PREPARATION OF IRON SULFIDES AND THE STUDY OF THEIR ELECTROCHEMICAL CHARACTERISTICS FOR USE IN A NON-AQUEOUS–LITHIUM BATTERY

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Summary

A variety of iron sulfides was prepared by changing both the mixing ratio of iron to sulfur and the reaction heating temperatures. Samples were then subjected to chemical and X-ray diffraction analyses to check their composition. These iron sulfides were polarized in a nonaqueous electrolyte. As a result, the sample prepared with a S/Fe ratio of 1.1/1 and heated at 800 °C showed the highest electrochemical capacity and had the molecular formula FeS. A button-type, nonaqueous electrolyte–lithium battery using the FeS as the cathode material was constructed and evaluated. The energy density of the battery was calculated to be 0.448 W h/cm^3 and 0.137 W h/g.

Introduction

At the present time, a variety of materials is being studied for their suitability for use as cathode materials in nonaqueous–lithium batteries. Among these, several materials such as $(CF)_n$ [1], MnO_2 [2], SO_2 [3], $SOCl_2$ [4], are attracting special attention, and lithium batteries using these materials are under industrial development. The working voltages of all these batteries are approximately 3 volts, and although advantageous because of their high energy density, a voltage compatibility problem does accompany them in that 3 V batteries are not convenient for use in modern equipment designed to use 1.5 V batteries.

Because of the initial success of cathodes designed for lithium batteries, and because of the voltage incompatibility problem, we have tried to develop a high energy, 1.5 volt battery consisting of a lithium anode and a ferrous sulfide cathode in a nonaqueous electrolyte. In previous work we have found [5] that ferrous sulfide in partnership with lithium was electrochemically active in a nonaqueous electrolyte at ambient temperature and demonstrated a voltage of 1.5 volts.

McCoy *et al.* reported that iron sulfide showed higher energy density, greater availability and lower cost than other metal sulfides as the cathode material of a high temperature lithium/molten salt battery [6]. The specific capacity of the cathode was 1.10 A h/cm^3 [6]. Nelson *et al.* obtained 121 W h/kg as the specific energy density of the lithium/iron disulfide molten salt battery [7]. Both FeS$_2$ and FeS are known as cathode materials. Nelson *et al.* considered that the FeS electrode would result in a slightly lower performance capability than the FeS$_2$ electrode because of the lower sulfur content and lower cell voltage [7]. However, they also stated that the FeS electrode has the advantages of reduced corrosion, longer life and lower cost [7]. Hall reported that the FeS$_2$ electrode discharges in two steps, while the FeS electrode discharges in a single voltage plateau [8]. For these reasons, FeS is preferred as the cathode material [8, 9].

On the other hand, lithium, room temperature nonaqueous electrolyte batteries employing iron sulfide cathodes have not previously been reported. In this report, various iron sulfides were prepared and subjected to electrochemical polarization tests. Among these iron sulfides, FeS prepared from an S/Fe ratio of 1.1/1 and at a reaction temperature of 800 °C showed the highest electrochemical capacity and was used as the cathode of a lithium–nonaqueous battery. The characteristics of the battery have been evaluated and are described in this paper.

Experimental

Materials

The sulfur and iron used in this work were commercially available reagent grade chemicals and were used without further treatment. Iron powder was 98.7 wt.% pure and contained 76 wt.% particles with a diameter of 10 - 45 μm. Sulfur powder was 99.7 wt.% pure and contained 87 wt.% particles with a diameter of 10 - 45 μm. Lithium metal used as the anode material for test cells was 99.8% pure (of commercial quality). LiClO$_4$, propylenecarbonate (PC) and dimethoxyethane (DME) were purified by the following procedures. For dehydration and purification, PC was distilled under vacuum and DME was distilled at atmospheric pressure, while LiClO$_4$ was dried under vacuum at 150 °C. PC and DME were mixed in the volume ratio 1:2. 0.5 mol of LiClO$_4$ was dissolved in 1 liter of the mixed solvent to prepare the electrolyte, the dissolution being carried out in an Ar atmosphere. The water content of the electrolyte was 30 ppm when measured by the Karl Fischer method.

Preparation of iron sulfides

A porcelain boat containing approximately 5 g of the mixture of iron and sulfur powder was placed in a porcelain tube 15 mm dia. and 60 mm long which was filled with nitrogen gas. The mixture was heated at a rate of (temperature rise of) 10 °C/min to a prescribed temperature, and kept at
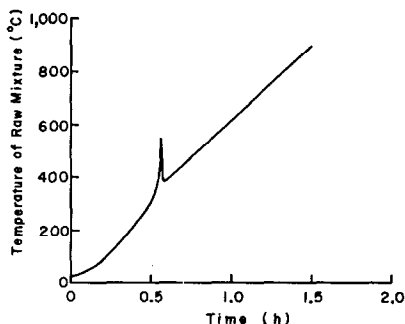
Fig. 1. Temperature change of mixture.

that temperature for 2 h. After cooling to room temperature, the product was pulverized to under 100 mesh and subjected to experimental use. The temperature change of the mixture during the heat treatment procedure is shown in Fig. 1. When the temperature of the mixture reached 350 °C, it then rose steeply to 550 °C, followed by a decrease to furnace temperature again. This steep temperature rise was caused by the heat of reaction of the mixture.

Analysis

The resultant iron sulfides were subjected to chemical and X-ray diffraction analyses to determine their composition. The sulfur content, in the forms of $Fe_{0.95}S$ and FeS, of the samples was measured by the amount of H_2S evolved when dissolved in HCl (1 mol/l). The total Fe dissolved was measured by atomic absorption spectroscopy. The iron (metallic Fe and Fe in iron compounds other than iron sulfides) content was calculated by subtracting the Fe corresponding to $Fe_{0.95}S$ and FeS from the dissolved Fe. The undissolved part of the sample was leached in a hot alcoholic alkaline solution, and the sulfur dissolved (in this case) was determined by atomic absorption spectroscopy as elementary sulfur. Finally, the residue was dissolved in concentrated HNO_3 and the FeS_2 content was calculated from the eluted amount of Fe.

The $Fe_{0.95}S$ and FeS contents were determined by the respective peak areas of the X-ray diffraction patterns of individual samples. Sample No. 8 contained 50.4 wt.% $Fe_{0.95}S$ and its peak at 55.8° was used as the $Fe_{0.95}S$ standard. Sample No. 12 contained 95.9 wt.% FeS and its peak at 55.2° was used as the FeS standard.

Test cell

The test cell used in the electrochemical studies is shown in Fig. 2. A variety of samples was prepared from Fe and S mixtures by changing the mixing ratio and heating temperature and they were used for cathode materials. The sample (0.1 g) and 0.1 g of graphite were mixed and pressed to a pellet of dimensions 11.0 mm dia. and 0.85 mm thickness. This pellet was
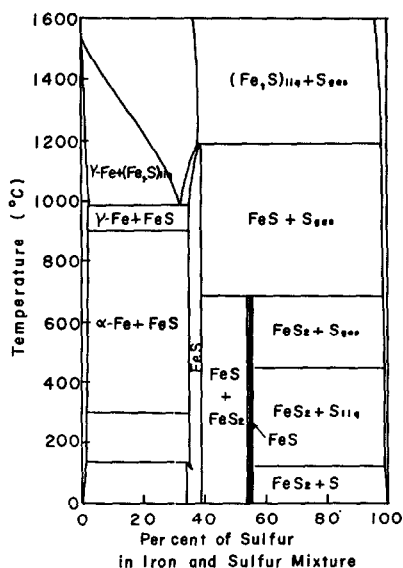
Fig. 4. Equilibrium diagram of the Fe–S system.

and 0.78 mm thickness. This cathode was dried for 2 h at 200 °C under vacuum before use. Lithium metal having dimensions of 7.3 mm dia. and 1.2 mm thickness was used as the anode. 55 μl of the electrolyte were poured into the battery and the battery construction was performed in an Ar atmosphere.

Results and discussion

Composition of reaction products

The equilibrium diagram of the Fe–S system is well-known and is shown in Fig. 4 [10]. We prepared six kinds of iron sulfide by mixing sulfur and iron in ratios of 0.8/1 to 2.0/1 and by heating at 800 °C for 2 h. Seven more kinds were prepared by mixing sulfur and iron in the ratio 1.1/1 and heating at 300 - 900 °C for 2 h.

We first investigated the effect of the S/Fe ratio on the product composition. X-ray diffraction patterns of these products are shown in Fig. 5. Several peaks other than Fe and FeS are observed in Fig. 5. These peaks were identified, according to ASTM cards, as $Fe_{0.95}S$. Analytical results of these products are listed in Table 1 and, as expected from Fig. 4, Fe and FeS were produced at a S/Fe ratio of 0.8/1, and in the ratio range of S/Fe = 1.0/1 to 1.5/1, the main product was FeS. At higher sulfur ratios between S/Fe = 2.0/1 and 1.5/1, $Fe_{0.95}S$ was produced in addition to FeS. As the product with the highest FeS content was produced with the highest yield at a S/Fe ratio of 1.1/1, subsequent experiments were performed with this ratio.
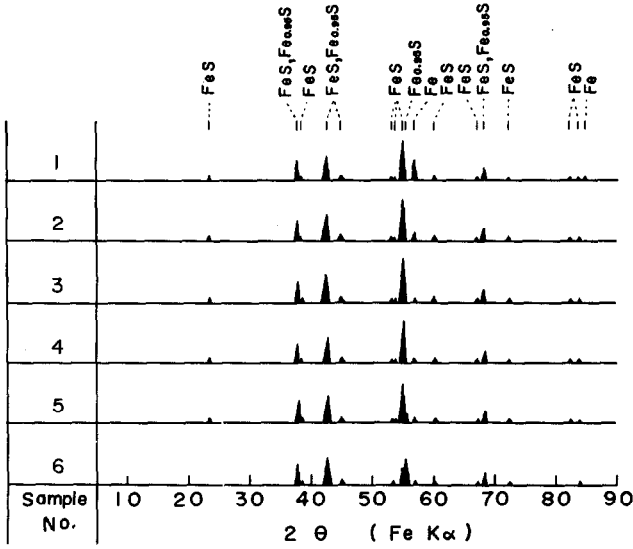
Fig. 5. X-ray diffraction patterns of samples prepared from various Fe/S mixing ratios. No. 1, 0.8/1; No. 2, 1.0/1; No. 3, 1.1/1; No. 4, 1.2/1; No. 5, 1.5/1; No. 6, 2.0/1.

TABLE 1

Effect of S/Fe mixing ratio on yield and composition of products

Sample no.	S/Fe mixing ratio	Yield* (%)	Composition of product (wt.%)					
			FeS_2	$Fe_{0.95}S$	FeS	Fe	S	Others
1	0.8/1	98	0.1	–	74.2	22.6	0	3.1
2	1.0/1	96	0.1	–	87.9	9.1	0	2.9
3	1.1/1	96	0.1	–	95.9	2.6	0.4	1.0
4	1.2/1	91	0.2	–	95.5	4.1	0	0.2
5	1.5/1	85	0.3	4.0	91.0	3.9	0	0.8
6	2.0/1	76	0.3	58.0	36.0	2.5	1.6	1.6

*Yield means the weight ratio of the product to raw mixture.

Next, the effect of reaction temperature on product composition was investigated. X-ray diffraction patterns of the products investigated are shown in Fig. 6. In spite of the fact that FeS is the sole product at the S/Fe ratio of 1.1/1 and in the temperature range 200 - 900 °C, as shown in Fig. 4, peaks corresponding to $Fe_{0.95}S$ also appeared, as shown in Fig. 6. The compositions of these products are listed in Table 2. Below 300 °C, the reaction was inefficient and the products contained FeS_2, $Fe_{0.95}S$ and unreacted raw materials. FeS was not detected in these products. When the heating temperature ranged from 500 to 700 °C, both FeS and $Fe_{0.95}S$ were obtained and at the higher temperature, a higher content of FeS was found.
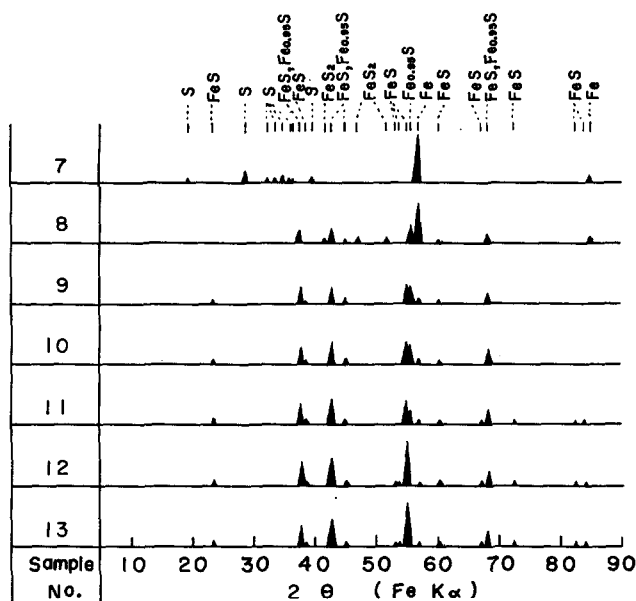
Fig. 6. X-ray diffraction patterns of samples prepared at various heating temperatures. No. 7, 200 °C; No. 8, 300 °C; No. 9, 500 °C; No. 10, 600 °C; No. 11, 700 °C; No. 12, 800 °C; No. 13, 900 °C.

TABLE 2

Effect of heating temperature on yield and composition of products

Sample no.	Heating temperature (°C)	Yield* (%)	Composition of product (wt.%)					
			FeS_2	$Fe_{0.95}S$	FeS	Fe	S	Others
7	200	87	2.3	16.1	—	49.2	29.1	3.3
8	300	85	10.1	50.4	—	34.5	0.5	4.5
9	500	94	0.2	43.9	44.6	8.8	1.2	1.3
10	600	96	0.1	37.3	54.7	4.7	0.6	2.6
11	700	96	0.2	28.2	65.5	3.6	0.8	1.7
12	800	96	0.1	—	95.9	2.6	0.4	1.0
13	900	95	0.1	—	95.3	3.5	0	1.1

*Yield means the weight ratio of the product to raw mixture.

Above 800 °C, only FeS was produced in higher concentration and $Fe_{0.95}S$ was not detected. From these evaluations, it is evident that the product with the highest FeS content was obtained from a ratio of S/Fe of 1.1/1 and at a reaction temperature of 800 °C.

Electrochemical test

A variety of iron sulfides and mixtures of iron sulfides has been synthesized. In order to find the best cathode material for a nonaqueous–
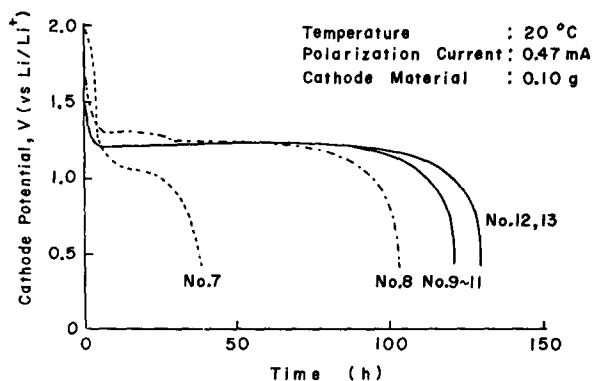
Fig. 7. Effect of heating temperature on polarization curves. No. 7, 200 °C; No. 8, 300 °C; No. 9, 500 °C; No. 10, 600 °C; No. 11, 700 °C; No. 12, 800 °C; No. 13, 900 °C.

TABLE 3

Effect of heating temperature on electrochemical capacity of products

Sample no.	Heating temperature (°C)	Electrochemical capacity (mA h/g)				
		Theoretical*				Experimental**
		FeS_2	$Fe_{0.95}S$	FeS	Total	
7	200	20	101	−	121	170
8	300	90	318	−	408	470
9	500	2	277	272	551	550
10	600	1	235	334	570	550
11	700	2	178	400	580	550
12	800	1	−	585	586	600
13	900	1	−	581	582	600

*Theoretical electrochemical capacity means the sum of the calculated electrochemical capacities of FeS_2, $Fe_{0.95}S$ and FeS in the products.
**Experimental electrochemical capacity is the discharge capacity to 1.0 V.

lithium battery, cathodic polarization tests of these iron sulfides and mixtures were performed. The results of these tests are shown in Fig. 7. Experimental electrochemical capacities of samples calculated from the data shown in Fig. 7 were compared with theoretical electrochemical capacities calculated from Table 2, as shown in Table 3. The experimental electrochemical capacities of all the samples were nearly equal to the theoretical electrochemical capacities and their electroactivities were high, demonstrating each iron sulfide to be an active cathode material in a nonaqueous electrolyte.

Because of their poor iron sulfide content, electrochemical capacities of materials from preparations Nos. 7 and 8 were low. The discharge curve of material No. 8 showed a slightly higher potential at the start of the discharge plateau. This was probably caused by discharge of FeS_2, contained
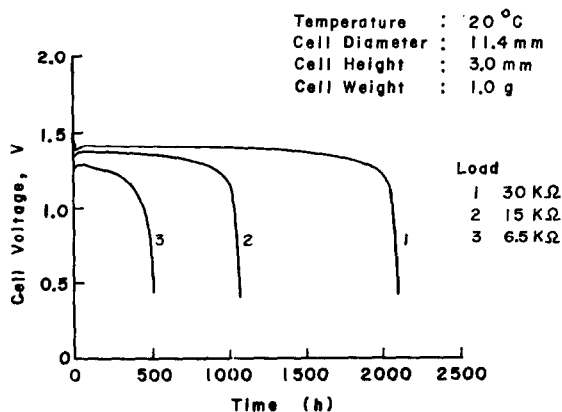
Fig. 8. Discharge curves of button-type battery.

to an amount of 10 wt.% in this sample. The five samples Nos. 9 - 13 had high contents of $Fe_{0.95}S$ + FeS and showed large electrochemical capacities. Although each sample had almost the same theoretical electrochemical capacity, samples Nos. 9 - 11 had slightly lower experimental electrochemical capacities than those of Nos. 12 and 13. This may be due to the fact that samples nos. 9 - 11 were a mixture of $Fe_{0.95}S$ and FeS, while Nos. 12 and 13 contained FeS only. Consequently, it is considered that $Fe_{0.95}S$ has slightly less available electrochemical capacity than FeS. From these experiments, it is demonstrated that FeS prepared with a S/Fe ratio of 1.1/1 and at a temperature of 800 °C (No. 12) was most suitable for use as a cathode material in a nonaqueous battery.

We selected material No. 12 as the cathode nearest to the optimum composition for use in a Li/FeS button cell. Various discharge curves of a button cell with this cathode material are shown in Fig. 8. The working voltage of the battery is 1.4 V and its capacity is 98 mA h. The energy density of the battery was high and was calculated to be 0.448 W h/cm^3 or 0.137 W h/g.

Conclusion

The experimental results of this study can be summarized as follows:
(1) In the mixing ratio range S/Fe = 0.8/1 - 2.0/1 at a heating temperature of 800 °C for 2 h, the product with the highest FeS content was obtained at a ratio of S/Fe = 1.1/1.
(2) In the heating temperature range from 200 to 900 °C with a S/Fe ratio of 1.1/1 and a heating period of 2 h, the product with the highest FeS content was obtained in the highest yield at 800 °C.
(3) Electrochemical tests revealed that FeS prepared with a S/Fe ratio of 1.1/1 and at a temperature of 800 °C is the most suitable for use as the cathode material in a nonaqueous battery.

(4) A button type nonaqueous lithium battery using the above FeS was constructed and demonstrated the following characteristics: working voltage 1.4 V, energy density 0.448 W h/cm^3 or 0.137 W h/g.

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