

## Short Communication

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### Synthesis of FeS for Lithium Batteries

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Our studies on lithium batteries based on the Li/CuS system have been pursued as far as the laboratory technology stage [1]. The specific feature of the technology was the direct synthesis of CuS in the copper cathode holder. By this means excellent electrical contact of the cathodic material with the current collector was obtained. Good cathodic mass electrical conductivity and favorable pore orientation in the material are two advantages of the method.

In the course of further studies we turned our attention to the Li/FeS system, which has the important advantage of a more "standard" voltage of 1.5 V. The system has been studied for some years [2, 3] on both a primary and a secondary battery basis, including high temperature applications. The reduction mechanism of FeS in lithium cells is far from being fully understood. However, compounds such as  $\text{Li}_2\text{FeS}_2$  have been found [4].

In the literature there are numerous procedures for the preparation of FeS cathodes [5]. All are based on the addition of graphite (to improve conductivity), and binder (to obtain better mechanical strength) to the synthetic FeS powder. The mixture is then pressed onto the current collector — usually in the form of steel mesh. Such an approach has its advantages and disadvantages. It is much more easy to control the stoichiometry of the sulphide and its grain size — Fe and S have a very strong tendency to form nonstoichiometric sulphides. A disadvantage lies in the introduction of substantial amounts of substances which do not contribute to the battery capacity and are a potential source of impurities which can affect the shelf life of the battery.

In the course of our study we attempted the direct synthesis of FeS in the cathode holder. We prepared the mixture of Fe and S (equimolar or with slight excess of S) in a dry box because of the high sensitivity of Fe powder to moisture. Hydrogen-reduced iron (p.a., SERVA) and S (POCh) were used. Weighed portions of the mixture were pressed into shallow, bowl-shaped steel cathode holders, placed in a close fitting mould, transferred to a

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furnace, and heated at 700 °C for a few hours. In this way cathodes 20 mm in diameter and 3 mm thick were obtained. The material was solid and well-bonded to the holder, with excellent mechanical properties including easy machining and polishing of the outer surface. This polishing approach has often been used to remove traces of slag from the faces of samples and to normalize their thickness. Sample porosity (determined from the material density) was easily controlled within the range 35 - 60%.

Samples of FeS obtained according to the procedure outlined above were subjected to further examination to determine the composition and microstructure of the material. The tests were carried out using a JEOL scanning microscope with microprobe and a Siemens diffractometer (with Mo

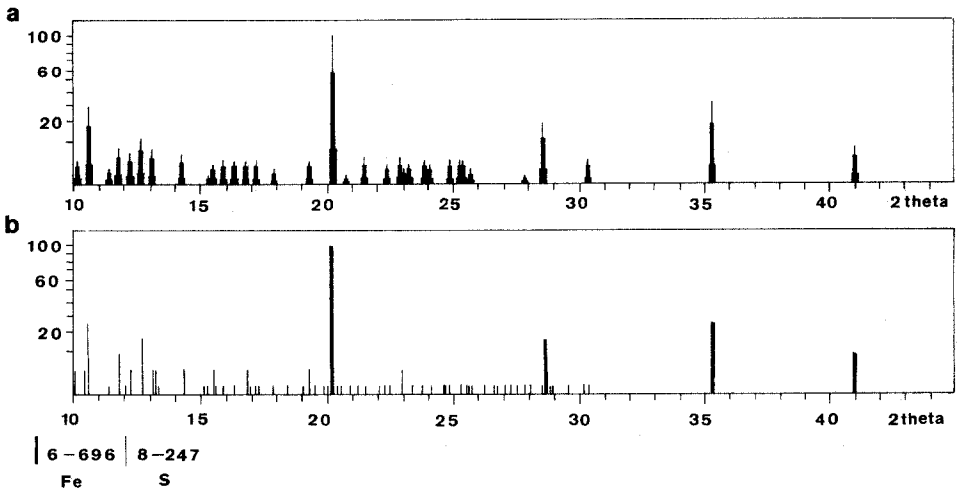


Fig. 1. X-ray powder diffraction pattern for: (a) Sample No. 297; (b) the standards.

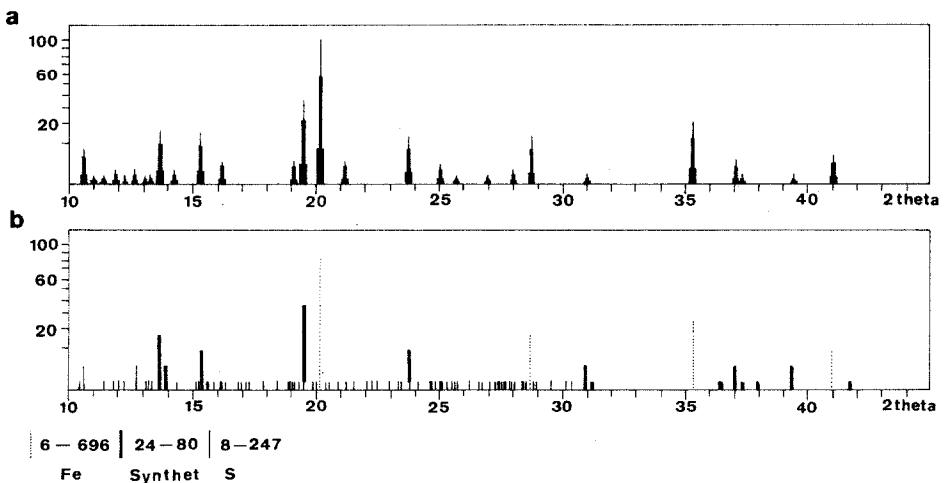


Fig. 2. X-ray powder diffraction pattern for: (a) Sample "SF"; (b) the standards.

source). The crystalline phases present were identified using the XAF computer program run on an IBM PC/AT with the ICPDS database comprising 40 000 standards. The Hanawalt method of identification was adopted. The main points found in the course of this investigation are summarized below:

(i) In the sample of the mixture before baking no substantial amounts of FeS were found (sample No. 297, Fig. 1).

(ii) In the sample of commercial FeS (FLUKA) (sample "SF", Fig. 2) in addition to the FeS present in the form of synthetic triolite some amounts of Fe and S were detected.

(iii) In all the samples of FeS synthesized according to our procedure only two crystalline phases were detected, namely, natural and synthetic

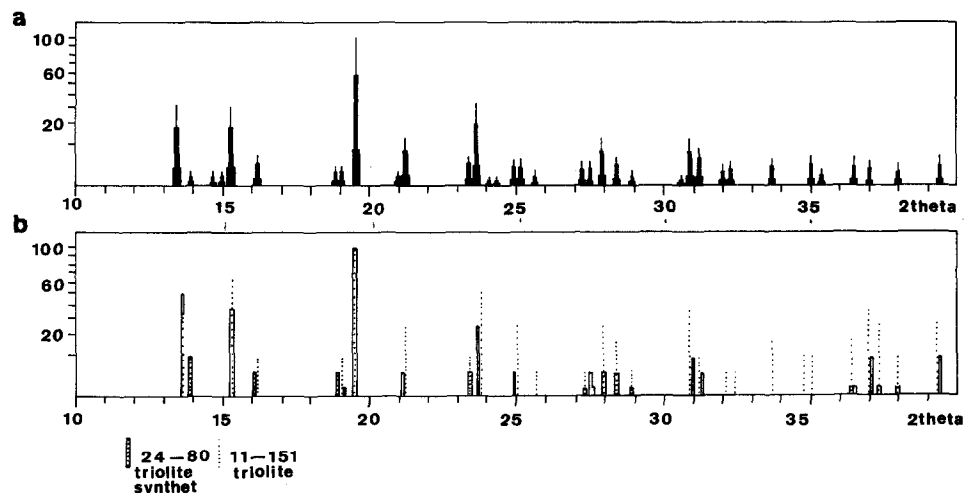


Fig. 3. X-ray powder diffraction pattern for: (a) Sample No. 237; (b) the standards.

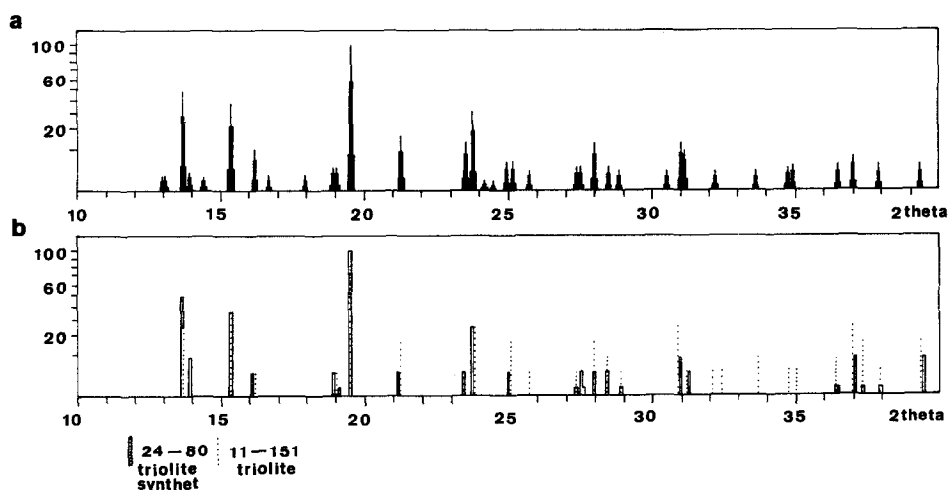


Fig. 4. X-ray powder diffraction pattern for: (a) Sample No. 148; (b) the standards.

triolite (*e.g.*, samples Nos. 237 and 148, Figs. 3 and 4). At this stage in the investigation it can only be said that the two were present in different proportions in the various samples.

Judging from the results of diffractometric studies, the successful synthesis of iron sulphide free from substrates (Fe and S) and undesirable phases such as sulphates or oxides may be claimed.

In the course of the microscopic study, a preliminary understanding of the morphology of grains and pores was established. In Fig. 5 the large grains of commercial FeS (sample "SF") may be seen. For comparison, in Fig. 6 (sample No. 237, similar magnification) a much more developed grain surface is shown. This structure may be regarded as being typical of all our samples. The only exceptions to this characteristic were grains found in the surface layer of the samples. Here the material has often been melted (this can be seen even without an instrument). On the microphotographs large crystals with large, flat faces can be seen (Fig. 7) as for sample No. 148. In this photograph the distribution of sulphur in the material along the line A in the

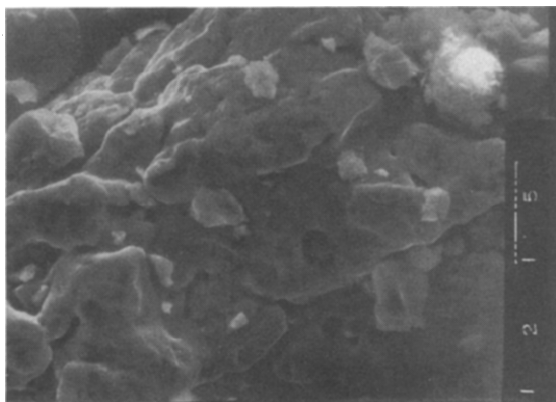


Fig. 5. Grains of commercial FeS (sample "SF") ( $\times 1050$ ).

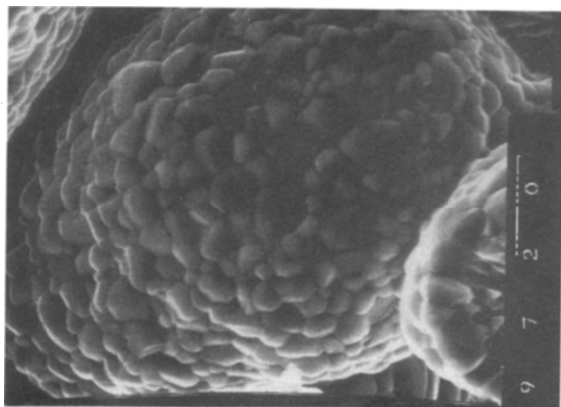


Fig. 6. Typical morphology of the surface of grains in sample No. 237 ( $\times 1400$ ).

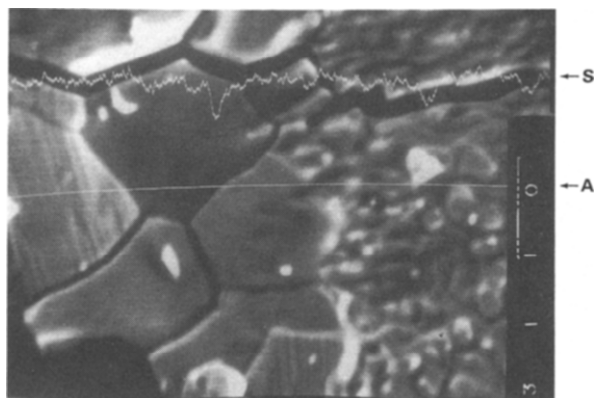


Fig. 7. Grains in the melted zone of sample No. 148 ( $\times 700$ ). The sulphur content distribution profile (line "S") measured along the line "A" is shown.

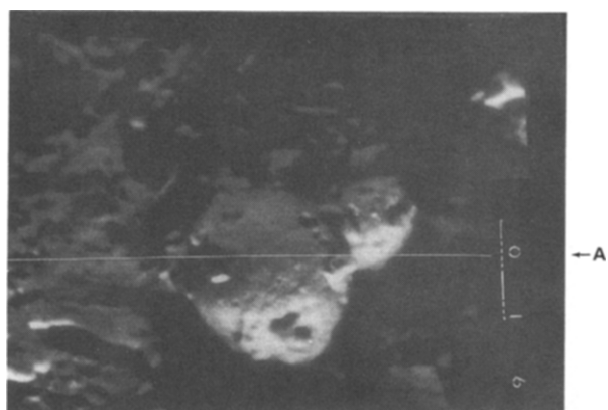


Fig. 8. Grains of commercial FeS (sample "SF") ( $\times 1400$ ). The distribution of Fe and S have been determined along line "A" in the center — see Fig. 9.

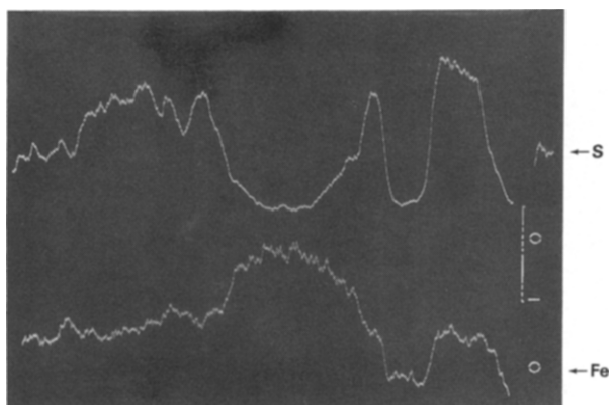


Fig. 9. Distribution of S and Fe contents along line "A" in Fig. 8 ( $\times 1400$ ).

center of the picture is shown. The distribution is much more uniform than in the commercial compound (*cf.* Figs. 8 and 9 for sample "SF").

In general, the results suggest that the method has possibilities and the product obtained appears not to be inferior to the commercially available material. Selected samples remain under investigation in the course of a separate electrochemical study. They are being used as components of laboratory models of lithium batteries. Discharge curves, internal resistances, and other parameters of the batteries are being studied, but this kind of study requires time for its completion. The voltammetric characteristics of our cathodes will be studied shortly using solvents such as THF, DME or BL, and their mixtures.

### References

- 1 L. Werblan, J. Lesinski, A. Suzdorf, J. Izydorek and R. Drachal, *J. Power Sources*, 9 (1983) 409.
- 2 F. W. Dampier, *J. Electrochem. Soc.*, 128 (1981) 2501.
- 3 Z. Tomczuk *et al.*, *J. Electrochem. Soc.*, 128 (1981) 760.
- 4 C. A. Vincent (with F. Bonino, M. Lazzari and B. Scrosati), *Modern Batteries — An Introduction to Electrochemical Power Sources*, Edward Arnold, London, 1984.
- 5 E. M. Shembek *et al.*, *Elektrokhimiya*, 22 (6) (1986) 824; E. M. Shembek *et al.*, *Elektrokhimiya*, 21 (11) (1985) 1560.