Development of a Sodium Ion Secondary Battery

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Recently, the demand for large storage batteries for electricity supply has been increasing remarkably. We have been developing a sodium ion secondary battery which has large storage capacity and which can work at ambient temperature without using rare elements.

In this paper, we introduce the trends in the development of the anode and cathode materials for sodium ion secondary batteries. Moreover we report on the electrical and safety properties of the sodium ion secondary batteries which contain our anode and cathode materials.

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Introduction

Lithium ion secondary batteries have already been made practical as small power supplies for devices such as mobile phones and notebook computers. In addition, there has been increased demand for large power supplies such as power supplies for automobiles, including electric vehicles and hybrid vehicles and power supplies for distributed power storage and so on. The small power supply range of 10kWh or less, where energy density is given the top priority, has become the exclusive territory of lithium ion secondary batteries, centered on applications in mobile information terminals. However for large power supplies, where the weight of material cost increases, environmental impact and cost-performance relationships are given the top priority instead of energy density. What becomes a problem here is reserves and constraints on the annual production of lithium, which is the charge transporter within batteries, and transition metals such as cobalt for redox couples that have the function of maintaining charge neutrality for cathodes. In research and development for the next generation of secondary batteries, known as post-lithium ion secondary batteries, extensive investigations are being carried out on batteries that do not use rare metals.

One of the candidates for the next generation of secondary batteries that has been proposed to meet this demand for large power supplies is the sodium ion secondary battery that uses sodium instead of lithium as the charge carrier and iron, manganese and other transition metals instead of cobalt for redox couples, and such batteries are being investigated.1), 2) If sodium ion secondary batteries can be made practical, there will be an approximately three digit relaxation in the constraints on reserves accompanying this, and we can expect that the environmental impact and cost will be greatly reduced.

On the other hand as shown in **Table 1**, sodium has a normal electrode potential of approximately 0.3V higher or, in terms of ion volume, twice or greater than lithium and an atomic weight that is three times greater.3) Therefore the guidelines for searching for electrode active materials for lithium ion secondary batteries cannot be appropriated for sodium ion secondary batteries.

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Table 1 Comparison with lithium and sodium[3)]

	lithium	sodium
ratio of reserves	1	1,000
cost (for carbonate)	\$ 5,000/t	\$ 150/t
atomic weight	6.9 g/mol	23 g/mol
ionic volume	1.84 Å^3	4.44 Å^3
theoretical capacity	3,829 mAh/g	1,165 mAh/g
normal electrode potential vs. SHE	–3.045 V	–2.714 V

For example, it is impossible for graphite, which is typically used as a anode material for lithium ion secondary batteries, to store and release sodium ions both theoretically and in practice because of its crystal structure.[4), 5)] Around the beginning of the 2000's, it was discovered that carbon materials as hard carbon having disordered structures could electrochemically store and release sodium ions,[6)] and even though anode materials with sufficient cycle life had not been found up to several years ago, work was being done on developing and making practical sodium ion batteries, and a small number of researchers were investigating them.

We have focused on carbon materials as hard carbon having disordered structures and have carried out development of anode materials that have both charging and discharging capacity and cycle life that are practical for sodium ion secondary batteries. In addition, we have been developing layered oxides with superior balance in capacity and cycle life for cathode materials too. In this article, we will describe these anode materials and cathode materials and also report on the results of carrying out verification testing on sodium ion secondary batteries that operate at room temperature and that combine these electrode materials with an organic electrolyte that uses carbonate solvents.

Anode Materials for Sodium Ion Secondary Batteries

1. Anode candidate materials for sodium ion secondary batteries

The development of anode materials for sodium ion secondary batteries follows a history similar to that of anode materials for lithium ion secondary batteries. In the early investigations into sodium ion secondary batteries, starting at the beginning of 1980, Delmas et al. used metallic Na for the anode, and started evaluating characteristics for layered oxides as cathode active materials.[7)] Since then, metallic Na for the counter electrodes has been most typically used in evaluations of materials for sodium ion secondary batteries. However, metallic Na is highly active, even though it has a low melting point of approximately 98°C. In particular, since it reacts explosively with water, the use of metallic Na for practical use and commercialization of sodium secondary batteries operating at room temperature is thought to be difficult even now from the standpoint of battery safety. The sodium-sulfur (NAS) batteries, which are practical batteries that are successful in using metallic Na in the anode by using β alumina as a solid electrolyte and working at high temperatures, are the sole example.

Thus, there has been a need for a safety anode material that is inexpensive and that has a large capacity for storage and release of sodium ions to replace metallic Na. In terms of Na alloys, which are one answer for this, a group from Showa Denko K. K. investigated and disclosed a sodium ion secondary battery that used an alloy of sodium and lead for the anode material at the end of the 1980s.[8)] However, because of the addition of lead, which is a heavy metal, the energy density was reduced, and because of the toxicity and environmental impact, no more examples of investigations into Na-Pb alloys have been seen since then. In terms of other alloy based anodes, sodium ion secondary batteries using as anode materials thin films of metallic tin, germanium and bismuth, which also underwent a variety of investigations for lithium ion secondary batteries, were investigated by a group from Sanyo Electric Co., Ltd. in the middle of the 2000s.[9)]

Recently, the group of Komaba et al. discovered that, with an anode using a nano-powder of tin, a large capacity of approximately 500 mAh/g with excellent cycle retention characteristics could be obtained.[10)]

Problems with volume changes and forming fine powders that accompany reactions to create alloys are problems that are common to sodium as well as lithium, but conversely, appropriation of the movement toward making alloy anodes practical by improving binders, which have progressed with lithium ion secondary batteries, is a possibility for overcoming these problems.

In addition, carbon materials are being examined for practical anode materials that replace metallic Na. However, it is widely experimentally known that graphite which has a layered structure that is typically used in lithium ion secondary batteries was developed, but does not electrochemically store and release sodium ions. This is because the ion radius of sodium ions is larger than those of lithium, and therefore, it is difficult for them to enter between the graphene layers. Furthermore, this is backed up by the fact that lithium and potassium can take a stable position on the hexagonal mesh-like structural surface of the graphene layer, but sodium cannot find a stable position (cannot form a commensurate structure).4), 5)

Fig. 1 shows the results of charging and discharging tests carried out after fabricating a R2032 coin cell in a glove box with an Ar atmosphere, making an electrode with graphite applied to a copper foil using polyvinylidene fluoride (PVdF) as a binder as the operating electrode, making metallic Na the counter electrode and, further, using an electrolyte solution (1 M $NaClO_4$/EC-DMC) in which $NaClO_4$ electrolyte salt was dissolved in an ethylene carbonate (EC): dimethyl carbonate (DMC) solvent at a ratio of 1:1 (volume ratio) at a concentration of 1 mol/L.3)

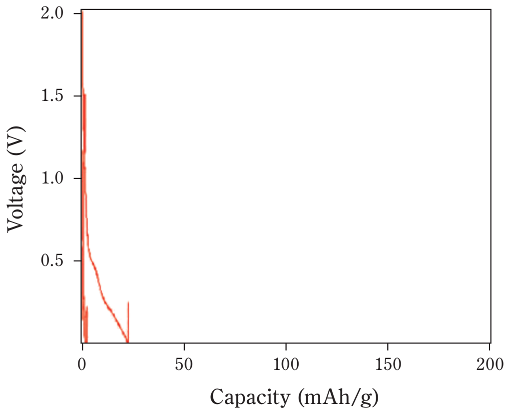


Fig. 1 Charge and discharge curves of graphite vs. Na metal 3)

During the initial discharge (the direction storing the Na is called "discharge", denoted similarly for the half cell for evaluating anode carbon materials in the following), a small amount of capacity was observed, but absolutely no charging (direction releasing of Na) capacity was obtained. It was confirmed that graphite is not appropriate as an anode material for sodium ion secondary batteries.

On the other hand, at the beginning of the 2000s, some researchers started discovering that carbon materials with hard carbon having disordered structures could electrochemically store and discharge sodium ions. The group of Dahn et al. carried out evaluations using metallic Na as a counter electrode for hard carbon derived from glucose and reported that approximately 300 mAh/g was obtained for an initial reversible capacity.6) However, the problem that cycle retention characteristics were not enough for practical secondary batteries remained. Starting in the middle of the 2000s, there were reports of hard carbons derived from resins that had aromatic rings with hydroxyl groups being suitable for anode materials for sodium ion secondary batteries.11)

2. Sumitomo Chemical hard carbon

Sumitomo Chemical also started focusing on these hard carbons and investigating them as anode materials for sodium ion secondary batteries. As a result, it was found12), 13) that a large charging and discharging capacity of approximately 320 mAh/g and excellent cycle characteristics could both be established in hard carbon derived from calixarenes as shown in **Fig. 2**.3)

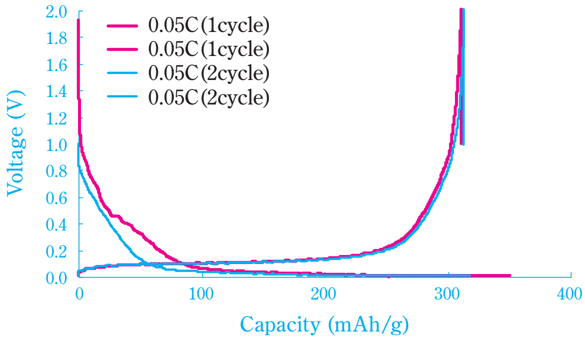


Fig. 2 Charge and discharge curves of the hard carbon heat-treated at 1600°C vs. Na metal 3)

If high temperature heat treatment is carried out with an inert gas flow at 1500°C to 2000°C after the carbonization process during synthesis, the capacity of these hard carbons increases.

(1) Measurement of quasi-OCV

To indirectly observe the Na charge and discharge reaction potential, we carried out quasi-measurements of open circuit voltage (OCV) with various Na storage states for hard carbon after high temperature heat treatment at different temperatures.

For the quasi-OCV measurements, various types of hard carbon were used, and a coin cell with a configuration of metallic Na for the counter electrode and an electrolyte solution (1 M $NaPF_6$/PC) in which $NaPF_6$ electrolyte salt was dissolved in a propylene carbonate (PC) solvent at a concentration of 1 mol/L was fabricated. A continuous operation (**Fig. 3** (a))3) in which, after

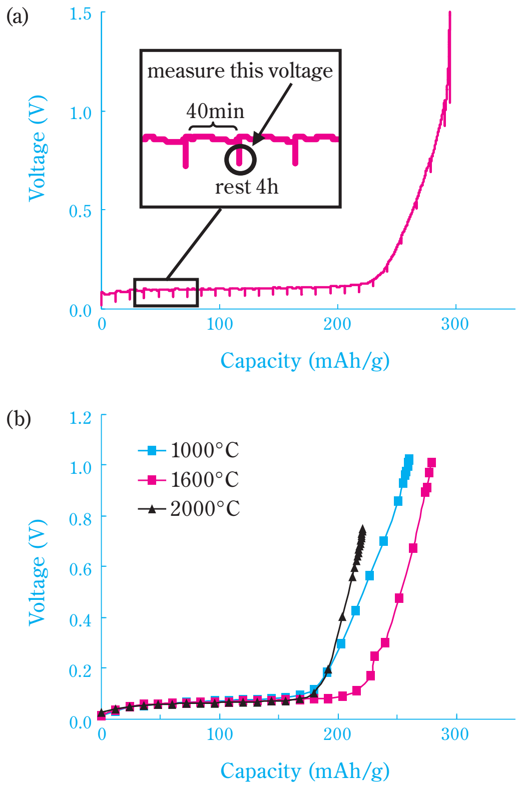


Fig. 3 (a) Measurement of quasi-open-circuit-voltage (QOCV) and (b) the QOCV plots of hard-carbons[3)]

complete discharging, charging was carried out at 0.05C, with four hours rest given for every 40 minutes of charging, and the potential after four hours recorded as quasi-open circuit voltage, was repeated 30 times.

The 0.05C here is a value known as the "C rate" where discharging is carried out over 20 hours, and there is a relationship in which current value (A)/battery capacity (Ah) = C rate.

In the quasi-OCV plot, the open circuit voltage (**Fig. 3** (b))[3)] in a state where there is a large amount of Na storage (potential is low) stayed constant regardless of the temperature of the high temperature heat treatment for the hard carbon; therefore, it could be assumed that the low potential of the Na storage mechanism was common to all and not dependent on the treatment temperature.

(2) NMR measurements

To further analyze the Na storage state in hard carbon using nuclear magnetic resonance (NMR), a coin cell was fabricated with metallic Na for the counter electrode, techniques of discharging used, carbon anode materials with different sodium ion storage capacities prepared and ^{23}Na-NMR measurements carried out.

The hard carbons storing sodium ions which were prepared were the five shown in **Fig. 4**: (1) approximately 20 mAh/g (≈ 0.6 V), (2) approximately 40 mAh/g (≈ 0.3 V), (3) approximately 70 mAh/g (≈ 0.1 V), (4) 200 mAh/g and (5) approximately 300 mAh/g.[3)] A Bruker Avance 300 WB (7T) was used for the measurement equipment, and ^{23}Na-NMR measurements were carried out under the condition of a 4 kHz rotational speed for the samples. For the reference sample (0 ppm) for sodium ions, an aqueous solution of NaCl and a blank were measured and used in processing the measurement results.

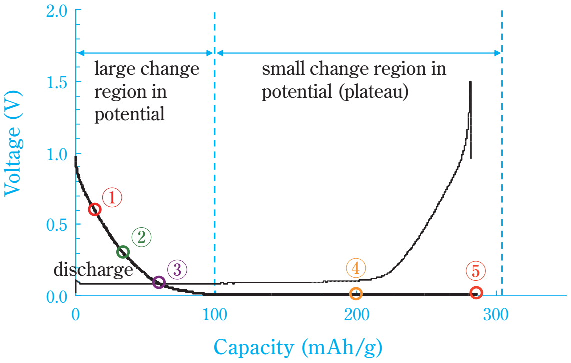


Fig. 4 The measurement points of ^{23}Na-NMR for hard-carbon[3)]

From the ^{23}Na-NMR measurements results shown in **Fig. 5**, no peak can be seen in the vicinity of 1000 ppm,[3)] and we were able to confirm that Na was present in the charged hard carbon in ionic form instead of metallic. In addition, no shift in the main peak was observed because of differences in sodium ion storage capacity. In particular, the shape of the peaks for (4) and (5) were identical; therefore, it could be assumed that there was a single Na storage mechanism, the same as in the results of quasi-OCV measurements at low potential.

(3) DSC measurements

DSC evaluations were carried out to clarify the thermal stability and reactivity of hard carbon in the state of storing sodium ions.

Coin cells were fabricated using hard carbon and metallic Na and discharging was carried out; the hard carbon was made to store sodium ions. These coin cells were disassembled, the electrode mixture recovered from the electrodes in which the sodium ions were stored in the hard carbon, and along with the electrolyte solutions, DSC measurements were carried out on these

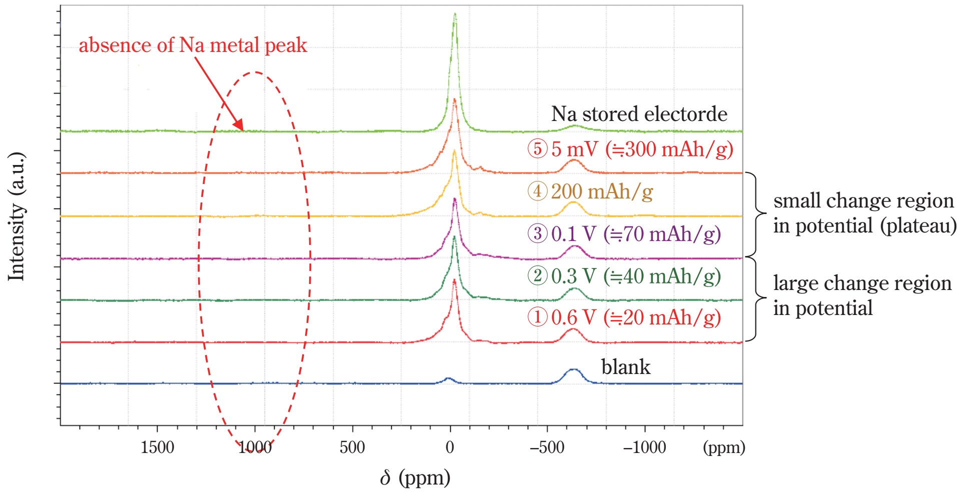


Fig. 5 ^{23}Na-NMR profile of various discharged hard-carbons[3)]

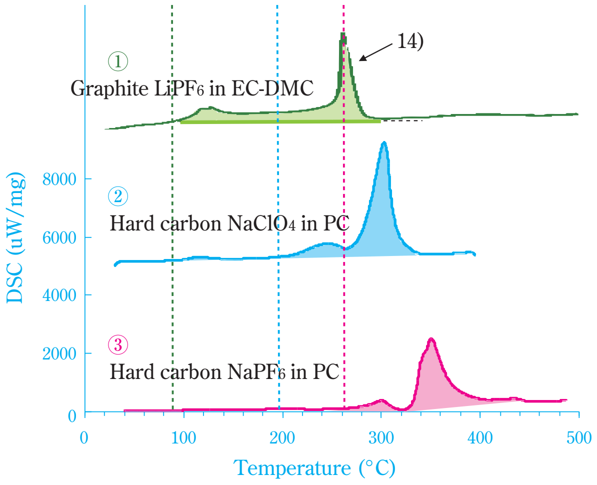


Fig. 6 DSC profile of carbons stored Li and Na respectively[3)]

to observe the exothermic activity. These results along with those denoted in the references[14)] for DSC measurements of graphite with lithium ions stored in it are shown in **Fig. 6**.[3)]

From the results of the DSC measurements, it can be seen that the starting temperature for heat generation in the hard carbon with sodium ions stored in it is higher than that for graphite with lithium ions stored in it. Therefore, hard carbon in which sodium ions have been stored has superior thermal stability, and there is a high possibility that even in a charging state, a sodium ion secondary battery would be safe. In addition, when the same solvent was used, we saw a tendency in which the starting temperature for heat generation was higher when $NaPF_6$ was used than when the perchlorate $NaClO_4$ was used.

Cathode Materials for Sodium Ion Secondary Batteries

1. Candidates for cathode materials for sodium ion secondary batteries

There is a long history of investigations into cathode materials for sodium ion secondary batteries, and starting with $NaCoO_2$ at the beginning of the 1980's by the group of Delmas et al., sodium secondary batteries were fabricated for layered oxides such as $NaMnO_2$ and $NaNi_{0.6}Co_{0.4}O_2$ with metallic Na for the counter electrode, and the electrochemical characteristics of these were reported.[7), 15)–17)] However, even though sodium has the same number of valences as lithium, the volume of ions is two or more times that of lithium and three or more times in terms of atomic weight; therefore, sodium-based materials are at an essential disadvantage to lithium-based materials from the standpoint of energy density, so we only saw a few examples of investigations up until the middle of the 2000s. In recent years, there have been investigations into candidate substances in which sodium is substituted for the lithium in substances that had generally been investigated as cathode materials for lithium ion secondary batteries for cathode materials for the sodium ion secondary batteries which have attracted attention.

(1) Oxide-based cathode materials

Starting with investigations of $NaCoO_2$ in which sodium is substituted for the lithium of $LiCoO_2$, which has a layered rock-salt type crystal structure, layered oxides with a $NaMO_2$ (M being a transition metal) composition have consistently been investigated as promising candidates for cathode materials for sodium ion secondary batteries.[18), 19)] These include sodium, which is a charge carrier, and a transition metal, for the redox couple, at a ratio of 1:1, and in addition, this is because the mass is small since they are constituted of a minimum of two oxygen atoms, making for a high energy density. On the other hand, the behavior as an oxidizing agent such as the release of oxygen in a charged state from the layered oxide cathode materials of lithium ion secondary batteries (the state in which the lithium ions are detached) can be assumed to be the same in sodium-based layered oxides.

For comparison, with oxides that have spinel type crystal structures, such as $LiMn_2O_4$, which are used in lithium ion secondary batteries, no substances exist in which sodium can be substituted in an amount that can be used in sodium ion secondary batteries; therefore, there are no candidates. This is because the ion radius of sodium ions is too large for the tetrahedral site in the spinel structure that the lithium ion occupies, and substitution is impossible.

(2) Phosphate-based cathode materials

Investigations of materials in which sodium is substituted for lithium in $LiFePO_4$, which has an olivine crystal structure and is used in lithium ion secondary batteries, and other phosphate-based cathode materials, such as $NaFePO_4$,[20)] $NaVPO_4$,[21)] Na_2FePO_4F,[22), 23)] $Na_3Fe_3(PO_4)_4$[24)] and $Na_3V_2(PO_4)_2F_3$[25)], are moving forward.

This material group can be expected to have a high degree of safety without the danger of oxygen release in a charged state because the bonds between phosphors and oxygen are strong. On the other hand, the masses of substances which contain many elements other than sodium, which is the charge carrier, and the transition metal, which is the redox couple, are large (and their volume is large), so from the standpoint of energy density, they are disadvantageous materials.

(3) Sulfide-based cathode materials

TiS_2 is a historical cathode material, and was the first commercialized in lithium secondary batteries, and it also exhibits an extremely good reversible charging and discharging profile as a cathode material for sodium ion batteries.[26), 27)] The flatness of the charging and discharging profile is good with metallic Li anodes, and the average discharge voltage is approximately 2.2 V while two steps are present in the charging and discharging profile for metallic Na anodes, with the average discharge voltage being about 0.4 V lower at 1.8 V. This difference in potential reflects the difference in normal electrode potential for lithium and sodium.

(4) Organic material based cathode materials

With lithium ion secondary batteries, organic material based cathode materials were too bulky and had too low a specific volume energy density for the problems, while we can see a number of examples of investigations into sodium salts of oxo-carbonates, Prussian blue and other materials for sodium ion secondary batteries.[28), 29)]

Organic material based cathode materials are not just bulky, but also can maintain a reversible host-guest function to the extent that the individual molecules themselves are not broken even if the macro-crystallinity of the molecule system as a whole is lost by storing sodium, which is large. In addition, they can present multiple sodium ions to battery reactions and can form large capacity cathode materials if they are materials with a low molecular weight.

2. Sumitomo Chemical layered oxides

At Sumitomo Chemical, we have focused on and started developing layered oxides thought to be promising from the standpoint of energy density. Initially we evaluated the characteristics of $NaFeO_2$, which has a crystal structure of layered rock-salt and uses iron which is the most abundant in terms of resources among the transition metals in the fourth period of the periodic table, for the cathode material of sodium ion secondary batteries. Though the discharge voltage of a sodium secondary battery using $NaFeO_2$ was comparatively high at approximately 3.5 V and activity that drew a flat discharge curve was exhibited,[30)] the resistance was high, and we determined that $NaFeO_2$ was a material with a problem in water resistance. Next, we carried out examinations of layered oxides that used manganese, such as $NaMnO_2$, which has a structure similar to $NaFeO_2$ and $Na_{0.7}MnO_2$, which has a layered structure in which Na defects reduce the symmetry, but materials that used manganese were determined to have a low discharge voltage of approximately 3–2.5 V. In addition, $NaNiO_2$, which is a layered oxide that uses nickel, tends to have a high discharge voltage, but use of the comparatively expensive nickel in large amounts can be said to be inappropriate for the purpose of development of sodium ion secondary batteries. Just in case, we evaluated $NaCoO_2$, a layered oxide that uses cobalt, but unlike the case of

$LiCoO_2$ in lithium ion secondary batteries, the discharge capacity with sodium was small, and good characteristics could not be obtained. Based on this knowledge, we moved forward searching for compositions with which we could obtain excellent battery characteristics by combining a, b and c in layered oxide compositions represented by $Na(Fe_aMn_bNi_c)O_2$ where a + b + c = 1, such that the iron was maximized and the nickel was minimized based on the purpose of developing sodium ion secondary batteries.

(1) XAFS measurements

In the search for compositions, we carried out XAFS measurements to investigate the valence number for each of the transition metal elements in the layered oxides. As a result, we determined that the iron was trivalent, the nickel bivalent and the manganese quadrivalent. In addition, in the results for layered oxides in a charged state, iron was in a mixed state of trivalent and quadrivalent, nickel being quadrivalent and manganese also being quadrivalent. In other words, we determined that the nickel mainly undergoes a redox reaction and that next, the iron also undergoes a redox reaction with charging and discharging.

In material design, the sodium is monovalent and the oxygen is bivalent; therefore, it is reasonable for the transition metal M in a layered oxide represented by $NaMO_2$ to be trivalent; therefore, materials with a ratio of 1:1 (in other words, an average of trivalent) for bivalent nickel and quadrivalent manganese in a three element cathode material combining iron, nickel and manganese can be thought of as not being unreasonable. Furthermore, since layered rock-salt crystal structures, which are typical for layered oxides, have three axes of symmetry in the direction of layering in a trigonal system, they can be thought of as including 1/3 each of the transition metal if there is some form of regularity in the positions of the transition metals in the crystal, and we started with an investigation of $NaFe_xMn_{1/2-x/2}Ni_{1/2-x/2}O_2$, in which the amount (x) of iron was varied centered on $Na(Fe_{1/3}Mn_{1/3}Ni_{1/3})O_2$.[31), 32)]

(2) Determination of cathode material composition

$NaFe_xMn_{1/2-x/2}Ni_{1/2-x/2}O_2$ was synthesized by mixing a $Fe_xMn_{1/2-x/2}Ni_{1/2-x/2}(OH)_2$ precursor (which was obtained by co-precipitation in which an aqueous solution of NaOH was added to an aqueous solution in which chlorides of the transition metals were dissolved) and NaOH, and calcining in a nitrogen atmosphere for 12 hours in the temperature range of 750°C to 900°C.

When x was any of 0.2, 0.33 and 0.4, in powder x-ray diffraction measurements of the $NaFe_xMn_{1/2-x/2}Ni_{1/2-x/2}O_2$, it was found that a single phase such as a layered rock-salt crystal structure was obtained. Using this, acetylene black as a conductor and PVdF as a binder, a combined paste was prepared with n-methyl pyrrolidone (NMP) as a solvent, and an electrode was fabricated in which this was applied to aluminum foil. A coin cell was fabricated combining this electrode, metallic Na as the counter electrode and 1 M $NaPF_6$/PC as the electrolyte, and evaluations of the battery characteristics of the layered oxide were carried out. The discharge curves obtained in the results are shown in **Fig. 7**, and the charging and discharging capacity in the range of 1.5–4.0 V vs. that of metallic Na and other values are given in **Table 2**.

No large difference was seen in the characteristics for the various compositions in which x was 0.2, 0.33 and 0.4 for the layered oxides represented by $NaFe_xMn_{1/2-x/2}Ni_{1/2-x/2}O_2$; therefore, the $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$

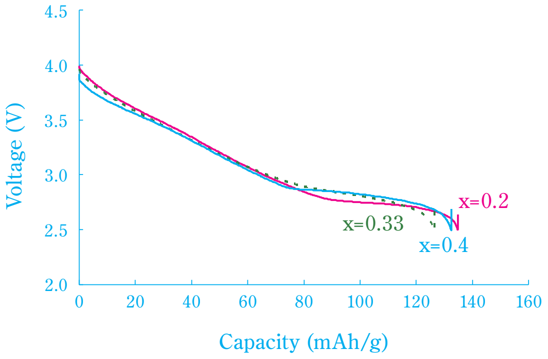


Fig. 7 Discharge curves of $NaFe_xMn_{1/2-x/2}Ni_{1/2-x/2}O_2$ vs. Na

Table 2 Capacity of layered oxide cathode materials in the range of 1.5-4.0V vs. Na metal

	theoretical capacity [mAh/g]	1st charge capacity [mAh/g]	1st discharge capacity [mAh/g]
$Na_{0.7}MnO_2$	182.09	67.0	167.3
$NaFeO_2$	241.82	103.6	60.8
$Na_{0.6}CoO_2$	153.55	84.6	63.1
$NaFe_{0.2}Mn_{0.4}Ni_{0.4}O_2$	240.13	151.4	134.8
$NaFe_{0.33}Mn_{0.33}Ni_{0.33}O_2$	240.54	153.1	126.6
$NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$	240.55	157.4	132.5

composition which included the most iron, for which resources are abundant, with x being 0.4 was thought to be most appropriate as a cathode material for sodium ion secondary batteries.

(3) DSC measurements

DSC evaluations were carried out to clarify the thermal stability and reactivity of the layered oxide $Na_{1-y}Fe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ in a charged state in which the Na was desorbed.

Coin cells in which $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ and metallic Na were used was fabricated; charging was carried out at 4.0V, and the sodium ions were desorbed from the $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ (roughly a $Na_{0.4}Fe_{0.4}Mn_{0.4}Ni_{0.3}O_2$ state). These coin cells were disassembled, the electrode mixture recovered from the layered oxide electrodes in which the sodium ions were desorbed, and along with the electrolyte solutions, DSC measurements were carried out to observe the exothermic activity. The results are shown in **Fig. 8**.

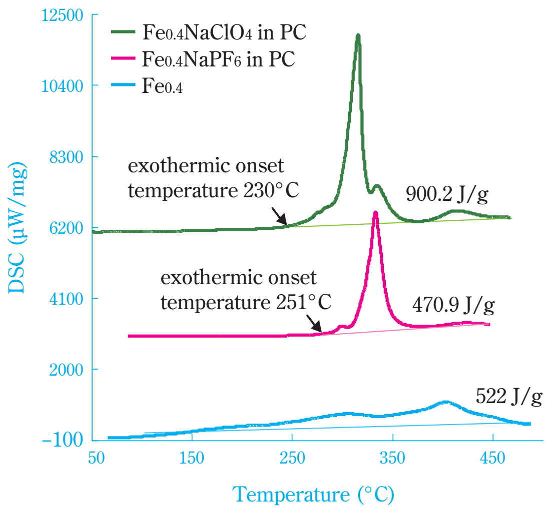


Fig. 8 DSC profile of charged $Na_{1-y}Fe_{0.4}Mn_{0.3}Ni_{0.3}O_2$

As a result of the DSC measurements, exothermic activity could not be seen at 200°C or less; therefore, the layered oxide with the sodium desorbed had superior thermal stability, and there was a high possibility of safety in sodium ion secondary batteries in a charged state. In addition, when the same solvent was used, we saw a tendency in which the starting temperature for heat generation was higher when $NaPF_6$ was used than when the perchlorate $NaClO_4$ was used.

Sodium Ion Secondary Batteries

1. Coin cell batteries

Up to now, the description has taken more than a small look at sodium secondary batteries in which metallic Na and Na alloys have been used for the counter electrodes, but up until the middle of the 2000s, anode materials having superior cycle stability and a sufficient reversible capacity for secondary batteries had not been discovered; therefore, it was difficult to get a look at actual measurement data for sodium ion secondary batteries constituted without using metallic Na or a Na alloy.

At Sumitomo Chemical, we started charging and discharging tests on coin cells around the end of 2007 for room-temperature type sodium ion secondary batteries made using hard carbon for the anode material and an oxide having a layered crystal structure for the cathode material, and we confirmed that charging and discharging characteristics that were promising for secondary batteries could be obtained.[1), 33)] In addition, there have been reports of sodium ion secondary batteries formed with layered oxide cathodes and hard carbon anodes from the group of Komaba et al. recently.[2)]

When R2032 coin batteries with a diameter of 2 cm, which were fabricated from a three element system cathode active material, $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ that made use of iron, manganese and nickel, a hard carbon anode, a 1 M $NaPF_6$/PC electrolyte and a polyethylene (PE) separator were evaluated in investigations at Sumitomo Chemical, a discharge capacity of approximately 120 mAh/g normalized by the weight of the cathode active

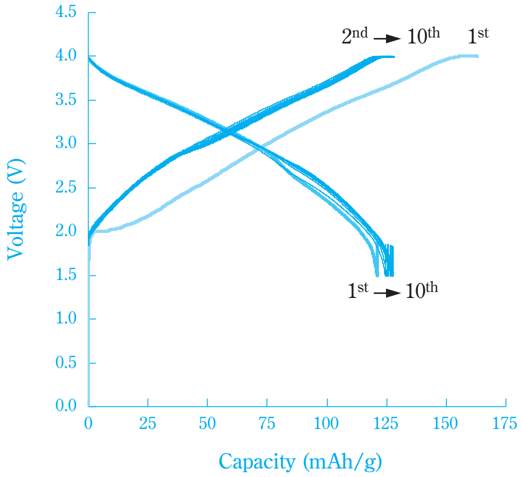


Fig. 9 Charge and discharge curves of the sodium ion battery consisting of $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ and hard-carbon[3)]

material was obtained in constant current constant voltage (cccv) charging and constant current (cc) discharging in a voltage range of 1.5–4.0 V and a 0.1 C rate as shown in **Fig. 9**.[3), 32)]

(1) Cycle (life) characteristics

As a result of carrying out accelerated tests at 10 times the current density for the sodium ion secondary batteries above, the retention rate for discharge capacity was approximately 90% at approximately 500 cycles. (In the accelerated testing, acceleration to a 1C rate,10 times the current density, was carried out after charging and discharging at a 0.1C rate for the initial 10 cycles, and the capacity was confirmed every 20 cycles by charging and discharging at the 0.1C rate.) **Fig. 10** shows a plot of the discharge capacity when discharging was carried out at the 0.1 C rate.[3)] When accelerated testing was carried out further up to 3000 cycles for this battery, the retention rate for discharge capacity was 50% after 3000 cycles. Thus, the life characteristics for this sodium ion secondary battery were superior.

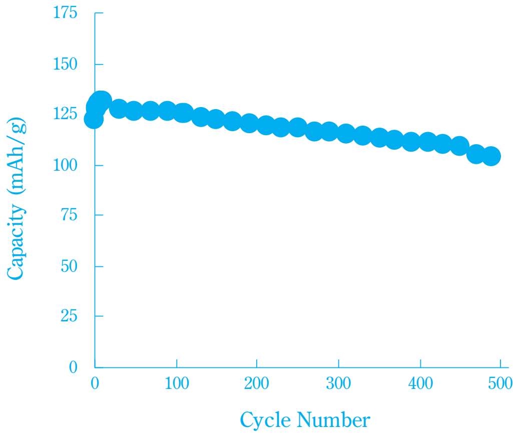


Fig. 10 Discharge capacity of the sodium ion battery consisting of $NaFe_{0.4}Mn_{0.3}Ni_{0.3}O_2$ and hard carbon at a rate of 0.1C[3)]

(2) Rate characteristics

In addition, when the changes in capacity when the current density was increased during discharging was measured, the discharge capacity at a 2C rate was maintained at 76% of that at the 0.1C rate, and these were rate characteristics that were not inferior to typical lithium ion secondary batteries.

(3) Low temperature discharging characteristics

The discharge capacity at a 0.1C rate at -40°C maintained 52% of that for 0.1C at 25°C. A reason that can be given for this is that PC, which has a low melting point, was used for the solvent in the electrolyte solution, and this can be thought of as a result superior to lithium ion secondary batteries that use typical ethylene carbonate (EC) based electrolyte solutions.

(4) Excessive discharge characteristics

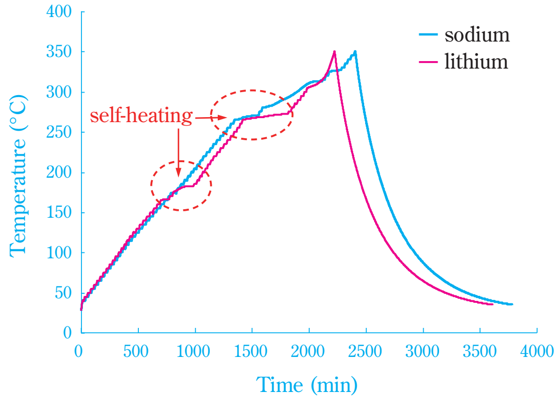
A sodium ion secondary battery identical to that used for the charging and discharging characteristics evaluations above was fabricated, and after confirming that there was no abnormal activity with several chargings and dischargings in a range of 2.0–4.0 V, excessive discharging tests were carried out in which discharging to 0 V was carried out after charging to 4.0 V and once again charging and discharging in a range of 2.0–4.0 V were carried out. As a result, we found that the sodium ion secondary battery maintained its original discharge capacity if it was charged once again.

We thought the reason for this was follows. In lithium ion secondary batteries, alloying reactions of the aluminum in the cathode current collector with the lithium and dissolving of the copper in the anode current collector arise if discharging is carried out at or below a certain voltage, and a large degradation arises. On the other hand, however, with sodium ion secondary batteries, no sodium and aluminum alloy arises; the changes in anode potential are large but do not reach the dissolution potential for copper; therefore, these batteries can be said to be essentially stable against excessive discharging.

(5) Self-heating behavior

We fabricated coin batteries for a sodium ion secondary battery identical to the one used for charging and discharging characteristics evaluation except for the separator being changed from PE to polypropylene (PP), and a lithium ion secondary battery with a typical configuration was used as a control test; after completely charging each of them, we measured the self-heating behavior using an accelerated reaction calorimeter (ARC) in which heating gradually took place in an insulated container (**Fig. 11**).

As a result, self-heating behavior was seen in the lithium ion secondary battery in the vicinity of 150°C and in the vicinity of 165°C, but self-heating behavior was not observed in the sodium ion secondary battery up to the vicinity of 260°C. Thus, sodium ion secondary batteries have the possibility of being batteries with superior thermal stability.



	sodium	lithium
cathode	NFMN	LNCM
anode	HC	Graphite
electrolyte	1M-$NaPF_6$ / PC	1M-$LiPF_6$ / EC : DMC : EMC (16/10/74)
separator	PP	PP

Fig. 11 Accelerated-reaction-calorimetry (ARC) profile of charged coin cell for sodium and lithium ion secondary battery respectively

2. Laminated batteries

Compared to the constitution of a commercial lithium ion secondary battery, the proportion of the material for the active material and other materials is smaller with respect to the battery container and the electrolyte is excessive with respect to the active material in this coin battery; therefore, we fabricated a larger laminated battery type sodium ion secondary battery to investigate more practical characteristics and evaluated the initial characteristics and safety.

The material configuration was made the same as the coin battery, and the electrode sheets and separator were cut into approximately 5 cm squares. With this group of the cathode, separator and anode as one layer, we fabricated one layer, 10 layer and 20 layer sodium ion secondary batteries (outside dimensions being substantially the same as those for smart phone batteries) and carried out evaluations of the characteristics such as charging and discharging.[34]

(1) Initial characteristics of laminated batteries

In constant current constant voltage charging and constant current discharging in a voltage range of 2.0–4.0 V and current of 0.1C and 25°C, all of these batteries exhibited a discharge capacity of approximately 120 mAh/g normalized by the weight of the cathode active material. The capacity of each of the batteries was approximately 30 mAh per layer. A photograph of the 20 layer battery is shown in **Fig. 12** and the charging and discharging curves are shown in **Fig. 13**.

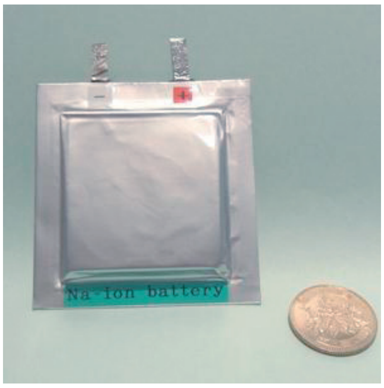


Fig. 12 Photo of the 20 layered sodium ion secondary battery with 500yen coin for the comparison

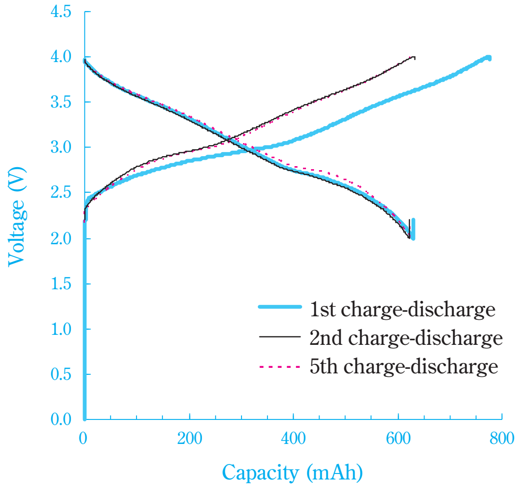


Fig. 13 Charge-discharge curves of the 20 layered sodium ion secondary battery

In the initial charging and discharging of all of the batteries, generation of a small amount of gas was seen; therefore, a gas removal operation was carried out after completion of the second cycle. The gas that was generated was 37% CO and 62% CO_2. Stable cycle behavior was exhibited after degas treatment (**Fig. 14**).

(2) Heating tests

Heating tests were carried out as the temperature of the 20 layer battery (600 mAh) in a state of being charged to 4.0 V was raised from room temperature at 5 K/min and maintained at 150°C for one hour. As a result, the voltage began to drop when the temperature

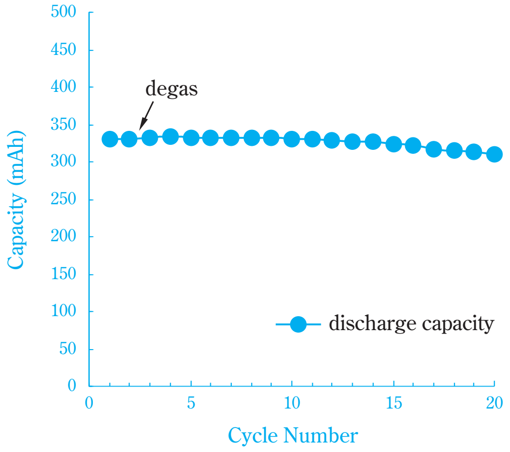


Fig. 14 Cycle behavior of the 10 layered sodium ion secondary battery

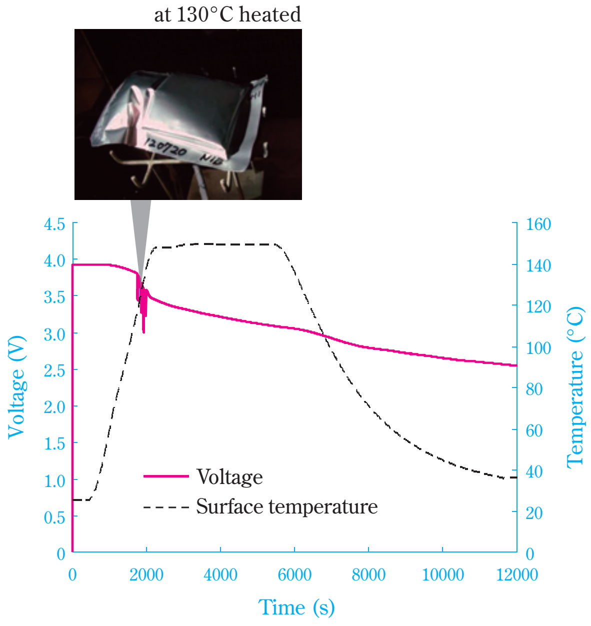


Fig. 15 Heating test profile of the charged 20 layered sodium ion secondary battery

of the battery surface rose above 75°C, and swelling of the battery was seen starting in the vicinity of 130°C, but it neither burst nor ignited (**Fig. 15**).

(3) Overcharging tests

Overcharging tests were carried out on the 20 layer battery at 25°C starting from a discharged state at three times the normal current rate. As a result, heat started being generated and the battery was seen to swell starting when the battery voltage exceeded 5V, but even when the battery was charged in excess of 200% of the capacity and reached 12V, it neither burst nor ignited (**Fig. 16**).

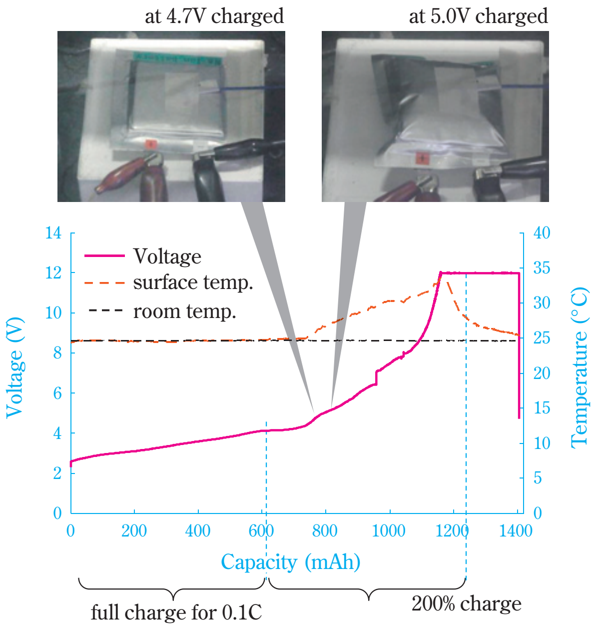


Fig. 16 Over-charging test profile of the 20 layered sodium ion secondary battery

Conclusion

In this article, we have introduced the initial characteristics of electrode active materials for sodium ion secondary batteries and practical batteries.

When we first started investigations into sodium ion secondary batteries, the situation was one in which we heard voices to the effect of "will sodium work?" even within the industry, but with the discovery of promising anode materials, verification data kept being accumulated by several research groups other than Sumitomo Chemical, and reports of sodium ion secondary batteries at academic conferences and in scientific journals have suddenly increased recently. It may not be possible to overcome all of the various disadvantages of sodium compared with lithium that were introduced at the beginning of this article, but we are discovering characteristics that would only be possible with sodium ion secondary batteries. In addition, we have found that sodium ion secondary batteries "work" in the investigations up to now, but there are still many things that have not been clarified.

Moving forward, we would like to carry out investigations that take into account the market for large power supplies, particularly, actual fabrication of large batteries and carrying out verifications, and we would like to progress with development aimed at early entry into the marketplace while making progress with various basic evaluations and analyses for the materials and battery reactions in sodium ion secondary batteries.

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