

Development of Molten Salt Electrolyte Battery

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A molten salt electrolyte battery (MSB) is a sodium secondary battery that uses molten salt as its electrolyte and features high energy density and safety. Our molten salt has a melting point of 61°C and needs to be heated to 90°C for battery usage. As the battery has a high energy density (290 Wh/L) and requires no cooling space, small and lightweight battery systems can be established. Although lithium ion batteries (LIBs) and sodium sulfur (NAS) batteries are currently drawing attention for large-scale energy storage, LIBs have limited lithium supply and safety problems, while NAS batteries require high operating temperature (350°C). For these problems, our sodium-based nonflammable MSB offers a comprehensive solution.

Keywords: battery, molten salt, sodium, bis(fluorosulfonyl)amide salt

1. Introduction

To use energy obtained through photovoltaic or wind power generation at end users for the purposes of peak shift, backup power supplies, charging electric vehicles, and the like in houses and buildings, storage batteries are indispensable for storing or supplying electric power. As a storage battery for these purposes, the lithium-ion battery, characterized by its high-energy density and compactness, is spotlighted and deployed in a variety of applications. Because of the diversity of its applications and an increase in demand for it, however, the battery has posed a resource problem that has come under close scrutiny. The 2005 total worldwide production of lithium as a metal was 21,400 tons, some 68% of which were produced by the main producers — Chile produced 8,000 tons, Australia produced 4,000 tons, and China produced 2,700 tons. In terms of the estimated amount of lithium deposits, four South American countries, Bolivia, Chile, Argentina, and Brazil, account for 84%. The scarcity of annual production is anticipated to be addressed by an increase in production based on refining by separation from saline lakes and oceans. However, the uneven distribution of the resources is a critical issue for Japan, a country that depends on imported raw materials. In addition, cobalt, used as the positive electrode active material, is a rare metal, and accordingly, a sharp increase in demand has caused a serious situation. On the other hand, sodium, found in the form of salt in a nearly inexhaustible quantity in oceans, has no problem with resources or uneven distribution at all. In terms of battery performance, the standard electrode potential of lithium is -3.045 V vs. SHE, while that of sodium is -2.714 V vs. SHE, which is slightly lower than the corresponding value for lithium. In terms of specific gravity, however, both elements are lighter than water, and sodium can compare favorably with lithium when viewed from the standpoint of specific energy.

Recently, batteries using sodium as a battery active material are gaining attention, and research and development activities on such batteries are being carried out vigorously. Batteries using molten sodium and solid electrolyte have already been put into practical use, being applied in uses

such as large-scale backup power supplies and power system stabilization. As large-capacity batteries using molten sodium, only NAS batteries⁽¹⁾ are in commercial use; however, it is necessary to raise their temperature to as high as 300 to 350°C for them to be operated. Against this backdrop, we are newly carrying out the development of a molten salt electrolyte battery consisting of molten salt as electrolyte as well as of sodium bis(fluorosulfonyl)amide salt, which is characterized by non-combustibility and non-volatility (hereinafter referred to as MSB).

2. State of the Development of MSB

2-1 Application of alkali metal bis(fluorosulfonyl)amide salt to battery electrolyte

An MSB is a battery that uses molten salt as electrolyte, has a high energy density of as high as 290 Wh/L under the current state and is characterized by perfect non-combustibility, allowing assembled batteries to be downsized and lightweight. Molten salt is characterized by features such as non-volatility, non-flammability, and high ionic concentration. Molten salt generally needs to be heated to remain molten, and a battery using molten salt with a melting point at a temperature below 373 K as electrolyte has not been realized. Recently, however, we have succeeded in developing a mixed molten salt, based on an alkali metal amide, that can be used as battery electrolyte. **Table 1** shows the thermal properties of (FSO₂)₂N salt and (CF₃SO₂)₂N salt of alkali metals^{(2),(3)}. (FSO₂)₂N salt is bis(fluorosulfonyl)amide, denoted as FSA salt, while (CF₃SO₂)₂N salt is bis(trifluo-

Table 1. Thermal properties of alkali metal amide salts^{(2),(3)}

Anion	Melting point	Alkali metal cation				
		Li+	Na+	K+	Rb+	Cs+
(CF ₃ SO ₂) ₂ N-	K	506	530	472	450	395
(FSO ₂) ₂ N-	K	403	379	375	368	365

romethylsulfonyl)amide, denoted as TFSA salt. Melting points of FSA salts are lower than those of TFSA salts, allowing them to be used at lower temperatures. In addition, it is possible to further lower the melting point by mixing two or more salts and thereby widening the liquid temperature domain.

Figure 1 shows a NaFSA-KFSA binary system phase diagram⁽²⁾. Of the FSA salts shown in **Table 1**, the NaFSA-KFSA system is considered to be one of the most promising systems for use in sodium-based secondary batteries operating at about 100 °C at present. All binary alkali metal FSA mixed salts, including the above mentioned, become simple binary eutectic systems⁽²⁾, with a eutectic temperature of 334 K (61 °C) for the NaFSA-KFSA system. The decomposition temperature of a salt with a eutectic composition (NaFSA: KFSA = 56: 44 (molar ratio)) is 463 K, and this substance can be used as a thermally stable electrolyte within a temperature range of about 130 K (334 – 463 K).

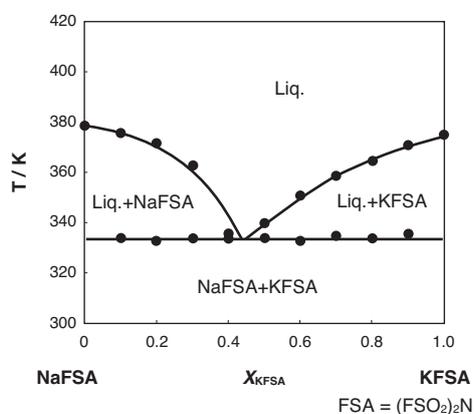


Fig. 1. NaFSA-KFSA binary system phase diagram⁽²⁾

Figure 2 shows cyclic voltamograms measured with a nickel electrode used as the working electrode on the cathode side and a glassy carbon electrode used as the working electrode on the anode side⁽⁴⁾⁻⁽⁶⁾. At the cathode limit, a peak attributable to the deposition and dissolution of sodium is observed at 0 V against the sodium metal electrode reference. At the anode limit, an irreversible oxidation

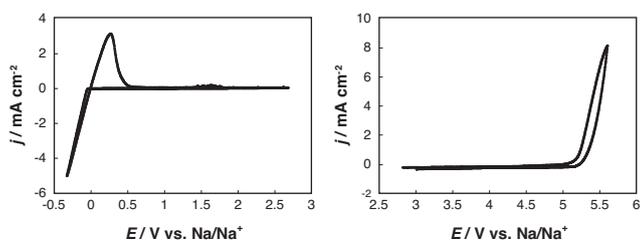


Fig. 2. Cyclic voltamograms for NaFSA-KFSA eutectic salt⁽⁴⁾⁻⁽⁶⁾
The cathode side (the graph at right) uses a Ni electrode and the anode side (the graph at left) a glassy carbon electrode.
Temperature: 363 K

reaction of anions starts at about 5 V. This shows that the electrochemical window of this molten salt is about 5 V, and that this molten salt can be used as electrolyte for a secondary battery within this range of potential.

2-2 Charge-Discharge properties

Figure 3 shows the basic composition of this battery. Regarding the arrangement of basic elements, the positive and negative electrodes composed of sodium compounds sandwich a separator impregnated with electrolyte, and when this battery is charged, sodium ions move from the positive electrode to the negative to form sodium alloy. Discharge is a reverse reaction in which sodium ions move from the negative electrode to the positive, with a voltage of 3.0 V being exhibited on the average.

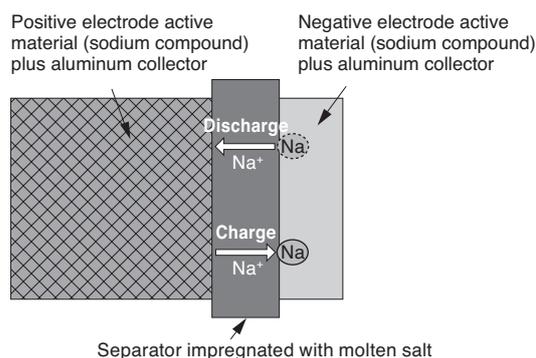


Fig. 3. Basic construction of an MSB

Using the coin cell shown in **Fig. 4**, the charge-discharge properties were measured under the battery composition and test conditions shown in **Table 2**. **Figures 5 and 6** show the results of the measurement^{(5),(6)}. The upper limit voltage for charging was set at 3.5 V and the lower limit voltage for discharging at 2.5 V. This was to prevent an irreversible transformation in the crystal structure from starting that is caused by excessive detachment of sodium ions from the positive electrode active material, NaCrO₂, which occurs when the charging voltage is about to exceed 3.7 V⁽⁷⁾. The measurement showed that the charging capacity is 74.7

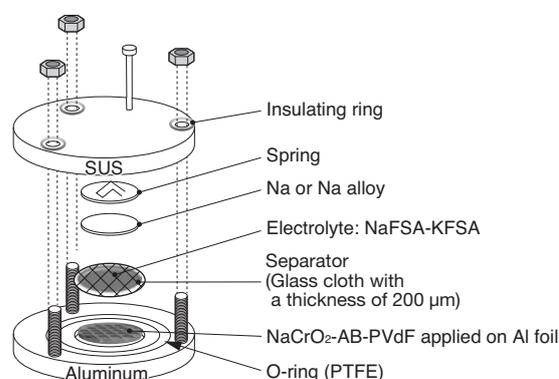


Fig. 4. Coin cell used in the two-electrode-type charge-discharge test

Table 2. Composition of the cell system and conditions for the charge-discharge test

Cell system		Test conditions	
Electrolyte	NaFSA-KFSA	Test battery	Coin cell
Positive electrode	NaCrO ₂	Temperature	80°C
Negative electrode	Na	SOC	100%
Separator	200- μ m-thick glass cloth	Charge-discharge rate	0.2 C

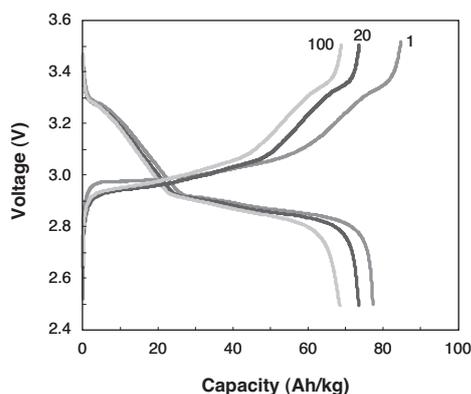


Fig. 5. Charge-discharge curves in the cycle test^{(5),(6)}

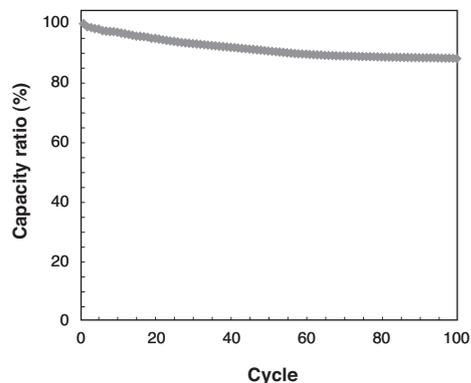


Fig. 6. Change in capacity referred to the initial capacity of 100%^{(5),(6)}

Ah/kg and the discharge capacity 74.0 Ah/kg, with a good value for the Coulomb efficiency of 99.1% exhibited.

Since an average voltage of 3 V was available, the specific energy attained a value of 224 Wh/kg, which is a sufficiently large value compared with the energy density of an NAS battery of 111 Wh/kg. The charge-discharge properties, with the data available only up to 100 cycles, show a satisfactory result in spite of the severe condition of an SOC (state of charge) value of 100%. The gentle lowering of the battery capacity from 1 to 20 cycles was considered to be due to the decomposition of active materials caused by the water content taken in during the battery case assembling process.

The effect of water contents is shown in **Fig. 7**, a result

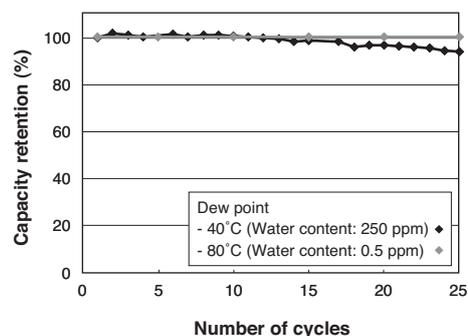


Fig. 7. Effect of the environmental water content on the capacity retention

of the examination on the cell system shown in **Table 2**. It has been confirmed that, as in other non-aqueous batteries, deterioration of capacity occurs under the effect of environmental water contents. Regarding the growth of dendritic lithium, which is regarded as problematic in connection with the mechanism of deterioration of lithium-ion batteries, it is feared that a similar mechanism could occur in sodium-ion batteries. However, since an MSB is a battery operating immediately below the melting point of sodium, sodium is likely to be electrodeposited smoothly on the electrode without growing into dendrites; for this reason, the capacity deterioration due to the falling of dead sodium can be avoided. **Figure 8** shows the cycle properties in the charge-discharge operation with the battery operating temperature set at 90°C. Although the battery was operated under the limited conditions of a charge-discharge rate of 0.2 C and an operating voltage range of 3.15 to 3.30 V, it is confirmed that the battery was capable of being charged and discharged for 1000 cycles without any capacity deterioration.

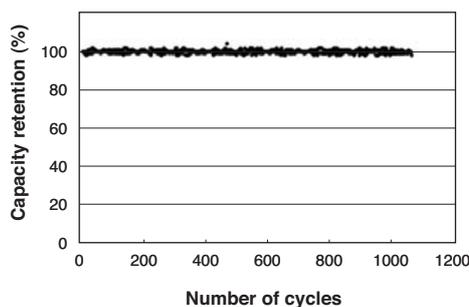


Fig. 8. Cycle properties in a charge and a discharge at 90°C (Charge-discharge rate: 0.2 C; cut-off voltage: 3.15 V and 3.30 V)

Figure 9 shows the discharge rate property examined under the test conditions shown in **Table 3**. In this test, it was investigated at what current density the battery could be discharged for a short period of about 10 seconds. The result shows that, for a short period, the battery can be discharged at a current density of 15 C (50 A/cm²).

2-3 Float charging test

Float charging is a type of charging used frequently for

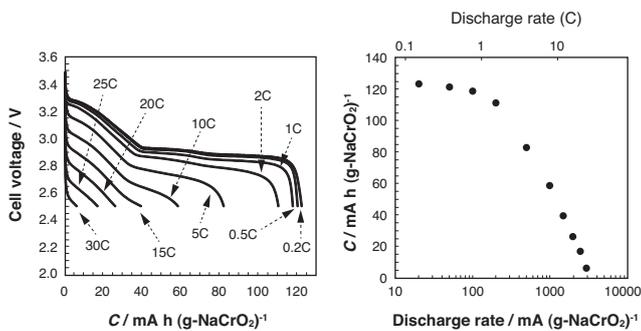


Fig. 9. Discharge rate properties⁽⁸⁾

Table 3. Composition of the cell system and conditions for the high rate charge-discharge test

Cell system		Test conditions	
Electrolyte	NaFSA-KFSA	Test battery	Coin cell
Positive electrode	NaCrO ₂	Temperature	90°C
Negative electrode	Na	Cut-off voltage	2.5 V
Separator	50- μ m micro-porous membrane	Charge/discharge rate	0.2 C~30 C

Application as a backup power supply for a mobile phone base station

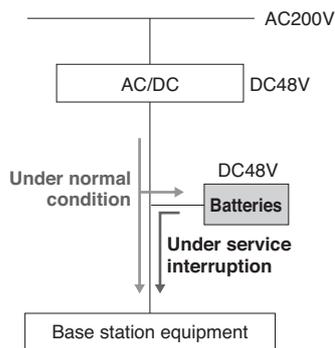


Fig. 10. Outline of the float charging test system

backup batteries, keeping the batteries fully charged in preparation for sudden service interruption. To do this, the float charging scheme as shown in Fig. 10 is often used. Float charging is a method of charging batteries in which batteries and a load — wireless equipment in this case — are connected constantly in parallel in order to charge the batteries while supplying power to the load. Since batteries are constantly charged by float charging and consequently battery deterioration due to overcharging must be minimized, the charging voltage is set at a value that allows only slight current necessary to compensate for self-discharge to flow. Figure 11 shows the initial condition of a battery composed of positive electrodes made of NaCrO₂, an electrolyte using eutectic melt made of a mixture of NaFSA and KFSA mixed in a molar ratio of 56 : 44, and negative electrodes covered with Al plates. At the start of float charging,

the battery is charged in a constant current control mode at 0.2 C, and when the cell voltage reaches 3.2 V, the charging mode is switched to constant voltage control. About 30 minutes after the switchover, the current fell to 4 mA, dwindling down to 0.01 mA in about a half day. The current of float charging after 100 hours was also 0.01 mA. The value measured with a higher-precision ammeter at this point in time was 0.008 mA, with no subsequent change observed and a steady state maintained. Figure 12 shows a discharge curve made up of two-week-interval measuring points. For three months during which MSB was evaluated, the capacity ratio maintained a value of 100%, with a satisfactory result also obtained in the float charging.

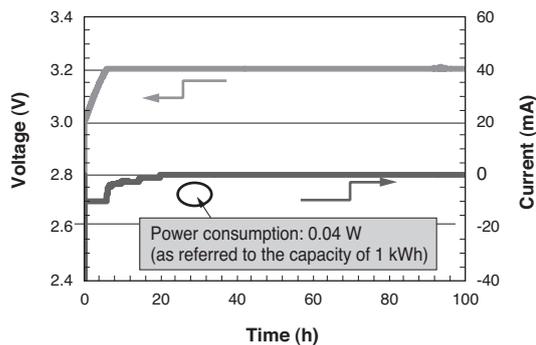


Fig. 11. Progress of the float charging test

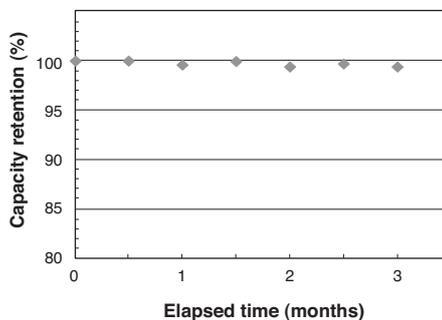


Fig. 12. Results of the float charging test (capacity retention rate for 3 months)⁽⁹⁾

2-4 Prototyping of assembled batteries

In terms of small-sized battery applications, our battery showed basic properties sufficiently comparable to those of NAS batteries already in practical use; however, we examined whether similar performance could be verified in kWh-class large-scale batteries. In 2010, we fabricated a 1-kWh 12-V unit, made up of 4 series-connected 250-Wh 3-V unit batteries (outside dimensions of 150 mm × 180 mm × 40 mm), starting charge-discharge tests in a battery composition based on this unit. The energy density of the batteries fabricated was 167 Wh/kg as referred to weight and 270 Wh/L as referred to volume. A unit battery was composed of a lamination of 20 positive electrodes and 20 negative

electrodes with separators sandwiched between the positive and the negative electrodes, placed in an aluminum casing and filled with molten salt, with a lid laser-welded to seal the assembly. The battery assembling work was conducted manually in all stages of fabrication, and an on-the-premises test battery combining 36 1-kWh units was fabricated. **Photo 1** shows an assembled battery with a total capacity of 36 kWh on which we are carrying out an on-the-premises test.

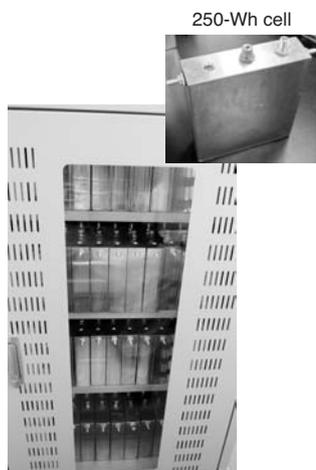


Photo 1. Test-purpose assembled battery with a capacity of 36 kWh

3. Examination of Battery Safety

The safety tests performed included one on an assembled battery and one on a battery cell. For the former, we performed vibration and shock tests on a unit battery, and for the latter, we performed a nail-penetrating, water-pouring, and immersion tests on laminate batteries. **Figure 13** shows a shock resistance test on a stationary battery conducted on the supposition of an earthquake. The earthquake resistance test was conducted by changing the temperature in a state of molten salt (on the supposition of an operating condition) and in a state of solidified salt under the conditions of a horizontal seismic coefficient of 1 G, a vertical seismic coefficient of 0.5 G, and the frequency being

1G (seismic intensity: 6-strong)
Guidelines for Disaster
Prevention Facilities
(Compiled under the
supervision of the Disaster
Prevention Section, the Fire and
Disaster Management Agency)
Under the conditions of a
horizontal seismic coefficient of
1 G, a vertical seismic
coefficient of 0.5 G, and the
frequency being swept from
10 Hz to 55 Hz over 6 minutes

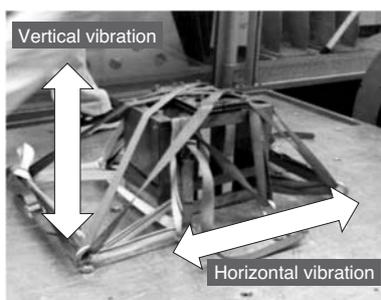


Fig. 13. Stationary application shock resistance test

swept from 10 Hz to 55 Hz over 6 minutes in accordance with the Guidelines for Disaster Prevention Facilities (compiled under the supervision of the Fire and Disaster Prevention Section, the Fire and Disaster Management Agency).

The battery under test was a 250-Wh MSB equipped with a gas-venting safety valve. This test did not show abnormalities of battery output, including internal short-circuiting, at all, demonstrating that the battery posed no problems with seismic vibration. **Figure 14** shows the outline of the collision shock test for vehicle-borne products. The battery used in a vibration test on the supposition of being used on a vehicle was a 250-Wh MSB, the same product as used in the earthquake resistance test. Although various conditions are prescribed in vibration resistance tests aimed at vehicle-borne parts, the test this time was based on JIS C 60068-2-27, a standard on “products rigidly fastened to vehicles running on rough terrain”; in the test, a unit battery in a low SOC was exposed to a shock of 5 G in all directions at 80°C. After the test, the battery exhibited no problems with its appearance or short-circuiting. Additionally, no abnormalities were observed in an examination of the dismantled battery.

Shock resistance test aimed at vehicle-borne parts (up to 5 G)

JIS C 60068 2-27
(Standard for products rigidly fastened to vehicles running on rough terrain)
Half-sinusoidal wave applied 3 times in each direction at intervals of 11 ms at 80°C

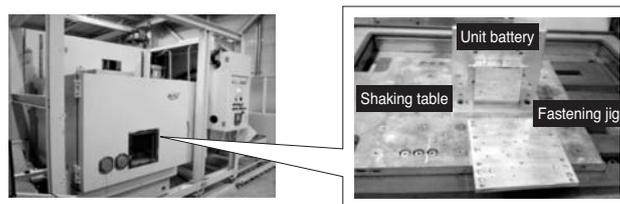


Fig. 14. Vehicle-borne application shock resistance test

The safety of the cell itself was evaluated in a safety test cubic chamber in accordance with the nail-penetrating test specified in SAE J2464, a method of testing automotive lithium-ion batteries, by using the laminate cell shown in **Table 4** and **Fig. 15**. **Figure 16** shows the outline of the nail-penetrating test. A SUS nail with a diameter of 3 mm was driven from the point perpendicularly above the center of

Table 4. Composition of the cell system and test conditions for the safety evaluation test

Cell system		Test conditions	
Electrolyte	NaFSA-KFSA	Test battery	10-cm-square single-layer battery
Positive electrode	NaCrO ₂	Temperature	90°C
Negative electrode	ZnNa alloy	SOC	100%
Separator	Polyolefin porous membrane with a thickness of 50 μm		

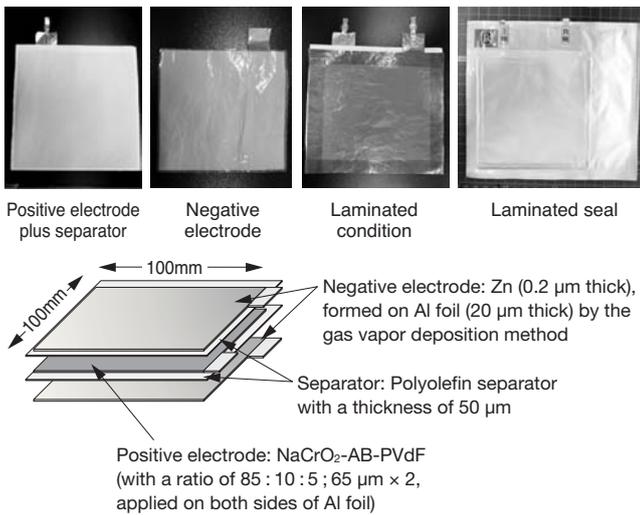


Fig. 15. Test laminated cell

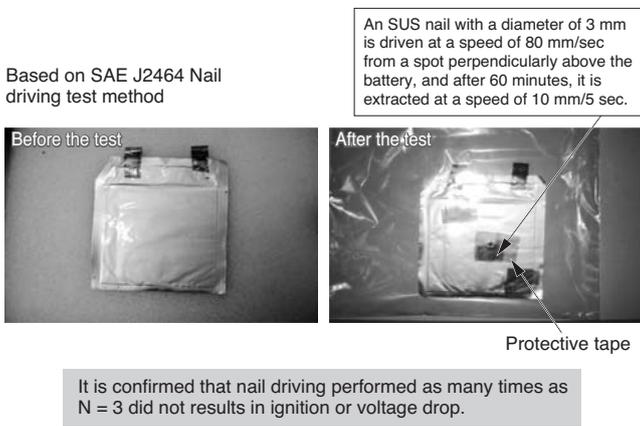


Fig. 16. Nail penetrating test

the fully charged battery onto it at a speed of 80 mm/sec. The items of measurement were the battery voltage and the temperature (near the part in which the nail was driven, on the outer edge below the tab, and three spots on the opposite side), as well as the temperature of the atmosphere and the gas pressure in the vessel, accompanied by video taking. The test did not show substantial changes in temperature, the occurrence of gas, or the like between the time immediately after the nail penetrating and 60 minutes after the test.

A lithium-ion battery may exhibit a gradual voltage drop and a temperature rise, leading to ignition in 30 to 60 minutes. With this possibility taken into consideration and no discharge observed after the battery had been left alone for 60 minutes, a nail-penetrating test at 10 mm/5 sec was conducted at the same time. Since the test was conducted in the atmosphere, it was feared that pulling out the nail could allow atmospheric moisture to react with metallic sodium in the negative electrode; however, no particular change in the appearance was observed. Figure 17 shows the outline of the immersion test and Fig. 18 that of the

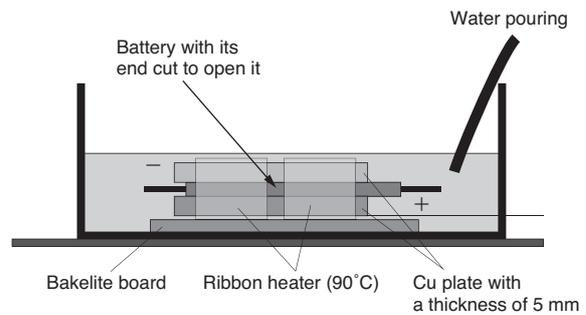


Fig. 17. Immersion test

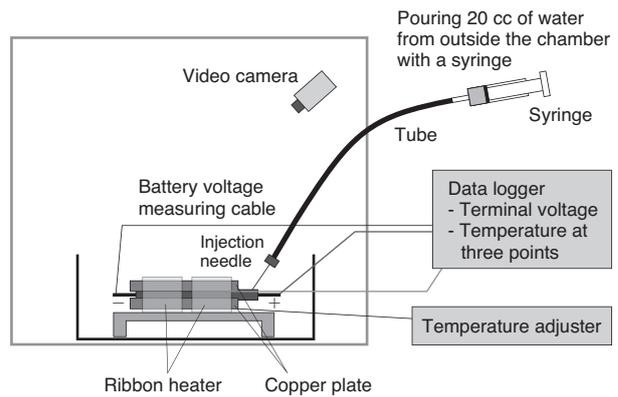


Fig. 18. Water pouring test

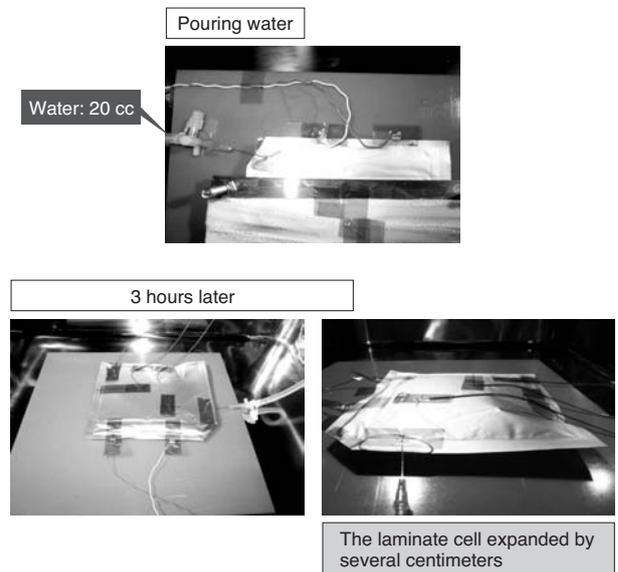


Fig. 19. Water pouring test

water pouring test. The battery used in the test is made up of laminate cells shown in Table 4, and the test was conducted in the safety test dome chamber as in the case of the nail-penetrating test. In the immersion test, the end portion of the laminate film of a fully charged battery was cut to

open the seal of the battery. The battery was heated for the salt to melt and then immersed in water. This caused bubbles to occur from the laminate cells at intervals but no conspicuous change was observed even after a lapse of two hours. It is thought that the cooling and subsequent solidification of the salt as a result of immersion prevented the negative electrode from coming into direct contact with the water, thereby making the reaction extremely slow. In the water pouring test, water was poured through an injection needle into the laminate of a battery kept at a normal temperature and another in a heated condition (20 cc) to observe the behavior. The laminate cell swelled gradually after the pouring, allowing the generation of gas to be confirmed; after a lapse of three hours, however, neither a definite temperature rise nor an abrupt reaction was observed, though the laminate cell swelled by several centimeters.

4. Conclusion

This paper has summarized the physical properties of alkali metal bis(fluorosulfonyl)amide salt that can be applied to an MSB using molten salt as electrolyte, the results of examinations on its safety and charge-discharge properties under the current state, and the trial fabrication of assembled batteries.

- An MSB is a battery using molten salt as electrolyte, having a high energy density, being characterized by perfect non-combustibility, and allowing assembled batteries to be downsized and lightweight.
- The upper limit voltage for charging is 3.5 V and the lower limit voltage for discharging 2.5 V.
- With an energy density in a coin cell condition of 224 Wh/kg exhibited, the charge-discharge properties, with the data available only up to 100 cycles, show a satisfactory result in spite of the severe condition of an SOC (state of charge) value of 100%.
- Although the battery was operated under the limited conditions of a battery operating temperature of 90°C, an SOC of 10%, and a charge-discharge rate of 1 C, it was confirmed that the battery was capable of being charged and discharged for 1000 cycles without any capacity deterioration.
- A test of float charging, a mode of charging for backup power supplies, was conducted with satisfactory results obtained.
- Vibration and shock tests were conducted as tests of the battery system, and nail-penetrating, water pouring, and water immersion tests as tests of the battery cell, with no occurrence of abnormalities confirmed.
- An assembled battery with a total capacity of 36 kWh was fabricated as an on-the-premises test battery by combining 250-Wh unit batteries. The energy densities of the unit battery were 270 Wh/L as referred to volume and 167 Wh/kg as referred to weight.

We will work on the establishment of the production technology for this battery while determining the safety under various environments through the implementation of further safety tests.

• MSB is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

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