used for plating the Li is substantially less than that used for stripping (10). By contrast, Li-ion cells can be recharged effectively in two hours or less (6), because dendrite formation is eliminated by using carbon.

3.2 Safety of Metallic Li and Carbon Anodes Probed by Accelerating Rate Calorimetry

The safety record of AA-size secondary cells with Li metal anodes is less than satisfactory (1,2,11). Furthermore, there have even been problems with primary Li/MnO₂ cells which led to product recalls (12). This suggests that safety is a central issue which must be resolved. When carbons or graphites are fully intercalated with lithium, they reach voltages within a few millivolts of metallic Li. Therefore, from a thermodynamic point of view, the lithium within LiC₆ is approximately as reactive as metallic Li. Although the melting point of metallic Li (180°C) is much lower than that of LiC₆ (> 700°C), reactions between organic electrolytes and lithium begin at temperatures far below the melting point of lithium. From these arguments alone, it is not obvious that switching to carbonaceous anodes will improve cell safety.

Most cell safety incidents involve a scenario where the cell is heated electrically (by a short circuit, through high-rate overcharge, by forced discharge, etc.) above a temperature

beyond which thermal runaway occurs. The thermal runaway in the case of cells with Li metal anodes is commonly caused by chemical reactions between the Li and the electrolyte which become serious above about 120°C in cycled cells. We have probed these reactions with an Accelerating Rate Calorimeter (ARC).

An ARC is a sensitive adiabatic calorimeter designed to follow an exothermic reaction. The sample is placed within an inner chamber of the instrument and a thermocouple is attached. Using radiant heaters, the sample is brought to a starting temperature just above the point where the chemical reactions reach runaway under quasi-adiabatic conditions. For our ARC this is a self heating rate of $0.02^{\circ}\text{C}/\text{minute}$. Then the sample is allowed to self-heat while the chamber wall temperature tracks that of the sample, thus maintaining adiabatic conditions. As the sample self-heats, the heating rate accelerates because the exothermic reactions speed up as the temperature increases. The measurements reported here were made using a Columbia Scientific Instruments ARC (Austin, Texas, U.S.A.), which is capable of making measurements on AA-size cells.

For the experiments on Li metal anode cells, we used Li/MnO₂ cells which had been cycled 5, 10 and 25 times at $\pm C/10$. The cells were housed in AA size cell cans, but the electrodes were wound on large diameter cylinders, thus limiting the number of electrode turns in the cell. The mass of lithium in these cells was 0.31g. The cell capacity was about 150mAh, or about 1/4 that of a standard AA cell. The electrolyte used was 1M LiAsF₆/PC/EC. In the ARC experiments, the cells were fully charged and then placed into the calorimeter. The cell voltage and temperature were monitored externally. The cell temperature was raised to 100°C by the radiant heaters and then the self-heating process was monitored.

Figure 1 shows the temperature versus time for cells which had been cycled 5, 10 and 25 times. Naively, these results suggest that the heating rates are low. However, one must keep in mind that the thermal mass of these cells is about 4 times larger than a standard cell (because of the large central cylinder around which the electrodes were wound) and that the 'reactant load' in the cell is only about 1/4 that of a real cell. This implies that a real AA-size Li/MnO₂ cell cycled 25 times would self heat from 100°C to 180°C in less than 2 minutes under adiabatic conditions. This agrees with our experience based on qualitative observations of real cells and is a *very serious problem*.

Figure 2 shows the logarithm of the heating rate plotted versus $1000/T$ for the same Li/MnO₂ cells. There is a clear and dramatic increase in the reactivity of the cells as a function of cycle number. Notice that the heating rate at 400°K (127°C) increases by a factor of more than 20 between the cell with 5 cycles and the cell with 25 cycles. For all cells, the heating rates continue to increase with temperature. We believe that the increase in reactivity with cycle number is caused the increasing surface area of the Li anode due to cycling. This leads to a larger area of contact between the reactants, i.e. the Li and the electrolyte. Since the surface area of lithium metal anodes is not easily controlled and depends upon battery operating conditions, exhaustive (and probably prohibitive) testing programs are required to confirm the safety of cells containing lithium metal anodes (13).