

# Safety Technology for High-Energy-Density Lithium-Ion Battery

INOUE Kazuhiko, KAWASAKI Daisuke, UTSUGI Kouji

## Abstract

By developing a high-energy-density battery, NEC has not only helped make life more convenient by facilitating the more compact design of products that use batteries, it is also supporting the broader goal of creating a more sustainable society through efficient utilization of energy. Successful development of a high-energy-density battery requires not only suitable material to accumulate and store energy, but also technology capable of controlling large amounts of energy and technology to ensure reliability and safety in the event of emergency. This paper introduces technology that uses NEC's original flame-retardant electrolyte and separator to increase the safety of high-energy-density batteries.

### Keywords



lithium-ion battery, electric vehicle, high-energy density, safety, flame-retardant electrolytes, phosphoric acid ester compound

## 1. Introduction

The NEC Group is developing high-performance batteries for a wide range of applications, including electric vehicles, household electricity storage, and large storage systems that support electric grids, as well as electronic devices (Fig. 1). In every case, users demand that battery capacity be increased without increasing battery size. Demand for batteries with higher density is particularly

intense in the electric vehicle sector, as battery capacity has a direct impact on the vehicle running distance.

Among materials that have recently attracted attention for their ability to facilitate storage of large amounts of energy are alloys such as silicon (which can be used for anodes) and layered oxide material such as lithium nickel oxide (which can be used for cathodes). Development of batteries using these materials is now underway (Fig. 2). However, if the stored energy in a battery using these ma-

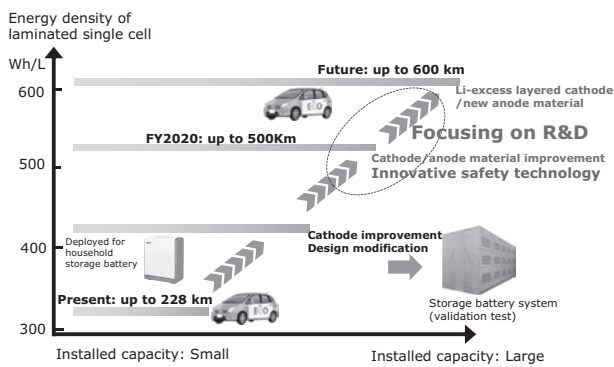


Fig. 1 NEC's lithium-ion battery R&D target.

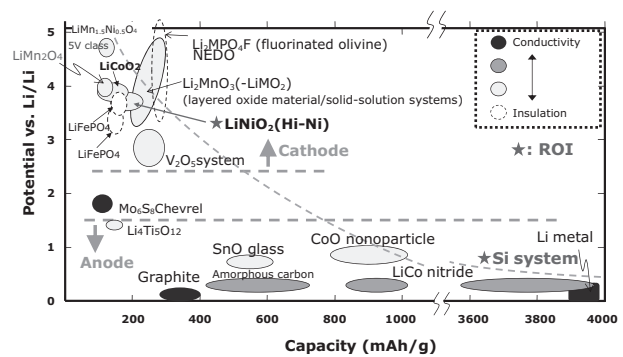


Fig. 2 Candidates for high-energy density active material.

materials becomes uncontrollable, thermal runaway can occur, leading to a potentially dangerous situation in which the components of the battery and the electrolyte (which is a flammable hazardous substance) are ignited.

Important technologies to maintain battery stability include circuit design technology that provides protection circuits, abnormality prevention technology that prevents deterioration of batteries by strengthening component properties (such as heat resistance, weather resistance, and chemical resistance), and flame-retardant technology that prevents ignition and spread of fire even in the case of thermal runaway.

In this paper, we will discuss the development of a non-flammable electrolyte and a separator with increased heat resistance.

## 2. Flame-Retardant Electrolyte

### 2.1 Electrolyte Used for Lithium-ion Batteries

Lithium-ion batteries are capable of storing large amounts of energy thanks to a high voltage of over 4 V. This high electric potential was made possible by using a nonaqueous electrolyte that has higher voltage resistance than a conventional aqueous electrolyte and is not electrolyzed even when the voltage exceeds 4 V.

However, the usable solvents for lithium-ion batteries are limited to compounds that have excellent capability to dissolve lithium salt and are also low in viscosity because high ion conductivity is required. Many commercially available batteries use solvents called carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC), and propylene carbonate (PC), but all of these are flammable organic compounds (**Fig. 3**).

### 2.2 Flame-Retardant Phosphorus-based Electrolyte

Candidates for non-flammable nonaqueous organic solvents include ion liquids, halogen-based organic compounds, and organophosphorus compound. However, none of these are really suitable for use as the principal component of an electrolyte because they have higher viscosity and are more expensive than conventional car-

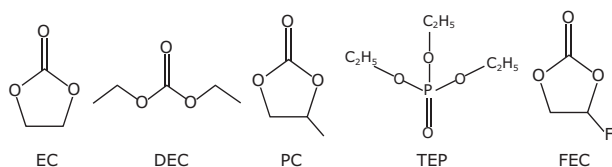


Fig. 3 Structural formulae of electrolytes.

Table 1 Values of electrolyte solvent physical properties.

	EC	DEC	PC	TEP	FEC
Boiling point(°C)	247	126	242	215	212
Melting point(°C)	35	-43	-49	-57	22
Autoignition temperature(°C)	465	445	510	470	426
Flash point(°C)	150	33	135	111	125
Viscosity(cP)	1.9(40°C)	0.83(20°C)	2.8(20°C)	1.7(20°C)	4.5(20°C)
Explosion limit(vol%)	3.6 to 16.1	1.4 to 11	2.3 to 10	1.7 to 4.9	4 to 28

bonate-based electrolytes. To solve this problem, it has been proposed to mix non-flammable solvents with a conventional carbonate-based electrolyte. At this time, none of these compounds have seen any significant practical use because none of the proposed methods can achieve sufficient flame retardancy.

In search of an appropriate compound, we decided to examine phosphoric acid ester. A comparison of the properties of phosphoric acid ester with conventional carbonates is shown in **Table 1**. As is the case with the carbonates, triethyl phosphate (TEP) - which is one of the phosphoric acid ester compounds - is low in viscosity, has excellent ion conductivity thanks to its excellent ability to dissolve lithium salt, and - for a non-flammable material - is relatively inexpensive. Consequently, we began working on an electrolyte whose principal component is phosphoric acid ester, which is a non-flammable compound.

The reason TEP has not previously attracted much attention is that its explosion point and flash point are even lower than PC. This would seem to indicate that its flame retardant capabilities are not very promising. Moreover, TEP cannot function as an electrolyte because it has poor compatibility with carbon materials used for conventional lithium-ion batteries and decomposes on the surface of the anode.

However, after performing actual combustion tests, we found that this substance is a self-extinguishing compound that ceases burning as soon as it is separated from a burner - although it continues to burn as long as it is held on a burner. We also found that the electrolytic property of the electrolyte for silicon oxide - which is one of the candidate materials for the high-density battery anode we are developing - can be significantly improved by adding a few percent of fluoroethylene carbonate (FEC), whose constitution is partially replaced using fluorine that also contributes to flame retardancy. The effects of this are shown in **Fig. 4**. Lithium nickel oxide is used for the cathode, silicon oxide is used for the anode, and polypropylene resin is used for the separator.

In the graph on the left, only TEP was used as an electrolyte solvent component, but charging was not possi-

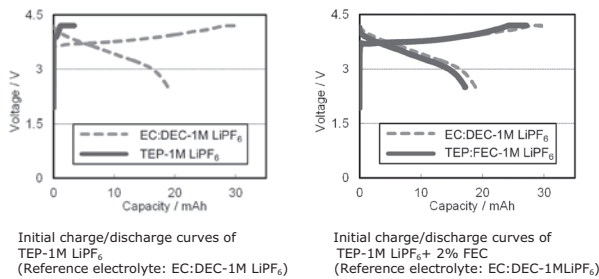


Fig.4 Suppression effects of FEC on TEP decomposition.

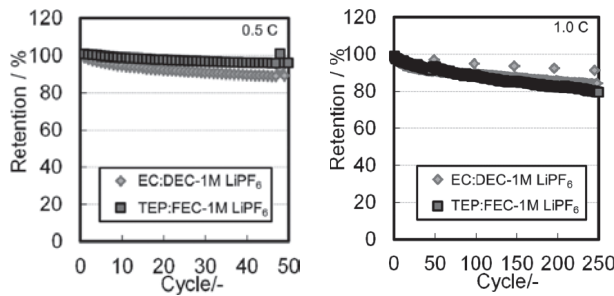


Fig.5 Cycle performance (comparison between the new electrolyte and conventional electrolytes).

ble because the TEP decomposed on the surface of the anode. On the other hand, the graph on the right is an example of what happened when 2% FEC was added. Since addition of FEC suppresses decomposition of the TEP, this makes it possible to obtain a charge/discharge curve equivalent to that of carbonate electrolytes.

### 2.3 Battery Properties

Fig. 5 shows the life property (cycle property) of the new electrolyte whose principal component is TEP. Compared to the electrolyte (EC/DEC-1M LiPF<sub>6</sub>) whose principal component is a conventional carbonate, the capacity (retention) after charge/discharge transits similarly. For practical use, some fine-tuning such as the addition of an additive would be required, but the results clearly indicate that the potential is there. In other words, it has been verified that this mixture offers performance equivalent to conventional electrolytes, as well as the additional benefit of being non-flammable.

### 2.4 Safety

We ran comparisons (external short-circuit test, high-temperature test, and impact test) between our newly developed battery and a conventional battery. Lithium nickel oxide was used for the cathode in the new

battery, silicon oxide for the anode, an inorganic (fiber) material with excellent heat resistance for the separator, and phosphoric acid ester for the electrolyte. The conventional battery used polypropylene resin for the separator and carbonate-based solvent for the electrolyte (Table 2). To maximize safety, a stacked multilayer laminated configuration was used for the new battery (Photo 1). This configuration provides a much a larger surface-to-volume ratio than is possible with a cylindrical or prismatic battery around which the electrode is wound. Based on this combination of design and materials, we anticipated that our new battery would offer excellent heat dissipation performance and higher safety even under conditions of abnormal heat generation.

#### (1) External short-circuit test

The external short circuit testing conditions are shown in Fig. 6. Photo 2 shows the external appearance of the batteries after the external short-circuit tests. When the reference battery with carbonate-based electrolyte was tested, the battery itself swelled and exploded. You can see the magni-

Table 2 Battery composition.

	Reference battery	New battery
Cathode	LiNiO <sub>2</sub>	LiNiO <sub>2</sub>
Anode	SiO	SiO
Electrolyte	EC/DEC	TEP/FEC
Supporting salt	LiPF <sub>6</sub>	LiPF <sub>6</sub>
Separator	Polypropylene	Inorganic



Photo 1 7 Ah battery used for safety evaluation.

\* 55 deg C environment

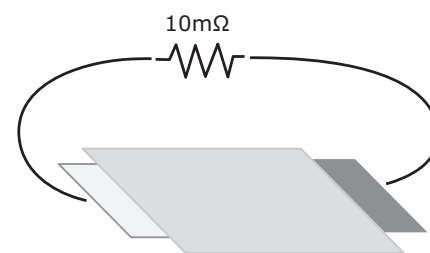
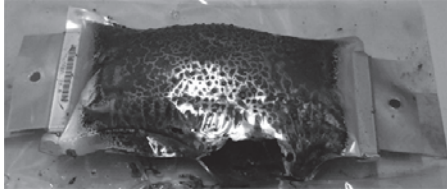


Fig. 6 External short-circuit test.

Reference battery



New battery



Photo 2 External appearance of the batteries after the external short-circuit test.

tude of the explosion in the photo. The new battery featuring the phosphoric acid ester electrolyte, on the other hand, displayed a few wrinkles on the outer covering due to slight vaporization, but otherwise appeared unchanged.

## (2) Heating test

In the heating test, we observed the effect on the batteries of exposure to a temperature of 150 deg C for 3 hours (**Fig. 7, Photo 3**). When the temperature exceeded about 120 deg C, the cell voltage of the reference battery with the polypropylene resin separator began to decrease rapidly. At the same time, the battery temperature increased considerably. After the high-temperature storage test, observation of the battery's appearance indicated that it had ignited (Photo 3, top). Ignition is believed to have occurred because the polypropylene resin with low heat resistance generated melting and contraction, causing the battery to short-circuit.

Thanks to the use of the inorganic separator and new electrolyte, the new battery, on the other hand, showed only a gradual decrease in cell voltage even when it had been exposed to 150 deg C heat for 3 hours. This indicates that high safety was ensured because the inorganic separator generated neither melting nor contraction even at the high temperature of 150 deg C.

## (3) Impact test

An impact test evaluates the safety of a battery when a strong impact is applied. Specifically, the test consists of placing a  $\phi 15.8$ -mm round bar on the charged battery and dropping a 9.1-kg weight on it from a height of 78.5-cm.

The electrodes were short-circuited inside the ref-

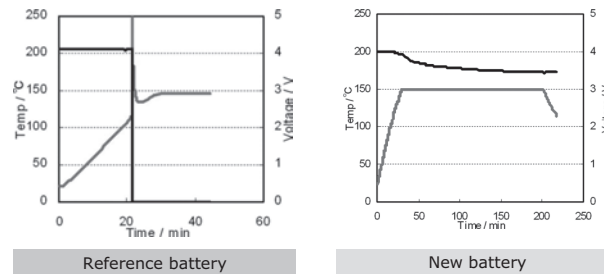
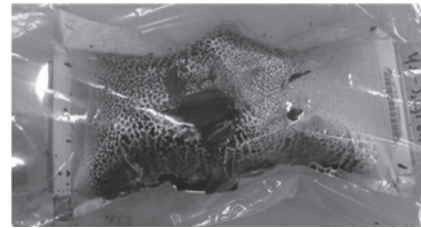


Fig. 7 Changes in battery temperature and voltage during the heating test.

Reference battery



New battery



Photo 3 External appearance of the batteries after the heating test.

erence battery, as was the lithium nickel oxide cathode, resulting in heat generation caused by the local flow of heavy current. The polypropylene resin also generated melting and contraction due to the heat, so the short-circuiting between the electrodes caused by the impact expanded, leading to the ignition of the flammable electrode. With the heat-resistant inorganic separator, on the other hand, there was no expansion of short-circuiting and no ignition, thanks also to the flame retardant properties of the electrolyte (**Photo 4**).

## 3. Conclusion

We have developed an electrolyte suitable for incorporation in high-energy density batteries. This electrolyte has almost the same life property as conventional carbonate-based electrolytes, with the added advantage that it is flame-retardant. In combination with an inor-

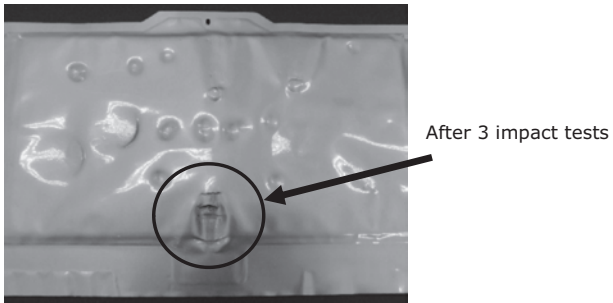


Photo 4 View of the new battery after the impact tests.

ganic separator featuring excellent in heat resistance, this ensures the highest possible levels of safety.

#### Authors' Profiles

##### **INOUE Kazuhiko**

Principal Researcher  
Smart Energy Research Laboratories

##### **KAWASAKI Daisuke**

Principal Researcher  
Smart Energy Research Laboratories

##### **UTSUGI Kouji**

Senior Manager  
Smart Energy Research Laboratories

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