

CASING MATERIALS FOR SODIUM/SULFUR CELLS*

B. HARTMANN

Brown, Boveri & Cie AG, Central Research Laboratory, Heidelberg (F.R.G.)

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Summary

Specifications for suitable casing materials for sodium/sulfur cells are discussed. In order to select the best materials three types of experiments have been performed: static corrosion tests, experiments which used the samples as electrodes in Na_2S_4 , and tests in Na/S cells. According to the results of the static corrosion tests the materials are arranged in three groups for practical reasons.

Aluminum in contact with Na_2S_4 at 350 °C develops an insulating layer. Corrosion layers formed on heavy metal alloys possess quite high conductivities. The structure of these layers is discussed. As the cell casing serves as a current collector, aluminum was coated with chromium containing iron, cobalt or nickel alloys. Plasma spraying was used as the coating method. The usefulness of coated aluminum was demonstrated in Na/S cells.

Zusammenfassung

Die Anforderungen, die an ein Behältermaterial für Natrium/Schwefel-Zellen zu stellen sind, werden diskutiert. Zur Auswahl geeigneter Materialien wurden statische Korrosionstests, Korrosionsversuche, bei denen ein elektronischer oder ionischer Strom durch die Probenoberfläche floss, und Zelltests durchgeführt. Die Materialien werden nach den Ergebnissen der statischen Korrosionstests unter praktischen Gesichtspunkten in drei Gruppen geordnet. Widerstandsmessungen zeigten, dass sich Aluminium in Na_2S_4 mit einer isolierenden Sulfidschicht bedeckt, während Schwermetalllegierungen oft leitfähige Korrosionsschichten ausbilden. Die Struktur der Korrosionsschichten wird diskutiert. Da der Zellbehälter als Stromkollektor dient, wurde eine Beschichtung von Aluminium mit chromhaltigen Eisen-, Kobalt- oder Nickellegierungen entwickelt. Die Beschichtung erfolgte durch Plasmaspritzen. Die Brauchbarkeit von beschichtetem Aluminium wurde in Na/S-Zellen gezeigt.

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Introduction

In sodium/sulfur cells the catholytic melt consisting of sulfur and sodium polysulfides respectively is separated from the liquid sodium anode by sodium ion conducting β -alumina. In the normal assembly the sodium is stored inside and the sulfur outside the β -alumina tube.

The cell casing which contains the catholytic melt is exposed to the severely corroding sodium polysulfides at the working temperature of sodium/sulfur cells of 300 °C to 350 °C. Using the inverse concept of Na/S cells, *i.e.* with the sulfur stored inside the β -alumina tube, similar corrosion problems arise at the current collector pole.

In early experimental sodium/sulfur cells only corrosion resistant materials such as graphite and glass were used. As these materials cannot be used as casings for technical cells because of their unfavourable mechanical properties, corrosion experiments were concentrated on practical materials. Suitable casing materials have to fulfil the following criteria: (1) good corrosion resistance. The corrosion rate must be small enough not to destroy the cell within the battery lifetime of approximately 3 years. The decrease in cell capacity due to the consumption of sulfur by corrosion has to be kept as small as possible. A maximum capacity loss of 20% is considered to be acceptable; (2) good electrical conductivity. In the central sodium electrode design, the wall of the cell serves usually as the current collector. The internal resistance of a sodium/sulfur cell is affected by both the conductivity of the bulk material and, in particular, the conductivity of the corrosion products at the interface with the melt; (3) low weight. The low weight of sodium/sulfur cells is of particular interest for traction applications. The advantage of the sodium/sulfur system compared with the lead-acid system with respect to energy density is partly lost if a heavy cell casing is used; (4) adequate mechanical properties. Being a structural member of the cell the casing material requires a certain mechanical stability. Therefore metals are favoured; (5) easy fabricability. Low raw-material costs of a material meeting the other criteria can be more than counterbalanced by difficulties in fabrication of the cell. Materials which allow the use of well-known technologies are strongly favoured; (6) sufficient availability. As the other parts of sodium/sulfur cells consist of abundantly available materials one should make use of cell casing materials for which large resources are known thus allowing good prospects for sodium/sulfur batteries in the future.

Experimental

To evaluate the corrosion properties of the candidate materials three types of tests have been performed: static corrosion experiments; corrosion experiments with applied electrical potentials; use of materials as casings in sodium/sulfur cell corrosion testing.

In static corrosion experiments which were used as a screening test [1] cylindrical samples of 5 mm diameter and 10 mm height were corroded in sulfur or sodium tetrasulfide. The evacuated ampoules containing the samples and the corroding agent were kept at 320 °C for periods of between 100 and 1500 h. The sodium tetrasulfide was prepared from an alcoholic solution [2] and had a residual alcohol and water content of less than 0.02%.

After the test, sulfur and sodium tetrasulfide were dissolved and the weight change of the samples was determined. In metallographic sections the thickness and structure of the corrosion layer were measured. It turned out that the best quantity to characterize the degree of corrosion was the metal consumption from the core, as this parameter was least disturbed by the solubility of the corrosion products or scaling of parts of the corrosion layers.

To examine the influence of an applied electrical potential on the corrosion rate two identical nickel wires of 2 mm diameter were exposed to the attack of Na_2S_4 at 350 °C for 100 h in an arrangement as shown in Fig. 1. One of the nickel electrodes served as reference electrode and remained current free while the other was the working electrode. A mean current of 250 mA/cm² was passed through the working electrode using an applied periodic triangular potential pulse. An aluminum crucible which had been coated with carbon served as a large area counter electrode.

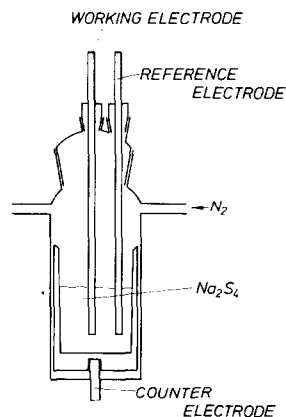


Fig. 1. Experimental set up for determination of the effect of applied potential on corrosion.

In another experiment a piece of graphite felt was pressed between two nickel plates. A potential was applied between the nickel plates in a sulfur melt at 350 °C, the current being purely electronic. The charge which passed through the surface of the two nickel plates was 260 Ah/cm². An additional nickel plate (electronically insulated) was attached with a glass ribbon at one of the electrodes.

Resistance measurements were performed with a Keithley Model 503 Milliohmmeter as the 40 Hz alternating current of this milliohmmeter left the composition of the polysulfide melts unchanged.

TABLE 1

Classification of materials for Na/S cells according to static corrosion tests

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- (a) **Heavily corrodible materials**
 These materials do not build up a protective layer and they or their corrosion products are often soluble in the melt.
 Examples: iron, copper, nickel but some noble metals as well, alloys such as Vacon or Monel and some sulfides such as Ag_2S and CuS .
- (b) **Corrodible materials developing a more or less protective coating.**
 Examples: cobalt, chromium, stainless steels and so-called superalloys with a basis of nickel or cobalt.
- (c) **Corrosion resistant materials**
 Examples: graphite, glass, some resins, aluminum, magnesium, titanium, molybdenum, some sulfides, *i.e.* those of cobalt, chromium or molybdenum, which have a low solubility in the melt and numerous oxides and refractories, especially α - and β -alumina.
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Results and discussion

According to the results of the static corrosion tests [1] the materials are divided into three groups as listed in Table 1. In the first group are those materials which suffer heavy corrosion in sulfur and sodium polysulfides. The fast chemical reaction rate is the main reason for the metal consumption. The corrosion layer is not protective in this case because of quick chemical diffusion [8] of the metal in the layer or high solubility of the corrosion products in the melt. The corrosion rate of nickel, a typical material from this group, is $7 \mu\text{m}/\text{day}$. Pellets of silver sulfide were dissolved completely within 100 h.

In the second group are those materials which corrode in the catholytic melt of sodium/sulfur cells. The rate of corrosion appears small enough to be acceptable for the expected applications of sodium/sulfur batteries. It is characteristic of this group of materials that the corrosion rate in sodium polysulfides decreases with time due to the protective nature of the corrosion layers. In the case of cobalt and chromium the layer consists of one or more sulfides of these elements. In the case of stainless steels and cobalt or nickel base super alloys there are two different corrosion layers [7, 10]. The inner one consisting of chromium thiospinels is a barrier against chemical diffusion [8] of the base metals thus limiting the corrosion rate. The outer corrosion layer consists of the base metal sulfides of mainly pyrite structure. The metal pyrites were dissolved in the melt according to their solubility [3]. The formation of these compounds in sodium/sulfur cells has been shown using X-ray electron microscopy [4]. A characteristic alloy of this group consisting of 53% nickel and 44% chromium had an average corrosion rate of $0.1 \mu\text{m}/\text{day}$ over more than 1000 hours.

The third group consists of materials which are practically corrosion resistant. Some of these materials are thermodynamically stable as, for example, graphite, glass, oxides and refractories. The other corrosion resistant materials consist of metals such as aluminum, magnesium, titanium and molybdenum which develop a very thin passivating surface layer in contact with the melt.

This classification is chosen for practical reasons and differs from that found in the literature [3]. With respect to corrosion resistance, group three materials are the most suitable. However, these materials exhibit disadvantages with respect to conductivity or mechanical properties. Therefore group two materials or coatings of base metals with group two or three materials are most promising.

In the experiments designed to establish the influence of current on corrosion the reference sample to which no potential was applied corroded with a rate of $7 \mu\text{m}/\text{day}$. In the test with an ionic current the corrosion rate was accelerated up to $19 \mu\text{m}/\text{day}$ while the electronic current effected no detectable increase in the corrosion rate. In consequence the quality of contact between the graphite felt and the metal current collector influences not only the internal resistance of the cell but the corrosion rate as well. Any ionic fractions of the current at the current collector surface diminish cell capacity due to the increased consumption of sulfur to form corrosion products. If the electrical contacts in the cell are insufficient the cells have to be polarized to a voltage of 1 V or even below due to the high internal resistance. Such large polarizations may cause additional scaling of the corrosion layers and corrosion at the new free surfaces [9].

Owing to the corrosion of sodium/sulfur cell casings it is not only the bulk conductivity of the material but especially the conductivity of the corrosion layer at the interface to the melt that influences the resistance of the cells. Though aluminum is one of the metals with the best electrical conductivity it is not possible to use it as current collector in Na/S cells, because the thin layer developed at the interface to the melt consists of aluminum sulfide which is a good insulator. The resistivity of aluminum sulfide, Al_2S_3 , has been measured between room temperature and 400°C using pressed pellets. At the working temperature of Na/S cells the resistivity of Al_2S_3 is still $10^9 \Omega\text{cm}$. Thus the cell resistance is increased to unacceptable values even by very thin layers. A powder of stainless steel which had been sulfurated in liquid sulfur for a long time and pelleted had a resistivity of $10 \Omega\text{cm}$ which is low enough for Na/S cells. Table 2 shows the resistivities of some binary and ternary sulfides, the data being partly taken from literature. Some of these compounds as for instance iron chromium thiospinel FeCr_2S_4 or pyrite FeS_2 have already been found in the analysis of Na/S cell casings [1].

Chromium rich alloys with iron, cobalt or nickel as basic metals are known from gas turbine applications to have low corrosion rates [6]. In contact with molten sulfur or polysulfides these alloys develop typical duplex corrosion layers [1, 4, 10]. The inner compact portion of the duplex

TABLE 2

Resistivities at room temperature

		$\rho/\Omega\text{cm}$
Metals	Al	3×10^{-6}
	stainless steel	5×10^{-5}
Graphite		2×10^{-3}
Binary sulfides	FeS ₂	2×10^{-2}
	CoS ₂	2.6*
	NiS ₂	4.5*
	NiS	1.5*
	Co ₃ S ₄	3×10^{-4}
	Cr ₃ S ₄	6×10^{-3}
	Cr ₂ S ₃	$1.3 \times 10^{2*}$
	MoS ₂	$1 \cdot 10 \times 10^4$
	Al ₂ S ₃	10^{10*}
	Mixed sulfides and thiospinels	FeCr ₂ S ₄
CoCr ₂ S ₄		5×10^3
FeCo ₂ S ₄		6×10^{-1}
Insulators	glass	6×10^{13}
	Al ₂ O ₃	10^{14}

*Pellet measurements.

layer adjacent to the core of the metal consists of the metal (II) chromium thiospinels. This layer can work as a barrier against the diffusion of the parent metals to the corrosion layer–melt interface. The outer corrosion layer, which is sometimes porous, consists of the mixed sulfides of iron, cobalt and nickel depending on the alloy composition. These sulfides usually have the pyrite crystal structure. Two mechanisms have been proposed as being responsible for the decrease of the corrosion rate of super alloys [7]: (i) the rate limiting process is the chemical diffusion of the parent metals through the inner compact layer of chromium thiospinels; and (ii) owing to the different molar volumes of the pyrite and thiospinel phases micro-cracks are formed in the corrosion layer. The cracks can only be filled by reaction of gaseous sulfur with the metal to form sulfides. As the partial pressure of sulfur in the gas phase in contact with the sulfides is very low, corrosion is limited by the gas phase transport of sulfur.

The corrosion rates of these alloys are lower by a factor of 100 and even more than those of pure iron, nickel, cobalt and even chromium.

Coating aluminum with heavy metal alloys can combine the low weight and low cost of aluminum with the good conductivity of the corrosion products which is characteristic of some heavy metal alloys. Some aluminum plates were plasma sprayed with various alloys and compounds, and the resistances *versus* carbon counter electrodes in Na₂S₄ were measured. In this arrangement pure aluminum showed a resistance of 140 Ω while samples with a suitable coating of a super alloy had resistances of only 1 to 4 Ω

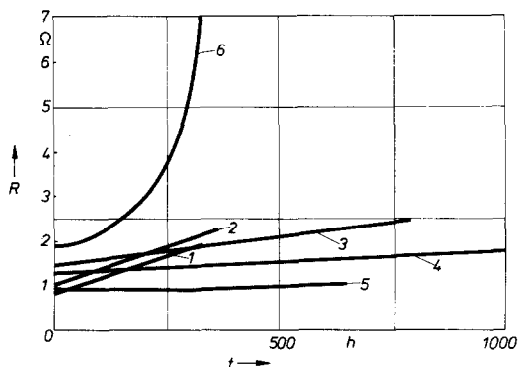


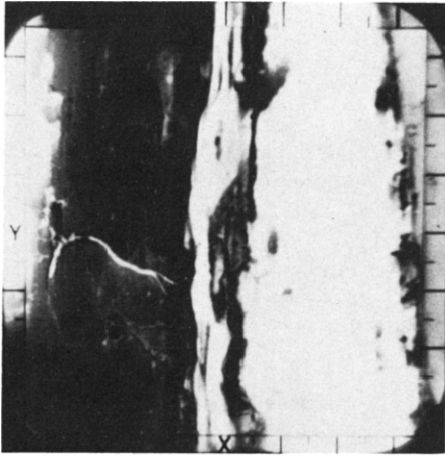
Fig. 2. Time dependence of resistance. 1, steel 1.4541; 2, aluminum with plasma sprayed steel coating; 3, IN 587; 4, aluminum with plasma sprayed Deloro SF 60 coating; 5, aluminum carbon coated; 6, aluminum covered with carbon mechanically.

under the same conditions. Owing to the slightly higher resistivities of the titanium and molybdenum sulfides compared to iron or nickel sulfides the resistances of titanium and molybdenum in this arrangement were also higher.

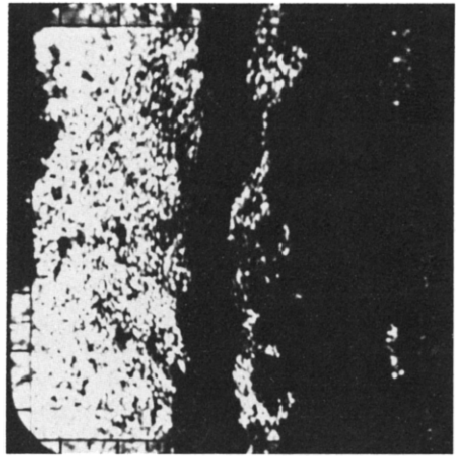
Figure 2 shows the results of some resistance measurements in molten Na_2S_4 at 350°C . As shown by the lines 1 and 2 the performance of a material in contact with the melt is the same whether it is massive or plasma sprayed. Line 3 gives the resistance of a superalloy IN 587 which is more corrosion resistant than steel and therefore the resistance increase with time is slower. Another nickel base plasma coating known as SF 60 is to be seen in line 4. Lines 5 and 6 show the resistance of aluminum which is carbon coated or mechanically covered with carbon respectively. In the latter case contact is lost due to formation of aluminum sulfide.

The most conclusive corrosion test is the use of the material under consideration as casing in sodium/sulfur cells, as the electrochemical potential as well as the stoichiometry of the melt vary periodically during operation. The changes in composition of the melt are accompanied by changes in the solubilities of corrosion products, in viscosity, in wetting properties and in the chemical aggressiveness.

Some sodium/sulfur cells have been operated with a nickel base superalloy coated aluminum cell casing instead of stainless steel, which was generally used. The lifetime of such a cell was about five months and 250 cycles respectively, the sulfur utilization being about 70%. The cell failed due to a defective weld. The maximum corrosion was found in those lower parts of the cell which were in contact with the melt. The upper part of the casing, however, was not so heavily attacked. The microprobe analysis of the metallographic sections (Fig. 3) shows the fully sulfided coating. As expected from the corrosion of the bulk alloys, chromium is enriched in a layer adjacent to the aluminum, and nickel is distributed all over the corrosion layer.



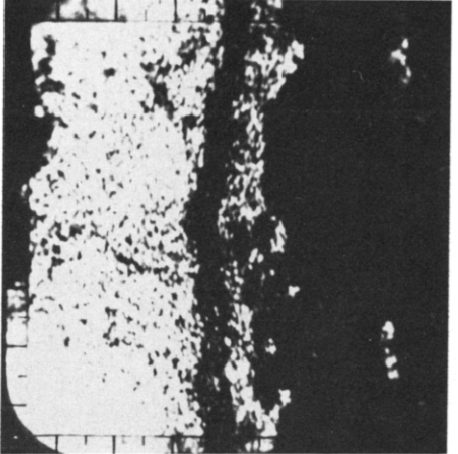
(a)



(b)



(c)



(d)

Fig. 3. Electron microprobe analysis of a metallographic cut through a Na/S cell casing (a) Normal; (b) S $K\alpha$ radiation; (c) Cr $K\alpha$ radiation; (d) Ni $K\alpha$ radiation.

Conclusions

Coating may be the solution to the casing problem as it has been found difficult to find a material which is satisfactory in all respects as cell casing for sodium/sulfur cells. With respect to corrosion the behaviour of a coating was essentially the same as that of the massive materials. This has been demonstrated by comparison of the resistances of samples in Na_2S_4 melts. Another factor that affects the corrosion rate is the nature of the current if an electric potential is applied during corrosion. Insufficient electronic contact results in ionic currents through the sample surface thus increasing the corrosion rate by a factor of almost three.

The possibility of using aluminum with a plasma sprayed super alloy coating has been demonstrated in sodium/sulfur cells. The performance and examination of these cells demands further optimization of the alloy compositions and plasma spraying conditions.

Acknowledgement

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References

- 1 R. Bauer and B. Hartmann, *Werkst. Korros.*, to be published.
- 2 G. Weddigen, H. Kleinschmager and S. Hoppe, *J. Chem. Res.*, (1978) 1110 - 1118.
- 3 Ford Annual Reports, Research on electrodes and electrolytes for the Ford sodium-sulfur battery.
- 4 R. Bauer, W. Haar, H. Kleinschmager, G. Weddigen and W. Fischer, *J. Power Sources*, 1 (1976/77) 109.
- 5 M. P. Y. Brennan, *Electrochim. Acta*, 22 (1977) 279.
- 6 T. Narita and K. Nishida, *Oxid. Met.*, 6 (1973) 181.
- 7 K. N. Strafford, *Metall. Rev.*, 138 (1969) 153.
- 8 H. Rickert and S. Mrowec, *Z. Phys. Chem. (N.F.)*, 36 (1963) 329.
- 9 R. J. Bones and T. L. Markin, Polarisation and corrosion in sodium/sulphur cells, presented at E.C.S. Atlanta Meeting, Oct. 1977.
- 10 S. Mrowec, T. Werber and M. Zastawnik, *Corros. Sci.*, 6 (1966) 47.