

Apology and Correction Notice

We would like to express our sincere apologies for the errors in the description found in KOBELCO TECHNOLOGY REVIEW No. 40, which was published in January 2023.

We understand that these errors may have caused inconvenience to our readers and other concerned parties.

Specifically, we would like to clarify the author names in the table of contents for the article on page 71.

Incorrect : Dr. Takayuki TSUBOTA, Dr. Takashi ACHIHA, Yoshiki HAYASHI,
Dr. Takuya MORI, Hiroshi OZONO

Correct : Dr. Takayuki TSUBOTA, Dr. Takashi ACHIHA, Yoshiki HAYASHI,
Dr. Takuya MORI, Hiroshi OZONO, Hidemasa TSUNEISHI

Technical Trends in, and Analysis of Evaluation Technologies of Secondary Batteries

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Abstract

The shift toward electric vehicles (EV shift) is being accelerated worldwide to reduce CO₂ emissions during running. In addition, more renewable energy is being introduced, increasing the demand for secondary batteries. Against this backdrop, studies are being conducted to increase the energy density of lithium-ion batteries for EVs and stationary battery storage. The company is also focusing on developing new batteries, e.g., all-solid-state batteries that can further improve energy density and sodium-ion batteries that use sodium instead of lithium, a rare metal. Kobelco Research Institute supports the development of batteries through its evaluation/analytcs technologies, including "the prototype production of lithium-ion batteries, all-solid-state batteries, and sodium-ion batteries," "battery characteristics evaluation technology," "reaction distribution analysis technology in battery cells," "redox reaction analysis technology," and "non-destructive deterioration diagnosis technology for reuse," thus contributing to the realization of carbon neutrality.

Introduction

Decarbonization is accelerating globally. The Paris Agreement, adopted at the 21st Conference of the Parties to the United Nations Framework Convention on Climate Change held in 2015, sets a common long-term global goal of keeping the average temperature rise well below 2°C above pre-industrial levels and pursuing efforts to limit global warming to 1.5°C." The 2021 Intergovernmental Panel on Climate Change 6th Assessment Report concludes that "there is no doubt that human influence has warmed the atmosphere, oceans and land." The EU, promoting decarbonization, has announced that it will reduce greenhouse gas emissions to virtually zero by 2050. In Japan, there was a declaration of "2050 carbon neutral, the realization of a decarbonized society," and in April 2021, the greenhouse gas reduction target was significantly raised to "reduce emissions in 2030 by 46% compared to 2013."

These trends of decarbonization have a significant impact on the automobile industry, which is a critical core industry that supports the Japanese economy. Europe has announced a

policy to ban the sale of gasoline and diesel vehicles, including hybrid vehicles, by 2035 and is ambitiously promoting the shift to electric vehicles (EVs). The secondary battery, a component of an electric powertrain, is a critical device that greatly affects the driving performance of automobiles, such as cruising distance and acceleration. Research and development for high energy density and high input/output are accelerating.

This paper describes the technological trends of lithium-ion batteries, including the next generation, and the latest analytical evaluation and analysis technology at the Kobelco Research Institute.

1. Technological trend of liquid lithium-ion secondary batteries

Lithium-ion batteries are smaller, lighter, and have higher voltage and energy density than conventional aqueous secondary batteries such as nickel-metal hydride batteries. In addition to small batteries for mobile devices, in recent years their application has expanded to in-vehicle batteries such as those for EVs and stationary large storage batteries. Akira Yoshino, the 2019 Nobel Laureate in Chemistry, established the fundamental concepts in 1985, including the structure of the lithium-ion battery with lithium cobalt oxide (LiCoO₂) as the cathode and carbon material as the anode, the cathode aluminum foil current collector, and the olefin microporous membrane for the shutdown function during heat generation.¹⁾ Later, in 1991, Sony Energytech Inc. (currently Sony Energy Devices Corporation) put lithium-ion batteries into practical use. A schematic diagram of the lithium-ion battery is shown in **Fig. 1**. In an example of a battery with lithium cobaltate for the cathode and graphite for the anode, the reaction of a lithium-ion battery during charging consists of the occurrence of the desorption of Li⁺, releasing electrons from the cathode to the external circuit and inserting them into the anode through the electrolyte. Conversely, during discharge, the desorption of Li⁺ occurs at the anode, with electrons being inserted into the cathode. The reaction equation is shown below. This is a simple reaction in which Li⁺ moves back and forth between the cathode and anode, which is called a "rocking-chair reaction."

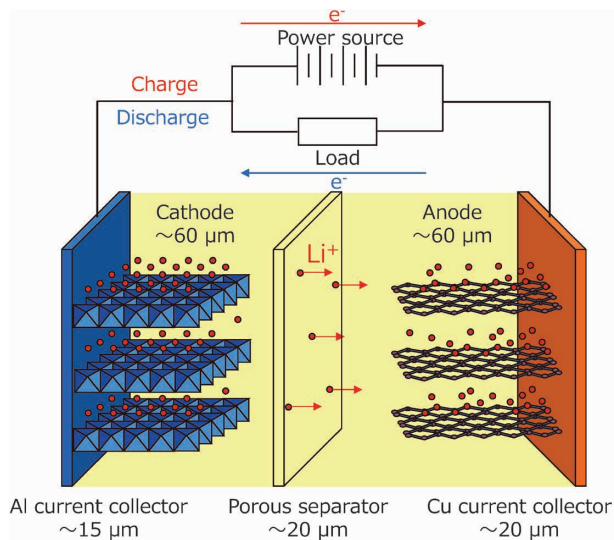
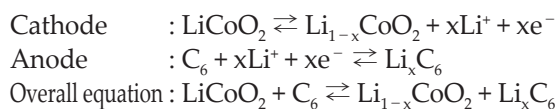


Fig. 1 Schematic diagram of a typical lithium-ion battery



Meanwhile, stationary storage batteries are becoming more common as the introduction of renewable energy sources such as photovoltaic and wind power generation expands. However, as the share of renewable energy--whose output fluctuates greatly depending on the weather conditions--increases, it flows back into the grid of electric power companies, causing large frequency fluctuations and adversely affecting the stable supply of electric power. Such cases are becoming apparent. For a stable supply of electric power, there are high expectations for ample MWh-class battery storage for peak-shaving and peak-shifting.

1.1 Further energy densification of cathode

The lamellar oxide LiCoO_2 used as a cathode material in lithium-ion batteries has been widely applied to mobile devices. However, approximately 60% of the world's production of Co, a rare metal, is produced in the Democratic Republic of the Congo (DRC), and the country's political instability makes the risky location and price hikes an issue. This has spurred the development of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM111), in which Co is partially replaced with Ni and Mn.^{2,3} In 2010, when the study for automotive applications was underway, LiMn_2O_4 with spinel structure and LiFePO_4 with a low cost and excellent thermal stability, despite its low operating voltage, were also used, in addition to NCM111. However, from the viewpoint of cruising distance, cathode materials with high energy density have been preferred, and cathode materials for in-

vehicle batteries have converged on NCM-based materials, which are being applied to lithium-ion batteries for EVs. In the charge/discharge process of NCM111, the preferential redox reaction is $\text{Ni}^{2+}/\text{Ni}^{4+}$. For even higher energy density, studies are being conducted to apply an increased Ni ratio, e.g., $\text{Li}(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\text{O}_2$ (NCM523), $\text{Li}(\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2})\text{O}_2$ (NCM622), and $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ (NCM811).^{4,5} Recently, LiFePO_4 , which has excellent thermal stability, has been attracting attention again from the viewpoint of safety when used in EVs.

1.2 Further energy densification of anode

The anodes of lithium-ion batteries are mainly made of carbon materials, but the theoretical capacity of graphite is 372 mAh/g, and more than 90% of the theoretical capacity has already been used as the effective capacity. For further energy densification of anodes, research and development are underway on Si-based alloy anodes with a greater theoretical capacity than graphite. Si has an excellent capacity to occlude lithium ions; however, the volume expands by approximately a factor of 4 when fully charged. The significant expansion and contraction associated with occluding and releasing lithium ions during charge/discharge cycles cause pulverization and a rapid decline in capacity. Hence, SiO with Si nanoclusters dispersed in a SiO_2 matrix has been commercialized to improve the cycle life.^{6,7} SiC and SiO-C are also being studied.^{8,9} Furthermore, the morphology control of particles, such as Si nanoparticles and nanowires, is also being investigated.^{10,11}

2. Analysis/evaluation technology contributing to the development of high energy density batteries

2.1 Visualization of reaction distribution in the depth direction of electrode

Kobelco Research Institute, Inc (KRIJ) is engaged in the prototyping and evaluation of lithium-ion batteries. The company can prototype electrodes using various materials, including developed products, and prototype batteries of cylindrical, laminated, and square types, as shown in Fig. 2. These are being used to elucidate cycle degradation and storage degradation mechanisms.¹² This section introduces new evaluation and analysis techniques for battery development oriented toward high energy density, such as in-vehicle batteries.

In-vehicle batteries are subjected to the charge/discharge of a large current during regenerative charging at startup/deceleration and quick charging.

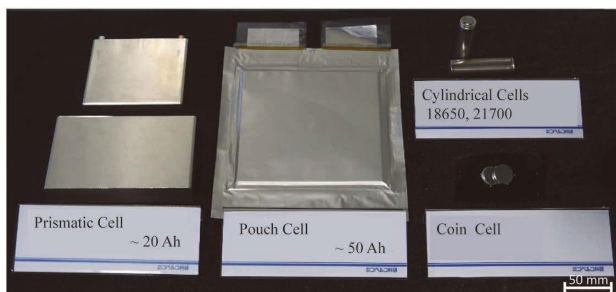


Fig. 2 Battery cells for testing

A large amount of lithium ion moves between electrodes inside the battery, resulting in lithium-ion distribution in the electrode's depth direction.¹³⁾ In other words, excessive reactions are repeated in the electrode surface layer near the opposite pole, resulting in localized degradation and a decline in capacity and input/output characteristics. However, in the case of the NCM cathode, lithium ion moves through the electrolyte to resolve its potential difference from the moment charge/discharge ends, and a relief phenomenon occurs, which averages the amount of lithium between active materials. Therefore, the analysis could not capture the reaction distribution after the relief. KRIJ has developed a new method of instantly removing electrolytes, which serve as relief paths, and has succeeded in solidifying the lithium-ion distribution in the electrode without relief.

A battery using a $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ cathode (NCA) was prototyped, and the electrolyte was removed after discharge at a 3C rate. The rate 1C refers to a current that discharges at the rated capacity of 1 h, and the rates 2C and 3C refer to currents that discharge at the rated capacity of 1/2 h and 1/3 h, respectively. Sampled electrodes were thinned in the cross-sectional direction using a microtome. Transmission imaging XAFS measurements were performed at BL08B2 at the SPring-8. Imaging XAFS is a technique to visualize the spatial distribution of chemical bonding states in a sample area of a few square millimeters using a two-dimensional X-ray detector. The Ni K-edge was measured, and machine-learning noise reduction was performed on the X-ray transmission images. Fig. 3 shows the distribution of Ni valence, which is a color intensity image of the energy value around the normalized intensity of 0.3 in the X-ray absorption near edge structure (XANES) region. A higher energy value indicates a higher state of charge (where discharge is not in progress). The upper part of Fig. 3 is on the side of the opposite pole (anode side), and the lower part is on the side of the current collector. It is confirmed that the reaction preferentially occurs on the electrode surface

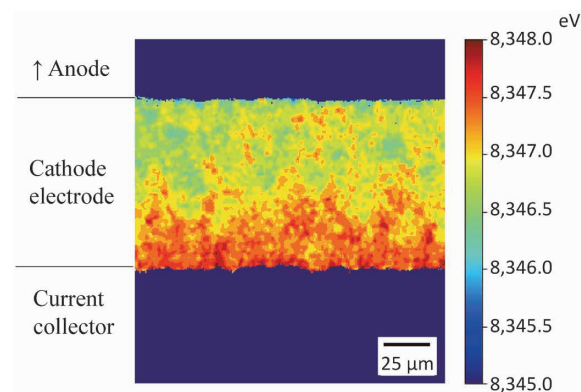


Fig. 3 Energy distributions of Ni K-edge XAFS in the NCA cathode

near the anode. For EV batteries, it is necessary to increase the amount of active material to achieve higher capacity. Designing an electrode with thick film and high density is prone to such a reaction distribution, which may cause rapid capacity decline and an increase in resistance. Understanding the reaction distribution of the battery to be used and controlling the charge/discharge rate appropriately will lead to longer battery life.

2.2 Visualization of electron conduction path in the depth direction of electrode

On the other hand, the formation and maintenance of an appropriate electron conduction path are necessary for the charge transfer reaction to proceed at the electrolyte/active material interface. Using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), a next-generation active material for 5 V-class high-potential cathodes, a cathode was prototyped for cycle degradation tests. After 300 cycles of charge/discharge at a 2C rate, the capacity declined significantly to 30% of what it had been initially. The cross-sectional shape of the LNMO cathode and the electron conduction path are shown in Fig. 4. The left column shows atomic force microscope (AFM) images; the upper row shows the initial product, and the lower row shows the degraded product. The degraded product shows more cracks in the active material than the initial product, especially in the upper part near the anode, which is pulverized by the expansion and contraction caused by charge/discharge. The electron conduction path detected, by scanning spread resistance microscope (SSRM) is visualized in the right column of Fig. 4. The SSRM is a method to visualize the distribution of resistance values by scanning the sample surface with a conductive probe. In the degraded product, the electronic conduction of the electrode surface layer near the anode has declined significantly. The repeated

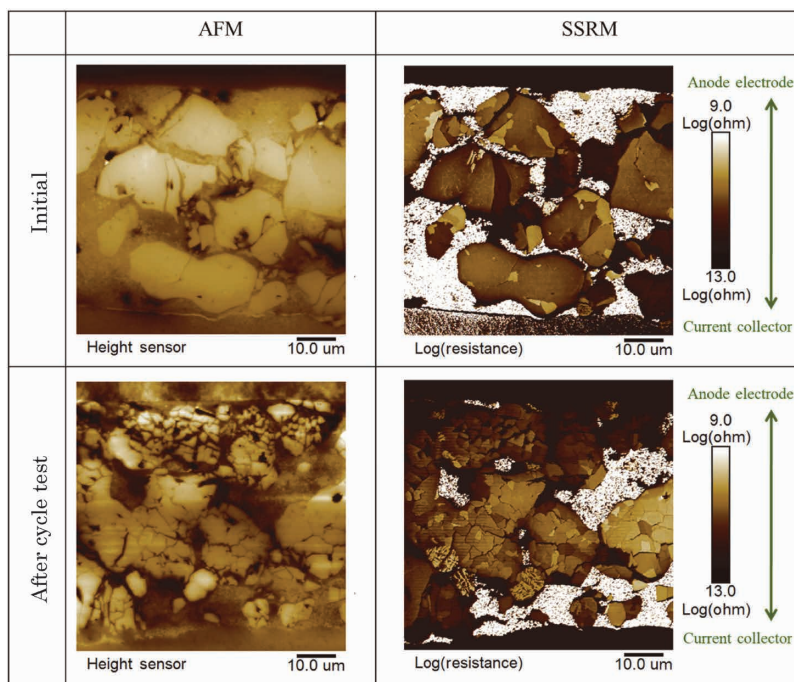


Fig. 4 Cross sectional views of LNMO cathodes and electron conduction paths

insertion desorption of excess lithium ion in the electrode surface layer is considered to have caused the active material of the electrode surface layer to be pulverized and the electron conduction path of the conductive agent to be cut off. Since no electrode reaction takes place unless electrons are supplied together with lithium ions, the breakage of the electron conduction path causes a significant decline in capacity.

2.3 Non-destructive degradation diagnostic technology for reuse

Used lithium-ion batteries are increasing with the spread of EVs, and efforts are underway to reuse them in stationary energy storage systems. The differential analysis of the charge/discharge curve is a method to evaluate cathode degradation and anode degradation by obtaining peaks corresponding to phase transitions of the active material without breaking down the battery. A storage test was conducted on a prototype battery using NCA as the cathode active material and graphite as the anode active material, and the battery was kept fully charged at 70°C for one week. Fig. 5 shows the charge/discharge curves before and after the storage test and the dV/dQ curve obtained by differentiating the charge/discharge curve. Fig. 5(b) indicates by arrows the peaks derived from graphite stage structure identified from KRIJ's monopole data. The peak shifts to the high voltage side due to storage degradation. In the charged

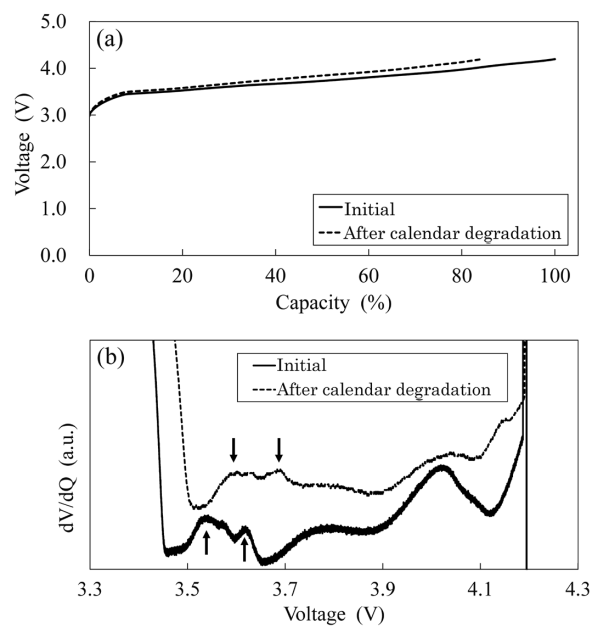


Fig. 5 Charge curves (a) and dV/dQ curves (b) before and after calendar degradation

state, the anode is exposed to a strongly reducing environment, and the electrolyte decomposition reaction occurs, during which the lithium ion inserted into the anode is incorporated into the sub-reaction of film formation and becomes carbonate or phosphate, thereby reducing the amount of lithium ion available for operation. This causes a gap between the cathode and anode capacities, and as the capacity range of the cathode used shifts to the high potential side, the anode peak also shifts relative to the high voltage side. Thus, utilizing the

monopole information allows the degradation state to be analyzed non-destructively.

3. Expectations for new batteries

3.1 Secondary battery project initiatives in Japan

In NEDO's "Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING)" (FY2009-FY2015) and "Research and Development Initiative for Scientific Innovation of New Generation Batteries 2 (RISING2)" (FY2016-FY2020), the development of an innovative battery with an energy density of 500 Wh/kg, which significantly exceeds the performance of conventional lithium-ion batteries, has been promoted through industry-government-academia collaboration, aiming at a cruising distance equivalent to that of current gasoline-powered vehicles. The candidates for new batteries include a fluoride shuttle battery with anion as a charge compensation carrier, a battery using conversion reaction, a zinc-air battery, and a lithium-sulfur battery. From FY2021 on, NEDO's "Research and Development Initiative for Scientific of New Generation Batteries 3" will focus on the research and development of fluoride batteries and zinc anode batteries that can achieve both high energy density and safety while using inexpensive materials with few resource constraints.

Basic research on all-solid-state batteries has been conducted by ALCA-Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING). Studies are underway from basic research to practical application, including the research and development of the production process of an all-solid-state lithium-ion battery, aimed at installation in EVs, in NEDO's "Development of Material Evaluation Techniques for Advanced and Innovative Batteries (Phase 2)", which began in FY2019.¹⁴⁾⁻¹⁶⁾

The Element Strategy Initiative of the Ministry of Education, Culture, Sports, Science, and Technology is developing sodium-ion batteries as eco-friendly post-lithium-ion batteries. As mentioned above, lithium-ion batteries have been commercialized and are being applied to EVs and sizeable stationary power sources. However, for large power supplies, in which material costs play a more significant role, the reduction of environmental impact and cost performance are prioritized. Therefore, there is a high expectation for the development of sodium-ion batteries, whose charge carriers use sodium, with reserves approximately 1,000 times greater than those of lithium,¹⁷⁾ a rare element with a small Clarke number.

The prototyping/evaluation technology for the all-solid-state battery and sodium-ion battery, which are nearing commercialization as new batteries, is introduced below.

3.2 Prototyping/evaluation technology of all-solid-state battery

KRIJ has been independently synthesizing solid electrolyte, prototyping and evaluating all-solid-state batteries based on sulfide, and is entering the phase of practical application. Fig. 6 shows the ionic conductivity of glass-ceramic $\text{Li}_7\text{P}_3\text{S}_{11}$, LGPS-type $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, and argyrodite-type $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$ at various temperatures as representative examples of sulfide-based solid electrolytes synthesized at KRIJ.¹⁸⁾ Some systems exhibit ionic conductivity close to the ionic conductivity of 10^{-2} S/cm^2 of electrolyte and are nearing practical application. The rate characteristics of a coated all-solid-state battery using $\text{Li}_6\text{PS}_5\text{Cl}$ are shown in Fig. 7. The discharge capacity of more than 80% is maintained even at a 5C rate, showing excellent

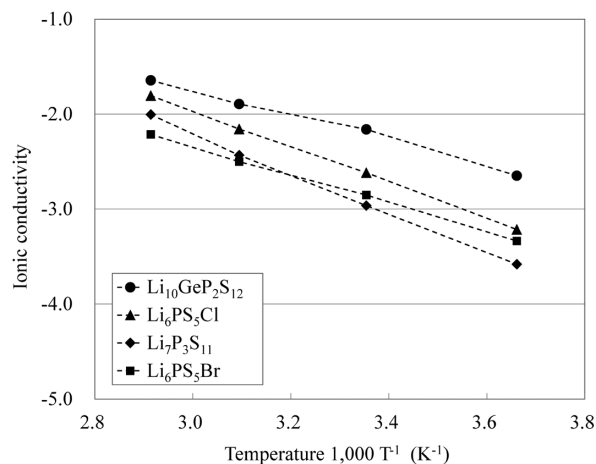


Fig. 6 Ionic conductivity of sulfide-based solid electrolytes

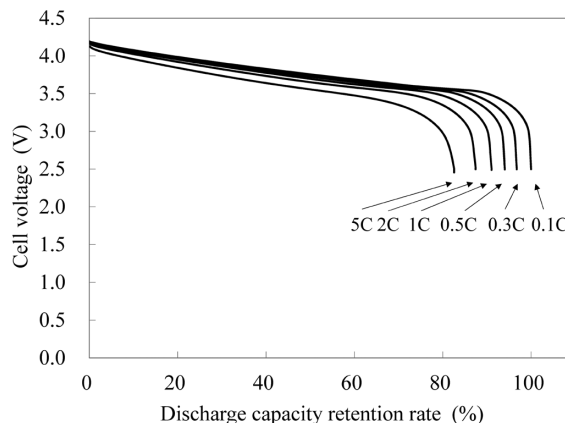


Fig. 7 Discharge rate characteristics of sulfide-based all-solid-state batteries

output characteristics. In electrolyte, in addition to lithium ion (cation), a counterpart anion is transferred, and the ion transport number of lithium ion, which contributes to ionic conduction, is about 0.3.¹⁹ On the other hand, solid electrolyte differs from the electrolyte in that the ion transport number of lithium ion is 1. In electrolyte, a solvothermal reaction occurs in which solvent molecules of electrolyte are coordinated around lithium ion, and a desolvation reaction occurs when lithium ion is inserted into active material. In a solid electrolyte, there is no reaction with the solvent, and the reaction occurs smoothly at the solid-electrolyte/active-material interface, making the battery system suitable for high-speed charge/discharge.

3.3 Prototyping/evaluation technology of sodium-ion battery

The history of investigating cathode materials used in sodium-ion secondary batteries is long, and many studies have been conducted on oxide, phosphate, sulfide, and other cathode materials.²⁰⁾⁻²³⁾ In the oxide system, starting with NaCoO_2 , the NaMeO_2 compound (Me: transition metal element) with a layered rock salt structure is a promising candidate. The ionic radius of transition metals Fe and Li are close, and cation mixing occurs quickly, making LiFeO_2 electrochemically inert. On the other hand, NaFeO_2 is electrochemically active, and inexpensive Fe can be selected as a transition metal.²⁴⁾ In the layered rock salt structure where the $\text{Fe}^{3+}/\text{Fe}^{4+}$ reaction is used, the P2 and O3 types have

been studied.^{25), 26)}

Focus was placed on the O3-type layered rock salt structure, which has been used in lithium-ion batteries, to synthesize $\text{Na}(\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$, $\text{Na}(\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Co}_{1/3})\text{O}_2$, and $\text{Na}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Fe}_{1/3})\text{O}_2$ based on $\text{Na}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ with lithium replaced by sodium, and Ni, Mn, and Co replaced by Fe, respectively. Sodium-ion batteries using these for their cathodes were prototyped, and their redox reaction and charge/discharge characteristics were investigated.

A case of $\text{Na}(\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ is shown as an example of redox reaction analysis. Mössbauer measurement of Fe by transmission ^{57}Fe Mössbauer spectroscopy was performed at room temperature in the velocity range ± 5.2 mm/s. Fig. 8 shows the Mössbauer spectrum of $\text{Na}(\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ adjusted to each voltage. A paramagnetic doublet spectrum is observed in each sample. The isomer shift reflects the s-electronic charge density and is also known as the chemical shift. On the other hand, the quadrupole split reflects the electric field gradient induced by the oxygen ligands in the matrix. At 2.5 V, Fe exhibits a typical quadrupole split and is in a single Fe^{3+} valence state. On the other hand, the shape of the Fe^{3+} doublet becomes gradually asymmetric with increasing voltage. The analysis with Fe^{3+} and Fe^{4+} has confirmed that the average valence of Fe increased due to an increase in the Fe^{4+} component by the desorption of sodium ions.

Fig. 9 shows the hard X-ray XAFS measurement results for $\text{Na}(\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ at the Fe-K

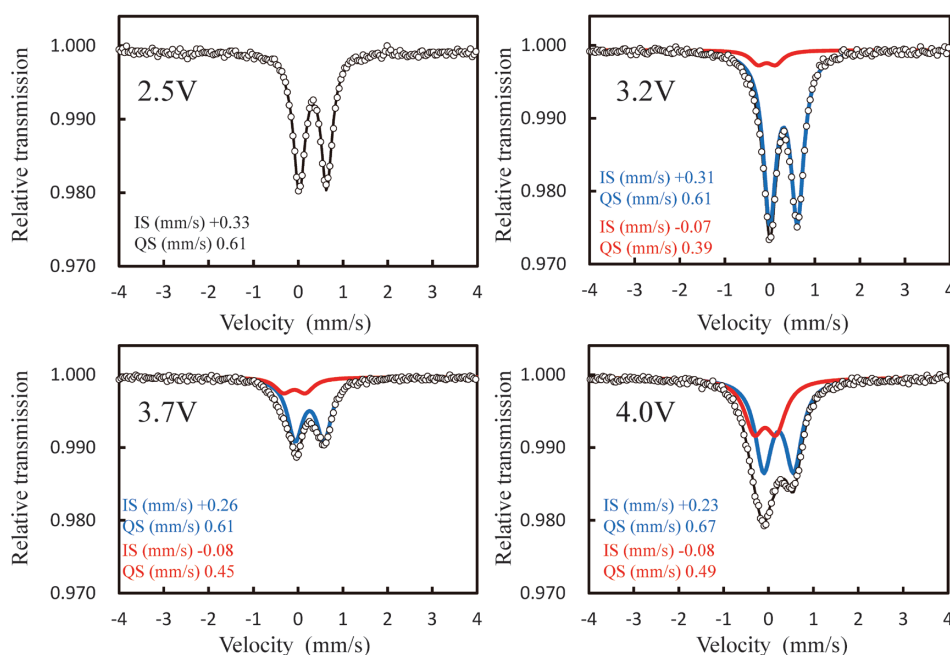


Fig. 8 ^{57}Fe Mössbauer spectra of $\text{Na}(\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$

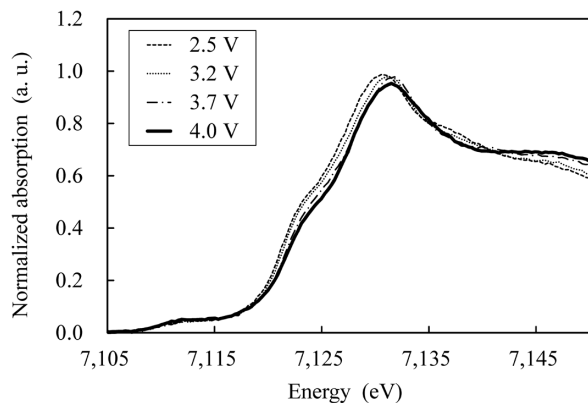


Fig. 9 Fe K-edge X-ray absorption spectra of Na($\text{Fe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$) O_2

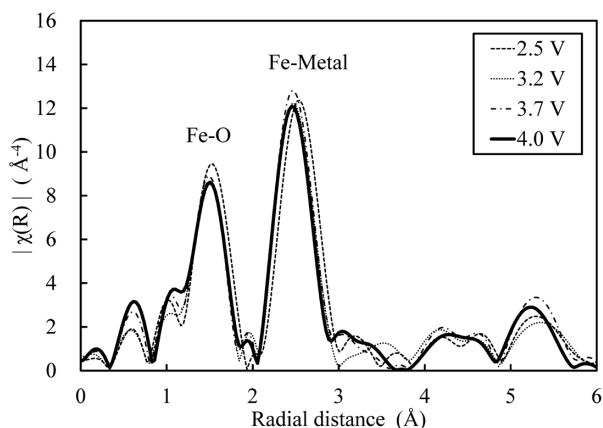


Fig.10 Radial distribution functions around Fe atoms

absorption edge adjusted to each voltage. Comparison with a reference sample has confirmed Fe to be Fe^{3+} after synthesis. As the voltage increases, the XANES spectrum shifts to the high-energy side, confirming an increase in the average valence of Fe, similar to the Mössbauer results. The radial distribution function around Fe is shown in Fig.10. In the radial distribution function around Fe, the lattice spacing of Fe-O, the first proximal lattice, shrinks as the voltage increases, suggesting an increase in valence, which indicates a redox reaction of Fe.

Fig.11 compares the discharge capacities. Thus, by appropriately selecting inexpensive transition metals such as Fe, various capacities and operating voltages can be expressed, and the creation of a wide variety of materials can be expected. The ionic radius of sodium is larger than that of lithium, so the Coulomb force is smaller, and if the desolvation process is diffusion-controlled,²⁷⁾ charge/discharge can be performed faster than with a lithium-ion battery. Combinations with high output characteristics have also been reported,²⁸⁾ and expectations for sodium-ion batteries as post-lithium-ion batteries are growing.

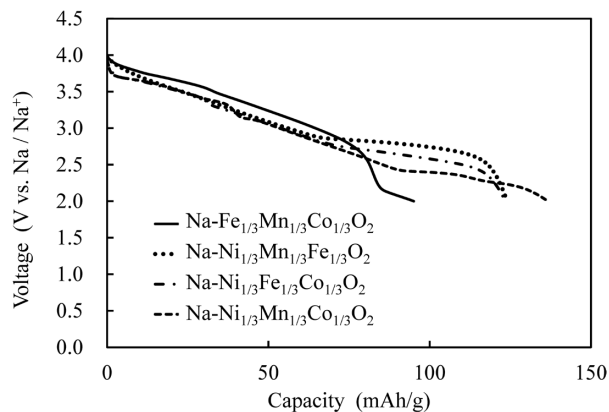


Fig.11 Comparison of discharge capacity of O3 type layered rock salt structure cathode materials

Conclusions

The promotion of decarbonization efforts in the international community is an urgent task. The decarbonization of power sources is progressing with the social implementation of hydrogen energy, the electrification of vehicles, and the introduction of renewable energy. Secondary batteries are an essential technology for EVs and electric power storage, and efforts are being made to improve the high energy density and safety of current liquid lithium-ion batteries. In addition, there are high expectations for the emergence of new batteries, such as all-solid-state batteries and sodium-ion batteries. Kobelco Research Institute will support the research and development of secondary batteries by providing prototypes of secondary batteries, physical analysis, chemical analysis, safety tests, and combined analysis with CAE, and will contribute to the realization of SDGs and carbon neutrality.

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