

Technical Review

The Lithium Ion Battery Technology

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Abstract

The performance of Li-ion system based on LiCoO₂ and Graphite is well optimized for the 3C applications. The charge-discharge mode, the manufacturing process, the cell performance and the thermal reactions affecting safety has been explained in the engineering point of view. The energy density of the current LIB system is in the range of 300~400 Wh/l. In order to achieve the energy density higher than 500 Wh/l, the active materials should be modified or changed. Adopting new high capacity anode materials would be effective to improve energy density.

Keywords : Lithium Ion Battery, Graphite, Anode material, Energy density, Safety Issues, thermal stability, Manufacturing process.

1. Introduction

The Li-ion battery had been commercialized by Sony in 1991. Now Li-ion battery is a leading secondary battery in 3C (Camcorder, Notebook PC, Cellular Phone) market due to its high voltage, high energy density and light weight. In the world market, the shipment of Li-ion cell was 410 million cells (282 billion yen) in 1999, and it will be 550 million cells in 2000. The shipment increased by 35 %. Currently more than 10 companies are producing or preparing to produce the Li-ion batteries. In Korea LG Chemical started mass production of Li-ion battery in 1999.

Most of the Li-ion technology is based on Graphite-LiCoO₂ system. Even if the energy density has been increased from 220 wh/l to 400 wh/l for 8 years in this LIB system, it is expected to be increased continuously. The safety of Li-ion battery was a big issue when the LIB had been introduced to the secondary battery market. However, this safety issue has been cleared by introducing the protective circuit and safety devices.

2. The Li-Ion System

2.1. LIB System and Charging Method

Current Li-ion technology is based on Graphite-LiCoO₂ system which is illustrated in the Fig. 1. Anode material is graphite and cathode material is LiCoO₂. When the battery is charged the lithium ion moves from cathode material through separator into the graphite in the non-aqueous electrolyte system. When the battery is discharged the lithium ion moves from graphite to LiCoO₂. In order to avoid the dendrite formation of lithium metal on the graphite surface, the capacity

of the anode electrode is always designed bigger than that of cathode electrode. CC-CV (constant current – constant voltage) charging has been introduced for the Li-ion system in order to avoid overcharge of the cell. When LIB is overcharged, the lithium ions in LiCoO₂ move to anode and intercalate into the graphite and the excess lithium deposit on the anode surface as a lithium metal dendrite. The metallic lithium is much more unstable than the lithium ion intercalated into the graphite. The deposition of metallic lithium on the graphite surface also decreases the amount of the reversible lithium in the cell which results in a reduced cycle life of the cell. The schematic diagram of CC-CV charging is shown in Fig. 2. The change of the cell voltage, the charge current and charged capacity is plotted as a function of time. On CC-CV charging, the cell is charged at constant current until the cell volt-

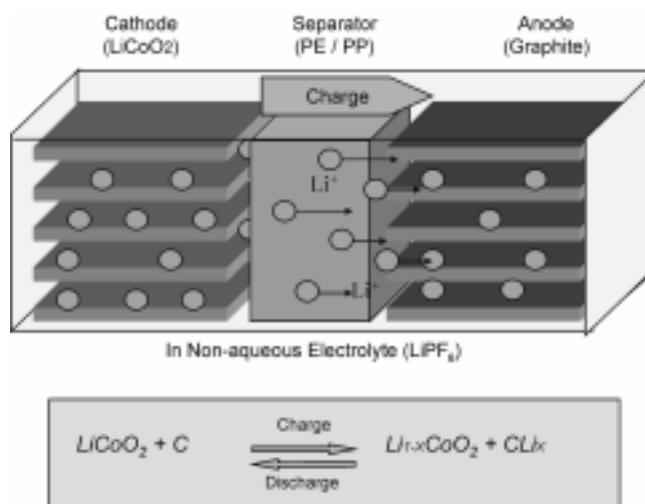


Fig. 1. The schematic diagram of Graphite-LiCoO₂ system.

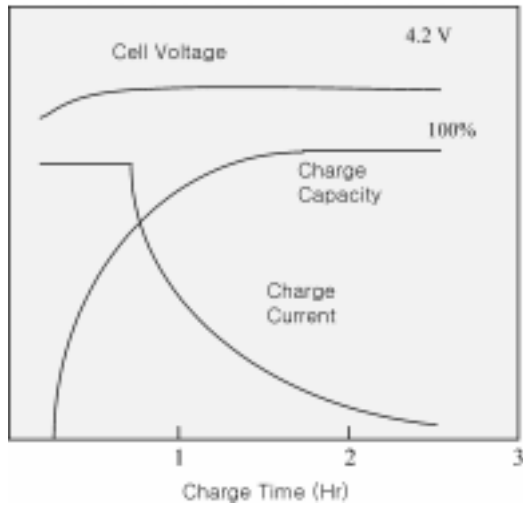


Fig. 2. The CC-CV charging characteristics.

age reaches up to 4.2 volt. And then, the constant current charging mode shifts to the constant voltage mode. The current decreases gradually maintaining the constant voltage until the cell is fully charged. Usually it takes more than one hour for 1 hour rate CC-CV charging. The CC-CV charging method prevents the Li-ion cell from overcharging and ensures cyclic characteristics.

2.2. Active Materials

The capacity of lithium metal is much higher than that of the graphite, however its cycle life and safety is not satisfactory for an anode material [1-2]. By introducing lithium alloys [3-4] safety had been improved. However, the cycle life was poor for lithium metal anodes because of the degradation of alloys on insertion/desertion reaction due to large volume change [5-6].

The intrinsic problems of the lithium metal or alloys have been solved by applying graphite as an anode material.

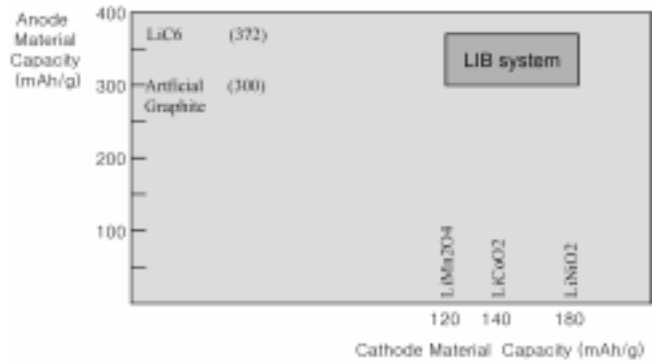


Fig. 3. The active materials for LIB system.

The capacity of anode and cathode materials of LIB system are illustrated in Fig. 3. In the anode material, the capacity of the artificial graphite is around 300 mAh/g and that of Graphite (LiC₆) is 372 mAh/g. In the cathode material, the capacity of LiMn₂O₄, LiCoO₂ and LiNiO₂ is 120 mAh/g, 140 mAh/g and 180 mAh/g, respectively.

The commercialized cathode materials for LIB system are LiCoO₂, LiMn₂O₄ and LiNiO₂. LiMn₂O₄ is safer than other materials however its capacity is smaller than others.

The capacity of LiNiO₂ is higher than LiCoO₂ or LiMn₂O₄, however LiNiO₂ is thermally unstable. The cycle life of LiMn₂O₄ and LiNiO₂ is being improved by the modification of the composition. Even if LiNiO₂ and LiMn₂O₄ are more cost effective than LiCoO₂, LiCoO₂ has been being utilized for most LIB system due to its good overall performances.

2.3. Manufacturing Process

The schematic diagram of the manufacturing process of LIB is shown in Fig. 4. The manufacturing process is composed of mixing, coating, roll pressing, slitting, winding, assembly, formation and inspection. The active materials, binder, conducting materials and solvent are mixed together in the

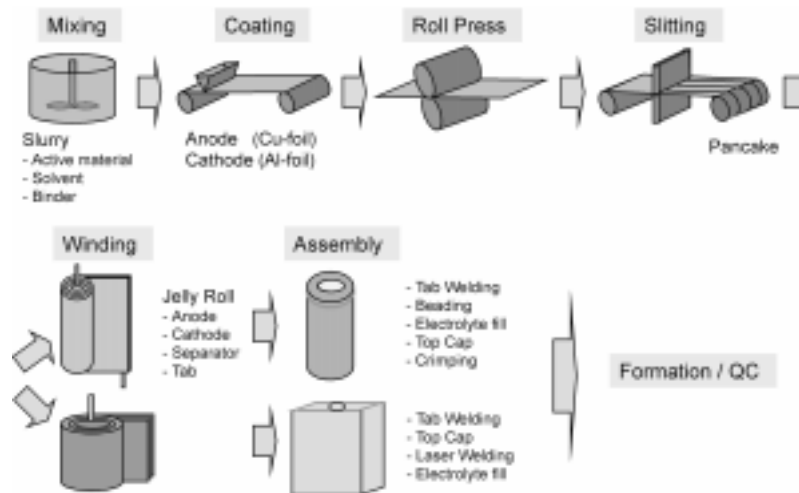


Fig. 4. The manufacturing process of cylindrical and prismatic LIB.

mixer to make a slurry. The slurry is coated on the metal foils. After drying the electrodes, the thickness and porosity of the electrodes are controlled uniformly by the roll press. After slitting the electrode by the slitting machine into a specified width, the positive and negative electrodes are wound with separators into a jelly roll by winding machine. In the jelly roll, positive and negative tabs are welded to the metal foils. The jelly rolls are inserted into the cans. One of the tab is welded to the can and the other one is welded to the top cap. After filling electrolyte into the can, top cap parts are laser welded or mechanically crimped for sealing. The final step is the formation process by which the cells are charged. After formation the bad cells are removed by the quality control scheme. The steel cans are used for cylindrical cells and prismatic cells while the aluminum cans are used for the prismatic cells.

2.4. Cell Performance and Safety

The capacity, cycle life, rate performance, low temperature dischargeability and storage characteristic are main cell performances. As there is a trade-off between the cell performance and safety, the cell is designed to maximize the performance while meeting safety regulations. The performance of the commercialized lithium ion batteries are as follows.

1. Energy density of the prismatic cells: ~300 Wh/l
2. Energy density of the cylindrical cells: ~400 Wh/l
3. Cycle life: 80 % of initial capacity after 300~500 cycles.
4. Rate performance: more than 90 % of the nominal capacity at 2C. (30 minute discharge rate.)
5. Low temperature dischargeability: 40~60 % of the nominal capacity at -20°C (0.5C)
6. Storage characteristics: the capacity recovery higher than 95 % after one month storage.

The cells should not explode or fire when abused electrically, mechanically or environmentally. Major safety test standards from UL1642 and JSBA (Japanese Storage Battery Association) are shown in the Table 1. These abuse tests are performed on bare cells without protective circuit.

In the electrical abuse test, abnormal charging test is one of the most severe test. As the cell is overcharged without protective circuit, the temperature of the cell is increased and the active materials and electrolyte are decomposed into gases. For longer overcharge, the cell may explode or fire without any protective devices. However in the commercialized cells, as the protective devices such as PTC (positive temperature coefficient), CID (circuit interrupt device) and safety vent are installed, the cells are protected from overcharge. The PTC device regulates the maximum current of the cell and the CID disconnect the electrical circuit of the bare cell mechanically using inner pressure of the cell which has been built up by the gases evolved during overcharge. The protective circuit additionally protect the bare cell from overcharging by regulating maximum voltage.

In the Fig. 5, various thermal reactions between cell components of LIB are schematically shown [7-9]. When the LIB cell is abused, the temperature of the cell is increased to initiate the thermal reactions. If the lower temperature reactions initiates higher temperature reactions, it results in a thermal runaway and the cell may explode or fire. So the cell should be designed to avoid this chain reaction.

3. Advanced Area in LIB

3.1. Energy Density

In the Fig. 6, the energy density of 18650 cell is shown.

Table 1. Safety test standards from UL1642 and JSBA (Japanese Storage Battery Association)

Safety test scheme	Test	Requirements
<Electrical abuse test>		
- External short circuit	UL	No Explosion, No fine, No Vent, $< 150^{\circ}\text{C}$
- External short circuit (60°C)	UL	No Explosion, No fine, $< 150^{\circ}\text{C}$
- Forced Discharge ($2.5\text{C}/I_a$ hr, at I_a)	UL	No Explosion, No fine
- Abnormal charge ($2.5\text{C}/3I_c$ hr, at I_c)	UL	No Explosion, No fine
- High current charge ($3I_c$, 100 % charge)	JSBA	No Explosion, No fine
<Mechanical abuse test>		
- Impact test (8 mm bar, 9 kg, 60 cm)	UL	No Explosion, No fine
- Crush test (17.2 Mpa/P, 3000 pound/F)	UL	No Explosion, No fine
- Drop test (1.9 m, 10 times)	UL	No Explosion, No fine
- Drop test (10 m)	JSBA	No Explosion, No fine
- Nail penetration test (d = 3 mm, for 6 hr)	JSBA	No Explosion, No fine
<Environmental abuse test>		
- Heating test ($5^{\circ}\text{C}/\text{min}$ to 150°C , 10 min)	UL	No Explosion, No fine
- Thermal cycling ($-20\sim 60^{\circ}\text{C}$, 2 hr, 10 cycles)	JSBA	No Explosion, No fine, No distortion
- Water immersion (24 hr)	JSBA	No Explosion, No fine
- Vacuum test (11.6 kp, 6 hr)	JSBA	No Explosion, No fine

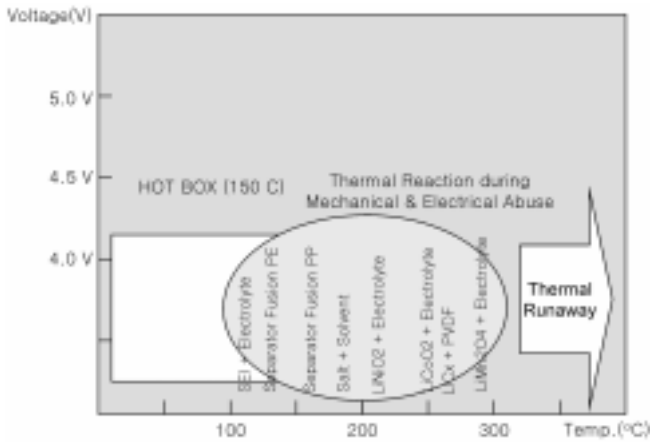


Fig. 5. Thermal reaction of LIB and abuse tests.

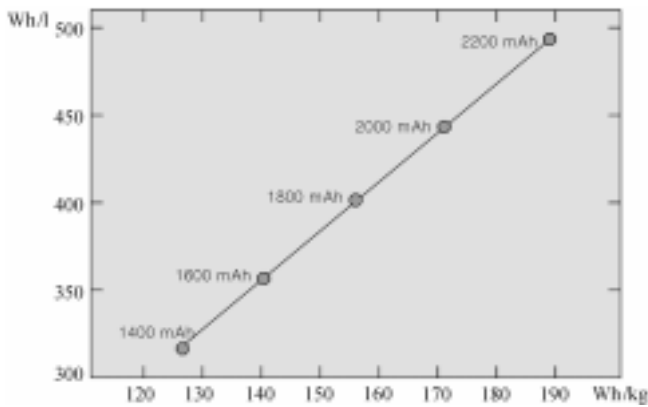


Fig. 6. The capacity of 18650 cell and energy density.

Several years ago, the energy density of LIB was 310 wh/l. Recently it has been increased up to 400 wh/l by adopting higher capacity graphite. As the capacity of the commercialized graphite is around 350 mAh/g which is almost close to the theoretical capacity of LiC_6 , new anode or new cathode materials are to be adopted in order to increase the energy density of LIB. The capacity of LiNiO_2 is around 180 mAh/g, however the capacity decreased to 160~170 mAh/g after modifying its composition to improve the cycle life and safety. No drastic increase of energy density is expected by adopting Ni based cathode material. More efforts should be concentrated on developing new high capacity anode materials. The schematic diagram of the anode materials and the energy density forecast is shown in Fig. 7.

3.2. Safe LIB

By adopting LiMn_2O_4 instead of LiCoO_2 , the safety of Li-ion system can be improved because LiMn_2O_4 is robust against overcharging and thermally more stable. In the Fig. 5, the reaction temperatures (and the exothermic energy [7]) between electrolyte and LiNiO_2 , LiCoO_2 and LiMn_2O_4 are about 200°C (600 J/g), 250°C (450 J/g) and 300°C (450 J/g),

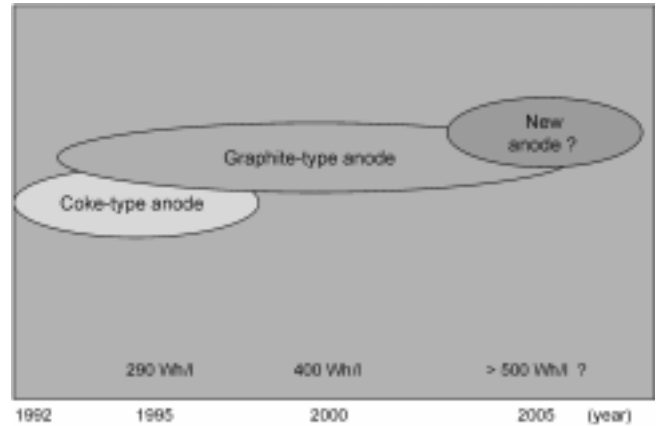


Fig. 7. The anode materials for the high capacity Li-ion system.

respectively. As the reaction temperature of LiMn_2O_4 is much higher than those of LiCoO_2 and LiNiO_2 , the Li-ion battery using LiMn_2O_4 cathode is more thermally stable and robust against overcharge or other abuse tests. In the current LiCoO_2 -Graphite system, the protective circuit is attached to prevent overcharge of the cell. However, it may be removed or simplified for the safe LIB.

4. Summary

Most of the Li-ion technology is based on LiCoO_2 and Graphite system. Even if this system is well established and optimized in the secondary battery market, more diverse LIB system will be developed. The energy density of LIB system will be increased continuously by adopting new high capacity anode materials and more safe LIB system will be commercialized to remove the protective circuit.

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