

Properties of Flexible Nickel Coated Steel Sheets for Battery Case

Takehiro TAKAHASHI* Kenichiro MATSUMURA
Kiyokazu ISHIZUKA Yasuto GOTO

Abstract

Ni-coated steel sheets are used for several battery cases including the Li-ion battery. As Ni coating provides barrier corrosion protection, the corrosion resistance of Ni coating for steel sheet worsens when the Ni coating contains some defects. Therefore, we developed SUPERNICKEL™ as a flexible Ni-coated steel sheet to prevent cracking during forming of battery cases. SUPERNICKEL™ shows higher coverage compared to an ordinary Ni-coated steel sheet especially after forming. As the Ni-coated steel sheet shows good coating adhesion by the Fe-Ni diffusion layer between the Ni layer and the steel sheet, it has higher flexibility than an ordinary electrodeposited Ni layer. Since dissolution of metal to electrolyte can be reduced by fewer defects in coating, using a battery case with high Ni coverage can improve the safety of Li-ion batteries.

1. Introduction

Ni-coated steel sheets have been used for cases of various types of batteries containing concentrated alkaline electrolyte solutions, such as alkaline manganese batteries, Ni-Cd batteries, and Ni-MH batteries, due to Ni's high resistance to chemicals and low surface electric resistance.¹⁾ In addition, Ni-coated steel sheets have been used as cases for cylindrical Li-ion batteries containing organic electrolyte solutions (Fig. 1). Cylindrical Li-ion batteries have often been used for notebook computers and power tools and, recently, they are adopted for batteries for electric vehicles (EVs). EVs often

have prismatic-type batteries; therefore, application of Ni-coated steel sheets to prismatic-type battery cases has been studied (Fig. 2).

There are two Ni coating methods for battery cases: post-coating in which formed cases are coated using a barrel or other similar tool and pre-coating in which coated sheets are formed into cases. For post-coating, a thick coating layer can be formed on the outer surface of a case; however, coating the inside of a case—the bottom, in particular—is difficult. On the other hand, in the case of pre-coating, evenly coated sheets can be formed; therefore, the bottom inside a case has an even coating layer and thereby the quality is high-



Fig. 1 Cylindrical lithium-ion battery cell cases (left: 18650 cell, right: 21700 cell)



Fig. 2 Prismatic type battery cell case

* Senior Researcher, Dr. Eng., Surface Treatment Research Lab., Steel Research Laboratories 20-1 Shintomi, Futttsu City, Chiba Pref. 293-8511

ly stable. However, for pre-coating, the coating may crack or separate during forming and the steel sheet (base material) may be exposed in some cases. Ni coating provides barrier corrosion protection and does not provide sacrificial protection like Zn coating, so, if a coating layer has a pinhole or crack, the corrosion resistance may worsen in some cases.²⁾

Therefore, to reduce coating defects after forming that deteriorate the corrosion resistance, Nippon Steel Corporation has developed SUPERNICKEL™ as flexible Ni-coated steel sheets for battery cases. Usually, electroplated steel sheets are first annealed and then coated as shown in the lower row in Fig. 3. On the other hand, SUPERNICKEL™ is manufactured by coating a cold-rolled sheet first and then annealing it as shown in the upper row in Fig. 3.

This paper describes the operation mechanism in which battery cases made of Ni-coated steel sheet SUPERNICKEL™ shows higher Ni coating coverage property than battery cases made of ordinary Ni-coated steel sheets along with the effects of Ni coating on cases for Li-ion batteries.

2. Experimental Procedure

2.1 Basic properties of Ni-coated steel sheets that are first coated and then annealed

The test pieces shown in Table 1 were prepared. No. 1 is an ordinary Ni-coated steel sheet that was annealed and then coated. No. 2 is a Ni-coated steel sheet that was coated and then annealed and that is equivalent to SUPERNICKEL™. The amounts of the Ni coatings were 17.8 and 900 g/m². Those with 900 g/m² of coating were used to measure the hardness. In addition, No. 3 is a Ni-coated steel sheet that was coated and then annealed as is the case with No. 2. To examine the alloy layer formed at the interface between the Ni coating layer and the steel sheet by annealing in detail, the amount of Ni coating was 900 g/m² only and the sheet was annealed for 9 h to form a thick diffusion alloy layer. As the electrodeposition bath, a Watts bath shown in Table 2 was used. As the positive electrode, a Ni sheet was used. The cathode current density was maintained at 20 A/dm². The substrate steel sheet was an extra-low-carbon steel sheet with a thickness of 0.25 mm. It was annealed at 800°C for 20 s.

The surface structure of the Ni coating was observed by second-

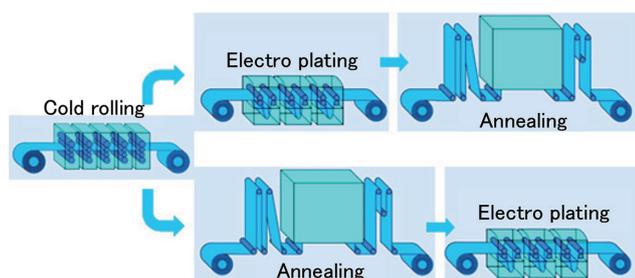


Fig. 3 Production process of nickel coated steel sheets (above: SUPERNICKEL™, below: ordinary Ni-coated steel sheet)

ary electron images (SEI) of a field-emission scanning electron microscope (FE-SEM) (JEOL JSM-7000F). The cross-sectional microstructures of the Ni coating were observed by backscattered electron images (COMPO images) of FE-SEM (JEOL JSM-7000F), and each Ni-coated steel sheet was vertically implanted into resin. Only No.3 was subjected to line analysis of Ni and Fe by energy-dispersive X-ray spectrometry (EDS). The hardness of the Ni coating layers was measured by a micro Vickers hardness tester, and each Ni-coated steel sheet was vertically implanted into resin. Micro Vickers hardness was measured at 10 points from the cross section of the coating with a load of 49 mN. The average was calculated.

The formability of the Ni coating layer was examined by a bending test. Each test piece was bent by 180° (1T bending) with a sheet of the same thickness (0.25 mm) as that of the Ni-coated steel sheet itself, put in-between as shown in Fig. 4, and implanted into resin to observe the cross-sectional microstructure. The cross-sectional microstructure was observed by SEI images of the FE-SEM (JEOL JSM-7000F). In addition, cases with a diameter of 15 mm and a height of 40 mm were produced using five-stage stamping and their corrosion resistance was evaluated. A salt spray test (SST) was conducted for 3 h in accordance with JIS Z 2371 and the appearance was photographed to see the corrosion resistance. The Ni coating coverage condition on cases, and the outer surfaces of cases that were not subjected to the salt spray test were analyzed by Ni and Fe mapping of an electron probe micro analyzer (EPMA) (JEOL JXA-8230).

2.2 Evaluation of dissolution resistance to Li-ion battery electrolytes

In the production of cylindrical Li-ion batteries for which mainly Ni-coated steel sheets are used, wound electrodes are put into a cylindrical case and it is left for a few days or more for the electrolyte to permeate. Then, it is covered and charged. The cylindrical case is connected to the negative electrode; therefore, the inside of the case is polarized to the negative electrode potential. Once charged, the

Table 2 Electrodeposition bath composition

	Concentration (g/dm ³)
NiSO ₄ ·6H ₂ O	240
NiCl ₂ ·6H ₂ O	45
H ₃ BO ₃	35

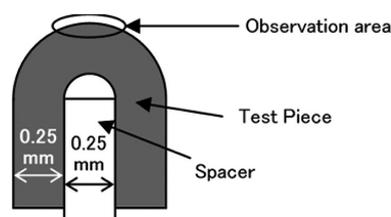


Fig. 4 Schematic diagram of bending test

Table 1 Test pieces

No.	Coating amount		Process		Note
	17.8 g/m ²	900 g/m ²	1st	2nd	
1	○	○	Annealing (20 s)	Ni coating	Common Ni-coated steel sheet
2	○	○	Ni coating	Annealing (20 s)	Equivalent to SUPERNICKEL™
3	—	○	Ni coating	Annealing (9 h)	For interface analysis

negative electrode potential is normally 1.2 V or less based on Li even during discharge, so the possibility of dissolution of Fe and Ni is low. However, the negative electrode potential before the initial charge when the electrolyte permeates is approximately 3.2 V based on Li, and Ni and Fe may therefore dissolve. Once Ni and Fe dissolve into the electrolyte, a dendrite-shaped substance may be generated through deposition on the negative electrode during charge to break through the separator, causing a minute short circuit.³⁾ A minute short circuit may result in self-discharge and cause fire, so it is desirable that metal dissolution from the case while the electrolytes are allowed to permeate is smaller.

The dissolution resistance to electrolytes was compared between non-coated steel and Ni-coated steel sheets in potentiostatic electrolysis simulating conditions when an electrolyte permeates the steel sheets. A three-electrode laminated cell illustrated in Fig. 5 was used for measurement. As the working electrode, a non-coated steel sheet or Ni-coated steel sheet was used. As the non-coated steel sheet, the extra-low-carbon steel sheet that had been used as the substrate steel sheet for the coating was used. As the Ni-coated steel sheet, No.2 in Table 1 was used. A Ni tab was spot welded to the back of each sheet. A PP hot melt film was used to heat seal each including the Ni tab except for an area of 10×10 mm. Each was washed ultrasonically in acetone and then pickled using 5% sulfuric acid for 10 s. It was washed with water, dried, and then put into a glove box in an Ar atmosphere with a dew point of -67°C.

The operations from this step to seal the laminated aluminum foil were conducted in the glove box in the same environment. As the counter and reference electrodes, metal Li foils were used. A metal foil was crimped to each Ni tab. The part of the Ni tab that did not make contact with the Li foil was heat sealed using a PP hot melt film. These were arranged in the laminated aluminum foil with separators in-between. Three sides of the laminated aluminum foil were heat sealed into a bag shape. An electrolyte solution of 1 mL was added to it and the laminated aluminum foil was then hermetically heat sealed. It was taken out from the glove box.

The laminated cell was put between 1-mm-thick steel sheets with sponges with a thickness of 10 mm in-between as shown in

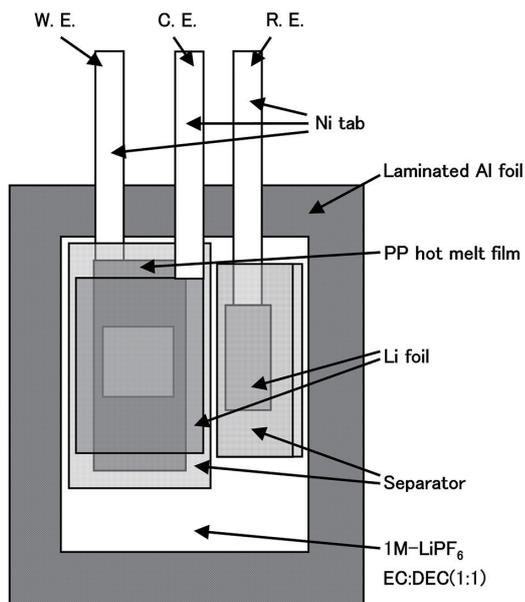


Fig. 5 Schematic diagram of electrochemical measurement cell

Fig. 6 such that the distance from the working electrode to the counter electrode became even at the time of electrochemical measurement. They were tightened with bolts such that the distance between the two steel sheets was 10 mm.

The potential was held at 3.2 V vs. Li/Li⁺, which was the negative electrode potential before initial charge, for 24 h. The product of anode current and time (electricity quantity) was calculated to compare the solubility between the non-coated steel and the Ni-coated steel sheet.

3. Basic Properties of Ni-coated Steel Sheets that are First Coated and then Annealed

3.1 Results

Figure 7 shows FE-SEM SEI images of the coating surfaces. On No.1, micro Ni crystals due to electrodeposition are seen. Meanwhile, on No.2, the surface is flat where fine projections and depressions that were seen on No. 1 are not observed. In addition, the crystal grains grew to 10 times or more in diameter.

Figure 8 shows FE-SEM COMPO images of the cross sections of the coating layers. On No. 1, the interface between the Ni coating layer (a) and steel sheet (b) is clear. Meanwhile, on No.2, a new layer (e) is seen at the interface. From the analysis results of No.3, the concentration of Ni at this section is uniform at approximately 5 mass%. Section d shows graded composition due to diffusion. Only the surface (c) is a pure Ni layer. Table 3 lists the hardness of the Ni coating layers measured before and after annealing. The hardness of the Ni coating layer significantly decreased as a result of annealing. That is to say, although both sections a and c are pure Ni layers, section c that was annealed along with the base material is softer.

Figure 9 shows the observation results of the cross sections of the coating layers after 1T bending. On No.1, cracks are seen on sections not coated with Ni. On the other hand, on No.2, the Ni coating is thinner at some sections; however, the section has been almost entirely coated with Ni and no cracks are seen.

Figure 10 shows the cases after the salt spray test. On No. 1, red rust is seen over a wide area on the side while, on No.2, red rust is clearly less compared to No.1.

Figure 11 shows the area analysis results of the sides of the cases by EPMA. On No. 1, the Ni coating is largely lost and Fe is exposed

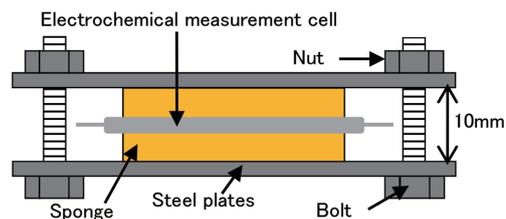


Fig. 6 Schematic diagram of stacked electrochemical measurement cell

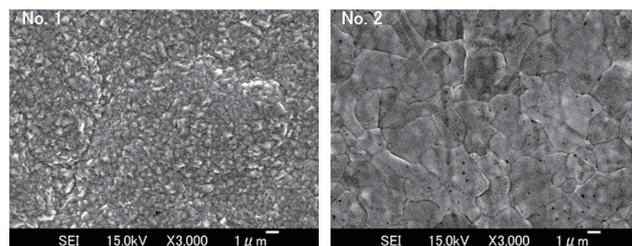


Fig. 7 SEM image of nickel coating surfaces

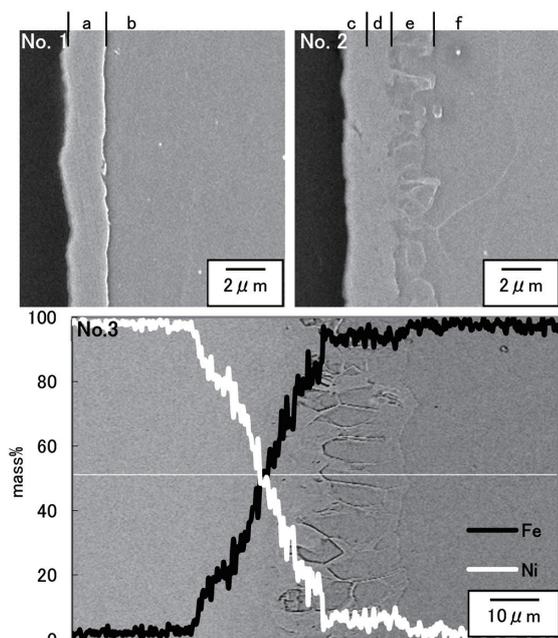


Fig. 8 Cross sectional SEM images and EDX line analysis of nickel coatings

Table 3 Hardness of nickel coatings (10-points average)

	Hardness (HV 49mN)
No.1 (as coating)	231
No.2 (after annealing)	120

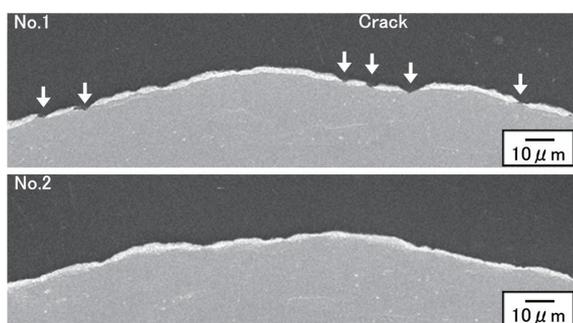


Fig. 9 Results of bending

at some sections. On No.2, the surface is almost entirely coated with the Ni and Fe is little exposed.

3.2 Considerations

The reasons that the Ni coating layer is softened by annealing may be because the Ni crystal grain size became coarser from the electrodeposited structure to the annealed structure as shown in Fig. 7,⁴⁾ and the tensile stress that remained on the Ni coating due to bathing in the Watts bath⁵⁾ was reduced by heat treatment.

The corrosion resistance of No.2 after processing was improved compared to No.1. This is because, as shown in Fig. 11, the coverage rate of the Ni coating after processing was higher for No.1 than for No.2. This difference is may be caused because the Ni coating layer on No.2 became softer by annealing as shown in Table 3, which made No.2 easily deform; and, as shown in Fig. 8, a Fe-Ni diffusion alloy layer was formed at the interface between the Ni

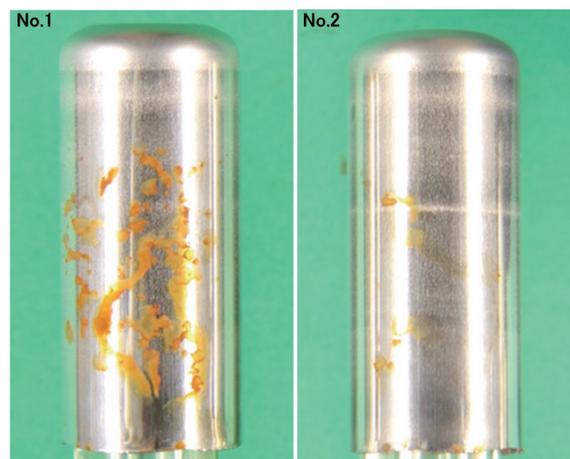


Fig. 10 Corrosion test results of nickel coated steel cases (SST: 3 h)

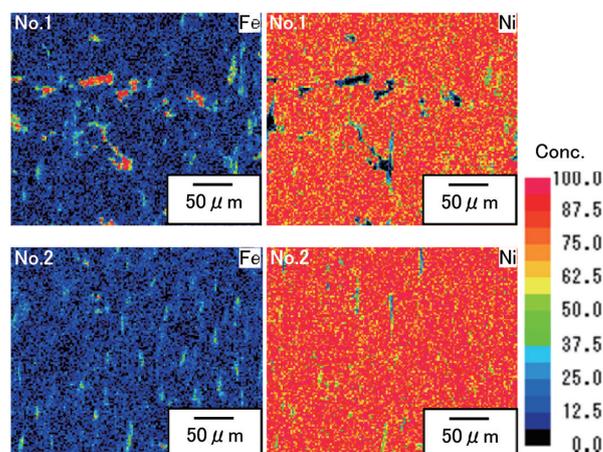


Fig. 11 Element mapping results of formed nickel coated steel sheet

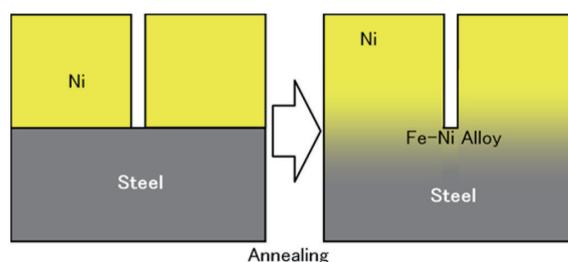


Fig. 12 Schematic diagrams of nickel coating pin pole (left: as plated, right: with annealing)

coating layer and steel sheet,⁶⁾ which enhanced the adhesion, which in turn enhanced the properties against processing. The bending test results in Fig. 9 clearly show that the properties against processing of No.2 are higher than those of No.1. In addition, another possible reason is that Ni diffused to the bottom of the pinhole that had been made during the electrodeposition hindered the section from being corroded as shown in Fig. 12.

4. Dissolution Resistance to Li-ion Battery Electrolytes

4.1 Results

Table 4 lists the electricity quantities calculated from the anode

Table 4 Anode electricity quantities and dissolved volumes

	Anode electricity quantities (mC)	Dissolved volumes (m ³)
Ni-coated steel sheet (No.2)	16	5.46×10^{-11} ^{*1}
Non-coated steel sheet	142	5.22×10^{-10} ^{*2}

^{*1} Calculated as Ni, ^{*2} Calculated as Fe

current in the potentiostatic electrolysis and electrolysis time. The table also shows the dissolved volumes calculated from the electricity quantities where the anode current on the Ni-coated steel sheet was generated by the dissolution of Ni and where the anode current on the non-coated steel sheet was generated by dissolution of Fe. At this time, Fe and Ni were regarded as dissolved as divalent cations. The anode electricity quantity on the Ni-coated steel sheet was 16 mC and that on the non-coated steel sheet was 142 mC. The anode electricity quantity on the Ni-coated steel sheet was approximately 1/9 that on the non-coated steel sheet. In addition, when it was assumed that the anode current was all generated by the dissolution of Ni for the Ni-coated steel sheets and by the dissolution of Fe for the non-coated steel sheet, the dissolved volume calculated from the anode electricity quantity is 5.46×10^{-11} m³ for the Ni-coated steel sheet and 5.22×10^{-10} m³ for the non-coated steel sheet. The dissolved volume for the Ni-coated steel sheet is approximately 1/10 that of the non-coated steel sheet.

4.2 Considerations

The average current density during potentiostatic electrolysis was $1.64 \mu\text{A}/\text{cm}^2$ even for the non-coated steel sheet with a large anode electricity quantity. It can be said that the negative electrode potential before initial discharge is not an active potential for either Ni-coated steel or non-coated steel sheets.⁷⁾ In addition, when it is assumed that the current flowing during the potentiostatic electrolysis was all generated by the dissolution of the metal and that the dissolved metal deposited at 1/100 of the melting area (1 mm²) concentratedly, the thickness is $0.546 \mu\text{m}$ for the Ni-coated steel sheet and $5.22 \mu\text{m}$ for the non-coated steel sheet. Therefore, even for a non-coated steel sheet, when the thickness of the separator is at least $10 \mu\text{m}$, the metal does not break through the separator and will not cause a minute short circuit. The Ni coating case even further reduces the risk of minute short circuits. That is to say, using cases made from SUPERNICKEL™ with high Ni coating coverage after proc-

essing may reduce the risk of minute short circuits on Li-ion batteries compared to cases made from ordinary Ni-coated steel sheets.

5. Conclusions

To clarify the mechanism of the basic properties of SUPERNICKEL™, two test pieces were fabricated at a laboratory: No. 1 of an ordinary Ni-coated steel sheet and No.2 obtained by simulating flexible Ni-coated steel sheet SUPERNICKEL™. The performance and physical properties were examined. It has been found that the Ni coating layer on SUPERNICKEL™ is softer than that on the ordinary Ni-coated steel sheet and that it has excellent adhesion; therefore, the coverage rate of the Ni coating after processing is high and the corrosion resistance is excellent. In addition, Ni coating can suppress dissolution of metals when the electrolyte solution permeates before the initial charge of Li-ion batteries. Using SUPERNICKEL™ as a case material may reduce the risk of minute short circuits in Li-ion batteries.

6. Closing Remarks

Enhancing the safety of batteries is essential for EVs and SUPERNICKEL™ satisfies such need. Nippon Steel is the only manufacturer in Japan that can perform processing from steelmaking to Ni coating seamlessly. The characteristics of base materials can be adjusted in a number of ways while the properties of the Ni coating described in this paper are given. In addition, the Nippon Steel group has developed many materials suitable for batteries and EVs such as steel foils for battery current collectors, Ni tabs for negative electrode leads, and high-strength surface-treated steel sheets for battery packs for vehicles, in addition to Ni-coated steel sheets. We will continue providing materials that satisfy customers' needs using this comprehensive knowledge.

References

- 1) Nippon Steel Corporation: SUPERNICKEL™ Catalog
- 2) Ukai, Y. et al.: Complete Guides of Surface Technologies. Tokyo, Koshin-sha, 1983, p.305
- 3) Japanese Patent Application No.2007-66530. March 15, 2007
- 4) Nishikawa, S. et al.: Seisan Kenkyu. 18 (1), 16 (1966)
- 5) Konishi, S.: Journal of the Metal Finishing Society of Japan. 12 (2), 47 (1961)
- 6) Okada, K. et al.: Journal of the Metal Finishing Society of Japan. 26 (8), 358 (1975)
- 7) Hara, N.: J. Vac. Soc. Jpn. 44 (10), 860 (2001)



Takehiro TAKAHASHI
Senior Researcher, Dr. Eng.
Surface Treatment Research Lab.
Steel Research Laboratories
20-1 Shintomi, Futtsu City, Chiba Pref. 293-8511



Kenichiro MATSUMURA
General Manager, Head of Lab.
Surface Treatment Research Lab.
Steel Research Laboratories



Kiyokazu ISHIZUKA
General Manager
Intellectual Property Dept.-I
Intellectual Property Div.
(Former Chief Researcher, Hirohata R & D Lab.)



Yasuto GOTO
Senior Researcher, Dr. Eng.
Hirohata R & D Lab.