Fe-based Metal Foils for Current Collectors in Li-ion Secondary Batteries

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Abstract

In lithium-ion secondary batteries for vehicles, focus on safety and cycle life has been required in addition to improvement of energy density and input/output performance concerning the traveling distance and power generation accepting characteristics. Therefore, materials for constituting the batteries are facing realignment of some fundamental functions. Fe-based materials including stainless steel are excellent in high electrolyte resistance, exhibit excellent mechanical properties, and also have a wide electric potential window. As a result, Fe-based metal foils for current collectors would significantly improve the performance and quality of batteries.

1. Introduction

Recently, it is said that the automotive industry is facing a turning point that occurs once every 100 years. With various countries' environmental regulations as a background, demand has clearly been shifting to motorized vehicles. Properties required for on-vehicle secondary batteries that control the vehicle performance vary depending on the vehicle type such as hybrid vehicle (HEV), plug-in hybrid vehicle (PHEV), and electric vehicle (EV). Generally, importance is attached to the safety and cycle life in addition to improvement of the energy density and input/output performance that are related to the traveling distance and power generation accepting characteristics. As the levels of required properties become higher, materials constituting secondary batteries, such as materials for positive and negative electrodes and electrolytes, need to be reformed. Various materials for positive and negative electrodes have previously been studied for higher energy density of lithium-ion secondary batteries (LIBs). In addition, recently, to satisfy both higher energy density and safety, all-solid-state LIBs for which electrolytes and all components are solids have been actively studied.

Due to environmental changes to which battery component materials are subjected, studies to apply Fe-based metal foils having corrosion resistance and mechanical properties superior to those of conventional materials to current collectors, being one battery component, have been actively conducted. These current collectors do not contribute to the battery capacity directly and there is demand for them to be as thin as possible. As a result, a technology for reducing the thickness to approximately 10 μ m by cold rolling is required. The Metal Foil Division of Nippon Steel Chemical & Material Co., Ltd. has an overwhelming share of ultra-thin stainless steel foils for hard disk drive suspensions in the world. The Nippon Steel Corporation group has strong points—rolling technologies that can control the thickness and flatness highly accurately even for very thin sheets and an integrated production and quality management system in which all processes from the procurement of raw materials to foil rolling are conducted within the group. This paper outlines ultra-thin Fe-based metal foil for current collectors that have been studied to realize high-capacity, long-cycle-life LIBs with high safety and reliability.

2. Structure of Liquid-based LIBs and Positive and Negative Current Collectors

Figure 1 illustrates the structure of a liquid-based LIB.¹⁾ A positive electrode and negative electrode face each other with a separator to prevent a short circuit in-between. A tab lead has been welded to each electrode to take current out from the electrode to the outside of the battery. An electrode consists of an electrode layer and current collector. The electrode layer consists of active materials that can occlude and release lithium (Li) ions during charge and discharge, conductive additives that improve electro-conductivity, and binders that bind active materials to each other and active materials to the current collector. The space enclosed by the case including voids in the electrodes and separator is filled with an organic elec-

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<Requirement matters for current collectors>

Conductivity, Mechanical strength, Adhesion with an electrode layer, Thin, Lightweight Corrosion resistance, Non-reactivity with Li, Heat resistance, Work-ability, Weld-ability

Fig. 1 Structures of (a) Li-ion secondary batteries and (b) Electrodes

trolyte into which Li salt has been dissolved. The current collector is a passage to flow a current to the electrode layer and tab lead, and also plays the role of a base of the electrode layer from a mechanical perspective. Therefore, current collectors need to have conductivity and mechanical strength. In addition to such, they require various characteristics, for example, they should have adhesion with electrode layers and corrosion resistance in electrolytes and they should be thin and lightweight. From a practical perspective, they should be easy to obtain and inexpensive.

The non-reactivity in electrolytes is a particularly important property that significantly affects the cycle life of devices. **Figure 2** shows the oxidation-reduction potentials of candidate materials of current collectors that were obtained by simply converting values for aqueous solutions into the Li electrode potential reference.¹⁾ The oxidation-reduction potential of copper (Cu) foils, which are often used as negative current collectors, is around 3.5 V (vs. Li/ Li⁺) at present and therefore they are not suitable for positive electrodes that are exposed to 4 V or more. Meanwhile, in the normal operating potential range of negative electrodes, Cu foils are stable in the metallic state. The oxidation-reduction potential of nickel (Ni), which is often used for tab leads, is around 2.8 V (vs. Li/Li⁺), so it is stable in the metallic state in the operating potential range of negative electrodes. Ni-plated steel foils manufactured by coating Ni on the plain steel surface have been suggested as negative current collectors.²

The oxidation-reduction potential of aluminum (Al) foils, which are often used for positive current collectors, is approximately 1.4 V, so they are not suitable for positive electrodes from a thermodynamical perspective. However, they easily passivate in typical LIB electrolytes, so it is known that they show rather good corrosion resistance in practice.³⁻⁶⁾ This is because Al is covered with an oxide film in the air, but, in fluoro-acid salt-based electrolytes represented by LiPF₆, a fluoride (AIF₃) film is formed on this oxide film; so, even when an Al foil is in contact with a positive electrode active material having strong oxidizability, Al does not significantly oxidize.³⁻⁶⁾ However, when Al is polarized to 1 V or less in an electrolyte, it alloys with Li, so Al cannot be used as a negative current collector.⁷⁾



Fig. 2 Oxidation-reduction potential of various metals (vs. Li/Li⁺)

Stainless steel has a passive-state film formed on the surface as is the case with Al and it does not alloy with Li, so it is expected as both a positive and a negative current collector. The passive-state film on stainless steel may consist of two layers of chromium (Cr) oxides on the metal base side and hydroxides consisting of iron (Fe) and Cr on the atmospheric side. The layer thickness may be approximately 1 to 3 nm although it varies depending on the conditions. A passive-state film is naturally formed in an environment where stainless steel is placed and this contributes to maintaining corrosion resistance. It is said that, in a normal environment, the higher the content of Cr (Cr/(Cr+Fe) ratio) in the passive-state film of stainless steel is, the higher the corrosion resistance is, and thereby the elution of metal ions decreases.

Meanwhile, regarding the passivation behavior of stainless steel in electrolytes used for liquid-based LIBs, some researchers have studied the details using SUS304, which is austenitic (γ) stainless steel in which Cr and Ni were added to Fe.8,9) These studies have reported that, in an electrolyte of a fluoro-acid salt represented by LiPF, the stainless steel reacts with anions including fluorine to form fluorides (CrF, and FeF,) on oxides, so excellent corrosion resistance is retained up to 5 V (vs. Li/Li⁺). Figure 3 shows a cyclic voltammogram (CV) of SUS316L (y stainless steel) in 1M-LiPF₄+EC:DEC (EC: ethylene carbonate, DEC: diethyl carbonate) (volume ratio of 1:1).¹⁰⁾ As is the case with the aforementioned SUS304, the anodic current is very small at 25 μ A/cm² or less up to 4.2 V (vs. Li/Li⁺) and the peaks of the cathode and anode are similar to those of SUS304. Therefore, it is expected that, for SUS316L, fluorides are formed on oxides in an electrolyte and the corrosion resistance is retained up to high potential.

Figure 4 shows the CV of the Nippon Steel group's representative stainless steel grades in 1M-LiPF₆+EC:EMC (EMC: ethyl methyl carbonate) (volume ratio of 1:3). The CV was measured by voltage sweep at a constant sweep rate of 5 mV/s under cyclic conditions of 2.5 V \rightarrow 4.7 V \rightarrow 2.0 V \rightarrow 4.3 V \rightarrow 2.3 V. The anodic current at each potential is very small at 4 μ A/cm² or less for all the





Fig. 4 Electrolyte resistance behavior of typical stainless steel grades

stainless steel grades, so it can be said that the levels compare favorably with those of Al foils that are currently used as positive current collectors. The anodic current values of ferritic (α) stainless steel NSSC430D, NSSC436S, and NSSC190 in which 17 wt% or more Cr is added and γ stainless steel SUS304, NSSC27AS, NSSC304JS, and SUS316L are particularly small. The anodic current values of NSSCFW1 and NSSCFW2 in which a smaller amount of Cr is added and a minute quantity of tin (Sn) is added instead are relatively small.

Therefore, an optimum steel grade can be selected based on characteristics such as mechanical properties and productivity in which the required levels vary depending on the application purpose, in addition to the non-reactivity in electrolytes. In any case, these types of stainless steel can be used as positive electrode current collectors that are exposed to 4 V or higher in the Li electrode potential reference. They are the only materials that can be used in practice for current collectors of both positive and negative electrodes.

3. Work to Improve the Energy Density of On-vehicle LIBs

3.1 Alkali resistance required for high-capacity positive electrodes and current collectors

Research and development of LIBs began in the 1960s and various combinations of materials for positive and negative electrodes have been studied. LIBs using LiCoO_2 (LCO) positive electrodes and carbon negative electrodes were first put on the market in Japan and they completed the basic structure of current LIBs. However, combining only such positive and negative electrode materials cannot further improve the energy density, so high-capacity active materials for positive electrodes that replace LCO have been actively studied.¹¹⁾ The capacity per weight of $\text{LiNi}_{1-X-Y}\text{Co}_X\text{Al}_Y\text{O}_2$ (NCA) mainly consisting of Ni is particularly large at 190 mAh/g or more compared with 120 to 150 mAh/g of LCO, so NCA is expected as a promising positive electrode material that can improve the energy density.

The NCA is synthesized by sintering lithium compounds (e.g., lithium hydroxides) with hydroxides containing Ni, Co, and Al, but unreacted lithium compounds may remain in the material. Such remaining alkaline component gelatinizes slurry and causes corrosion on current collectors according to formulas (1) to (3). Such corrosion reaction forms an insulating layer on the surface of an Al foil and reduces the adhesion between the positive electrode active material and the current collector, which may cause the active material to fall off. To prevent such problems, rinsing of positive active materials with water and neutralization processing by carbonic acid gas have been proposed, but such treatment unavoidably reduces the capacity of the active materials.¹²

- Whole reaction: $Al + H_2O + OH^- \rightarrow AlO_2^- + 3/2H_2\uparrow$, (1)
- Anode reaction: $Al + 4OH^- \rightarrow AlO_2^- + 2H_2O + 3e^-$, (2)
- Cathode reaction: $3H_2O + 3e^- \rightarrow 3OH^- + 3/2H_2$. (3)
- 3.2 Realization of high-capacity positive electrodes by drawing on the excellent alkali resistance of stainless steel

Current collectors made of an Al foil (positive current collectors currently used) and an NSSCFW2 stainless steel foil foliated to a thickness of 10 μ m were coated with an NCA positive electrode slurry and then dried, and the electrode layers were peeled. **Figure 5** shows their measured AC impedance.¹¹ When the imaginary part is zero, the resistance value of the real part does not change for the stainless steel foil before and after coating, but the resistance in-



Fig. 5 AC impedance measurement results before and after NCA electrode coating when using (a) NSSCFW2 stainless steel and (b) Aluminum foils



Fig. 6 SEM images of the NCA electrodes when using (a) NSSCFW2 stainless steel and (b) Aluminum foils

creases for the Al foil after coating. This may be because the stainless steel foil has corrosion resistance against strongly basic slurries, while a high-resistance film was formed on the surface of the Al foil due to corrosion.

Figure 6 shows scanning electron microscope (SEM) images of electrode plates made by coating an NSSCFW2 stainless steel foil and Al foil with an NCA positive electrode slurry and then drying.¹¹⁾ The electrode plates with slurry coated were dried at 80°C. For the stainless steel foil, spherical NCA particles densely gather, showing high packing properties. On the other hand, for the Al foil, voids possibly caused by hydrogen (H₂) gas generated by corrosion are seen. In addition, cellophane adhesive tape was used for a peeling test of the electrode layers. In the test, only the layer on the Al foil peeled off. This may be because the generated gas reduced the adhesion between the positive electrode active material and the current collector. Thus, generation of gas due to corrosion of current collectors significantly affects the packing properties of the electrode layer and the adhesion at the interface between the electrode layer and the current collector.

Figure 7 shows the evaluation results of 2032-type coin cells: one has an NCA positive electrode made of NSSCFW2 stainless steel foil and the other has an NCA positive electrode made of Al foil. Both have an Li metal foil as the opposite pole.¹¹) For the NCA positive electrode using the stainless steel foil, the initial discharge capacity is 192 mAh/g and the initial charge/discharge efficiency is 90%, being close to the theoretical values. In addition, the charge/

discharge efficiency in the second cycle and after is 100%, so it can be said that the stainless steel foil is electrochemically stable in the operating potential range of the positive electrode from 2.0 to 4.3 V (vs. Li/Li⁺). On the other hand, the initial discharge capacity of the NCA positive electrode using the Al foil is low at 178 mAh/g, showing that corrosion on the current collector affects the battery characteristics. **Figure 8** shows the evaluation results of the cycle performance of these NCA positive electrodes.¹¹) The NCA positive electrode using the stainless steel foil does not greatly deteriorate as the cycles are repeated: the capacity retention rate in the 30th cycle is 97% compared with the second cycle. On the other hand, the capacity of the NCA positive electrode using the Al foil decreases gradually as the cycles are repeated. The capacity retention rate in the 30th cycle decreases to 92% compared with the second cycle.

Next, the authors made coin cells for which each of these two types of NCA positive electrode was combined with a graphite negative electrode (coin-type NCA positive electrode/graphite negative electrode cell). **Figure 9** shows direct current resistance at 2, 5, and 10 seconds when the state of charge (SOC) was 50%.¹¹⁾ The capacity ratio between the negative electrode and positive electrode in these cells was 1.2 and the cell was designed such that the capacity was limited to that of the positive electrode. Figure 9 shows that the resistance is lower for both input and output when the NSSCFW2 stainless steel foil was used for the positive electrode. Although the electric characteristics of the stainless steel will be described later, the volume resistivity of general α stainless steel is 53.5×10⁻⁶ Ω·cm



Fig. 7 Charge and discharge curves of 2032-type coin cells with NCA and Li metal electrodes when using (a) NSSCFW2 stainless steel and (b) Aluminum foils



Fig. 8 Cycle performance of the NCA positive electrodes when using NSSCFW2 stainless steel and aluminum foils

and that of Al is $2.7 \times 10^{-6} \Omega$ -cm. It is expected that the internal resistance of a battery using α stainless steel would be higher under normal conditions. However, for materials showing corrosiveness like NCA, the stainless steel foil has better characteristics. The excellent alkali resistance of stainless steel may contribute to realizing high-capacity NCA positive electrodes.

3.3 High-capacity negative electrodes and mechanical properties required for current collectors

Carbon-based materials are mainly used as negative electrode materials at present. The theoretical value of the charge/discharge capacity is 372 mAh/g. Meanwhile, that of SiO, which is regarded as a promising material for high-capacity negative electrodes, is 1 500 to 2 000 mAh/g and that of Si and Sn that alloy with Li is very high at 4000 mAh/g or more. 10, 13, 14) These high-capacity active materials occlude and release many Li ions during charge and discharge. Therefore, crystal lattices expand and contract significantly at that time. The volume change during charge is approximately 10% of the original volume for graphite. Meanwhile, the change is 2.5 times for SiO and 3 to 4 times for higher-capacity Si.^{10, 13, 14)} These large volume changes apply large stress to the current collectors binding the active materials, which deteriorates the cycle performance of batteries due to changes in the shapes of the current collectors and deteriorates the adhesion between the current collectors and the active materials.¹³⁾

Furthermore, recently, flexible secondary batteries have been gaining attention as the wearable market has been developing, so materials of battery components need to resist repeated bending. With these circumstances as a background, Fe-based metal foils with excellent mechanical properties, such as Ni-plated steel and stainless steel foils, as compared with conventional Cu foils, have been gaining attention as negative electrode current collectors. **Table 1** lists the typical mechanical properties of these Fe-based metal



Fig. 9 Input/output characteristics of the NCA/graphite coin cells when using NSSCFW2 stainless steel and aluminum foils

	Symbol of	Symbol of	Thickness	Hardness	Tensile strength	Yield strength	Elongation
	steel grade	thermal refining	(µm)	(HV)	(N/mm ²)	(N/mm^2)	(%)
Austenitic stainless steel	SUS304	Н	10	417	1 198	1 099	1.0
	SUS316L	Н	10	366	1062	992	1.5
Ferritic stainless steel	NSSC190	Н	10	320	1 0 4 6	978	0.5
	NSSCFW2	Н	10	263	959	928	0.6
Ni-plated steel	_	Н	10	175	851	713	1.0

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Table 1 Mechanical properties of various Fe-based metal foils for current collectors



Fig. 10 Tensile strength of Fe-base metal foils and pure copper foil heat treated at various temperatures

foils. Although the mechanical properties vary depending on the steel grade and refining, the tensile strength of all the grades is 850 N/mm² or more. In addition, the application of high-strength rolled copper alloy foils, like Fe-based metal foils, to current collectors has been studied. Their tensile strength is approximately 800 N/mm² at maximum.¹⁵⁾ Therefore, Fe-based metal foils are clearly superior from the perspective of mechanical properties.

As binders that bind these current collectors and active materials, those with relatively low adhesive capacity such as polyvinylidene fluoride (PVdF) used for nonaqueous solvents and styrene-butadiene rubber (SBR) used for aqueous solvents have been employed. Therefore, when the materials used for binders are limited to the currently used ones, the only means used to suppress the expansion and contraction of the volume during charge and discharge is adding a small quantity of a high-capacity Si-based active material to a carbon-based material, so there is a limit to improving the capacity.

On the other hand, application of polyimide (PI) binders with high adhesion has been studied when negative electrodes are formed only with high-capacity active materials. Such PI binders require heat treatment at 200 to 350°C for imidization, so current collectors (base) need to resist heat to some extent.¹⁵⁾ **Figure 10** shows changes in the tensile strength of various Fe-based metal foils and a Cu foil due to heat treatment temperature.¹⁰⁾ The strength of the Cu foil rapidly decreases in heat treatment over 100°C. On the other hand, the strength of the Fe-based metal foils does not obviously change until approximately 400°C, showing excellent thermal resistance. Therefore, Fe-based metal foils are not softened as a result of heat treatment for PI binders and maintain high mechanical strength, and thereby they can be used as current collectors for high-capacity Sibased negative electrodes.



Fig. 11 Cycle performance of the Si electrodes when using the Ni-plated steel and copper foils as current collectors

3.4 Realization of high-capacity negative electrodes by drawing on the excellent mechanical properties of Fe-based metal foils

Figure 11 shows the evaluation results of 2032-type coin cells. One had an Si negative electrode current collector made of an Niplated steel foil. The other had one made of a Cu foil. Each had an Li metal foil as the opposite pole.¹¹⁾ The thickness of the Ni-plated steel foil was 10 μ m and that of the Cu foil was 20 μ m. PI binders were used for both types of Si negative electrodes. The initial discharge capacity of the negative electrode using the Ni-plated steel foil is high at 2760 mAh/g. On the other hand, that of the Cu foil is inferior at 2650 mAh/g. The Si negative electrode using the Ni-plated steel foil maintains the initial high capacity as the cycles are repeated. The capacity retention rate in the 50th cycle to the first cycle is 99.7%. On the other hand, in the case of the Cu foil, the capacity starts rapidly decreasing in the 30th cycle. The retention rate in the 50th cycle to the first cycle decreases to 85%.

Next, Fig. 12 shows the cycle performance and charge and discharge curves of a half cell consisting of an SiO electrode and Li as the opposite pole as an example where PI binders and a highstrength stainless steel foil were used.^{10, 13)} As the negative electrode active material, amorphous SiO with an average grain size of 5 μ m was used. As the electrode composition, SiO:conductive additive:PI =80:5:15 (weight%). As the current collector, an NSSC190 stainless steel foil with a thickness of 10 μ m was used. As the electrolyte, $1M-LiPF_6 + EC:DEC$ (volume ratio of 1:1) was used and, as the separator, polypropylene microporous membrane was used. The capacity at the first Li occlusion is approximately 2700 mAh/g and the capacity after the first Li occlusion is approximately 1500 mAh/g stably. The capacity retention rate after 100 cycles is 97.8% (100th/ 10th) and no increase in the polarization is seen. On the other hand, when conventional PVdF is used as the binder without using PI, the binder does not withstand the volume changes during charge and



Fig. 12 (a) Cycle performance of the SiO electrodes when using NSSC190 stainless steel foil with PI and PVdF binders and (b) Charge and discharge curves of the SiO electrode when using NSSC190 stainless steel foil with PI binder



Fig. 13 Various kinds of current collector foils after charge and discharge of 2032-type coin cells with SiO and Li metal electrodes

(a) Copper foil



(b) NSSC190 stainless steel



Fig. 14 (a) Copper and (b) NSSC190 stainless steel foils as current collectors after charge and discharge of SiO/LiFePO, cells

discharge and the cycle life is several tens of cycles.

Figure 13 shows current collectors after 2032-type coin cells each of which had an SiO electrode with Li as the opposite pole were repeatedly charged and discharged.¹⁾ The Cu foil had a thickness (18 μ m) approximately double the common thickness of conventional LIBs. The Cu current collector does not withstand volume changes during charge and discharge and it deforms and breaks. On the other hand, when the stainless steel foil with a thickness of 10 μ m was used, no apparent damage is seen. The influence of such volume expansion of the electrode layer is more obvious on the electrode having a large area (e.g., wound type) as shown in **Fig.**



Fig. 15 Calculation results of cell energy density when using thinner various metal foils for current collectors

14.¹⁾ Even using conventional Cu foils, it is possible to increase the thickness of the current collector to approximately 35 μ m so that it has sufficient strength to withstand volume changes during charge and discharge.^{10, 13} However, as a current collector is thicker, the entire electrode becomes thicker, so the energy density per volume significantly decreases. Therefore, when high-capacity negative electrode materials whose volume changes during charge and discharge are large are used, technologies for comparing and adjusting current collector materials and binders is important.

3.5 Thickness of Fe-based metal foil current collectors

As described above, the thickness of current collectors is an important characteristic for realizing high-capacity batteries. There is demand for current collectors to be as thin as possible because they do not contribute to the battery capacities. The hardness of Fe-based materials is much higher as compared with Al and Cu in the cold rolling process to manufacture Fe-based metal foils with a thickness of approximately 10 μ m, so a multiple-stage cluster rolling mill using small-diameter work rolls is used due to restrictions on rolling loads. Nippon Steel Chemical & Material uses a high-accuracy 12-stage rolling mill for ultra-thin stainless steel foils to achieve an excellent thickness accuracy of ±0.3 μ m even for ultra-thin foils with a thickness of 10 μ m.

 $LiFePO_4$ (LFP)/SiO cells (58×35×3.6 mm) for mobile devices were actually designed using current collectors made of various materials with a minimum thickness. **Figure 15** shows the calculation

results of their energy density.¹⁰ The Fe-based metal foils can withstand volume changes due to charge and discharge of high-capacity negative electrodes even when the thickness is 10 μ m. Therefore, the ratio of the volume that the current collector occupies in the battery can be made smaller and the resultant available space can be filled with active materials. The energy density per volume is higher by approximately 16% compared with cases using Cu foils. In addition, the specific gravity of general Cu foils is 8.96 g/cm³, while that of SUS304 is small at 7.93 g/cm³, so the energy density per weight is higher by approximately 8%, contributing to weight reduction.

4. Improvement of Input/Output Performance of On-vehicle LIBs and Electric Characteristics of Fe-based Metal Foils

Improving the input/output performance of on-vehicle LIBs, which is related to the characteristics for acceptance of power and regenerated energy, is an important task and thereby there is demand for the internal resistance of LIBs to be reduced. In the structure of a liquid-based LIB shown in Fig. 1, positive and negative electrode active materials, conductive additives, binders, and their interfaces are also resistance elements in a battery in addition to the electrical resistivity in current collector metals.

Table 2 lists the electric characteristics of candidate materials for current collectors and acetylene black that is a typical conductive additive.¹⁰⁾ When the International Annealed Copper Standard (IACS) of Cu, whose electrical conductivity is the highest, is determined as 100%, that of the α and γ stainless steel and Ni-plated steel are low at approximately 2 to 13%. However, compared with acetylene black (conductive additive), the IACS of the Fe-based metal foils is higher by five digits or more. The IACS values of LCO and LiMn₂O₄ (LMN), LFP, and other types of oxides, which are typical positive electrode active materials, are very low at 10^{-9} to 10^{-1} S/ cm.¹⁶ Even for graphite materials (negative electrode active materials) with excellent electrical conductivity, the IACS is lower than that of Fe-based materials. Therefore, when it is regarded that the element with the largest resistance among the resistance elements in the battery determines the responsiveness of the entire battery, it may be possible to ignore the low IACS of Fe-based materials.

Figure 16 compares the output characteristics of an LFP electrode using an NSSC190 stainless steel foil with one using an Al foil as an example.¹⁰⁾ The capacity density of the electrodes is 1.3 mAh/ cm² and half cells were used for evaluation. For both types of current collectors, the capacity density is 138 mAh/g per LFP weight at a 10C rate (relative ratio of the current during charge and discharge to the battery capacity; 1C means a current value at which, when a nominal-capacity battery is charged or discharged at rating, the charge or discharge completes in one hour). It is 50 mAh/g at a 50C

rate. Polarization is almost at the same level. No influence of the differences in the IACS between the current collectors on the output characteristics is seen. **Figure 17** shows the output characteristics of LFP/SiO-based batteries using NSSC190 stainless steel foils at 25°C.^{10,13} The charge was fixed at 0.2C. The discharge was changed from a 0.1C rate to a 50C rate. Generally, the resistance of stainless steel is high and thereby it is said that it is unfavorable for higher output. However, the output is 140 mAh/g at a 10C rate discharge and, in discharge of only two minutes (30C rate), it is 110 mAh/g, which is equivalent to approximately two-thirds (2/3) of the total capacity. These results show that even batteries using stainless steel foils can have excellent output characteristics.

In addition, for LIBs for HEVs and PHEVs in which larger cur-



Fig. 16 Rate profiles of the LFP positive electrodes when using NSSC 190 stainless steel and aluminum foils as current collectors



Fig. 17 Rate performance of the LFP/SiO cell using the NSSC190 stainless steel foil for the current collector

Material		Thickness	Electrical resistivity		IACS
		(µm)	$(\Omega \cdot cm)$		(%)
Stainless steel	SUS304	10	71.2	$\times 10^{-6}$	2.4
	NSSC190	20	53.5	$\times 10^{-6}$	3.2
Carbon steel	Ni-plated steel	10	12.8	$\times 10^{-6}$	13.3
		15	12.6	$\times 10^{-6}$	13.5
Copper		15	1.7	$\times 10^{-6}$	100
Aluminum		12	2.7-3.6	×10 ⁻⁶	63.0
Conductive additive		_	3–5	$ imes 10^{0}$	0.00006

Table 2 Comparison of electrical resistivity between various metal foils for current collectors and conductive additives



Fig. 18 Structures of the bipolar and the laminated cell

rents flow, various measures are required to reduce the internal resistance of the batteries to the extent possible, such as the installation location of tab leads and refinement of welds. The weldability of Fe-based materials is higher than that of other types of metal materials. Therefore, in addition to ultrasonic welding that has often been used for joining with tab leads, other welding processes with higher reliability (e.g., resistance welding) can be applied, so Febased materials have an advantage.

In addition, as described above, stainless steel can be applied to current collectors of bipolar batteries where positive and negative electrodes are arranged on the two sides of a single current collector. **Figure 18** illustrates the structure.¹⁾ As current collectors for bipolar batteries, a clad metal in which a metal material specific for positive electrodes and that for negative electrodes are laminated has been studied.¹⁷⁾ When stainless steel is used, a single type of current collectors are connected in series in a wide plane direction, which makes the series connection resistance smaller, which can make the influence of the high electric resistance of stainless steel foils smaller.

Meanwhile, stainless steel has a natural oxide film having an electric insulation property formed on the surface as is the case with Al. It improves the corrosion resistance by protecting the steel from electrolytes and this in turn contributes to preventing the electrolytes from deteriorating. However, the resistance at the interface between the stainless steel foil and the electrode layer by such a passive-state film hinders electron transfer, so there is a room for improvement in applications where there is demand for higher output.

For conventional Al foil current collectors, to improve the input/ output characteristics, coarsening the surface, lining (primer coating), carbon coating, and other means have been studied and applied. The same measures could be applied to stainless steel foil current collectors to improve the characteristics. In addition, in LIB manufacturing processes, the surfaces of current collectors are coated with electrode layers and dried. Then, they are stamped to increase the electrode density. Because the hardness of Al and Cu foils is low, such stamping bites the active materials, which reduces the interface resistance. However, stainless steel foils are particularly hard, so such effects cannot be readily obtained. Therefore, it can be said that, in order to reduce the internal resistance of batteries, technologies for comparison and adjustment based on the electrode manufacturing conditions and application purpose are required, for example, using softer Ni-plated steel foils and, when stainless steel is used, softening it based on chemical components and through heat treatment

5. Work to Improve the Safety and Reliability of Onvehicle LIBs

5.1 Improvement of overdischarge resistance

General LIBs contain flammable organic electrolytes and their energy density is high, so, if their conditions become severe such as overcharge, overdischarge, external short circuit, overcurrent, and abnormally high temperature (100°C or more), thermal runaway may occur starting from normal heat generation, resulting in rupture and fire. To prevent such dangers, many safety measures have been implemented such as shutdown separators, positive-temperature-coefficient (PTC) thermistors, protective circuits, current interruption mechanisms, and safety valves.¹⁸⁾ Safety must also be considered from the perspective of battery component materials. Stainless steel is electrochemically more stable than Cu whose oxidation reduction potential is around 3.5 V (vs. Li/Li⁺), so stainless steel may realize batteries that can resist overdischarge where negative electrodes are exposed to high potential.

Figure 19 shows the charge and discharge characteristics of batteries using various types of current collectors.¹⁾ Although the design is different in preciseness between battery types, for the battery having a Cu foil negative current collector and an Al foil positive current collector, when they were discharged deeply to 1.5 V in the first cycle for 10 hours (0.1C rate), charge and discharge became completely impossible in the second cycle and after or the battery having a negative current collector using an Ni-plated steel foil and a positive current collector using an NSSCFW1 stainless steel foil, even after it was overdischarged to 0 V, the initial charge and discharge characteristics were retained. These results show that the electrochemical stability of the current collector materials significantly affect the overdischarge resistance of batteries.

5.2 Realization of all-solid-state LIBs

As mentioned previously, all-solid on-board LIBs are gaining particular attention, as the next-generation high-performance storage batteries satisfying both high energy density and safety. In all-solid LIBs, all of the positive electrodes, negative electrodes, and electrolytes consist of solid materials. Therefore, all-solid LIBs are free from risks of electrolyte leakage and fire. The high safety is one characteristic. Meanwhile, the environment in which current collectors (battery component) are placed is very different from that for conventional organic electrolytes. Mainly for on-board batteries, sulfide-based solid electrolytes, whose ion conductivity is as high as twice that of organic electrolytes, have been found so far. However, corrosion of other component materials caused by these sulfides is of concern. It has been reported that, when conventional Cu foils are used for negative electrode current collectors, copper sulfides are formed on the surfaces of the current collectors, so coating the surfaces with Ni plating and carbon has been studied.¹⁹⁾ Meanwhile, stainless steel and other Fe-based materials have excellent corrosion resistance in various environments. Therefore, it is expected that they will be applied for more application purposes by drawing on their excellent corrosion resistance in the all-solid LIB sector for which a market will be formed in the future, and which will likely expand.

5.3 Improvement of the safety by current collector materials

Al with a low melting point of approximately 660°C that has been used as LIB positive electrode current collectors is an active substance with high affinity with oxygen as known by the thermite reaction. Therefore, if a battery exhibits thermal runaway due to some cause, the Al may accelerate the combustion. To verify this, an



Fig. 19 Charge and discharge curves when using four different current collectors; using NSSCFW1 stainless steel and Cu foils, using Al and Ni-plated steel foils and using NSSCFW1 stainless steel and Ni-plated steel foils



Fig. 20 Differential thermal analysis results of LCO coated (a) Aluminum foil and (b) NSSC190 stainless steel foil

LCO positive electrode material was applied to an Al foil and stainless steel foil and nitrogen gas was used to conduct differential thermal analysis (DTA) under its gas flow. **Figure 20** shows the results. Even when the stainless steel foil was heated to 700°C, no obvious thermal reaction was recognized. On the other hand, the Al foil showed exothermic reaction before melting and endothermic reaction at 600°C or more. This may be because a thermite reaction occurred in which oxygen (positive electrode oxide materials) and Al reacted in an inert gas atmosphere. If the temperature of the battery rises due to such heat of reaction, there may be a risk of thermal runaway including thermolysis of the electrolyte and positive electrode materials. On the other hand, stainless steel with a high melting point of approximately 1400°C has excellent thermal stability, so using stainless steel for current collectors may enhance the safety of batteries.

6. Conclusions

Current collectors made from stainless steel foils and other Febased metal foils have excellent characteristics such as high corrosion resistance, high mechanical strength, and a wide potential window unlike other types of metal foils. Using high-strength ultra-thin Fe-based metal foils can improve the performance in sectors for, for example, realization of high-capacity NCA positive electrodes and Si-based negative electrodes and drastically longer cycle life, which used to be thought impossible. Regarding electric resistance, which is regarded as a problem, solutions have been studied by optimizing the structure of electrodes and the application of bipolar batteries. Realization of high-capacity LIBs with high safety and high reliability is expected in the future by applying Fe-based metal foils.

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