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Lithium Ion Secondary Battery Technologies, Present and Future

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SUMMARY: Since the introduction of lithium ion secondary batteries (LIB) in 1991,the ceaseless and remarkable improvement has been done and the energy density has been doubled. New classes of anode and cathode active materials with possibly large charge and discharge capacity are in the course of development and further improvement in LIB performances can be expected by their adoption. The present status and future trends of LIB are discussed here including new types of LIB with polymer gel electrolytes.

Introduction

Since LIB was introduced into the market by Sony first in the world in 1991, they have been made the best use of as power sources for diverse portable electronic products such as cellular phones, notebook computers, video cameras and so on.

The principal features of LIB are as follows: 1) high energy density (both gravimetric and volumetric), 2) high operating voltage, 3) low self-discharge rate, 4) no memory effect, 5) high drain capability, 6) wide temperature range of operation, and 7) quick-charge acceptance. These excellent characteristics have enabled the LIB market to extend with so rapid strides.

Incessant and extensive improvement of LIB have been effected immediately after its first appearance in the market, and for example, a two-fold increase was achieved in last 10 years in regard to energy density, deriving from the advances in the materials for cathodes, anodes, electrolytes etc.

In this article, the present status and future trends of the LIB technologies will be discussed including so-called polymer batteries.

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Anode materials

The carbon anode has been a key component of LIB, and various carbon materials ranging from graphite to amorphous carbon have been proposed.

Graphite, a typical anode material, has a layered structure and it is generally understood that lithium can intercaltes (or dopes) between the layers of graphite to form lithium graphite intercalation compounds (Li-GIC), whose composition is LiC_6. In an aprotic organic solvent containing lithium salts, graphite is reduced by electrochemical lithium doping to form Li-GIC, and the Li-GIC can be electrochemically oxidized by lithium undoping. This indicates that a Li-GIC can be charged and discharged as anodes for nonaqueous rechargeable cells.

Several types of carbonaceous materials as well as graphite can be doped with lithium to form similar lithium insertion compounds. We have given the name 'carbon intercalation compounds' (CIC) to these compounds on the analogy of GIC. It has been confirmed that certain Li-CIC's can be utilized as anodes of LIB in place of Li-GIC.

At present, graphite and hard carbon are mainly put to practical use and both have their merits and demerits. TABLE I shows the comparison between graphite and hard carbon as the anode materials for LIB.

TABLE I Comparison of Graphite and Hard Carb

Description	Graphite	Hard Carbon
Cyclability	Acceptable	Excellent
Anode Bulging	Large	Very Small
Discharge Curve Profile	Flat	Sloping
Lithum Doping Capacity	<372 mAh/g <825 mAh/cm^3	<ca. 700 mAh/g <ca. 1000 mAh/cm^3
Efficiency at 1st Cycle	>95%	>85%

Graphite has a orderly layered structure and lithium can intercalate only into the spacings between its layers to form LiC_6, and the lithium storing capacity of graphite is subject to the stoichiometry of LiC_6 (calculated at 372 mAh/g). Hard carbon, however, consists of randomly oriented small crystallites, and lithium can be electrochemically inserted into the ultramicropores (with diameters of about 0.7 to 0.8 nm). These ultramicropores are assumed to be able to trap lithium in clusters, and this cluster lithium can also be electrochemically discharged. Thus the capacity limitation due to LiC_6 stoichiometry can be eliminated in the case of the hard carbon anode as a whole.

From the point of view of the improvement of the lithium doping capacity, keen attention has been attracted to amorphous carbon including hard carbon and carbon materials calcined at low temperature. Carbon materials heat-treated at $<1000°C$ shows higher capacity than graphite, around 500 mAh/g1), and H. Azuma2) reported that ideally designed hard carbon might have capacity of greater than 700 mAh/g.

It should be stressed that hard carbon can be economically prepared from agricultural wastes. We have been developing carbonaceous materials for the LIB anode by carbonization of bamboo saw dusts and coffee grounds followed by the heat treatment at various temperatures.

TABLE II shows charge / discharge capacities of bamboo saw dusts and coffee grounds derived carbonaceous materials.

TABLE II CHARGE AND DISCHARGE CAPACITY OF BAMBOO AND COFFEE GROUNDS DERIVED CARBONACEOUS MATERIALS

Raw Materials	HTT/℃	CC/mAh•g^{-1}	DC/mAh•g^{-1}	Eff/%
Bamboo	1100	775	630	81.3
	1200	710	580	81.7
	1300	560	500	89.3
Coffee Grounds	1200	615	525	85.4

HTT: Heat Treatment Temperature, CC: Charge Capacity
DC: Discharge Capacity, Eff: Efficiency at first cycle

These data are encouraging to further studies on these materials. Focus should be on improvement of efficiency and verification in practical cells.

In addition to carbonaceous materials, several candidates for the LIB anodes have been investigated, such as tin compounds, silicon compounds, metal (Co, Ni, Cu, Fe etc.) nitrides, and PAS 3)(polyasenic semiconductor).

Large capacity, good cyclability, and no reaction with electrolytes are indispensable characteristics for the LIB anodes. It cannot be stressed too strongly, however, that "small bulging" and "high efficiency" are not at all less important than these.

Charge / discharge efficiency in initial cycles is not neglected from the viewpoint of the cell design. PAS, for example, has very high lithium doping capacity, almost 1100 mAh/g, but irreversible capacity (trapped lithium which cannot be discharged) is also significantly large (around 300 mAh/g), which means that preceding lithiation of PAS or the excess cathode material usage equivalent to 300 mAh per gram of the anode are needed to compensate this irreversible portion, and this is not favorable for the cell design.

Lithium doping capacity of amorphous tin complex compounds (ATCO), $SnB_xP_yO_z$ is close upon 1000 mAh/g$^{4)}$. Its charge / discharge efficiency at the first cycle, however, is rather low, around 60~65%. Moreover, lithium doping into ATCO brings about anode bulging greater than 100% which causes poor cyclability. The situation seems to be the same to silicon compounds. Further effort is needed to put the anode candidates discussed above to practical use.

Cathode material

As discussed above, the anode materials for LIB are initially devoid of lithium species, and thus, cathode materials are required to contain lithium which can be reversibly extracted and inserted. Three compounds, $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ are the cathode candidates which are most vigorously investigated.

$LiCoO_2$ has fairly high discharge capacity and charge / discharge efficiency is favorable. It is relatively stable at high temperature, which results in desirable safety characteristics of LIB. $LiCoO_2$ is the sole cathode material which shows comprehensively sufficient properties including capacity, cyclability, safety etc.

Cobalt is scarce natural resources and its production district is maldistributed. Thus, its price is high and very fluctuating, which stimulates the development of new cathode materials with a lower cost.

$LiNiO_2$ and $LiMn_2O_4$ are the alternative candidates and much effort has been made to replace $LiCoO_2$ with these compounds. While $LiNiO_2$ has considerably higher discharge capacity than $LiCoO_2$, its charge / discharge efficienncy at the first cycle is lower than that of the latter. Thermal stability of $LiNiO_2$ is second to $LiCoO_2$, which brings about poor safety properties of the former at high temperature. Another difference between $LiNiO_2$ and $LiCoO_2$ is in their discharge curve profiles. The latter shows a rather flat profile when discharge voltage is plotted against discharge time. That of the former, however, is sloping, the discharge voltage going down bit by bit in the course of discharge time.

Moreover, the crystal structure of $LiNiO_2$ is changeable and the shift from the $R\overline{3}m$ to a rock-salt structure is observed especially in the case of the Li extracted (in other words, charged) compound, which causes poor cyclability of resulting cells.

Much effort has been done to improve the safety and cyclability issues of $LiNiO_2$ by the introduction of the third elements such as Co, B, Sr, Ti, Mg etc. We have developed the novel nickel complex compound with 20% higher discharge capacity than $LiCoO_2$. The new cathode material shows equivalent safety characteristics and cyclability to $LiCoO_2$.

This improvement was achieved by the introduction of a small amount of several elements and by optimizing the preparation process of raw materials.

As manganese is abundant and inexpensive resources, $LiMn_2O_4$ is a very attractive cathode material and it shows the most excellent thermal stability and is hardly over-charged, which enables it easier to design a resultant cell with passable safety characteristics.

$LiMn_2O_4$ has several drawbacks and poor cyclability and low discharge capacity are most important among them. Dissolution of Mn into the electrolyte is observed especially during high temperature storage of a cell, and this phenomenon is considered to be one of the causes of poor cycle performance of $LiMn_2O_4$ cells. Addition of selective elements such as Cr, Fe, Al etc. are effective to improve cyclability, but effectiveness is still insufficient and further investigations are needed.

Novel materials such as $LiMnO_2$ with the $R\bar{3}m$ structure and Nasicon-type Fe compounds are theoretically attractive from the capacity and cost point of view, and many works on them have been made with keenness.

Polymer gel electrolyte battery

Non-aqueous aprotic solvents in which Li salts such as $LiPF_6$, $LiBF_4$, $LiClO_4$, or $LiAsF_6$ is dissolved are generally used as electrolytes for LIB. In the case of organic solvents, however, there is a possibility of the leakage of flammable electrolytes. Thus, polymer gel electrolyte batteries have been investigated with might and main.

LIB with PVdF, PAN, and PEO based polymer gel electrolytes have been developed extensively. Polymer gel electrolyte batteries (LPB) have several advantages, including higher gravimetric energy density than conventional LIB, no electrolyte leakage, excellent safety characteristics and flexibility of shape.

It has been believed that LPB always goes with poor drain capability and unfavorable discharge characteristics at low temperature. We have developed LPB with comparable performances to conventional LIB including low temperature properties, drain capability and cyclability. The trial results are summarized in TABLE Ⅲ

TABLE III PRINCIPAL PERFORMANCES OF TRIAL LPB CELLS

Description	Conventional LIB	LPB
Drain capability		
1 C/0.2 C	99 %	98 %
2 C/0.2 C	96 %	94 %
3 C/0.2 C	94 %	91 %
Temperature Dependence of Discharge capacity		
10 ℃/23 ℃	96 %	96 %
0 ℃/23 ℃	85 %	85 %
−10 ℃/23 ℃	41 %	54 %
Cyclability		
1st cycle/300th cycle	90 %	92 %
Energy density		
Wh/dm^3	260	270
Wh/kg	92	127

* Cell size: 6×30×48 mm

Conclusion

LIB was first introduced into the market by Sony in 1991, and has been widely accepted as power sources for PC, cellular phones, AV equipments etc. Energy density has been improved year by year, and at present it has reached over 380 Wh/dm^3 and 150 Wh/kg.

LIB continues evolution. New cathode and anode active materials with higher capacity than conventional ones are being investigated vigorously, and capacity of LIB will be further elevated by adopting them.

Introduction of polymer gel electrolyte has realized a new type of LIB with lighter weight, thin and flexible shape and high safety properties.

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