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The effect of metal sulfides in the cathode on Na/S battery performance

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Abstract

The effect of metal sulfides in the cathode on Na/S battery performance was investigated. Battery capacity was heavily decreased by doping with FeS₂, CoS₂ and Cr₂S₃, and little influenced by doping with NiS₂ and Al₂S₃. A FeS₂ 3.0 wt.% doped cell exhibited a 65% resistance rise and a 65% capacity loss during cycling. Such a degradation causing by the metal sulfides was mainly attributable to a low charge acceptability of the cathode and closely related to the cathode structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Na/S battery; Corrosion; Metal sulfide

1. Introduction

Na/S battery has been in development for utility energy storage application [1]. For this application, the Na/S battery is expected to have a long cell life and high reliability [2].

As operating temperature of the Na/S battery is relatively high (280–380°C) and cathode active materials (sulfur and sodium polysulfide) are so corrosive, corrosion of cell case is considered as one of the major failure modes of the Na/S battery [3,4].

The corrosion of the cell case contains two problems [3]. First is the leakage of the cathode active material through pin-hole generated by the cell case corrosion, and the other is degradation of cell performance caused by metal sulfides formed by the cell case corrosion. Actually, most of long time tested Na/S batteries show degradation of cycle performance before beginning of the leakage [1]. This means that the latter is a more major problem of the Na/S battery, than the former.

So, It is important to study the effect of the metal sulfides in the cathode on battery performance in order to improve the life and the reliability of the Na/S battery. Yasui et al. investigated the effect of FeS on β''-alumina with a Na₂S₄/β''-alumina/Na₂S₄ cell. They reported that no degradation was observed in the FeS doped cell, and Fe³⁺ ion was not observed in the tested β''-alumina crystal structure [5]. Weiner et al. added metallic Fe, Cr, Mo and FeS to the cathode of Na/S batteries. They reported that addition of FeS <0.1 wt.% unexpectedly improved rechargeability of the cathode [4].

In previous works, kinds of the investigated metal sulfides were restricted, and metal sulfides such as CoS₂, Cr₂S₃, NiS₂, Al₂S₃ which are major corrosion products of the cell case, were not reported. In this paper, the effect of these metal sulfides on Na/S battery performance was investigated, and the relationship between cathode structure and degradation of cell performance caused by the metal sulfides, was also investigated.

2. Experimental

Fig. 1 shows construction of a single cell for testing. Molten sodium metal, which serves as anode, is contained with a porous metal wick in a β''-alumina tube. A pre-cast matrix of graphite felt impregnated with molten sulfur, which serves as cathode, is placed in a gap between the β''-alumina tube and chromized steel cell case. To improve rechargeability of the cathode, a highly resistive layer made of ceramic fiber cloth, is placed closely to the β''-alumina tube (This cathode structure is called 'A-type'). Effective area of the β''-alumina tube and that of the cell case are 123 and 192 cm², respectively.

Five commercial reagent grade metal sulfides, FeS₂, CoS₂, Cr₂S₃, NiS₂ and Al₂S₃ (Kojundo Chemical Laboratory Co., Ltd.) were used. Purity level of these metal sulfides were over 99% except for Al₂S₃, whose purity level was 98%. Quantity of adding the metal sulfides was defined by metal weight percent of the metal sulfides to sulfur weight in the cathode. In this experiment, 0.1–3.0 wt.% metal sulfides were added to the cathode.

The Na/S batteries doped with the metal sulfides, were heated up to 330°C in an electric oven, and then operated for

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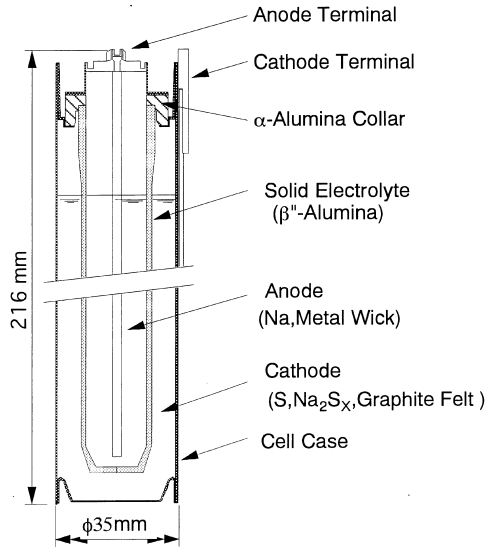


Fig. 1. Cross-sectional view of Na/S cell.

70 charge/discharge cycles. Charge and discharge currents were 10 and 20 A, respectively. Cut-off voltages of charge and discharge were 2.52 and 1.42 V, respectively. Cell capacity and cell resistance were measured at every cycle. Cell resistance was calculated from a highest voltage in discharge. So, the cell resistance means the minimum resistance at a discharge state. After 70 charge/discharge cycles, the Na/S batteries at a fully charged state were cooled to a room temperature and dissected. Amount of Na, S and impurities in the cathode were analyzed by EDX (Seiko, SEA2010).

3. Result

3.1. Cell testing

Fig. 2 shows effect of doping the metal sulfides on the cell capacity when the 3.0% metal sulfides were doped. The NiS₂ and Al₂S₃ doped cells showed a little capacity loss compared

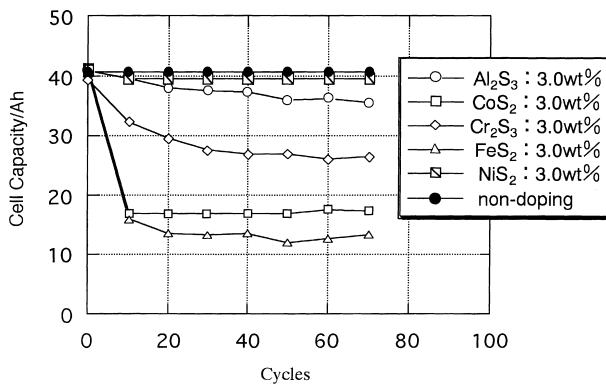


Fig. 2. Effect of metal sulfides doping in cathode on cell capacity.

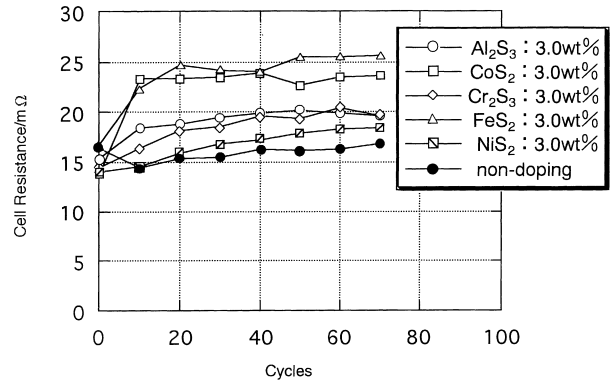


Fig. 3. Effect of metal sulfides doping in cathode on cell resistance.

with the non-doped cell during cycling. On the other hand, a large capacity loss was observed in the FeS₂, CoS₂ and Cr₂S₃ doped cells until 20 to 40 charge/discharge cycles with little capacity loss in subsequent cycles. Capacity loss observed with the FeS₂ doped cell was 65% of the initial cell capacity. It was apparent that the metal sulfides, FeS₂ and CoS₂ in particular, caused a large capacity loss, and about 40 charge/discharge cycles were necessary to stabilize the cell capacity in these cells.

Fig. 3 shows change in the cell resistance with cycles. Like the capacity loss, a large resistance rise was observed in the FeS₂, CoS₂ and Cr₂S₃ doped cells. Similarly, a little resistance rise was observed in the NiS₂ and Al₂S₃ doped cells. In the case of the FeS₂ doped cell, about 65% resistance rise was observed during cycling.

There was a marked similarity in capacity loss and resistance rise. The metal sulfides which were responsible to the large resistance rise are considered to cause the large capacity loss. Actually, most of Na/S batteries use Cr–Fe alloy as the cell case material. So this result presents a serious problem.

Charge curve of the metal sulfide doped cells are shown in Fig. 4. The charge voltage of the FeS₂ doped cell abruptly increased after 1.5 h (15 A h) charging, as well as the CoS₂ doped cell.

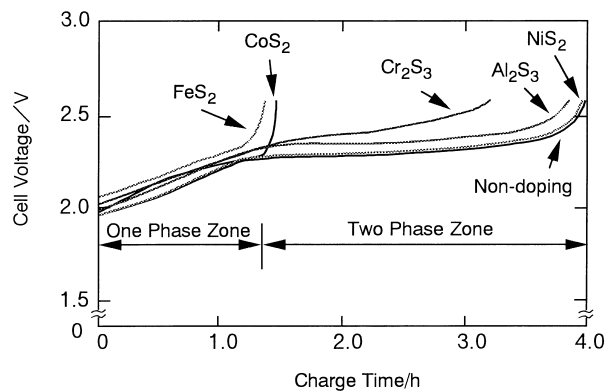


Fig. 4. Charge curves of metal sulfide doped cells.

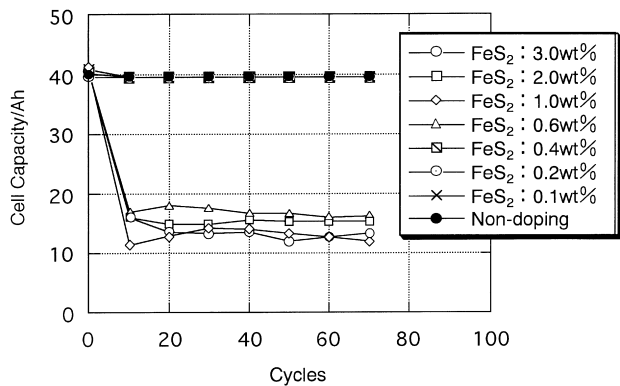


Fig. 5. Relationship between the doping amount of FeS₂ and capacity change with cycles.

Next, the relationship between the doping amount (0.1–3.0 wt.%) of FeS₂ and cell performance was investigated. Fig. 5 shows the cell capacity change with cycles. Little capacity loss was observed <0.4 wt.% doping, but steep capacity loss occurred >0.6 wt.% doping at almost the same rate.

The cell resistance change with cycles is shown in Fig. 6. Cell resistance was lowered in somewhat <0.4 wt.% doping. This phenomenon seems to be caused by improvement in wettability of carbon felt to the cathode active materials [4]. The cell resistance rise was observed with addition of the FeS₂ over 0.6 wt.%. Here again, the relativity in the capacity loss and the cell resistance rise was observed. In general, corrosion of cell case is considered to decrease the amount of effective active material in the cathode by formation of

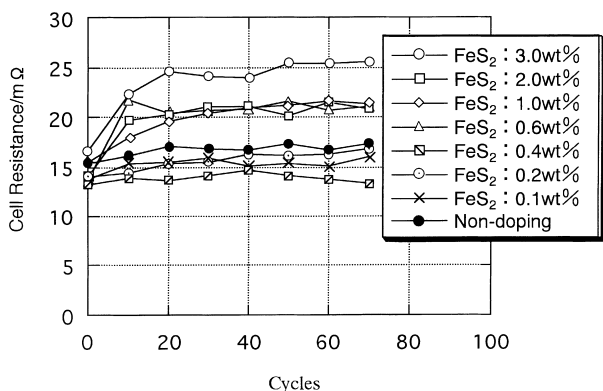


Fig. 6. Relationship between the doping amount of FeS₂ and cell resistance change with cycles.

Table 1
Composition of elements in cathode matrix

Sample	Cell case side (wt.%)				Electrolyte side (wt.%)			
	Na	S	Fe	Cr	Na	S	Fe	Cr
FeS ₂ 3.0 wt.% doped cell	59.1	32.9	4.9	3.2	38.1	58.8	1.6	1.6
Non-doped cell	22.4	76.7	0.3	0.6	25.1	73.8	0.7	0.4

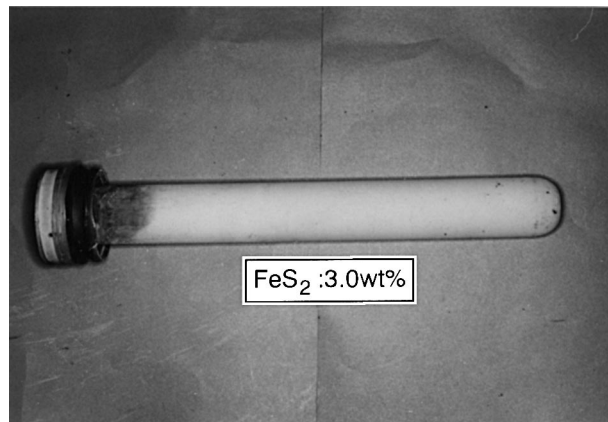


Fig. 7. Appearance of β''-alumina tube in the FeS₂ 3.0 wt.% doped cell.

metal sulfides [3]. However, the calculated capacity loss of this effect is only 1.8 A h in the case of the FeS₂ 3.0% doping. So, actually this effect seems to be negligible.

3.2. Post test analysis

After 70 cycles, the FeS₂ 3.0 wt.% doped cell and the non doped cell were dissected. It was observed that the cathode matrix of the non doped cell showed bright yellow which is characteristic color of sodium polysulfide, while the cathode matrix of the FeS₂ 3.0 wt.% doped cell showed dark yellow. Fig. 7 shows the appearance of the β''-alumina tube in the FeS₂ 3.0 wt.% doped cell. Discoloration and precipitation of impurities were not observed on the surface of the β''-alumina except a little sulfur deposition.

In order to investigate distribution of elements in the cathode matrix, the amount of Na, S and impurities were analyzed by EDX, and the peaks corresponding to Na, S, Fe and Cr were found. The proportions of each element in the dissected cells are listed in Table 1. When paying attention to Na content, the Na contents of the FeS₂ doped cell were 38 and 59%, which were relatively high compared with the non doped cell (22 and 25%).

In particular, the Na content at the cell case side was fairly higher than that at the electrolyte side. This means that charge reaction was not carried out successfully in the FeS₂ doped cell especially at the cell case side.

When paying attention to Fe and Cr content, both the Fe and Cr contents of the FeS₂ doped cell were relatively high compared with the non doped cell, and the Fe and Cr content at the cell case side was much higher than that at the

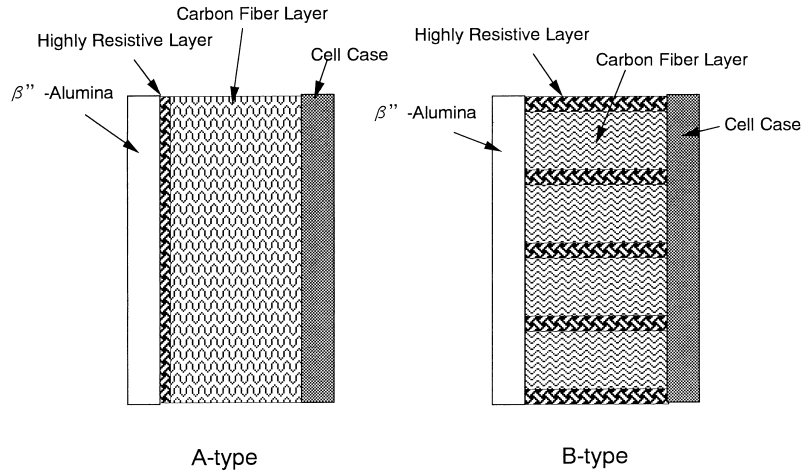


Fig. 8. Schematic of cathode structures.

electrolyte side. This result would indicate that the FeS₂ doping to the cathode caused not only increasing Fe content in the cathode, but also accelerating cell case corrosion, resulting in formation of the chromium sulfide in the cathode as a corrosion product of chromized layer.

3.3. Improved cathode structure

In general, the cathode composition change of Na/S battery during the initial stage of charging, (usually Na₂S₃~Na₂S_{3.5}) to Na₂S_{5.2}, is in one phase zone, representing Na₂S_x. A more charged state beyond Na₂S_{5.2}, in other word, a sulfur rich state, is in the two phase zone representing Na₂S_{5.2} + S. As shown in Fig. 4, the capacity loss observed in the metal sulfide doped cells were attributable to inadequate charging at the two phase zone.

It is well known that charge acceptability at the two phase zone is closely related to the cathode structure [3]. A new type cathode structure, called ‘B-type’, was then developed as an alternative to the usual ‘A-type’ cathode. Fig. 8 shows

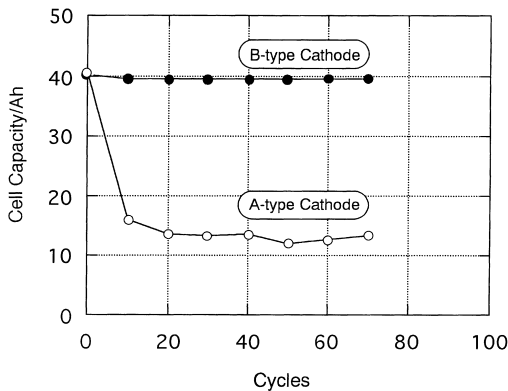


Fig. 9. Relationship between the cathode structures and cell capacity changes with cycles in the case of FeS₂ 3.0 wt.% doping in cathode.

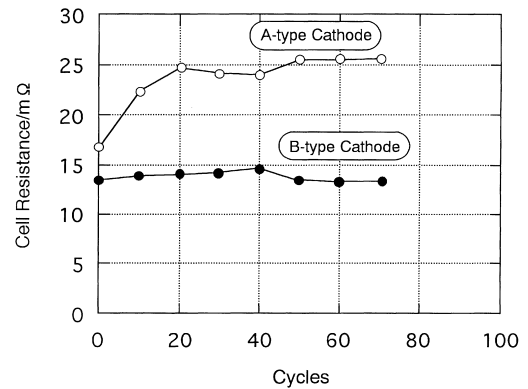


Fig. 10. Relationship between the cathode structures and cell resistance changes with cycles in the case of FeS₂ 3.0 wt.% doping in cathode.

the schematic structures of both cathodes. The ‘B-type’ cathode consists of a layered structure containing a carbon fiber layer and a highly resistive layer attached perpendicular to the β''-alumina tube

Effect of the FeS₂ doping on the ‘B-type’ cell was then investigated. Figs. 9 and 10 shows the cell capacity and the cell resistance of the FeS₂ doping ‘B-type’ cell, compared with the ‘A-type’ cell. It was apparent that the ‘B-type’ cell showed almost no capacity loss and no resistance rise in spite of the FeS₂ doping. This means that the degradation of cell performance caused by the metal sulfides is closely related to the cathode structure.

4. Discussion

The sulfur deposition on the β''-alumina surface is responsible to the degradation of charge acceptability at the two phase zone [3]. Since sulfur is an electronic insulator, if sulfur is formed on the β''-alumina surface, Na⁺ ion current is blocked by this layer hindering further charging.

To prevent sulfur deposition on the β'' -alumina surface, a highly resistive layer is usually placed to the β'' -alumina side of the cathode. Because no charging reaction occurs in the highly resistive layer, the highly resistive layer is always impregnated with sodium polysulfide which is a good Na^+ ion conductor during cycling. In other words, the highly resistive layer functions as a Na^+ ion current passage way to the β'' -alumina.

The large capacity loss, observed in the metal sulfide doped 'A-type' cell, is thought to be caused by the degradation of the highly resistive layer. Two mechanisms about the degradation of the highly resistive layer are considered as shown below.

1. Charge current density increases by the metal sulfide deposition on the highly resistive layer.
2. The resistance of the highly resistive layer decreases by the metal sulfide deposition.

In this study, a large discharge resistance rise was also observed in the metal sulfide doped cell with a large capacity loss, and 'B-type' cells were little affected by the addition of metal sulfide. So, the degradation of the highly resistive layer observed in this study seems to have been caused by the increased charge current density in the cathode. In any event, degradation of cell performance caused by metal sulfide is considered to be closely related to the cathode structure, and a cathode structure like the 'B-type' will be little affected by the addition of the metal sulfides.

5. Conclusion

The effect of the metal sulfides in the cathode on the Na/S battery performance was investigated. Based on the present work, the following conclusions can be drawn.

1. Battery capacity was heavily decreased by doping FeS_2 , CoS_2 and Cr_2S_3 and little influenced by doping metal sulfides, NiS_2 and Al_2S_3 .
2. An FeS_2 3.0 wt.% doped cell exhibited about 65% capacity loss and 65% resistance rise.
3. The degradation of cell performance caused by the metal sulfides, was closely related to the cathode structure, and the cathode structure like the 'B-type', was little affected by the addition of the metal sulfides.

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