Development of large, highly safe, high-performance lithium ion batteries for stationary use to support a smart society

Sept. 24, 2013

ELIIY Power Co., Ltd.
Kiyomoto Kawakami - Director, Managing Executive Officer

Company overview

- Sept. 28, 2006
  Company established by four people based on the ”noble aim” of solving environmental problems

▪ Investment of over ¥30 billion, primarily from industrial companies

▪ Product development policy making the safety of rechargeable batteries the top management priority

▪Advanced Technology management (MOT)

▪Venture spirit of creating a market from the ground up

2007
Developed battery cell using lithium iron phosphate as the cathode material

Oct. 2009
Completed Research and Development Center
(Shiga Prefecture)

Apr. 2010
Completed first phase of mass production plant (Kanagawa Prefecture)

Sept. 2010
Began selling Power iE portable power storage system

Oct. 2011
Began selling Power iE portable power storage system

June 2012
Completed second phase of mass production plant (Kanagawa Prefecture)

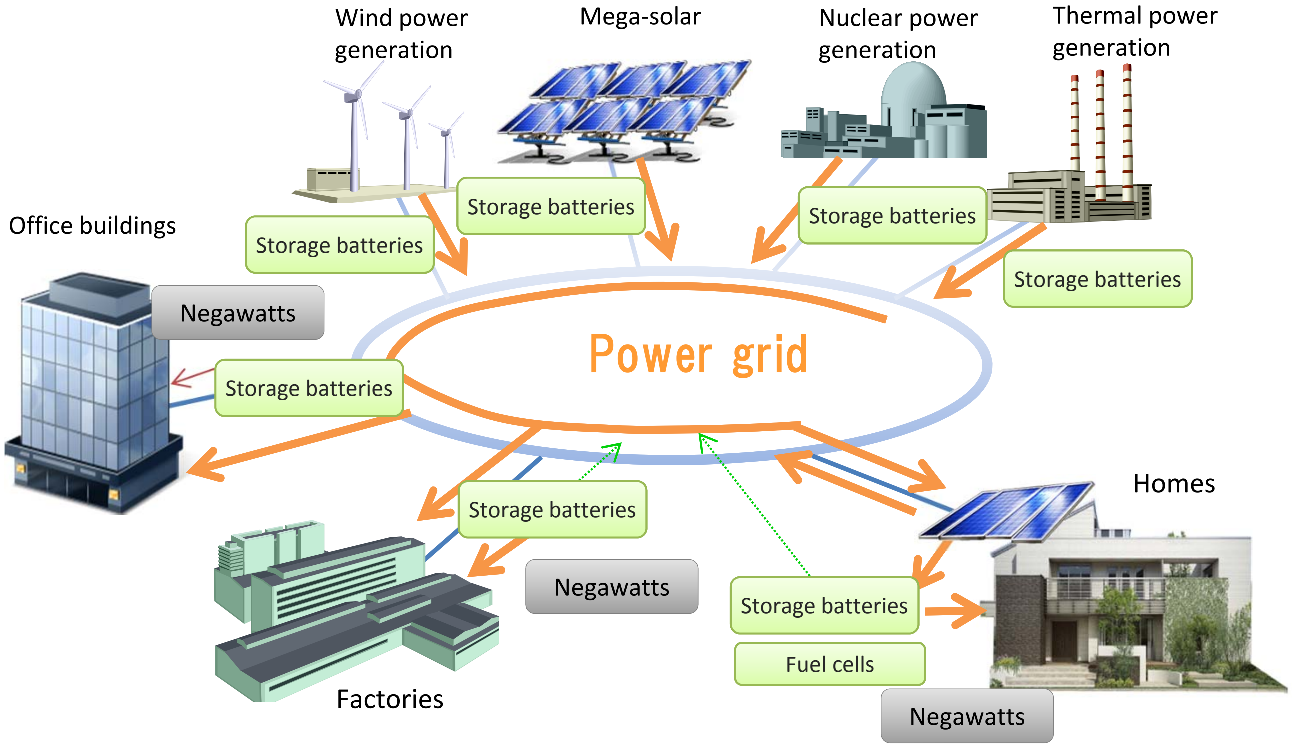
Dec. 2012
Began selling power storage systems for industry

Mar. 2013
Began selling residential power storage systems

Reasons why storage batteries are needed for a smart society

Storage batteries are essential to achieve the best energy mix

Ingenuity is needed to effectively use energy without any waste.



[Role of storage batteries]
Stabilizing (smoothing) the system by suppressing peak power of the load.
Excess power is accumulated in storage batteries for later use.

Types of storage batteries used for power storage applications

Lithium ion batteries are the current favorite

The current favorite is lithium ion batteries, which feature normal temperature operation, high energy density and long service life!

	Operating voltage	Operating temperature	Energy density	Power density	Expected service life	Battery efficiency	Structure		
							Cathode	Anode	Electrolyte
Lead storage battery	2.0 V	Normal	20-35 Wh/kg 50-90 Wh/liter	100 -200 W/kg	7-10 years 1500 cycles	65-80%	Lead oxide	Lead	Dilute sulfuric acid
Nickel metal hydride battery	1.2 V	Normal	20-70 Wh/kg 30-200 Wh/liter	150 -1000 W/kg	500- 1500 cycles	Up to 84%	Nickel hydroxide	Hydrogen absorbing alloy	Potassium hydroxide + Sodium hydroxide
Sodium-sulfur battery	2.0 V	280-350℃	120 Wh/kg 170 Wh/liter	150 W/kg	15 years 4500 cycles	Up to 88%	Sulfur	Sodium	β-alumina
Redox flow battery	1.4 V	10-40℃	10-20 Wh/kg 20 Wh/liter	Unknown	10 years or more	75-85%	V4+/V5+ ion s	V2+/V3+ ions	Sulfur-vanadium
Lithium ion battery	2.4-3.8 V	Normal	70-160 Wh/kg 200-400 Wh/liter	400-1000 W/kg	10 years or more 3600 cycles or more	Up to 95%	Lithium oxide	Carbon Lithium titanate	Lithium salt + Organic solvent

An in-company investigation

Subject for stationary using of Lithium ion batteries

Merits to other batteries (e.g. Ni-MH, Lead acid)

- ✓ **Low self-discharge**
- ✓ **High energy density**
- ✓ **High energy efficiency**

Demerits (safety risk)

- ✓ **overcharge/ overdischarge**
- ✓ **thermal runaway**

Subjects for stationary using

* Large energy capacity

* Keep long system life

* Will be used in homes, public facilities and other buildings

* Not enough low enforcement or regulation for popularization

It must be safety first to use LIB for stationary using!

Factors which make lithium ion batteries unstable

If a battery heats up abnormally due to internal or external factors, it will become unstable.

internal factors

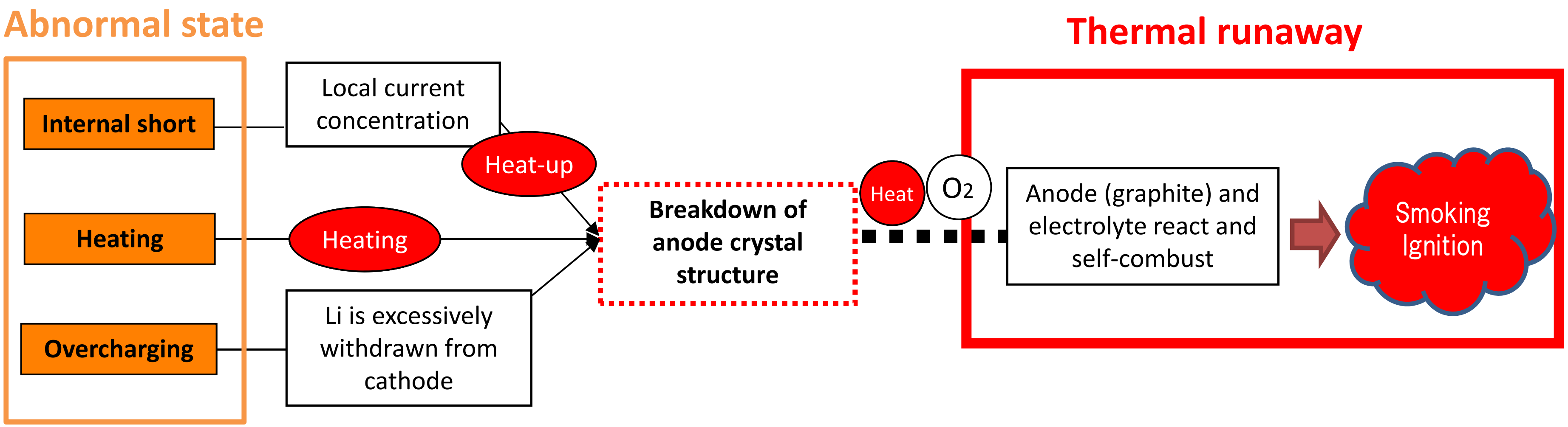
✓**Thermal runaway due to breakdown of the cathode crystal structure…Overcharging**

✓**Abnormal heat-up due to internal short…Li dendrites, current collector short, infiltration of foreign matter**

external factor

✓**Abnormal heat-up due to internal short caused by external factors…Crushing, collision**

✓**Forced heat-up due to external factors…Heating, fire**



It is best if the causative factors can be eliminated, but it is difficult to suppress external factors, and thus it is necessary to consider methods which can suppress abnormal heat-up.

Factors which make lithium ion batteries unstable

At present, safety assurance depends on the system

Factors

✔Overcharging ✔Internal short
✔Thermal runaway due to forced heating

Take measures by BMU ⟶ System provides safety assurance

Battery Management Unit (BMU)

Monitors voltage and temperature of each battery cell to prevent any improper operation such as overcharging.

+

Battery system
(Storage battery part)

Ordinary concept of battery protection

The development system is clear, and the technique is effective for set products
・Mobile phones ・Laptop computers ・Cars, etc.

⇕

With systems for stationary use, the development system is unclear, and separate products are included.

[Most important point]

Safety of single cell

※not depend on BMU

The approach must be changed between small cells and large cells for power storage

1. **High degree of "safety"**
2. **Long life time**
3. **High capacity storage**
4. **Enables input/output of large current**
5. **Easy maintenance**
6. **Low cost**
7. **Disposable**

Stationary lithium ion batteries for power storage must balance conflicting requirements: high battery capacity and large current flow on the one hand, while prioritizing safety on the other.

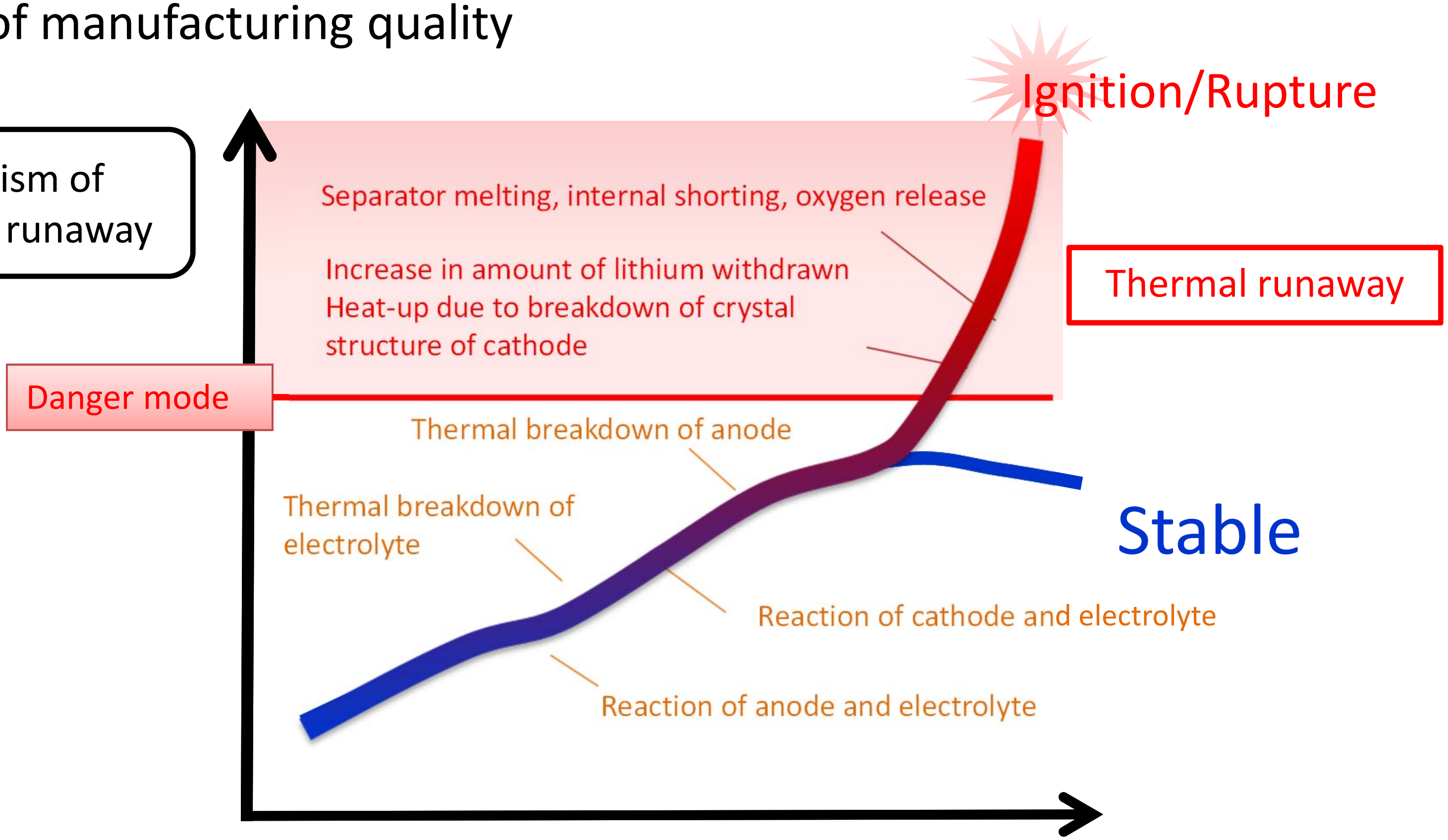
Key points for developing highly safe batteries

Thermal runaway can be suppressed through multilateral optimal design

- Materials with high thermal stability → We noticed iron phosphate lithium cathode
- Structure with no local heat-up
- Metal case
- Optimization of each component
- Control of manufacturing quality

(Structure with no local heat-up / Metal case) → Produced heat << Heat capacity + Radiated heat

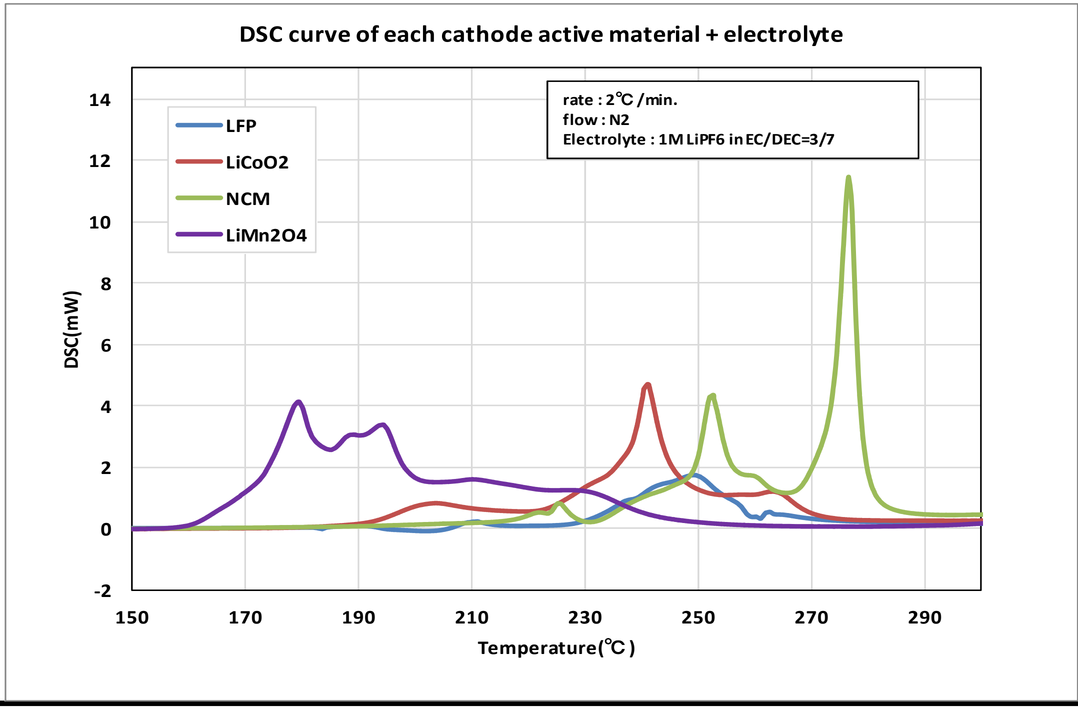
Mechanism of thermal runaway



Types of cathode active materials and their thermal stability

Lithium iron phosphate has the advantage in terms of thermal stability

Cathode active material	$LiNiO_2$	$LiCoO_2$	NCM	$LiMn_2O_4$	$LiFePO_4$
Thermal stability Thermal breakdown temperature in charged state	× (Approx. 180℃)	△ (Approx. 200℃)	○ (Approx. 320℃)	○ (Approx. 300℃)	◎ (Approx. 600℃)
Produced heat ※1	1330J/g	770J/g	563.6 J/g	230J/g	150J/g



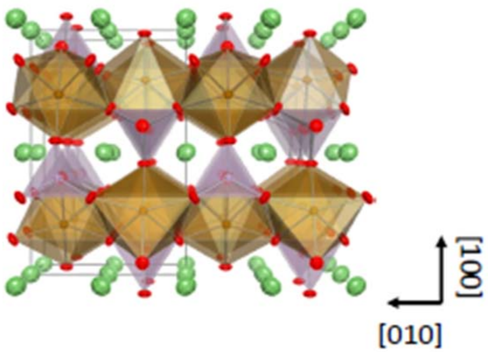
※1 NNIKKEI ELECTRONICS 2010.2.22 NE ACADEMY P97 table1

Thermal breakdown characteristics of cathode materials (charged state)

Features of lithium iron phosphate cathode material

Crystal structure is highly stable by olivine type structure

Safety

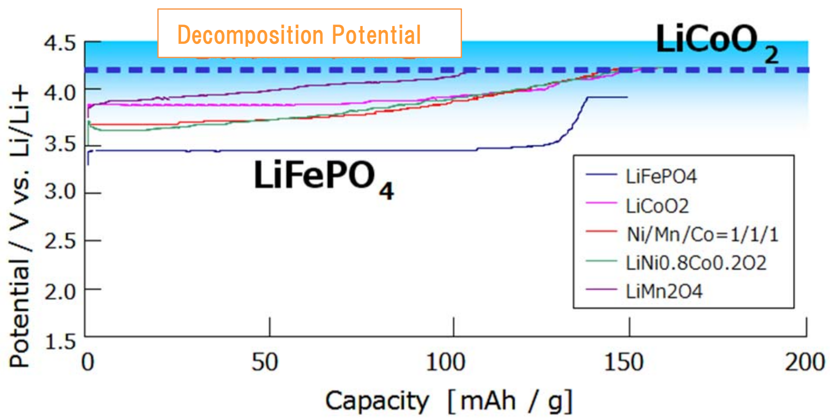


Li Fe PO_4

Lithium does not contribute to stability of the crystal structure → crystal structure is stable without enough lithium of the anode by overcharge

Anion Li is in the crystal structure not involved The phosphorus (P) anion does not release oxygen → high thermal stability

Long life



Can be charged with a safe potential

✔ Safety and long life

Abundant resources

Uses iron (Fe) for the transition metal. → ✔ **Abundant resources** ✔ **Low cost**

※1 Shin-ichi Nishimura, Genki Kobayashi, Kenji Ohoyama, Ryoji Kanno, Masatomo、Yashima, Astuo Yamada, Nature Materials, 7, 707-711 (2008)

Among those battery test samples , changed only cathode materials for burning test

Lithium iron phosphate which has high thermal stabilities burns gradually with combustion test.

Cathode materials	Burning time	burning test scene
$LiFePO_4$	14’41’’	
$LiMn_2O_4$	5’00’’	
30% of $Li(Mn/Co/Ni)O_2$ + 70% of $LiMn_2O_4$	4’27’’	
$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	3’47’’	

Comparison of overcharge resistance characteristics due to differences in cathode active material

Overcharge testing: testing using prototype batteries (50Ah class) with different cathode materials

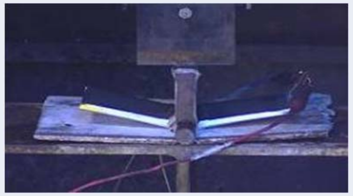
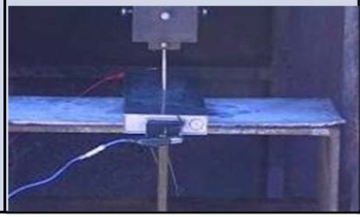
Thermally stable $LiFePO_4$ will not induce thermal runway due to breakdown of crystal structure , even in the case of enforced overcharge

Cathode active material	Phenomenon	Max. temperature
Lithium iron phosphate($LiFePO_4$)	Vent1	104℃
Lithium manganese oxide($LiMn_2O_4$)	Vent2	470℃
Ternary-based (30%) + (70%) ($LiMn_2O_4$)	Vent3	509℃
Ternary-based ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$)	Vent3	526℃

Vent1 Safety valve operation (at battery surface temperature of 150℃ or less), only vapor of electrolyte
Vent2 Intense white smoke (at battery surface temperature of 150℃ or higher)
Vent3 Ignition (including catching fire)

Is it safe to use lithium iron phosphate?

Relationship between safety and battery structural design

	Overcharge (20V)	Nail penetration	Crushing	Combustion
48Ah = ELP's Cell Cathode: $LiFePO_4$ Anode: Carbon SUS case				
8Ah Cathode: $LiFePO_4$ Anode: Carbon Laminated				
46Ah Cathode: $LiFePO_4$ Anode: Carbon SUS case				Not conducted

- Chemical phenomena relating to battery safety (e.g., white smoke, ignition) are caused by thermal breakdown resulting from a rise in battery temperature.
- Battery temperature depends on the relationship between the amount of heat produced, heat capacity, and the amount of heat radiated. These factors mainly depend on the battery structure.
- Therefore, even if cells are comprised of the same material, differences in battery structure will affect the results of safety testing.

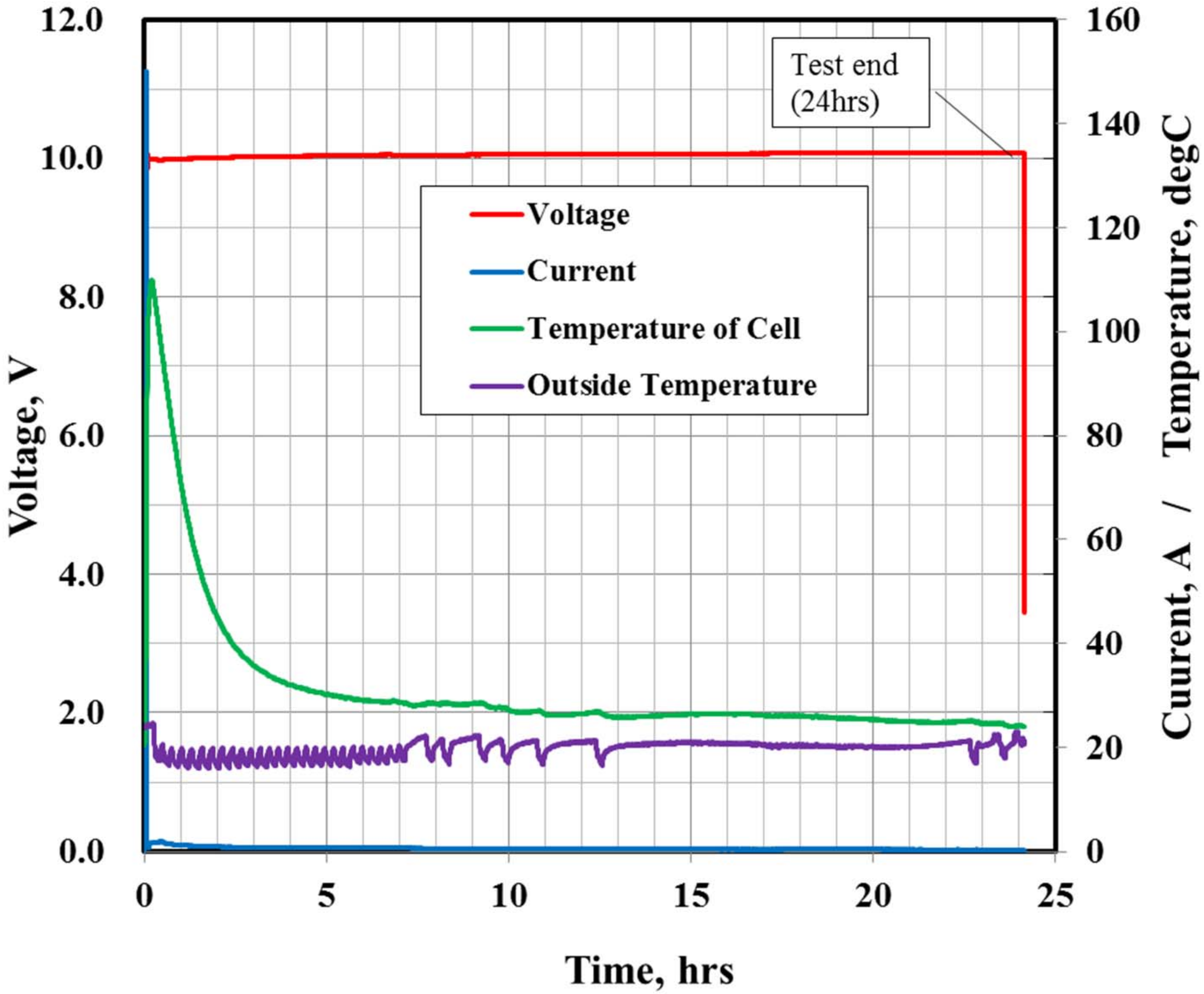
Using lithium iron phosphate does not always ensure safety

Risk scenario and related test to create safe battery

Possible risk	Possible test item
✓ Malfunction or miss use of BMU	▶24hrs overcharging
✓ Internal short circuit	▶Nail penetration test
✓ Short circuit of coursed by crush	▶Crush test
✓ Fire or forced burning	▶Heating ▶Forced burning test

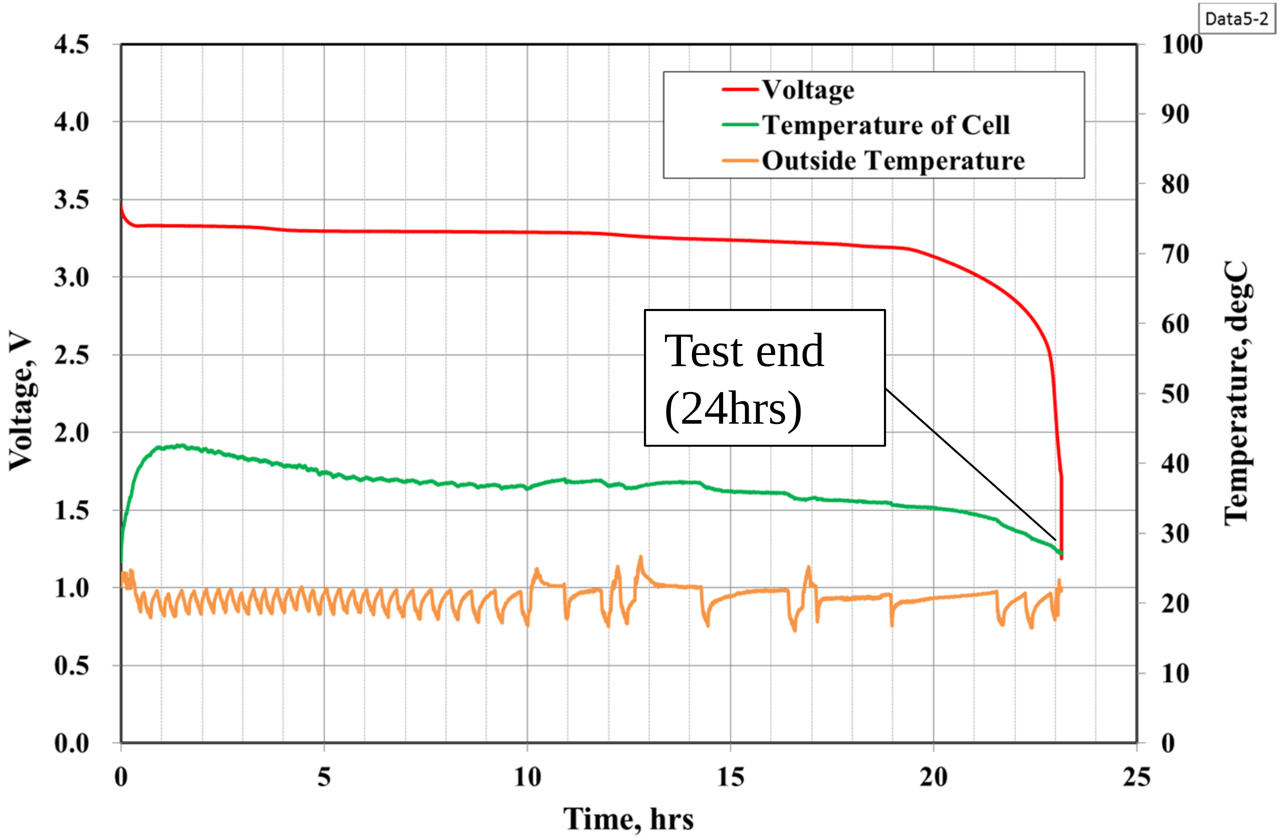
Test result of overcharge

150ACC (3C) , Max. 10V



Test result of penetration

SOC100%, φ3.0mm



Discussion of nail penetration test results

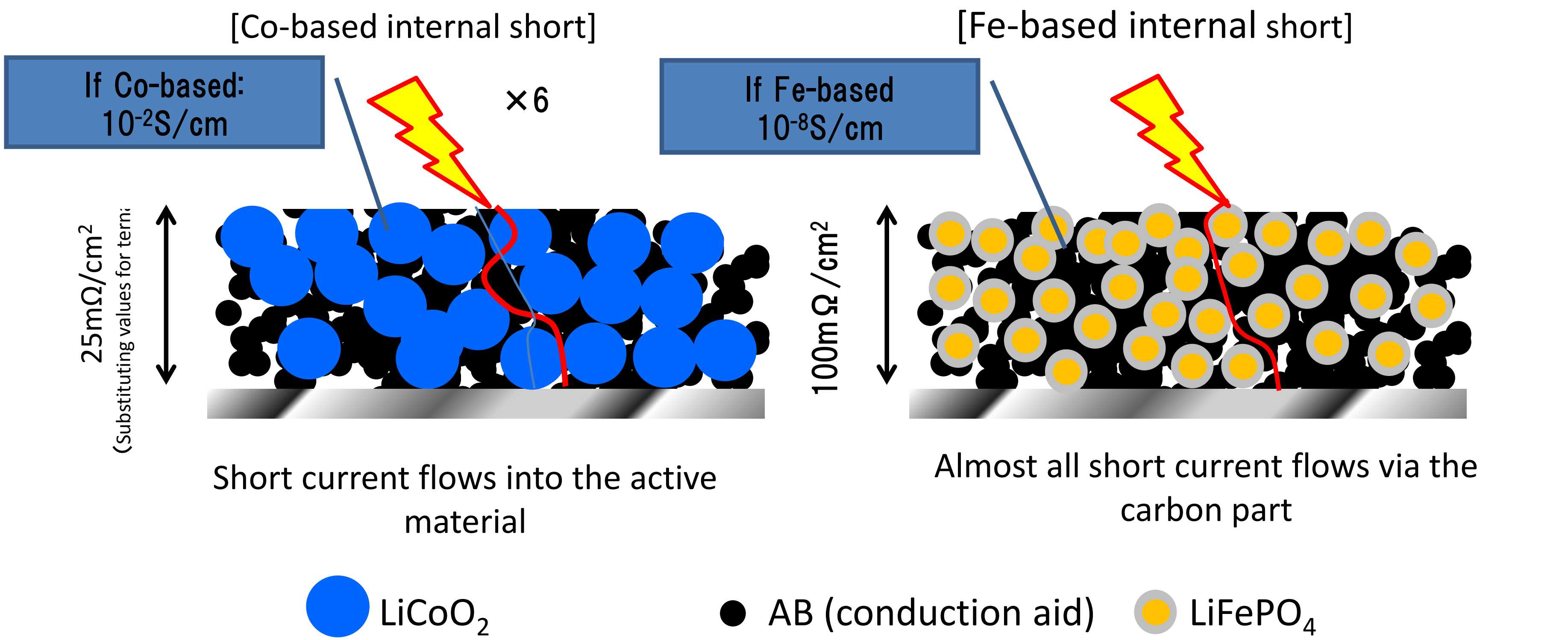
Conductivity of each type of single cathode material

Even with a single cathode material, an iron-based cathode has conductivity orders of magnitude lower than other types.

Conductivity of each type of single cathode material (order of magnitude)

Carbon	Ni-based	Co-based	Mn-based	Fe-based
10^{2}	10^{-1}	10^{-2}	10^{-5}	$10^{-8\sim-9}$

（Unit: S/cm）



Conclusion

Triggers of thermal runaway and key points for design of highly safe batteries

- ✓ Unsafe states of lithium batteries are caused by internal shorts, heating and overcharging, but self heat-up due to breakdown of the cathode crystal structure and thermal breakdown due to increased battery temperature also have an effect.

- ✓ In this presentation, I have evaluated various cathode materials, and shown, using experimental results, the stability and thermal stability of the crystal structure of lithium iron phosphate.

- ✓ On the other hand, experimental results shows that the separator material cannot achieve heat resistance commensurate with the thermal stability of lithium iron phosphate, and thus in order to suppress internal shorting due to thermal breakdown (meltdown) of separators and ensure battery safety, it is crucial to suppress the amount of internal heat produced by optimizing battery structure.

To ensure safety of lithium ion batteries, it is crucial to optimize thermal stability of the cathode material and structure-based thermal design

First in the world to pass safety certification by TÜV Rheinland (TUV)

Safety evaluation from the perspective that single cells should be safe

ELIIY Power

The only battery cell to pass TUV severe safety evaluation testing* stricter than public standards

TUV test item	Measurement conditions	Acceptance criteria	Results for Eliiy cells	SBA S 1101/JIS measurement conditions
Vibration	10Hz-500Hz, 0.35mm peak, 3 axes, 5 cycles	No leakage, No ignition/rupture	Pass	None
Dropping	100cm	No leakage, No ignition/rupture	Pass	100cm
Forced internal short	Nail penetration, 3mmΦ stainless steel rod, 80mm/sec	No ignition/rupture, Cell temperature 170℃ or less	Pass（26℃）	Insertion of piece of nickel, 0.1mm/sec, 800N
Salt water immersion	Salt water with 3.5% concentration	No leakage, no rupture	Pass	None
Impact	Average 75g, maximum 175g	No leakage, No ignition/rupture	Pass	SOC 50%, place rod on top Drop 9.1kg from 61cm
Crushing	13kN	No ignition/rupture	Pass	None
Thermal shock	−40℃ to 80℃	No ignition/rupture	Pass	None
Heating	130℃, 10min	No venting, No ignition/rupture	Pass	5℃/min, 85℃, held for 3hrs.
Forced external short	5mΩ	No ignition/rupture, Cell temperature 150℃ or less	Pass（118℃）	30mΩ
Overcharging	50A or 150A, 10V CCCV, 24hrs	No ignition/rupture, Cell temperature 150℃ or less	Pass（105℃）	0.2℃, up to 120% of max. voltage（However, this is not mandatory）
Forced discharge（reverse charging）	100A（2 cycles）, 1hrs	No venting, no ignition/rupture	Pass	50A（1 cycle）, 90min

TÜV Rheinland Group: A leading international certification body with offices in 60 countries worldwide. The group handles safety inspections for electrical products and automobiles etc.

* Severe Condition Testing Manual for Lithium Ion Cells, v2: 2011