리듐망간과 인산철 비교특성

I. Choice of cathode material

In li-ion battery, cathode material's property has an important influence on battery's comprehensive performance. As cathode material, structural stability's comparison of iron phosphate lithium (LFP) material and lithium manganate (LMO) material is shown in the table below:

	LMO	LFP
Material's crystal structure (phase)	Spinel structure	Olivine structure
Ion stability of material	Mn^{3+} is easy to have disproportionated reaction，cause decrease of manganese and catalytic decomposition of SEI(solid electrolyte interface) layer on anode surface	Structure is stable, iron ion is not easy to dissolve out
Material's crystal structural stability	Lattice distortion in charge& discharge, easy to occur Jahn-Teller effect	LFP under condition of discharge& charge, change of cell parameters is comparatively small, structure is very stable
Material's thermostability/ oxidability	LMO 's DSC (Differential scanning calorimetry) test in charged state，exothermic peak occurs at about 250℃	LFP 's DSC test in charged state, exothermic peak occurs at about 330℃
Operation voltage	3.8V	3.2V
Float charge performance	Float charge at 4.2V, electrolyte is easy to dissolve, cell safety and cycle performance is bad	Float charge at 3.6V, electrolyte is not easy to dissolve, cell safety and cycle performance is good

1. The structural stability of LFP and LMO material have a comparatively large difference.

The material's basic property and its crystal microstructure are closely related.
Fig. 1 & 2 show LMO material's spinel structure and LFP material's olivine structure respectively.

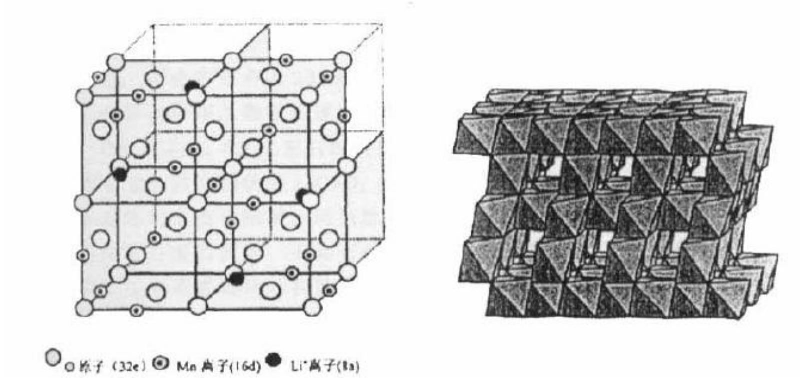

Fig.1： LMO material's spinel structure

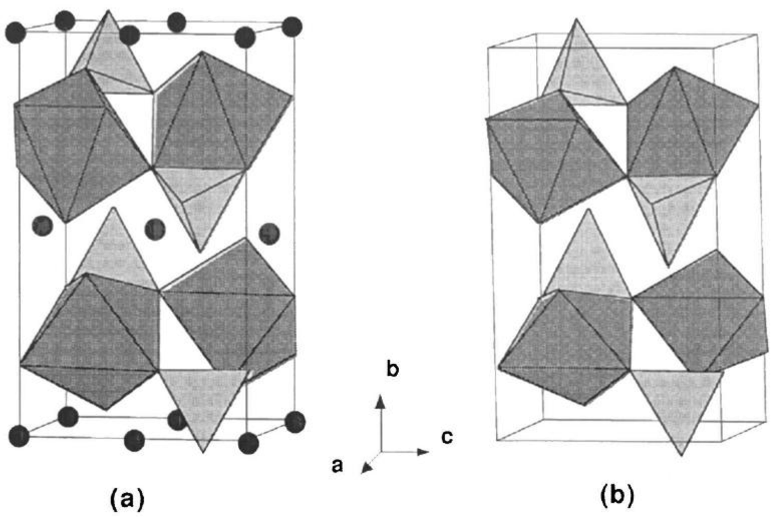

Fig.2： LFP material's olivine structure

The Mn^{3+} in spinel structural LMO can have disproportionated reaction, which would produce Mn^{2+} and Mn^{4+}. Under the condition of high temperature, such reaction will speed up, and Mn^{2+} will easier to dissolve to the electrolyte, which will cause decrease of manganese and catalytic decomposition of SEI layer on anode surface, and finally cause decrease of battery's capacity, while there is no disproportionated reaction of iron ion in olivine structural LFP. Its structure is more stable.

Then, in the battery, as SOC(state of charge) increases, because of lattice distortion, the spinel structural LMO is easy to occur Jahn-Teller effect, Mn's average valence to be lower than 3.5 flaw spinel phase will form on particle surface, which will make the structure unstable, cause capacity loss and material property deterioration; But the change of cell parameters of olivine structural LFP is comparatively small under the condition of discharge& charge, as a result, its structure is very stable as SOC increases, the representation on performance is battery's storage & cycle performance are both good no matter of high or normal temperature.

2. The thermostability of these two materials have a comparatively large difference.

Let's make a DSC test on LMO and LFP material in charged state and find out their oxidability differences. We can see from the DSC curve diagram (Fig. 3), as temperature increases, LMO's exothermic peak occurs at about 250℃, while LFP's exothermic peak occurs at about 330℃. And we can know that more heat is let out for the reaction of LMO and electrolyte, while the corresponding heat release of LFP is obviously less. This characteristic proves that the oxidability of LFP is obviously lower than LMO in charged state. Inside of battery, when the voltage or temperature is high, the LMO battery is easier to have oxidizing reaction of electrolyte, causing battery's safety problem.

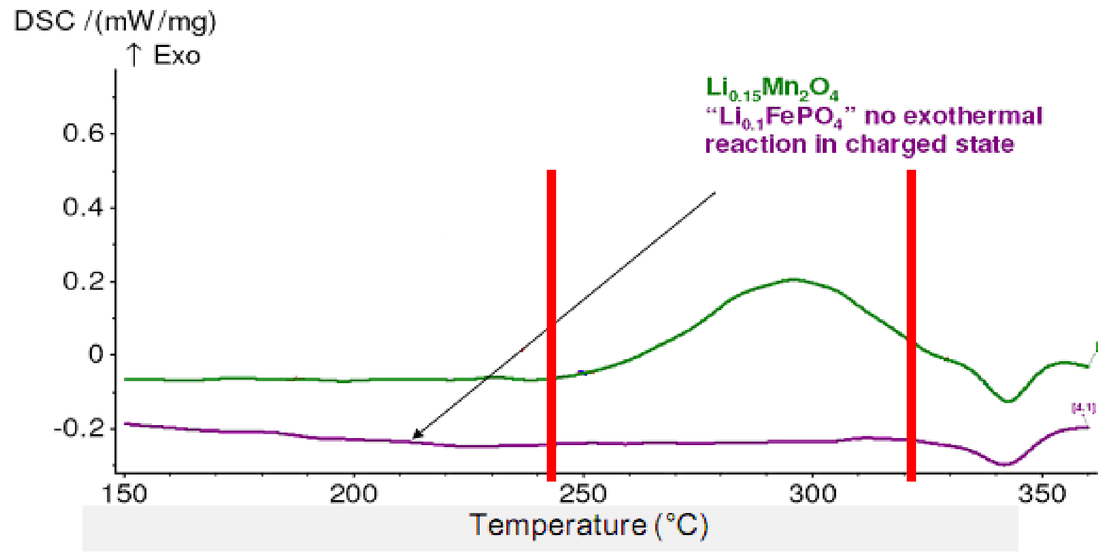

Fig.3： DSC curves of LFP and LMO material in charged state

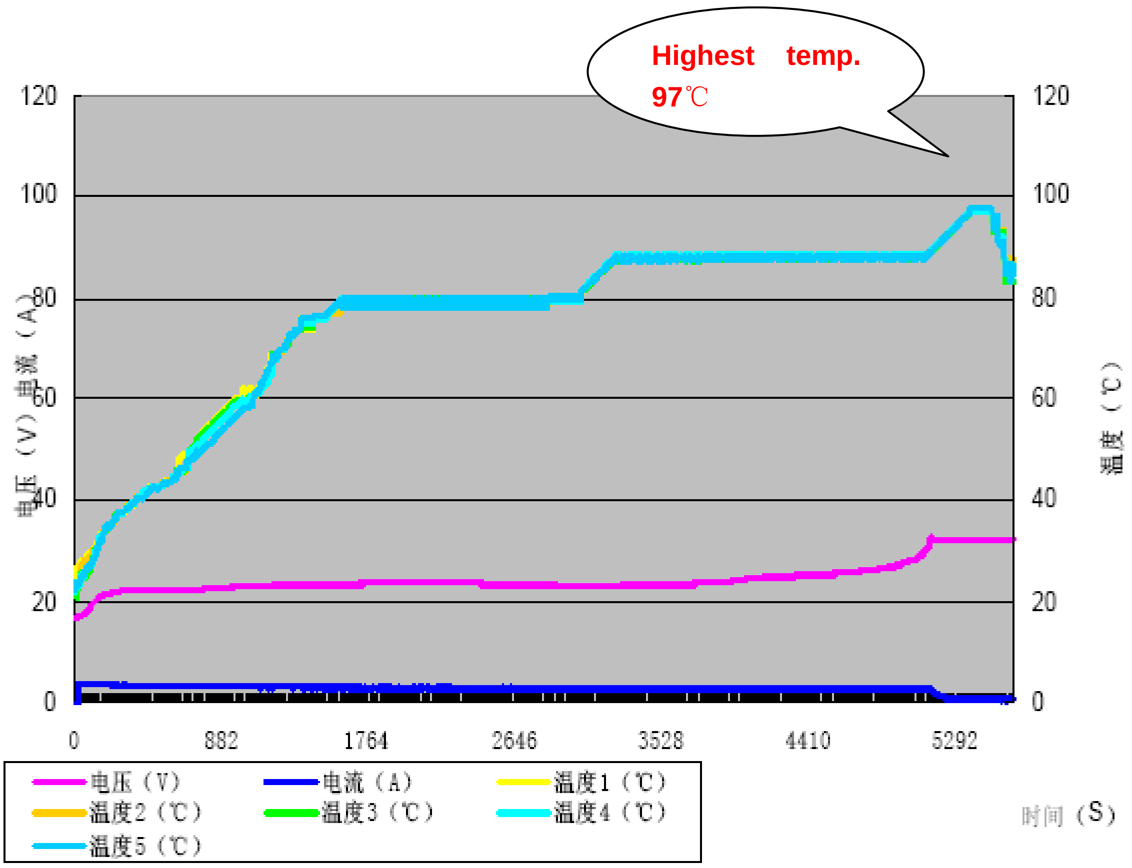

Fig.4： 0.2C&30V overcharge curve of 5-series LFP battery pack

Let’s charge for a 5-series battery pack manufactured with LFP and LMO material respectively with a 0.2C current. While charging, battery pack’s protection circuit is removed, meanwhile, upper limit voltage is set at 30V, then battery packs’ current, voltage and temperature are shown in Fig. 4&5. When the cells are overcharged to their limits, LFP battery’s temperature is obviously low and its safety is better.

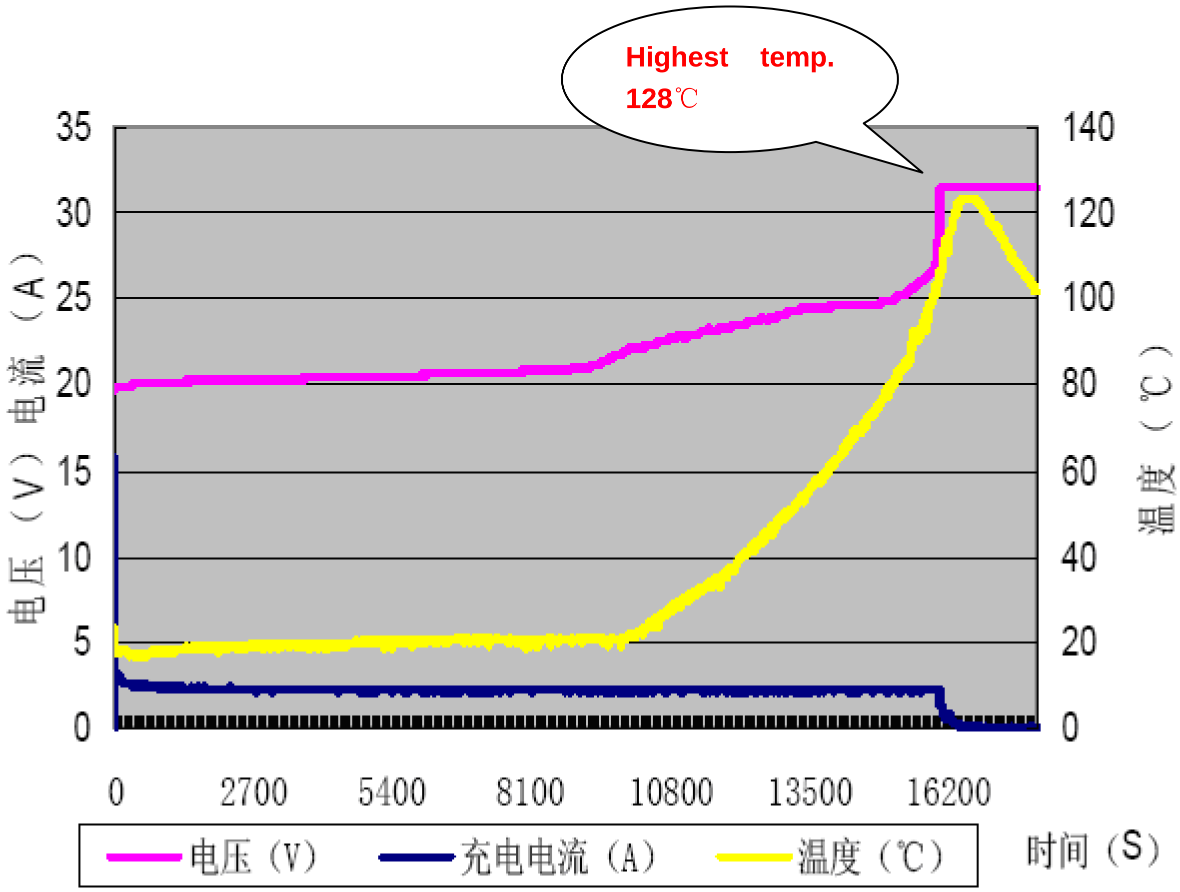

Fig.5：0.2C&30V overcharge curve of 5-series LMO battery pack

3. The float charge tolerance ability of these two materials have a comparatively large difference.

LMO cell's voltage is about 4.20V when full charged, float charge at this time would make LMO material's structural stability worse, and the electrolyte is under high voltage, which would make the solvent easier to decompose. These two factors would make LMO battery's storage and cycle performance slump.

LFP cell's voltage is about 3.6V when full charged, as LFP 's structure is more stable, and solvent in electrolyte would not decompose at this time, cell's performance would not be affected by float charge.

Compared with LMO material, as LFP material is better in thermostability, weaker in oxidability, LFP cell is better in safety, more tolerant with overcharge and high temperature. When LFP cell is in abnormal condition, it is not easy to occur thermal runaway, even if it occurs, its damage degree is less than LMO, therefore it is more suitable for manufacturing large capacity battery. Because LFP 's structure is more stable in the course of charging, and it will not occur dissolution similar with Mn dissolution in LMO, battery's cycle performance is better and the life will be longer. All of these show that LFP battery is more suitable for electric energy storage battery，this is also the most important reason why Phylion chooses LFP for cathode.

II Choice of anode material

Phylion uses MCMB (mesocarbon microbeads) for cell's anode active material.

When battery is in the process of a long-time cycle, MCMB can maintain a stable structure, thus it has a longer life than common graphite material.

Contrast of MCMB and non-MCMB artificial/composite graphite's main property is shown in the following table:

	MCMB	Non-MCMB artificial/composite graphite
Basic unit structure inside of particle	Layered graphite	Layered graphite
Particle appearance	Spherical	Irregular
Surface area	About $1m^2/g$	About $2\text{-}6m^2/g$
Whether need coating outside of particle	No need	Often need coating for making up structure flaw, but coating layer is different with particle itself, it will have damage or breakage in cycle, causing material property affected, thus affecting cell and battery's performance
Processing property	Easy	Processing difficulty is big, often cause plates' uniformity bad, thus affecting cell and battery's performance

III Choice of electrolyte

The operation voltage of LMO-MCMB system's cell is 2.7 to 4.2V, the choice of solvent in electrolyte is relatively difficult, and good oxidation-reduction additives are not yet found in this voltage sector, LMO battery‘s overcharge performance is relatively weak.

The operation voltage of LFP-MCMB system's cell is 2.0 to 3.65V, the choice of solvent in electrolyte is relatively easy, and good oxidation-reduction additives can be found, which increases LFP battery's overcharge performance.

IV Choice of cell structure

1. Case type comparison:

	Aluminum-plastic film soft-packing case	Aluminum case
Packaging case	Aluminum-plastic packaging film	Aluminum
Cell weight	Light	Heavy
Anti-water ability	Can't be used for a long time, moisture can permeate into cell	Can resist influence of environmental moisture completely
Anti external force ability	Packaging is easy to break and cause cell failure	Can resist external force, cell is not easy to be damaged
Cell's internal resistance	Use eduction of aluminum and nickel tags, high	Use riveting technique, low
Heat dispersion ability	Common	Good

1.1 Soft-packing cell and aluminum case cell both belong to main packaging forms of rectangular cell. The soft-packing cell's weight is light and the case is insulated. It is actually sealed by PP layer's fusion, but the PP layer itself is air-permeable and water-absorbable. When cell is placed for a long time, the environmental moisture can permeate through the PP layer to cell's interior gradually. At present, the common aluminum-plastic packaging film can only guarantee that moisture inside of cell reach standard within 3 years; while the aluminum case cell is sealed by metal fusion, and metal cannot permeate air or absorb water, so the moisture in cell can reach standard until cell expires. Nowadays, packaging film material with a better anti-water-permeate ability is developed abroad.

1.2 The case of soft-packing cell uses aluminum-plastic packaging film, the original thickness of aluminum layer is only 0.040mm, after stamping and forming, there is only 0.020mm in corner part , external collision or vibration both can possibly make damage of aluminum layer, and once the aluminum layer is broken, cell failure can be caused; while aluminum case cell uses aluminum with thickness of 0.50mm as case, making defect in this aspect not exist.

1.3 Soft-packing cell's positive and negative electrode use eduction of aluminum and nickel tags, however aluminum and nickel tags' internal resistance is high, and its strength is weak. Been bended for 6-8 times, problems of cracking or breaking can occur, which can cause cell failure; while for Phylion 's aluminum case cell, its positive and negative tags use riveting method, the external poles' strength is big, similar problems won't happen.

1.4 The case of soft-packing cell is aluminum-plastic packaging film, which has a bad heat dispersion ability. It can cause temperature rise of cell's interior, moreover, it can deteriorate cell's performance; while aluminum case which has a good heat dispersion ability.

1.5 Soft-packing cell is easy to burn in ultimate condition, while a special safety valve device is designed on aluminum case cell, fire or explosion can be avoided by venting of safety valve in ultimate condition.

2. Comparison of internal structures of coiling +lamination, coiling, Z-type lamination, bag-type lamination：

2.1 There is stress inside of cell with coiling structure, tension to separator is produced in charge& discharge of cell, structural change inside of cell can be affected. Ordered by stress inside of cell (from big to small): coiling +lamination, coiling, Z-type lamination, bag-type lamination;

2.2 Ordered by thermal distribution uniformity (from big to small) when cell is discharging: bag-type lamination, Z-type lamination, coiling, coiling +lamination;

V Comparison of LFP and LMO cell/battery pack's performance

	LFP cell	LMO cell
7-series 0.2C& 60V overcharge	Air-leakage, no fire, no explosion	**Fire,** no explosion
150℃ high temp. box	No air-leakage，no fire, no explosion	No fire, no explosion, but air-leakage proportional
Acupuncture	No air-leakage，no fire, no explosion	No fire, no explosion, but temp. up to 400℃ proportional
Impact	No air-leakage，no fire, no explosion	No air-leakage，no fire, no explosion
Normal temp. 1C cycle performance	3000-4000 times	1200-1500 times
High temp. performance	1C capacity at 60℃ close to normal temp.	1C capacity at 60℃ is 95% of normal temp.
Low temp. performance	1C capacity at -20℃ is 50% of normal temp.	1C capacity at -20℃ is 80% of normal temp.
Mass energy density [Note]	About 430Wh/kg	About 361Wh/kg
Volume energy density [Note]	About 950Wh/L	About 1040 Wh/L

Note: As manufacturing technique has a comparatively large effect on cell's energy density, the comparison here is only used by LFP and LMO material's mass/volume energy density themselves.