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RESEARCH AND DEVELOPMENT OF LITHIUM BATTERIES IN CHINA

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Summary

Basic research work on lithium cells in China was initiated in 1965, and a variety of primary cells has been developed and introduced to the market. Lithium–iodine (1978), lithium–thionyl chloride (1977), lithium–sulfur dioxide (1979) and lithium–manganese dioxide (1980) cells, and lithium thermal batteries (1982) have been successfully manufactured and have found wide application.

In this paper, the development and the state-of-the-art of various lithium battery systems in China are presented and the present applications and future markets are discussed.

Introduction

China has an abundant supply of lithium. To make full use of this asset, projects for the development of lithium batteries have been organized on a national basis by the Chinese government.

Basic research on lithium cells commenced in China in 1965. In the early stages, the work dealt mainly with the manufacture of pure lithium, the preparation and purification of aprotic solvents and electrolytes (including solid and fused-salt varieties), and studies of the physicochemical as well as the electrochemical properties of electrode materials for use in lithium cells [1 - 3]. In recent years, closer attention has been directed towards the study of electrode mechanisms, the selection and evaluation of additives and catalysts that can be used in lithium cells to improve the discharge characteristics and alleviate the voltage delay, and to the hazards of using some lithium battery systems [4, 5]. Basic research has also been undertaken on the electrochemical properties of conductive polymers and the insertion reaction of lithium into layer compounds (such as TiS_2, MoS_2, etc.) and non-layer types of metal oxides (such as TiO_2, PbO_2, etc.) in the development of secondary lithium cells. Most of the fundamental research work has been carried out at universities and various institutes. Prominant among those are Beijing University, Fu-dang University, Wu Han University, the Institute of Chemistry, Academia Sinica, and the Tianjin Institute of Power Sources.

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Since the middle 1970s, a variety of lithium primary cells has been developed and marketed. In 1977, low drain, bobbin-type lithium–thionyl chloride cells were used in cardiac pacemakers in Shanghai. One year later, lithium–iodine cells were also used in clinical pacemakers in Tianjin. Since then, lithium–sulfur dioxide (1979) and lithium–manganese dioxide (1982) cells have been successfully manufactured and have found wide application. Lithium battery activities in China are summarized in Table 1.

TABLE 1

Summary of activities in R & D of lithium battery in China

Category and type	Current status	Typical applications	Work venue
$Li–SOCl_2$			
Low drain (bobbin)	Limited production	memory; military, pacemaker;	a; b; c; d
Medium drain (spiral wound)	Limited production	military; telecommunications	a; b
High drain (reserve)	development	military	a
$Li–I_2$	Pilot production	pacemaker	a; c
$Li–SO_2$	Limited production	military, telecommunications	a; b; i
$Li–MnO_2$	production	calculator, memory back-up;	a; b; e; f; g; h; i
$LiAl–FeS_2$	Pilot production	military	a
$Li–TiS_2$	Research		
$Li–V_6O_{13}$	Research		a
Li–polyacetylene	Research		

Note: a. Tianjin Institute of Power Sources.
b. Wu-Han Chang-Jiang Battery Manufactory.
c. Xu-Zhou 4th Manufactory of Electronic Devices.
d. Chinese Great Wall Industry Branch, Shanghai.
e. Feng-Yun Manufactory of Equipment, Xin-Xiang, He-Nan.
f. Feng-Lei Manufactory of Equipment, Mian-Yang, Si-Chuan.
g. Tianjin Dry Battery Manufactory.
h. An-Yang Battery Manufactory.
i. Jian-Zhung Chemical Company — Battery Manufactory.

State of the art of various lithium battery systems in China

Lithium–thionyl chloride

The low drain, bobbin type, lithium–thionyl chloride cells that were first used in cardiac pacemakers have been found to provide a safe configuration for this electrochemical system. Such cells have been produced in small sizes (types C, AA, 1/2 AA, and even smaller) and have been successfully used in memory back-up circuits, small radios, cardiac pacemakers, etc. They are characterized by a high specific energy (about 400 W h kg^{-1}; 900 - 1000 W h l^{-1}) and a long shelf life (>5 years).

The moderate drain, spirally wound, D and C type cells were introduced in 1983 as trial products. Explosive hazards were encountered, however, especially in abusive use. These types of batteries should be operated with safeguards against short circuits and voltage reversals by using fuses and diodes, respectively.

High-rate Li–$SOCl_2$ cells are still under development. Test results on prototype reserve Li–$SOCl_2$ cells have shown good prospects for military applications.

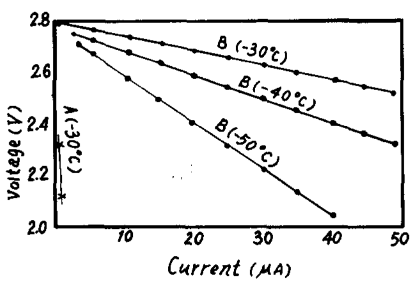
Lithium–iodine

The first successful clinical implantation of cardiac pacemakers powered by lithium–iodine cells was undertaken in Tianjin in 1978. Since then, there have been about 700 implantations; no failures have been observed as a result of battery problems. The calculated percentage of pacemaker failures is 3.6×10^{-4}/month, based on statistics collected over 6055 battery-months. In view of the fact that lithium–iodine cells are more reliable than lithium–thionyl chloride cells in cardiac pacemakers, it is reasonable gradually to replace the latter by the former in pacemaker applications.

It is recognized that lithium–iodine cells are suitable only for low current applications because of their high impedance. A new charge transfer complex compound has been discovered by the Institute of Chemistry, Academia Sinica; it has been successfully used by Tianjin Institute of Power Sources in lithium–iodine cells as an additive in the cathode. This additive can appreciably improve the discharge rate and low-temperature performance of lithium–iodine cells, as shown in Figs. 1 and 2. Furthermore, the self-discharge rate remains unchanged [6, 7].

Lithium–manganese dioxide

Coin type lithium–manganese dioxide cells were introduced to the market in 1979 by the Tianjin Institute of Power Sources. At present, there



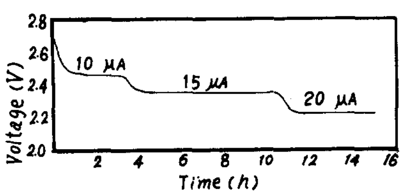


Fig. 1. V–I characteristics of lithium–I_2 cells at low temperatures. A and B cells were tested after eight months discharge at 30 μA, 37 °C. A-cell without additive; B-cell with additive.

Fig. 2. Discharge characteristics of B cell at −50 °C after eight months discharge at 30 μA, 37 °C.

TABLE 2

Catalog and performance of Li–MnO_2 cell

Types	Dimension		Weight (g)	Performance					
	Diameter (mm)	Height (mm)		Voltage (V)	Capacity (mA h)	Load resistance (Ω)	Initial current (mA)	Discharge duration (h)	Cutoff voltage (V)
LF 8	20	1.6	2	3	50	3×10^4	0.108	430	2.5
LF 9	20	2.5	2.5	3	120	1.5×10^4	0.236	450	2.5
LF 10	20	3.2	3	3	170	1.5×10^4	0.229	630	2.5
LF 14	24.5	3.0	4	3	200	1.5×10^4	0.230	735	2.5
LR 4	11.6	10.8	3	3	160	5.6×10^3	0.540	250	2.0

are about six manufacturers in China who are producing this type of cell. The largest manufacturer is Wuhan Changjiang Battery Manufactory; their annual output is about 1 million units. The main types are shown in Table 2.

Lithium–sulfur dioxide

Lithium–sulphur dioxide cells were first developed with crimping seal construction in 1979 by the Tianjin Institute of Power Sources. There are currently three manufacturers in China producing such cells. Hermetic technology has been introduced into cell construction in order to prolong the shelf life.

Lithium–thermal battery

Lithium aluminium–ferrous sulphide thermal batteries have been successfully produced since 1982 by Tianjin Institute of Power Sources and have been used for various special applications. They can be discharged at a very high current density (500 mA cm^{-2}) and with long discharge periods (100 - 300 s). LiSi–FeS_2 and LiB–FeS_2 thermal batteries are still under development in China. Prototype LiSi–FeS_2 cells have been tested; they deliver a service of more than 20 min.

Ambient temperature lithium secondary cells

Research and development work on ambient temperature secondary lithium cells was initiated in China in 1980. Much work has been devoted to the Li–TiS_2 and Li–V_6O_{13} systems in organic solvent-based electrolytes. It is claimed that a prototype C-type, hermetically-sealed, Li–V_6O_{13} cell with a spirally wound electrode configuration can deliver 50 cycles at a 50% depth of discharge.

Some exploratory research work on Li–polyacetylene and Li–TCNQ secondary cells has also been undertaken at the Tianjin Institute of Power Sources.

Outlook

Since the lithium–manganese dioxide battery has an adequate performance/cost ratio and gives a relatively higher reliability than other lithium batteries, it is probably the best suited product for the consumer market. In the future, the main task is to improve both the high rate and the low-temperature discharge performance, and to perfect mass-production techniques in order to reduce manufacturing costs.

Low-voltage lithium batteries (such as Li/FeS_2 and Li/CuO) are expected to be developed and put into the replacement market.

The lithium–iodine battery is the most reliable power source for implantable medical electronic devices. If the rate capability can be improved by the application of new materials and new technologies, lithium–iodine batteries may be developed for a wide range of applications in low power devices.

To date, the lithium–thionyl chloride battery is the most energetic unit among all the primary lithium systems. If safety problems can be solved, then large military and commercial markets will be developed in the near future for this battery. Lithium–sulfur dioxide batteries will probably be used in military applications in the intervening period. These are better suited to use in cold regions.

The research and development of ambient temperature secondary lithium batteries have been progressing slowly and continuously. Future success depends on breakthroughs in the areas of electrode materials and electrolytes.

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