

# **PRIMARY ELECTROCHEMICAL CELL TECHNOLOGY**

**Advances Since 1977**

Energy Technology Review No. 66

Chemical Technology Review No. 191

Edited by Robert W. Graham

# **PRIMARY ELECTROCHEMICAL CELL TECHNOLOGY**

**Advances Since 1977**

Edited by Robert W. Graham

**NOYES DATA CORPORATION**

Park Ridge, New Jersey, U.S.A.

1981

Copyright © 1981 by Noyes Data Corporation

No part of this book may be reproduced in any form  
without permission in writing from the Publisher.

Library of Congress Catalog Card Number: 81-38329

ISBN: 0-8155-0853-0

Printed in the United States

Published in the United States of America by

Noyes Data Corporation

Noyes Building, Park Ridge, New Jersey 07656

Library of Congress Cataloging in Publication Data

Main entry under title:

Primary electrochemical cell technology.

(Chemical technology review ; no. 191) (Energy  
technology review ; no. 66)

Includes index.

1. Electric batteries--Patents. I. Graham,  
Robert W. II. Series. III. Series: Energy tech-  
nology review ; no. 66.

TK2921.P76 621.31'2423'0272 81-38329

ISBN 0-8155-0853-0

AACR2

## FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued since January 1978, that deal with primary electrochemical cell technology. This title contains new developments since our previous title *Primary Batteries*.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced commercially oriented review of recent developments in the field of primary batteries.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

## 16 Reasons Why the U.S. Patent Office Literature Is Important to You

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source. Most important technological advances are described in the patent literature.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. *Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.*
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses—many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Identifying potential new competitors.
15. It is a creative source of ideas for those with imagination.
16. Scrutiny of the patent literature has important profit-making potential.

# CONTENTS AND SUBJECT INDEX

<b>INTRODUCTION</b> .....	1
<b>ALKALINE ZINC DRY CELLS</b> .....	3
<b>Electrodes</b> .....	3
Zinc Powder-Gel Anode Containing Methyl Cellulose .....	3
Zinc-Mercury Alloy .....	3
Graphite Body with Controlled Crystalline Orientation .....	4
Dispersion Based Carbon Binder Composition .....	4
Hetaerolite Addition to Cathode Mix .....	5
Nickel Oxide Cathodes from Dendrites .....	6
Stainless Steel Cathode Collector .....	7
Iron-Silicon Alloys as Anodes .....	8
Zinc and Magnesium Alloys of Aluminum .....	9
Indium, Gallium and Thallium Alloys of Aluminum .....	10
<b>Separators</b> .....	11
Polar Graft-Copolymerized Surface .....	11
Extraction Technique for Porous Polyolefin Film .....	12
Spiral-Wrapped Multilayer Cell Separator .....	12
Helically Braided Wire Device to Maintain Electrode Separation .....	15
Masked Separator for Magnesium Dry Cell .....	15
<b>Sealing and Leak Prevention</b> .....	19
Primary Radial Seal and Vent Closure .....	19
Improved Grommet and Metal Cover .....	21
Gasketing Technique .....	23
Resilient Plastic Disc .....	25
Synthetic Resin Sealing Technique .....	29
Plastic Encasement of Zinc Electrode .....	30
Sealing Device .....	30
Notched Flange Cover .....	31
<b>Holders, Adapters and Packaging</b> .....	34
Battery Cartridge and Connector .....	34
Open-Top Compartments for Battery Holder .....	35
Battery Case for Cassette Tape Recorder .....	35

Dry Cell Adapter . . . . .	38
Spring Contact . . . . .	39
Multiple Unsealed Cells in Sealed Container . . . . .	40
Heat-Shrunk Thermoplastic Film Packaging . . . . .	41
Hot Melt Plastic Enclosure . . . . .	43
Protectively Jacketed Female Terminal . . . . .	44
<b>Other Processes . . . . .</b>	<b>44</b>
Electrically Insulating Band on Inner Can Surface . . . . .	44
Cathode Depolarizer . . . . .	45
Zinc Perchlorate and Lithium Chloride Electrolyte . . . . .	47
Deferred Action Dry Cell Battery . . . . .	48
Catalyst for Air-Depolarized Cell . . . . .	49
<b>LITHIUM BATTERIES . . . . .</b>	<b>50</b>
<b>Lithium-Thionyl Chloride . . . . .</b>	<b>50</b>
Position Insensitive Battery . . . . .	50
Discrete Electrode Bodies . . . . .	54
Depolarizer and Liquid Cathode Heat Transfer Process . . . . .	59
Fluid Depolarizer to Control Heat Buildup . . . . .	60
Dithionite Salts as Charging Agents . . . . .	62
Lithium Clovoborate Salt Compounds Added to Electrolyte . . . . .	62
Hermetic Vent Structure . . . . .	63
Stabilized Glass-to-Metal Seals . . . . .	65
Laser Welding . . . . .	66
Addition of Copper to Current Collector . . . . .	66
<b>Lithium-Halogen . . . . .</b>	<b>67</b>
Pelletized Depolarizer . . . . .	67
Lithium Halide Coating on Electrode Leads . . . . .	69
Reactivation Device . . . . .	70
Organo-Metallic Polymers . . . . .	70
<b>Lithium-Halogen, Solid Electrolytes . . . . .</b>	<b>73</b>
Ternary Chalcogenides . . . . .	73
Lithium Iodide Doped with an Alkyl-Pyridinium Iodide . . . . .	77
Halogen-Chalcogen-Metal Solid Cathode . . . . .	78
Fluorinated Carbon Cathode . . . . .	79
Titanium Disulfide Conductive Separator . . . . .	80
Fused Lead Fluoride and Alkali Salt . . . . .	83
Treatment of Aluminum Oxide with an Organo-Metallic Compound . . . . .	85
Solid Lithium-Sodium Beta-Alumina Separator . . . . .	86
Lamelliform Oxides of Potassium, Indium and Tin . . . . .	89
Sodium Rare Earth Silicate Conductor Compositions . . . . .	91
Deposition of Thin Silver Iodide Films . . . . .	93
<b>Lithium-Silver Chromate . . . . .</b>	<b>93</b>
Flexible Cell . . . . .	93
Hermetic Ultraminiature Cylindrical Cell . . . . .	97
Pure Silver Chromate . . . . .	102
Gold Coating on Anode Collector to Improve Adhesion . . . . .	103
Silver and Bismuth Double Chromate Composition . . . . .	104
<b>Lithium-Sulfur Dioxide . . . . .</b>	<b>104</b>
Internal Fuse to Prevent Heat Build-Up . . . . .	104
Cell Reaction Barrier . . . . .	106
Resilient Neutralizing Material . . . . .	107
Aerosol Container Filling Procedure . . . . .	107

<b>Lithium-Carbon.</b>	110
Granular Graphite and Carbon Black Material	110
Carbon Monosulfide Polymers for Cathode	111
Flexible Cathode Design	114
Liquid Bromine Trifluoride as Catholyte	118
Organic Sulfahalogenide Electrolyte Compounds	119
Inorganic Lithium Salt in Methyl Acetate as Electrolyte	120
Ultrathin Battery	121
Thermal Switch	124
 <b>LITHIUM BATTERIES—ELECTRODES, ELECTROLYTES AND OTHER PROCESSES</b>	126
<b>Anodes</b>	126
Boron-Lithium Alloy	126
Calcium-Coated Anode	129
Deposition of Insoluble Film on Anode	130
Four-Prong Anode Collector	131
<b>Cathodes</b>	135
Lead Sulfate	135
Surface Alloy of Lead, Tin, Antimony and Silver	135
Bismuthate of Lead Oxide	136
Electrolyte Capillary Action for Lead Oxide System	137
Uncompressed Particles of Ferrous Sulfide as Cathode	139
Metallic Reducing Additives for Metal Oxide Cathodes	140
Solid Solution of Copper Oxide and Alkali Metal Oxide	141
Heat Treatment and Molding of Manganese Dioxide	144
Particle Size Control in Carbon-Manganese Dioxide Cathode	149
Vanadium-Chalcogen Compounds	150
Ammonium-Molybdenum-Chalcogen Compounds	151
Chalcospinel Compounds	152
Metal-Iron-Chalcogen Compounds	153
Stannous Sulfide	155
Lithium-Uranium Oxide-Fluoride Compounds	156
High-Surface-Area Metal Oxides of Manganese and Calcium	157
Amalgamated Aluminum, Magnesium and Calcium Anodes	157
Catalyst Layer on Cathode Current Collector	159
Bismuth Oxide	163
Chromium Oxide	164
<b>Electrolytes</b>	165
Dioxolane-Based Electrolyte Containing Lithium Perchlorate	165
Macroheterocyclic Compounds as Stabilizers	166
Stabilization of Lithium Hexafluoroarsenate Solutions	169
Additives for High Drain Lithium Cells	170
Three-Component Solvent Blend	172
<b>Venting, Sealing and Other Processes</b>	172
Casing Design Including Vent	172
Leakage Detection	174
Pressure Relief Insulator	175
Glass-to-Metal Seal	175
Double-Sealable Cell	178
Charge Sensing Grid	180



<b>METAL-AIR AND ZINC-SILVER OXIDE BATTERIES</b> .....	187
<b>Metal-Air</b> .....	187
Oxygen Diffusivity-Limiting Membrane .....	187
Step Configuration Rim to Control Seal Cracking .....	190
Depolarizer Mass Attached to Perforated Plastic Carrier .....	192
Battery Design .....	193
Electrically Operated Air Access Vent Cover .....	197
Restricted Gas Passageway .....	198
Float Type Metal-Air Battery .....	198
<b>Divalent Silver Oxide</b> .....	201
Foamed Silver Layer .....	201
Core of Silver(II) Oxide with Surface of Silver(I) Oxide .....	204
Zinc Oxide Additive to Cathode .....	204
Metal Sulfides as Electrolyte Additives .....	205
Sulfur Crosslinked Polyolefin Separator Material .....	205
<b>Zinc-Silver Oxide</b> .....	207
In-Situ Reduction to Form Silver Layer on Cathode .....	207
Metallic Silver Cathode Layer .....	210
Molded Electrode Using an Ethylene Acrylic Acid Additive .....	211
Chamfered Peripheral Edge for Positive Electrode .....	212
Mercury-Indium-Zinc Anode .....	213
Separator Beads Embedded in Electrode .....	215
Coated Absorbent Barrier Protecting Separator .....	216
Nylon Gasket for Leak Prevention .....	217
Glass Seal and Annular Packing .....	218
Compression Sealing .....	222
Long-Life Alkaline Cell .....	224
Design of Microconnector Contact .....	228
Silver Peroxide and Silver Oxide Composites .....	230
<b>SEAWATER, RESERVE AND THERMAL BATTERIES</b> .....	232
<b>Seawater Activated Batteries</b> .....	232
Multicell Battery .....	232
Bipolar Battery Construction .....	232
Cuprous Chloride and Silver Chloride Cathode .....	235
Flexible Lead Chloride Cathode .....	235
High Purity Aluminum-Gallium-Magnesium Alloy Anode .....	236
Cuprous Thiocyanate as Cathode Depolarizer .....	237
Electrolyte Access Design for Metal-Halogen Battery .....	238
<b>Reserve Batteries</b> .....	239
Lithium-Sulfur Dioxide Cell .....	239
Battery for Missiles .....	242
Latex Bonded Lead Dioxide Electrode .....	245
Lewis Acid Electrolyte Solute for Lithium-Carbon Cell .....	246
<b>Thermal Batteries</b> .....	249
Copper Chloride-Tetrachloroaluminate Battery .....	249
Molybdenum Chloride-Tetrachloroaluminate Battery .....	251
Fused Salt Thermal Cell .....	252
Fused Mixture of Vanadium Oxide, Boron Oxide and Bentonite as Depolarizer .....	256
Zinc as Fusible Heat Sink Element for Secondary Heat System .....	256
Exothermic Intermetallic Reactions as Heat Sources .....	262
Calcium Anode with Chloride and Nitrate Ion Catholyte .....	262

Percussion Activation .....	263
<b>Other Specialty Batteries.</b> .....	265
Water Cooled Construction for Torpedo .....	265
Acceleration Activated Battery for Missiles .....	271
Pyrotechnically Activated Cell .....	272
Room Temperature, Fused Salt, Electrolyte for Airborne Applications .....	277
High Temperature Cell Design for Molten Electrolyte .....	278
Electrode for Bio-Fuel Cell .....	281
<b>BATTERIES FOR PHOTOGRAPHIC APPLICATIONS</b> .....	282
<b>Laminar Batteries for Photographic Applications</b> .....	282
Lamination Process Using Cellophane .....	282
Coated Cellophane Structure .....	294
Carrier Web .....	304
Fabrication of Thermoplastic Laminate .....	309
Flat-Pack Battery Separator .....	314
Porous Inherently Sealable Separator for Flat Cells .....	317
Fiber-Filled Plastic Tubes as Vents .....	322
Hot Melt Adhesive Sealing Method .....	322
Slurry Electrodes .....	330
Zinc Particles Coated on Anode Sheet .....	338
Cadmium Patch Electrode .....	345
Cadmium Plated on Lead Foil .....	346
Electrolyte Corrosion Inhibitor .....	347
<b>PACEMAKER BATTERY TECHNOLOGY</b> .....	348
Construction of Lithium-Bromine Cell .....	348
Lithium-Iodine Cells .....	353
Two Electrically Independent Cells .....	361
Mixed Halogen Compositions .....	367
Mixture of Halogen and Activated Carbon .....	368
Aromatic Tertiary Amine-Halogen Complex .....	369
Pyridinium Bromide Perbromide .....	370
Leads Embedded in Lithium Anode Member .....	371
Palladium Metal as Hydrogen Getter in Mercury Battery .....	372
Silver Ferricyanide .....	377
Modified Grommet for Sealing .....	378
<b>INVENTOR INDEX</b> .....	382
<b>U.S. PATENT NUMBER INDEX</b> .....	385
<b>COMPANY INDEX</b> .....	387

# INTRODUCTION

Conventional primary cell batteries produce electric current through a chemical reaction. In particular, an oxidation-reduction reaction is carried out in such a way that its driving force produces an electric potential. The oxidation-reduction reaction is achieved by providing an oxidizing agent and a reducing agent which is separated from the oxidizing agent. The oxidizing agent removes electrons from one electrode and the reducing agent gives electrons to another electrode, the flow of current through the battery being carried by ions. A common dry cell battery is one type of primary cell battery.

The common dry cell battery comprises a zinc cylinder which acts as one electrode and contains a suitable electrolyte, such as a paste of ammonium chloride ( $\text{NH}_4\text{Cl}$ ), zinc chloride ( $\text{ZnCl}_2$ ), water ( $\text{H}_2\text{O}$ ) and diatomaceous earth or some other filler. A carbon rod and a surrounding paste, which includes a mixture of manganese dioxide ( $\text{MnO}_2$ ) and carbon particles, functions as the other electrode.

These familiar primary dry cells continue to be the conventional power source for flashlights and many portable electronic devices around the world. Improvements in reliability, leak-proofing and endurance are continually sought in the manufacture of billions of such batteries as they are now produced in most countries.

Modern technology has placed increased emphasis on producing an electrochemical power source having improved reliability, light weight, small size, high power and a relatively long or infinite shelf life. Power sources meeting these requirements find ready civilian and military applications in portable communication systems, in particular, systems which have short duty cycles, for example, on for short periods of time and then kept inactive for long periods of time.

Various high-voltage, high-energy density electrochemical cells have been the subject of recent investigations. Much of the work in this area has been involved with electrochemical cells having negative electrodes comprising highly reactive metals such as lithium. Work on electrolytes for lithium-based electrochemical power sources has progressed generally along two major lines: high temperature, inorganic molten salt electrolytes and organic solvent-based electrolytes.

A cell which utilizes a molten salt electrolyte provides a chemically stable system in which strong oxidants such as chlorine can be used as cathodes. For example, a molten salt cell utilizing a lithium anode and chlorine cathode provides exceptionally high energy and power density making development of a practical cell with these materials of particular interest. The molten salt lithium/chlorine cell (having a lithium anode, chlorine cathode and molten salt, typically lithium chloride, electrolyte) has many characteristics desirable in a high performance electrochemical cell. The anode is highly electropositive, the cathode is highly electronegative, the equivalent weight of the reaction product is low, and the anode, cathode and electrolyte conductivities are high.

In parallel with the development of lithium cells with molten salt electrolytes, lithium cells with nonhydroxylic organic solvents have been developed. These cells have been called "organic electrolyte cells," although typically they employ electrolytes consisting of inorganic salts in organic solvents. Cells of this type have

the advantage of being operable at room temperature.

The solid electrolyte primary battery has been developed to provide relatively high voltage and high energy density in a battery which is especially useful for long life, low current drain applications such as an implanted cardiac pacer. Of the alkali metals, lithium is generally recognized as the most satisfactory material for the negative electrode, i.e., the anode on discharge, in a nonaqueous cell. In selecting material for the positive electrode, i.e., cathode on discharge, it is appropriate to consider, among other factors, relative chemical activity, energy density and discharge characteristics during cell life.

Metal-air batteries have long been known, and comprise one or usually a plurality of air-depolarizable cells connected in series, parallel, or series/parallel so as to provide the required battery terminal voltage with the requisite current capacity. Most often the metal used in the metal-air cells of metal-air batteries is zinc, but cadmium, iron or other metals may also be used. In any event, metal-air cells have a higher energy density than the usual "dry" cells or other primary cells such as zinc/manganese dioxide or zinc/mercuric oxide cells; and in the most common instance, zinc-air cells may have three times or more the energy density of such other cells. There is, therefore, a great advantage in using such cells in multicell batteries.

Miniature button alkaline metal oxide cells, such as alkaline silver oxide cells, have gained wide commercial acceptance for many applications because they are characterized as being high capacity, small volume electric cells. In other words, they have a high power output and energy per unit weight and unit volume of active cathode material.

Flat or planar batteries comprise superposed planar anode/cathode combinations possessing a separator disposed intermediate each anode and cathode and electrolyte disposed on or impregnated in the separator and in contact with respective facing surfaces of the anode and cathode. Planar batteries of this type are generally intended to be employed as an individual power source for portable electrical devices wherein the selected device design parameters are optimized by the availability and employment of a planar battery exhibiting reliability with respect to its power delivery characteristics. Batteries of this type are employed commercially to operate the various electrically powered systems of photographic cameras. In such cameras, the battery, disposed as a component of a film pack for employment in and in combination with the camera, provides the electrical energy necessary to operate the camera's exposure control, film transport and photoflash systems, and, accordingly, such battery is required to operate in a sequential series of power generating modes which may or may not be interrupted by more or less extended recovery and/or storage times and under which conditions to deliver the required series of high current pulses dictated by the photographic system design.

Highly sophisticated technology associated with military and environmental requirements has been applied to the development of battery components for use at sea and under special thermally and reserve activated conditions. In the implantation field, highly reliable miniature batteries are used to power the pacemakers which have now become a routine part of the medical practice for heart disease.

This book describes over 200 processes relating to the worldwide development for primary battery chemistry, design, manufacture and applications technology. These processes, representative of the recent patent literature of the U.S., also encompass the newer technology developments in Japan, Europe and other countries.

# ALKALINE ZINC DRY CELLS

## ELECTRODES

### Zinc Powder-Gel Anode Containing Methyl Cellulose

*D.G. Clash; U.S. Patent 4,209,577; June 24, 1980; assigned to Union Carbide Corporation* describes powder-gel anodes comprising a major portion of a consumable anode material such as zinc, a minor amount of a gelling agent such as methylcellulose with or without carboxymethylcellulose and an aqueous alkaline electrolyte such as an aqueous potassium hydroxide solution.

The powder-gel anode is ideally suited for alkaline-MnO<sub>2</sub> cells. The amount of methylcellulose (MOC), Methocel, should range between about 1 and 6% based on the total weight of the extruded anode prior to its assembly in a cell. An amount lower than 1% would not provide sufficient binding for the anode while an amount above 6% would replace too much of the active consumable anode material for a given size anode and render the gel too viscous to properly extrude the anode without providing any additional advantage. Preferably, the range should be about 2 to 5% based on the weight of the extruded anode.

In addition to being a good substitute for carboxymethylcellulose in powder-gel anodes, methylcellulose, upon precipitating, will release or free electrolyte to the cell where it can be used in the electrochemical reaction and/or to improve ionic diffusion in the cell.

### Zinc-Mercury Alloy

*R. Nicaise; U.S. Patent 4,104,188; August 1, 1978; assigned to Metallurgie Hoboken-Overpelt, Belgium* describes a process for the manufacture of zinc powder for electrochemical batteries which require the presence of mercury. The process is characterized in that all or part of the mercury required in the battery is introduced into molten zinc, alloyed or not, the molten alloy being homogenized and transformed into powder by pulverization (atomization).

The powder obtained by the process is characterized in that the mercury contained in the powder forms a homogeneous alloy with the zinc. As a conse-

quence, mercury will be available in each grain of powder in an equal and predetermined amount until complete exhaustion of the metal.

#### Graphite Body with Controlled Crystalline Orientation

*M. Nagasawa, T. Ishida, and Y. Yoshikawa; U.S. Patent 4,157,317; June 5, 1979; assigned to Matsushita Electric Industrial Co., Ltd., Japan* describe a resin-bonded graphite body having controlled crystalline orientation and a density of at least  $2.05 \text{ g/cm}^3$ , the body comprising 3 to 12 wt % of a thermosetting resin and 88 to 97 wt % of a carbonaceous powder which includes at least 50 wt % of natural crystalline graphite powder.

The resin-bonded graphite body can be made by: uniformly mixing, into a dry powdered mixture, 3 to 12 wt % of a thermosetting resin and 88 to 97 wt % of a carbonaceous powder which includes at least 50 wt % of natural crystalline graphite; compressing the dry mixture by a first uniaxial pressure into a compressed powder rod having crystalline orientation; inserting the compressed powder rod in a hollow of a mold which hollow has a shape similar to the shape of the compressed powder rod and defines resultant graphite body shape with the crystalline orientation being kept; preheating the thus inserted powder rod to the softening temperature of the thermosetting resin; compressing the thus preheated rod by a second uniaxial pressure, the direction of which is perpendicular to the direction of the first uniaxial pressure, and heating the rod to a curing temperature of the thermosetting resin so as to harden the thermosetting resin; and taking the thus treated rod out of the mold.

The body has a high transverse strength and a very low electrical resistance in the direction parallel to the direction of the crystalline orientation, and is thus suitable for a dry battery electrode.

#### Dispersion Based Carbon Binder Composition

*G. Schneider, W. Riedl, and H.-M. Lippold; U.S. Patent 4,160,747; July 10, 1979; assigned to Varta Batterie AG, Germany* describe a method for the manufacture of a positive electrode containing a binder for primary cells with alkaline electrolytes. In this method, a binder is introduced into the cathode mass in the form of a dispersion in a hydrophilic medium. The binder is preferably an insoluble organic polymer which is nonswellable in water, for example, polyisobutylene. The polymer as well as the electrode must not swell in water so that the electrode can be manufactured with high accuracy to size and high stability.

The surfaces of the solid particles in the dispersion carry electrostatic charges opposed to the dipole moment of the dispersion medium, which is preferably water. A very uniform distribution of the binder, even when added in very small percentages, may be obtained by a conventional mixing operation, in which a binder in the form of a dispersion is introduced into the electrode mass, which is subsequently dried in air. The drying in air is necessary only when a dilute dispersion is used. An extremely uniform distribution of the binder in the cathode mass is, however, obtained. The distribution of the binder is not quite so good (although still adequate) when a concentrated dispersion (20 to 60%) is mixed with the mass, preferably by spraying; however, in that case, an electrode material is obtained which appears to be completely dry.

**Example:** 90 parts by weight of manganese dioxide as depolarizer and 10 parts

by weight of graphite as conductive material were mixed to produce a homogeneous mixture. About 1.5 parts by weight of polyisobutylene in the form of a 10% dispersion in water were introduced into the primary mixture, and the total charge was then mixed for a further 10 minutes. The mass was then suitable for molding; however, the mass was preferably first dried in air to ensure accurate metering of the mass.

A compression test along the longitudinal and transverse axes is an essential criterion for the physical properties of the cathode moldings. In a molding 23 mm in diameter, for a primary cell according to IEC Publication 86 Type LR 14, the following ultimate strength values in kilograms up to breaking point were obtained as a function of the admixture and quantity of binder used:

..... Breaking Load-Longitudinal Axis .....		
	1% Binder	2% Binder
	..... (kg) .....	
(Poly)isobutylene in (hydrophobic) solvent	19.5	26.0
(Poly)isobutylene in water	26.0	39.0
..... Breaking Load-Transverse Axis .....		
(Poly)isobutylene in (hydrophobic) solvent	1.5	2.0
(Poly)isobutylene in water	2.0	3.0

A further indication was provided by the absorption of electrolyte by the molding as a function of time (in minutes).

In moldings of equal size, the variations were as follows:

..... Electrolyte Absorbed After 10 Minutes (ml) .....			
Proportion of Binder	1%	1.5%	2%
(Poly)isobutylene in (hydrophobic) solvent	0.55	—	0.40
(Poly)isobutylene in water	1.65	1.50	1.30

The discharge time is a decisive criterion for the suitability of a cathode mass. Comparing a polyisobutylene binder dissolved in petroleum ether with one in the form of an aqueous dispersion, it was found that, in addition to processing advantages, the discharge times were also better for the dispersion.

Type of Discharge	Dispersion	Solution
10 ohm, continuous	44 hr	40 hr
6 hr - 50 mA	102 hr	95 hr
1 hr - 250 mA	890 min	867 min
10 <sup>1</sup> - 5 ohm	1,540 min	1,420 min
4 hr - 75 ohm	390 min	360 min

#### Hetaerolite Addition to Cathode Mix

*F.L. Tye, J.E.A. Shaw, and A.K. Agopsowicz; U.S. Patent 4,221,853; September 9, 1980; assigned to Berc Group Limited, England* describe a dry electric cell of the Leclanché type having a cathode mix which includes: (1)  $\text{MnO}_2$  having a  $\beta$ -crystal structure, and (2) either hetaerolite ( $\text{ZnO} \cdot \text{Mn}_2\text{O}_3$ ) or materials which enable hetaerolite to be generated in situ at a sufficiently rapid rate so that it constitutes the major discharge product even at moderate to high rates of discharge.

**Example: Pretreatment of  $\beta$ -MnO<sub>2</sub> to Produce Hetaerolite** — A solution was prepared by mixing equal volumes of aqueous zinc chloride solution (SG 1.45) and water. The solution was then saturated at 25°C with respect to ammonium chloride and zinc oxide. To 100 ml of this solution were added:

	Grams
92% grade $\beta$ -MnO <sub>2</sub> ore of Moroccan origin	50
Hydrated manganous chloride MnCl <sub>2</sub> ·4H <sub>2</sub> O	3.25
Zinc oxide	3
Ammonium chloride	4

The slurry was stirred for 4 days at temperatures in the range 80° to 90°C. The solids were then filtered off, washed and dried. X-ray diffraction analysis of the resultant treated ore showed, in addition to the phases originally present in the ore, a trace of hetaerolite ZnO·Mn<sub>2</sub>O<sub>3</sub>.

Two separate cathode mixes were prepared using treated and untreated ore according to the formulation:

	Grams
Manganese dioxide (treated or untreated)	23.08
Zinc oxide	0.25
Ammonium chloride	11.36
Acetylene black	3.55
Zinc chloride solution (SG 1.45)	7.47
Water	4.25

Two paper-lined R20 size cells containing 48.1 g cathode mix per cell were made. Each cell was subjected to a discharge test through a 5  $\Omega$  resistance for 30 minutes per day, 7 days per week at 20°C. The discharge curves and the open circuit voltages measured immediately before each discharge cycle were recorded. It was noted that the cell which had been made with the untreated ore give a steeply falling discharge curve. Its on load voltage fell below 0.75 V after 8.5 hours total discharge. On the other hand, the cell which had been made with treated ore gave a flatter discharge curve and sustained an on load voltage above 0.75 V for 21.5 hours of discharge.

After discharge, the cells were opened, the discharged cathode mixes extracted and subjected to x-ray diffraction analysis. No hetaerolite could be detected in the mix made with untreated ore while a strong diffraction pattern corresponding to hetaerolite was recorded on the mix made with treated ore.

#### Nickel Oxide Cathodes from Dendrites

S. Ruben; U.S. Patent 4,074,030; February 14, 1978 describes a process for producing a high coulombic capacity nickel oxide cathodic reactant or depolarizer for primary electric cells. The process includes the steps of growing large nickel oxide dendrites on the exterior surface of a suitable base, converting the dendrites to a higher oxide of nickel, which is then removed from the base and ground to small particles for use as a cathodic reactant or depolarizer.

The following procedure illustrates the process. A dry mixture of 90 pbw of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10 pbw of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O is heated to liquefaction in a water bath, brought to 90°C, and maintained at this temperature. Using a 600 cc Pyrex beaker containing 500 cc of the above molten mixture, two 0.030" thick Ni



strips  $1\frac{1}{4}$ " wide positioned  $2\frac{1}{2}$ " apart are connected as positive electrodes; a  $2\frac{3}{4}$ " wide piece of  $14 \times 14$  mesh screen formed from 0.020" Ni wire is immersed to a depth of  $3\frac{1}{2}$ " midway between the other two electrodes, and connected as the negative electrode. A current of 2 A is applied for 4 hours, or a total of 8 Ah. An output of approximately 2.0 g of green  $\text{Ni}(\text{OH})_2$  dendrites per ampere hour is obtained. The dendrites extend outward from the exterior surface of the  $9.625 \text{ in}^2$  nickel screen.

After cathodization, the nickel screen carrying the dendritic formation of green  $\text{Ni}(\text{OH})_2$  is withdrawn from the molten bath, rinsed in hot tap water, and immersed in an aqueous 20/100 LiOH bath with a 2 ampere current again being applied. In this step, the dendrite coated nickel screen is connected as the positive electrode and two  $\frac{5}{8}$ " wide Ni strips connected as the negative electrode. A 2 ampere current is applied overnight (approximately 19 hours for a total of 38 Ah). The following day, a five cycle procedure of reversing polarity is applied as follows: the 2 ampere current is reversed, the dendrite coated Ni screen becoming the negative electrode for 20 minutes, the screen being then connected as the positive electrode for 20 minutes, this cycle being repeated five times, the final cycle with the screen connected as the positive electrode being maintained for 1 full hour. The  $\text{Ni}(\text{OH})_2$  dendrite coated Ni mesh is then removed from the LiOH bath and rinsed in hot tap water.

The use of a lithium hydroxide electrolyte in the anodization procedure results in better distribution of current, thus providing a more uniform oxidation of the  $\text{Ni}(\text{OH})_2$  than that obtainable with the sodium or potassium hydroxide electrolytes used in the prior art.

The dendrites, after oxidation to maximum oxygen valency state by the above step, are hard, dense, friable and readily brushed off the surface of the screen on which they have been formed. After drying, they are micronized or ground to a fine state. The high current density obtained by carrying out the process on the nickel screen is responsible to a great extent for the low electrical resistance and friable state of the dendrite.

For use as a cathode in primary cells, the oxidized dendrite powder is mixed with 5% of graphite or carbon, serving as a binder, and compressed under high pressure into a pellet. The pellet is then assembled with a zinc or cadmium anode, an absorbent spacer between the electrodes, an alkaline electrolyte and a container, to provide an efficient primary cell.

The cathode is usable in conventional structure alkaline primary cells employing zinc or cadmium anodes and alkaline electrolytes.

Primary cells using the cathode and having an open circuit voltage of 1.7 may be used to replace the more expensive silver oxide alkaline cells, the open circuit voltage of which is 1.56. The cathode may also be used in some types of rechargeable cells.

#### **Stainless Steel Cathode Collector**

A process developed by J. Watanabe, A. Ohta, and S. Kobayashi; U.S. Patent 4,125,638; November 14, 1978; assigned to Matsushita Electric Industrial Co., Ltd., Japan provides for the use as a cathode collector of a Leclanche dry cell,