

Lithium ion secondary batteries; past 10 years and the future

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Abstract

Technologies of lithium ion secondary batteries (LIB) were pioneered by Sony. Since the introduction of LIB on the market first in the world in 1991, the LIB has been applied to consumer products as diverse as cellular phones, video cameras, notebook computers, portable minidisk players and others. Years of assiduous efforts and researches to improve LIB performances enabled LIB to play a leading role in the portable secondary battery market. In this article, the past 10 years' technological achievement is traced and future possibilities are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium ion secondary battery; Graphite intercalation compound; Lithium cobaltate; Non-aqueous electrolyte

1. Introduction

Lithium is a theoretically attractive material for negative electrodes of electrochemical cells owing to its least noble nature and low specific gravity. Primary cells with metallic lithium negative electrodes and non-aqueous electrolytes came into existence in early 1960s and they were successfully introduced into the market. Their outstanding features in comparison with conventional batteries with aqueous electrolytes are:

1. high voltage,
2. high energy density (both volumetric and gravimetric energy densities are very high),
3. low self-discharge rate, and
4. wide temperature range of operation.

Thus, secondary batteries with metallic lithium negative electrodes have attracted much attention as a candidate for the battery with high energy density, and much effort has been made in developing secondary lithium batteries.

Many practical problems, however, have been encountered in development of rechargeable lithium batteries. Several among them are

1. poor cycle performance,
2. need for long charging time, and
3. poor safety characteristics.

Almost all these issues are due to the dendritic lithium formation during cycling. Dendrites are apt to penetrate into the separator and to cause an internal short circuit between

positive and negative electrodes, which brings the problems including poor cycle performances and undesirable safety characteristics.

To overcome the weakness of the metallic lithium negative electrodes, some lithium-storing materials have been investigated as negative electrode materials including aluminium, Wood's alloy and carbonaceous materials and it has been confirmed that lithium/carbon alloys, a lithium–graphite intercalation compound (Li–GIC) being a typical one, is an excellent material for a negative electrode which inherits advantages of metallic lithium without the issue of lithium dendritic formation.

It is possible to synthesize lithium/carbon alloys by the direct chemical reaction of lithium and carbon, but they do not admit of mass production. The usual measure is that pure carbon is used in a negative electrode in place of an alloy and a lithium-containing compound like LiCoO_2 is applied to a positive electrode. Lithium ions are extracted electrochemically from LiCoO_2 during the charge of a cell in aprotic electrolytes and are doped into a carbon negative electrode to form a lithium/carbon alloy. During discharge, lithium ions are extracted from the alloy and doped back into LiCoO_2 .

Various investigations have been made on negative and positive electrodes, electrolytes, separators and others. A brief review on them will be described below.

2. Cell reaction

Negative and positive electrodes reactions in LIB in which graphite and LiCoO_2 are used as electrodes materials are as follows.

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Graphite has a layered structure and it is electrochemically reduced in an aprotic organic electrolyte containing lithium salts and lithium is intercalated (or doped) between the layers of graphite to form Li-GIC. Li-GIC is able to be charged and discharged as a rechargeable negative electrode for non-aqueous electrolyte cells according to the following reaction:

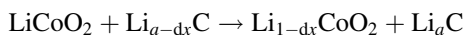


When a negative electrode is discharged, lithium is deintercalated (undoped) from lithiated graphite and lithium ions dissolve into the electrolyte.

The lithium content in the LiCoO_2 electrode reversibly changes during charge and discharge as indicated in the following equation:



In the LiCoO_2 /graphite cell system, the overall cell reaction is as follows:



This equation indicates that the cell reaction is simple migration of lithium ions between positive and negative electrodes and no metallic lithium is present in the system. To make a distinction from conventional lithium batteries, Sony gave the name “lithium ion secondary battery” to this battery system because a particular ionic bond compound (LiCoO_2) is used as a positive electrode and only lithium of an ionic state is found in a negative electrode.

LIB has outstanding properties as follows:

1. high voltage (average operating voltage is 3.6–3.7 V),
2. high volumetric and gravimetric energy density,
3. low self-discharge rate,
4. no memory effect,
5. quick charge acceptance,
6. excellent cycle life, and
7. wide temperature range of operation.

3. Positive electrode materials

As mentioned above, it was indispensable to develop lithium-containing materials for a negative electrode which could be electrochemically intercalated and deintercalated reversibly with lithium in non-aqueous electrolytes. In late 1970s we developed a novel cathode active material named silver nickelate, AgNiO_2 , for a primary silver oxide cell. It has a structure in which silver atoms exist between NiO_2 layers and Ag can be extracted from and inserted into the layers electrochemically in an alkaline electrolyte solution.

Our interests were as follows: “is it possible to synthesize LiNiO_2 in the same way as AgNiO_2 ?”, “can lithium be extracted electrochemically from LiNiO_2 ?”, “can lithium-extracted LiNiO_2 be doped again with lithium reversibly?” and “what is the optimum electrolyte system to be applied to the LiNiO_2 cathode if this compound is possible?”

We found a paper by Mizushima et al. [1], which was very closely related to LiNiO_2 , during our developmental course of the cathode material. They described in the paper that lithium-containing cobalt or nickel compounds, LiCoO_2 or LiNiO_2 , could be reversibly charged and discharged in aprotic solvents containing lithium salts and when they were applied to electrochemical cells as positive electrode materials, lithium could be extracted from them by electrochemical oxidation during charging and inserted into them by electrochemical reduction during discharging. The paper stimulated us to focus our effort on these materials.

We investigated intensely LiCoO_2 and LiNiO_2 as well as LiMn_2O_4 as a candidate for the positive electrode material. In Fig. 1 discharge curves of the three types of cells are shown in which these three materials are used as the positive electrode material. It has been confirmed that each material has the following merits and demerits.

LiCoO_2 :

1. flat discharge curve profile,
2. high charge/discharge efficiency at the first cycle,
3. passable discharge capacity on the weight basis,
4. stability at significantly high temperatures,
5. high cost,
6. scarcity of cobalt resources.

LiNiO_2 :

1. slightly sloping discharge curve profile and rather lower operating voltage than LiCoO_2 ,
2. lower charge/discharge efficiency at the first cycle than LiCoO_2 ,
3. higher discharge capacity than LiCoO_2 ,
4. instability at higher temperatures which is unfavorable for safety properties of resulting LIB,
5. poor cyclability.

LiMn_2O_4 :

1. flat discharge curve profile,
2. lower charge/discharge efficiency at the first cycle than LiCoO_2 ,
3. lower discharge capacity than LiCoO_2 ,

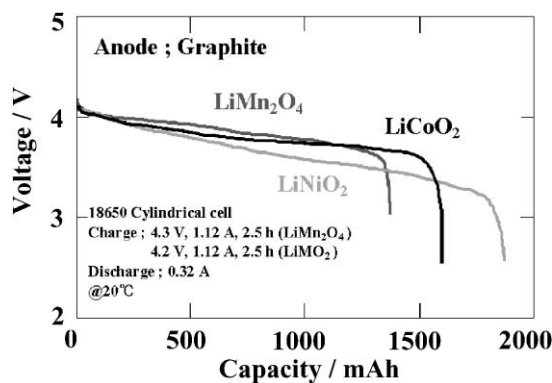


Fig. 1. Typical discharge curve profiles of LIBs with different materials for positive electrodes.

4. highest stability among the three candidates at high temperatures,
5. low cost,
6. abundance of manganese resources,
7. poor cyclability,
8. a little higher operating voltage than LiCoO₂.

We made detailed comparisons of these three materials in discharge capacity, charge and discharge efficiency (reversibility), a discharge curve profile and cyclability, and LiCoO₂ was selected as the positive electrode material. The decisive factors were cyclability, discharge capacity and safety characteristics (stability at higher temperatures).

In conventional synthesis methods for LiCoO₂, cobalt oxide (Co₃O₄) and lithium carbonate (Li₂CO₃) are mixed well and the resulting mixtures are calcinated in the air flow at a temperature of around 950°C. By this method, however, only fine particles with diameters of 1–3 μm can be obtained. Fine particles with a large specific surface area are unfavorable from the safety point of view. In the case of abuse such as external short circuit or crushing of a cell, fine particles react all together and all of the cell energy is released in a very short time with an accompanying sudden temperature rise and, in the worst case, the cell might catch fire.

We developed a novel synthesis process for LiCoO₂ with large particle sizes. The new process methods had two features that distinguished it from the conventional one. The first was that polyvinyl alcohol resin was added to the mixture of the raw materials to form granular pellets by using a granulator. By sintering of these pellets, LiCoO₂ particles with the average diameter of 20 μm were synthesized.

The second feature was that we used a slightly excessive amount of Li₂CO₃, and thus the Li/Co atomic ratio in the raw materials was greater than unity. While this procedure was favorable for obtaining coarse particles too, the resultant LiCoO₂ was desirable for safety characteristics as well.

A small amount of Li₂CO₃ was left unreacted in this method. When a cell is overcharged, for example, this residual Li₂CO₃ decomposes to evolve carbon dioxide gas resulting in build-up of the internal pressure in the cell and a safety device can be operated by the use of this internal pressure rise.

Though LiCoO₂ is the dominant positive electrode material at present in the LIB industrial world, alternative materials for a positive electrode have been developed including LiNiO₂, LiMn₂O₄ and other novel compounds.

It is expected that a higher energy density can be attained by using LiNiO₂ for positive electrodes in place of LiCoO₂ and the cost efficiency is assumed to be higher than for the cobalt compound. The former, however, has several drawbacks. A crystalline morphology transition, for example, is observed when LiNiO₂ is deeply charged, which adversely affects cyclability. Coulombic efficiency in the first charge/discharge cycle is significantly lower than that of LiCoO₂.

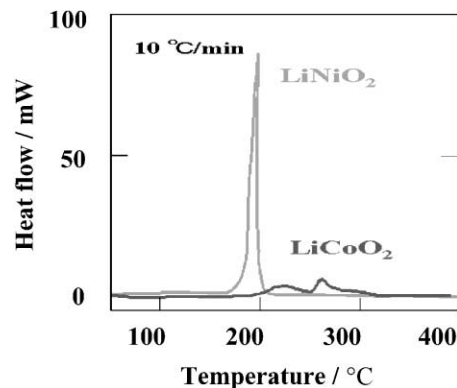


Fig. 2. DSC analysis of LiNiO₂ and LiCoO₂ charged up to 4.2 V vs. Li/Li⁺.

When LiNiO₂ is charged to lower voltages than 4.2 V, cyclability compares favorably with that of LiCoO₂, batteries involves a significant sacrifice of discharge capacity.

What is even worse, LiNiO₂ is unstable at higher temperatures. The DSC analysis result of LiNiO₂ is shown in Fig. 2 in comparison with that of LiCoO₂. It is clearly seen that LiCoO₂ generates only a small amount of heat at around 250°C, while in the case of LiNiO₂, however, heat is released at much lower temperature than LiCoO₂ and the heat evolved is excessive. Heat generation comes from the decomposition reaction of these materials to liberate nascent oxygen which is apt to react with lithiated carbon and electrolyte solvents and to result in further heat generation in great quantity.

Much effort has been made to get rid of the undesirable properties of LiNiO₂ mentioned above, and it is well established that the partial substitution of nickel with cobalt [2] and/or manganese is an effective way to prevent the morphology transition and to improve cyclability. Other substituents have been also tried and Toray Co. in Japan, for example, reported that the addition of strontium significantly improved the cyclability of LiNiO₂.

The safety properties of LiNiO₂ are promoted by the introduction of particular elements including boron, magnesium, and aluminium.

Many patents have been applied regarding the improvement of cyclability and/or safety characteristics of LiNiO₂ by the introduction of such an element and it is not too much to say that almost all the elements in the periodic table are listed in filed patents.

Poor cyclability of LiMn₂O₄ is considered to be due largely to the dissolution of manganese from the compound into electrolyte solutions. In a similar way to LiNiO₂, the addition of particular elements to this compound has been studied and chromium, for example, is reported to be an effective way to improve cyclability.

We have found that the extent of the irreversible capacity fade observed during the storage of LiMn₂O₄ cells, especially at high temperatures, depends on the depth of discharge (DOD). As shown in Fig. 3, the capacity loss during storage at 60°C for 125 h was largest at DOD of 80%, and

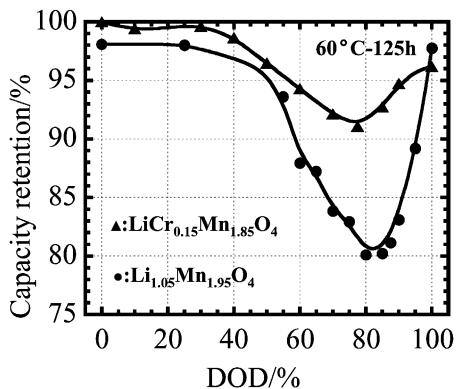


Fig. 3. Capacity Retention of LiMn_2O_4 based materials after storage at 60°C for 125 h, plotted against DOD of positive electrodes.

the loss was effectively suppressed by the addition of chromium.

Excellent stability at high temperatures and cost effectiveness put LiMn_2O_4 down as a candidate for the positive electrode material of the large scale LIB such as for electric vehicles (EV) and hybrid electric vehicles (HEV).

Novel materials have been investigated for positive electrodes. Among them are LiFePO_4 , FeSO_4 , vanadium compounds, molybdenum compounds and others. LiFePO_4 excels the others in safety characteristics and flatness of discharge curve profile. These features are desirable for EV or HEV applications. The discharge capacity on the weight basis, however, is less than LiNiO_2 and the average discharge voltage is lower than for LiCoO_2 , LiNiO_2 and LiMn_2O_4 . These drawbacks bring lower energy density to resultant cells.

4. Negative electrode materials

The energy density of Sony's LIB of the first generation (1991) was 200 Wh dm^{-3} and 80 Wh kg^{-1} . Much effort has been made to improve the performances, and at present it attains higher than 400 Wh dm^{-3} and 165 Wh kg^{-1} , almost twice as much as the values in 1991.

The energy density of the LIB depends largely on the negative electrode material because the noteworthy betterment in discharge capacity of positive electrode materials have not been achieved, and various kinds of carbonaceous materials have been investigated intensely.

We used so-called soft carbon in the first LIB, one of the reasons for the low energy density of a soft carbon cell in 1991 was that the charge voltage of 4.2 V, which is normal in current LIB, was not possible and 4.1 V charge was standard instead.

An improvement in cell performance has been attempted from that time by adoption of other classes of carbonaceous materials which can be charged at 4.2 V and which have higher charge/discharge capacity than soft carbon.

We utilized non-graphitizable carbon, or hard carbon, in LIB of the second generation. Hard carbon has many

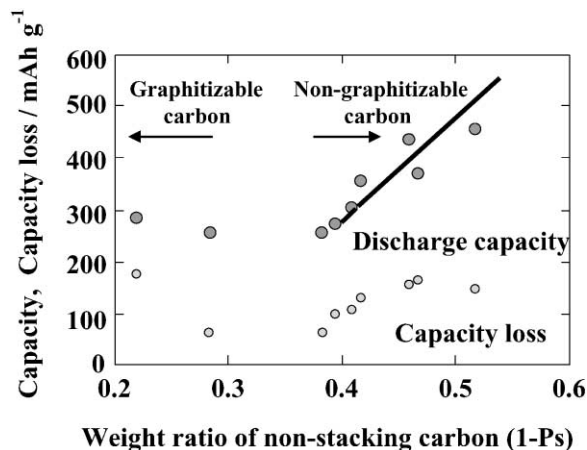


Fig. 4. Effect of weight ratio of non-stacking carbon ($1 - P_s$) on discharge capacity and capacity loss.

micropores surrounded by randomly oriented crystallites and the lithium doping capacity of this type of carbon can be increased by controlling the stacking structure of carbon layers. The number of layers in the stacks and the weight ratio of the carbon in the stacks to the total carbon (P_s) can be calculated from X-ray diffraction intensity data. As shown in Fig. 4, the lithium insertion capacity of hard carbon is improved with the increase of ($1 - P_s$). Accordingly, it is estimated that the non-stacking carbon plays an important role in the lithium doping/undoping mechanism. It may be concluded that high capacity can be achieved by increasing the ratio of non-stacking carbon ($1 - P_s$) of hard carbon. Furthermore, irreversible capacity is observed in the initial doping/undoping cycle (we name this "capacity loss") and it is desirable that the capacity loss should be as small as possible.

By deep investigations on various hard carbon raw materials, we have developed a new non-graphitizable carbon for a negative electrode with large charge and discharge capacity and high Coulombic efficiency.

A second generation LIB was able to be charged at 4.2 V and had energy densities of 220 Wh dm^{-3} and 85 Wh kg^{-1} . Particular mention must be made of the fact that hard carbon cells were outstanding in cyclability.

Both soft carbon and hard carbon cells have sloping discharge curve profiles and this attribute is undesirable for electronic equipment which has high cut-off voltages, above 3.0 V for example.

Graphite is a passable material as a negative electrode material because its discharge curve profile is flat. It is well-known that d_{002} spacings of undoped graphite are 0.335 nm and when lithium is inserted between the layers of graphite, d_{002} spacings expand to 0.372 nm and by undoping of lithium they shrink back to 0.335 nm. This means that during charge/discharge cycles, graphite repeats its expansion and shrink, which brings a deformation of the electrodes, resulting in poor cyclability. Hard carbon, however, has d_{002} spacings wider than 0.372 nm

and enjoys superior cyclability due to no expansion of the electrode.

The cell structure was optimized in graphite cells with the aim of compensation for the electrode deformation due to the d_{002} expansion. Cyclability was improved by this measure and the latest generation of LIB has high energy density greater than 400 Wh dm^{-3} and 165 Wh kg^{-1} with passable cyclability.

The maximum charge capacity of graphite is up to 372 mAh g^{-1} , which is calculated from the stoichiometry of Li-GIC (LiC_6). Amorphous carbon like hard carbon, however, has high charge capacity above 600 mAh g^{-1} . It was reported [3] that amorphous carbon heat-treated at low temperatures below 1000°C could trap lithium more than 1000 mg dm^{-3} . Although the specific gravity of amorphous carbon is low, the type with a charge capacity larger than 550 mAh g^{-1} has a higher volumetric capacity density than graphite (about 820 mAh cm^{-3}) even if its density is assumed to be 1.5 g cm^{-3} . A large irreversible capacity, as much as some 400 mAh g^{-1} , must be reduced before it is practical to use amorphous carbon in LIB.

Besides carbon, polyarsenic semiconductor (PAS) [4], tin or silicon oxides, metal nitrides, and others have been investigated as negative electrode materials with high lithium trapping capacity.

PAS was reported to be able to be charged up to the composition of LiC_2 and in that case the atomic lithium density of the compound is assumed to be greater than that of metallic lithium.

LIB with amorphous tin complex oxides (ATCO) [5] as a negative electrode was tried to be commercialized by a certain Japanese company. The company claimed that their tin based active material for negative electrodes, $\text{Sn}_{1.0}\text{B}_{0.6}\text{P}_{0.4}\text{Al}_{0.4}\text{O}_{3.6}$, had charge capacity of 1000 mAh g^{-1} and 2300 mAh cm^{-3} .

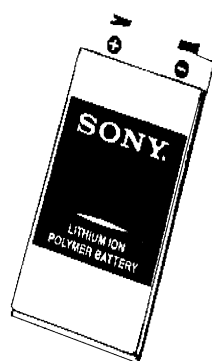
The charge and discharge efficiency at the first cycle is low (about 60%) for both PAS and ATCO, and the latter swells as much as 100–200% by the lithium insertion. These problems prevented these materials from being adopted as negative electrode materials.

Energy density of LIB with LiCoO_2 and graphite as a positive and negative electrode, respectively, is reaching the technological limits. It is indispensable that the novel materials for both positive and negative electrodes discussed above be developed and put into practical use in order to improve the energy density of LIB further.

5. Electrolytes

A non-aqueous electrolyte is used in LIB. It is formulated from solvents with high dielectric constants such as propylene carbonate, ethylene carbonate, dimethyl sulfoxide, etc. in which lithium-containing salts, including LiPF_6 , LiBF_4 , LiClO_4 and LiAsF_6 , are dissolved. Many lithium ions can be solubilized and solvated in these solvents. Solvents with high dielectric constants, however, have generally very high viscosity, even at room temperature, and this results in slow transfer of lithium ions, namely low ionic conductivity in the electrolyte. Practically, solvents with low viscosity are mixed with these solvents in order to lower the viscosity of the electrolyte system and to increase ionic conductivity. Among them are tetrahydrofuran, dimethoxyethane, diethyl carbonate, dimethyl carbonate and methyl ethyl carbonate.

Solidification of non-aqueous electrolytes has been investigated far and wide, and LIB with PVDF, PAN, and PEO based polymer gel electrolytes have been studied extensively. Polymer gel electrolyte batteries (LPB) have several advantages, including higher gravimetric energy density



Size (DxWxH)	3.8 mm x 35 mm x 62 mm
Weight	15 g
Nominal Capacity	760 mAh
Nominal Voltage	3.7 V
Charge Voltage	4.2 V
Charge Time	90 min
Energy Density (Volume)	375 Wh dm^{-3}
Energy Density (Weight)	190 Wh kg^{-1}
Cycle performance	~80 % @ 500 Cycle
Temperature Range	$-20^\circ\text{C} - 60^\circ\text{C}$
Cathode	LiCoO_2
Anode	Graphite

Fig. 5. Characteristics of Sony's LPB.

than conventional LIB, no electrolyte leakage, excellent safety characteristics and flexibility of cell shapes.

A new type of LIB in which gel polymer was used as an electrolyte began to be placed on the market in the beginning of 1999. These are called polymer batteries although the electrolytes are not genuine polymer but gel polymer.

It has been believed that LPB will always suffer from poor drain capability and unfavorable discharge characteristics at low temperatures. Sony has developed a LPB with comparable performance to the conventional LIB including low temperature properties, drain capability and cyclability (Fig. 5). They have a much higher gravimetric energy density than conventional LIB and are most suitable for small portable electronic equipment like cellular phones and personal digital assistants (PDA).

6. Conclusions

The LIB was first introduced into the market by Sony in 1991, and has been widely accepted as a power sources for

PC, cellular phones, AV equipment, etc. Energy density has been improved year-by-year, and at present it has reached over 400 Wh dm^{-3} and 165 Wh kg^{-1} . The LIB continues evolve. New positive and negative electrodes materials with higher capacity than the conventional ones are being investigated vigorously, and the capacity of the LIB will be further elevated by adopting them.

The introduction of a polymer gel electrolyte has given rise to a new type of LIB with lighter weight, thin and flexible shape and high safety properties.

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