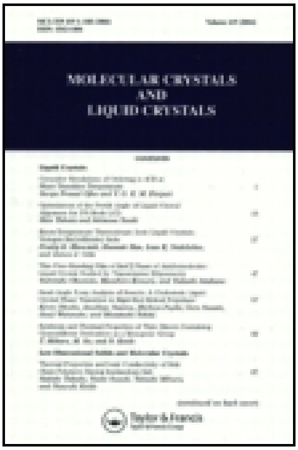

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DEVELOPMENT OF LITHIUM ION BATTERY

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The Lithium Ion Battery (LIB), using lithium cobalt oxide($LiCoO_2$) as a positive electrode and carbonaceous material as a negative electrode, has been used widely for note-book personal computers, cellular phones, camcorders and other applications. Development of this new battery system and recent technology trends are reviewed.

Keywords: lithium ion battery; lithium cobalt oxide; carbonaceous material

INTRODUCTION

Commercial production of the Lithium Ion Battery(LIB) has started from 1991. Fig.1 shows annual sales amounts of three secondary batteries, Nickel-Cadmium (Ni-Cd), Nickel-Hydrogen (Ni-MH), and LIB, in Japan from 1993 to 1998.

The trend for miniaturization of electronic equipment, such as computers, mobile phones, has led to unprecedented growth of LIB.

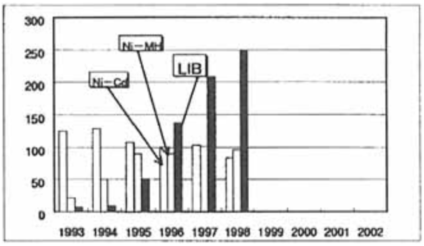

Fig.1 Annual sales amounts of secondary batteries in Japan (billion Yen)

The application of LIB in 1997 is shown in Fig.2.

Almost of all power sources of cellular phones, notebook personal computers, and camcorders manufactured in Japan have replaced by LIB.

Rectangular LIB is mainly used for cellular phones, and cylindrical LIB for notebook personal computers and, camcorders.

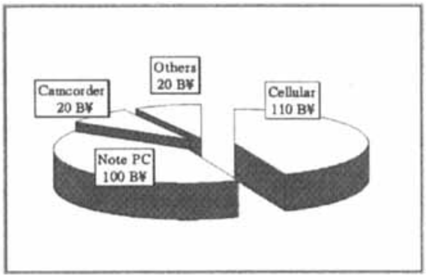

Fig.2 Applications of LIB

HISTORICAL REVIEW

Basic research on LIB started early 1980s. Fig.3 and Fig.4 show numbers of patent applications in Japan related to LIB, annual and cumulative numbers of applications, respectively. In Fig.3, a slight increase of applications is observed from 1985 to 1988. This fact suggests that basic key technologies of LIB had developed in these periods. In fact, most part of patents in these periods are applications related to carbonaceous materials for the anode.

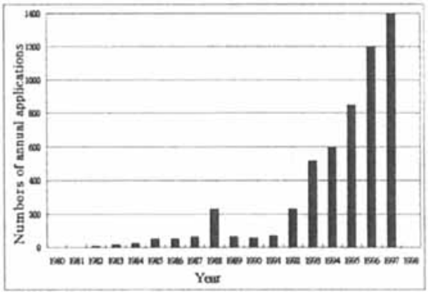

Fig.3 Numbers of Annual Applications

Rapid increase of applications is observed from 1992. It is obvious that this increase was due to commercialization of LIB. Asahi Chemical Industry Co. started basic research on new secondary batteries from 1981. We focused on development of new anode materials in place of lithium metal anode.

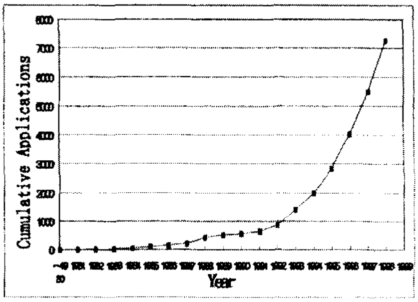

Fig.4 Cumulative Numbers of Applications

The first candidate for new anode material was Polyacetylene, which was able to be doped electrochemically both p and n type[1]. The reaction scheme is as follows:

p-Doping : $PA + X^- \Leftrightarrow PA^+X^- + e^-$

n-Doping : $PA + Li^+ + e^- \Leftrightarrow PA^-Li^+$

p-Doped Polyacetylene was thought as a hopeful cathode material, and also n-doped Polyacetylene as a hopeful anode material. We focused on n-doped Polyacetylene, and in 1982 we found highly n-dopable Polyacetylene, which was n-dopable 1 lithium ion per 3 CH units under certain conditions[2].

It means that reversible charge/discharge capacity was 687mAh/g, and we speculated "π allyl complex" as the electronic state of highly n-doped Polyacetylene, which is shown in Fig.5.

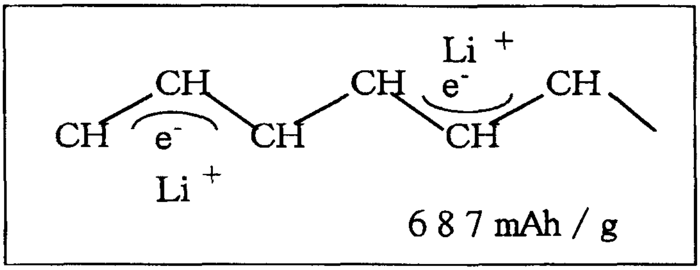

Fig.5 Hypothesis of electronic state of n-doped Polyacetylene

Unfortunately, this development was not successful, because of a lack of chemical stability and too low a real density of Polyacetylene.

In 1984, we found that some carbonaceous materials could be charged and discharged reversibly in high efficiency, and this material was much more stable and had a higher real density than Polyacetylene.

We continued further investigation focusing on the improvement of carbonaceous materials, and selection of cathode materials to be combined.

In 1985, we found LiCoO2 was the most suitable cathode material to be combined with a carbon anode[3] by following reasons.

1. **LiCoO2 contains lithium ion, which is necessary during charging and discharging.**
2. **LiCoO2 is very stable in ambient atmosphere and nevertheless it**

contains lithium ions.

3. $LiCoO2$ has high energy density.
4. $LiCoO2$ has very high redox potential, over 4V via Li^+/Li.

Afterwards this new battery system, C/$LiCoO2$, is named "Lithium Ion Battery (LIB)"

After further development, Asahi established A&TB Corporation in 1992, which is the joint company with TOSHIBA group, and started commercial production of LIB.

RECENT TRENDS OF LIB TECHNOLOGIES

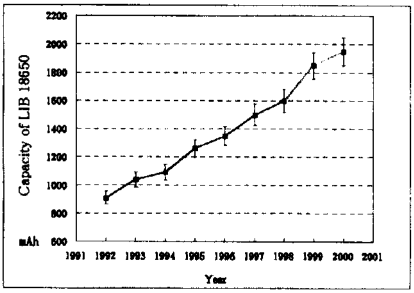

Fig.6 Capacity Enhancement of LIB

Fig.6 shows capacity enhancement of LIB 18650 in these 6 years, which is a standard cylindrical type cell. 1992, when commercial production of LIB had been started, the capacity of LIB 18650 was only 900 mAh. After that the capacity of LIB 18650 has been enhanced every year, and the standard capacity of LIB 18650, which was manufactured by Japanese LIB makers in 1998, was 1600mAh.

It is forecasted that the capacity of LIB 18650 will be 1850mAh in 1999, and 2000mAh in 2000.

These enhancements have been achieved mainly by improvement of carbonaceous materials. Table1 shows improvements of carbonaceous materials in capacity and first coulomb efficiency during these 6 years.

Table 1 Improvement of Carbonaceous Materials

Hard Carbon

	1992~	~1995	~1997	~1999	2000~
Capacity	200mAh/g	300mAh/g	400mAh/g	500mAh/g	650mAh/g
1st coulomb eff.	~80%	~80%	~85%	~85%	~85%

Graphite

		~1995	~1997	~1999	2000~
Capacity		250mAh/g	310mAh/g	350mAh/g	450mAh/g
1st coulomb eff.		~85%	~90%	~92%	~92%

Generally hard carbon has a higher charge/discharge capacity than graphite, but graphite has a higher real density (ρ_2) and higher value of first coulomb efficiency (η) than hard carbon, as shown in Fig.7.

Development of other materials such as new positive active materials or new electrolytes will realize further capacity enhancement of Lithium Ion Battery in the near future.

SUMMARY

1. **Development of Lithium Ion Battery and recent technology trends were reviewed.**
2. **Capacity of LIB 18650 has been increased from 900mAh to 1600mAh in these 6 years.**
3. **This capacity enhancement has been achieved by improvement of carbonaceous materials.**
4. **Capacity of LIB will reach 2000mAh in 2000 by further improvement of carbonaceous materials.**
5. **Further capacity enhancement must be achieved by improvement of other materials or other technologies.**

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