Characterization of Li_2FeS_2 from Li/FeS_2 Electrochemical Systems

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Abstract

This work surveys the complex and multi-phase discharge mechanism of Li/Fe_2S thermal batteries looking into the morphology and response to current density of the main intermediary compounds of this electrochemical cathodic system, namely Li_2FeS_2. Discharged cells of high power density battery were submitted to examination and characterization through SEM/EDS analysis. Those analyses allowed the access to the materials distribution and layers discrimination together with the identification of the cathodic interface.

The work wraps-up concluding that the needle-like-structures, characteristic of the Li_2FeS_2 compound, have their growth closely related to the current density drained from the battery. The elucidation of these phenomena will bridge the understanding of the cathodic mechanism leading to the optimization of this system.

Keywords: lithium battery, pyrite, molten-salt electrolyte, thermal battery.

Introduction

The Li/FeS_2 system is employed in high energy density molten salt electrolyte batteries frequently referred to as "thermal batteries". It plays extensive role as primary power sources in defense applications. Their main advantages are excellent environmental stability, both prior and during use, their wide range of operational temperatures, their long storage capability and high reliability. Thermal batteries are high temperature power sources that typically operate between 350^0C and 600^0C. They use a molten ionic conducting electrolyte, which is essentially inert prior fusion. Being hermetically sealed, they can remain in storage for 25 years or more without degradation. Once activated, however, power can be delivered at extremely high rates, in excess of $15\ kA/m^2$ for times on the order of seconds. At sufficiently low current densities (e.g., $< 500\ A/m^2$), lifetime can be easily extended to an hour or more.

Due to the open circuit potential of this particular electrochemical couple there's often a need of stacking a number of this cells, forming a battery, to achieve the required voltage. To thermally activate this battery, each cell incorporates a pyrotechnic pellet (thermite), which is ignited by a fuse strip. This strip is activated by an igniter (electroexplosive device) firing through a hole in the center of the stack. Activation times range from under 40 milliseconds for small pulse batteries to hundreds of milliseconds for the large power batteries (1).

Historically, a number of electrochemical cells have been used for different applications, but the $Ca/CaCrO_4$ couple was the main technology for thermal batteries from the early 1960`s (3). The key problems in obtaining extended duration from this system at high current densities are twofold. The first arises from the existence of exothermic side reactions of calcium chromate, which is soluble in the lithium chloride / potassium chloride electrolyte. The second comes from an undesired reaction of calcium in which the electrolyte forms the $CaLi_2$ alloy, molten at the battery operating temperature (approximately 600^0C), that can lead to intercell short circuiting if not controlled. At low current density, the formation of the $CaLi_2$ alloy at the anode-electrolyte interface sometimes causes serious voltage fluctuation (electrical noise) and occasional cell dropout, thus causing unreliability of the battery. At high current density, on the other hand, the formation of the double salt $KCaCl_3$ at the cathodic interface increases the internal resistance, reducing the system's life. The electrochemical reduction

of $CaCrO_4$ is complex and goes through different routes towards various reduced species. That cathodic process involves at first a one-electron reduction followed by a two-electron transfer.

The advent of the FeS_2 based electrochemical system was a welcome improvement to the previous $Ca/CaCrO_4$ system. It has few inherent problems due to chemical side reactions and variability when compared to the $Ca/CaCrO_4$ system besides being much more predictable. The iron disulfide can be obtained by synthesis or by mineral pyrite purification and is relatively inexpensive compared to the chemically synthesized $CaCrO_4$. In addition, it has improved power and lifetime without the deleterious consequences of the carcinogenic Cr (VI) contained in the calcium salt. The research and development of the various materials that are involved in the Li/FeS_2 battery technology has led to improved efficiencies and widened performance limits. In recent years this electrochemical system has emerged as viable candidate for new applications, such as in aerospace, emergency systems, vehicle propulsion and off-peak energy storage (6).

In this paper post-test cells examinations have been conducted on a Li/FeS_2 electrochemical system to characterize the main electrocathodic intermediate product, Li_2FeS_2. The cathodic interface has been investigated through Scanning Electronic Microscopy in order to evaluate the relationship between the current density and the Li_2FeS_2 formation mechanisms.

Materials and Methods

The high energy density battery is constituted of a lithium anode, a cathode, in which the iron disulfide is employed as a depolarizer, and an electrolyte that is composed of lithium and potassium molten chlorides. It is possible to discharge a typical single cell at variable currents producing cell voltages in the range of 1.9 to 1.5 V for periods of minutes to hours. Among the several special characteristics of these systems is the inertia up to circa 450°C, when the electrolyte melts and becomes conductive, which assures a long storage time (4, 5).

Many workers, through different techniques, have extensively studied the cathode reactions that occur during the discharge process. What is not generally realized is that the oxidation state of Fe in FeS_2 is not (IV) but (II). Tomczuk et alli (8) proposed the formation of $Li_3Fe_2S_4$, $Li_{11}Fe_4S_{10}$ and Li_2FeS_2 during discharge as lithiated intermediates. Although other products and electrochemical mechanisms are proposed in the literature, the majority of authors point out that the final reduction products are iron and polysulfides and that Li_2FeS_2 is the most important intermediate product (7). Further, it is identified that the same compound is generated in acicular habit away from the cathodic interface, consuming electroactive iron (2).

It should be remarked that the battery dimensions were 51 mm of diameter and 44.6 mm of height. It was composed of 14 single cells having each one having 4.45 cm of diameter, giving a surface area of 15.55 cm^2. There were five insulation layers around the stack with total thickness of approximately 4 mm.

The experiments were initiated with the battery ignition through an electrical surge, which ends up burning the thermites in all cells. There were no external temperature and pressure tampering.

The samples have been obtained from prototypes that underwent discharges in current densities over the range of 1.9 to 9.7 kA/m^2 for 60 seconds, keeping all other variables constant. These discharges do not usually consume the entire power capacity of the materials within each cell.

The interfaces of particular interest in this study involve the electrochemically active Li anode and FeS_2 cathode with lithium and potassium chlorides electrolyte. The cells have been broken through its center and had the exposed interface covered with an evaporated graphite film. It must be emphasized that the surfaces suffered no polishment to insure its original characteristics. Due to the high reactivity of electrodic components the dissection and macro-examination procedures have been conducted in a low-moisture room (air humidity below 5%) and under controlled atmosphere, with temperature nearby 15°C. Also the analysis using the SEM (Scanning Electron Microscope) techniques involves high vacuum, further insuring the stability of the samples.

Since it was not possible to separate the individual layers existing in the cells the X-Ray Diffraction samples have been prepared by grinding the whole cells down to a particle size of 295 μm. Further the electrocathodic reaction products, such as FeS, Li_2FeS_2, $LiK_6Fe_{24}S_{26}Cl$, have been submitted to analysis.

Results and Discussion

Extensive examinations of the transversal section from discharged cells have been conducted by the SEM equipped with EDS (Energy Dispersive X-Ray Spectroscopy) showing the material distribution and layers of different morphology. Photomicroscopic examinations under 50X magnification showed the entire cell having four layers, namely, the anode, electrolyte, cathode and thermite (Figure 1). It was identified a large amount of powdered iron in the first layer, which is used for immobilization of the pure lithium in the anode. The electrolyte layer, before the discharge, is composed of lithium and potassium chloride eutectic (45/55 wt %) and a magnesium oxide binder. The finely divided MgO acts as an immobilizer for the melted electrolyte, but does not react with either the anode or cathode, as showed by a magnesium mapping. The cathode layer, initially iron disulfide, lithium and potassium chloride eutectic, also

bears silicon oxide as a binder. The iron disulfide has a particle size less than 295 μm (50 mesh). The thermite layer was composed of high surface area iron powder and potassium perchlorate.

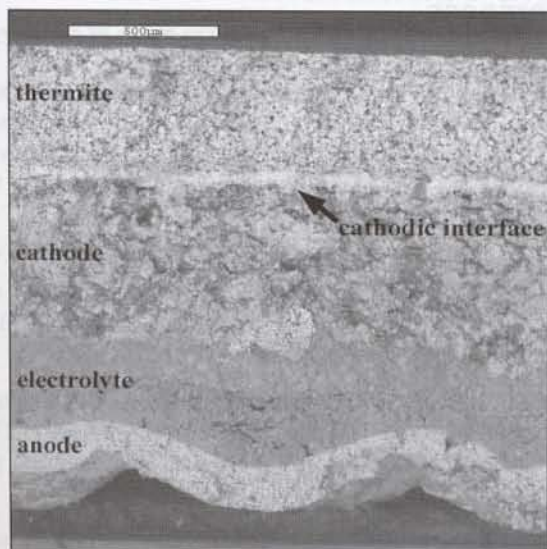Figure 1. SEM micrograph of the transversal section from Li/FeS$_2$ discharged cell (9.7 kA/m^2). X 50.

In the global cathodic mechanism FeS$_2$ is converted to Fe and Li$_2$S, however, a variety of multicomponent phases exist in this positive electrode at intermediate stages of discharge. For example, the main intermediate phases in FeS$_2$ systems are Li$_2$FeS$_2$ and LiK$_6$Fe$_{24}$S$_{26}$Cl, both identified by the X-Ray Diffraction. Thus the progression of equilibrium phases in the cathodic system is never as simple as FeS$_2$ ↔ Li$_2$S and Fe, instead it varies, depending on the composition of the electrolyte, the cell operating temperature and the rate of discharge.

Photomicroscopic examination of discharged cells had identified an interface between the cathode and the thermite. The compound under study, Li$_2$FeS$_2$ referred to as X-phase, is present in this cathodic interface. As suggested by the micrographs, the formed interface thickness and the morphology may be related to the current density. In the Figure 1, at higher current densities conditions (9.7 kA/m^2) the interface can be easily seen. In the other photomicroscopic examinations a magnification of 2000X has been chosen to identify the needle-like-structures characteristic of the X-phase structure.

At the lowest current condition, Figure 2 (1.9 kA/m^2), the cathodic interface is the thinnest and the structure of X-phase does not exhibit a defined pattern. The Li$_2$FeS$_2$ compound consists of acicular structures dispersed within a matrix of the catholyte indicating the beginning of the needle-like-structures' growth.

On the other hand, at higher current density conditions, Figures 3 and 4, the acicular structures become more distinctive and acquire a preferential growth

direction while the layer thickens. Qualitatively this structure increase is illustrated by the absence of potassium and chloride containing compounds in this region. This fact indicates that the LiK$_6$Fe$_{24}$S$_{26}$Cl, referred as J-phase, is not present in this interface. In the photomicroscopy with current density of 4.5 kA/m^2 (Figure 4) the boundary interface of the needle-like-structures and FeS$_2$ grain is clearly characterized.

In Figure 5 (9.7 kA/m^2), the needle-like-structures are wider as the result of a high rate reaction. As expected, at higher discharge rates, the formation of Li$_2$FeS$_2$ from FeS$_2$ electrodes becomes significant.
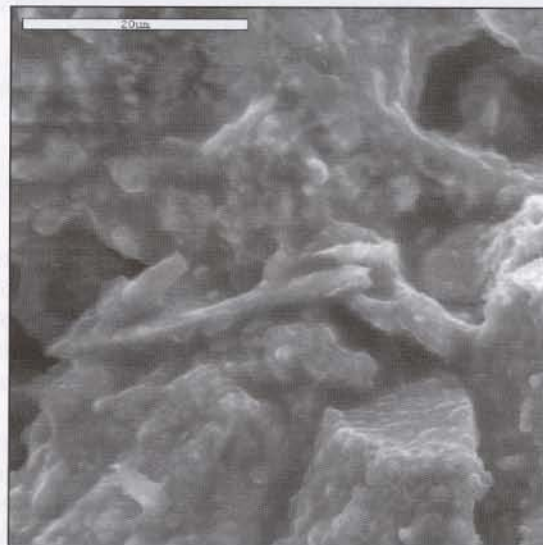

Figure 2. SEM micrograph of the cathodic interface from discharged cell (1.2 kA/m^2). X 2,000.

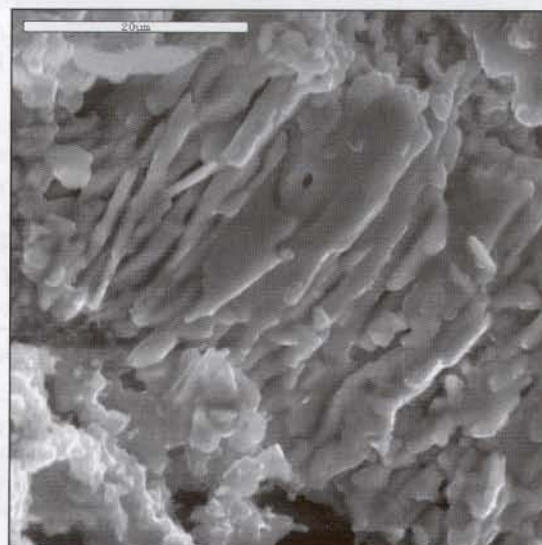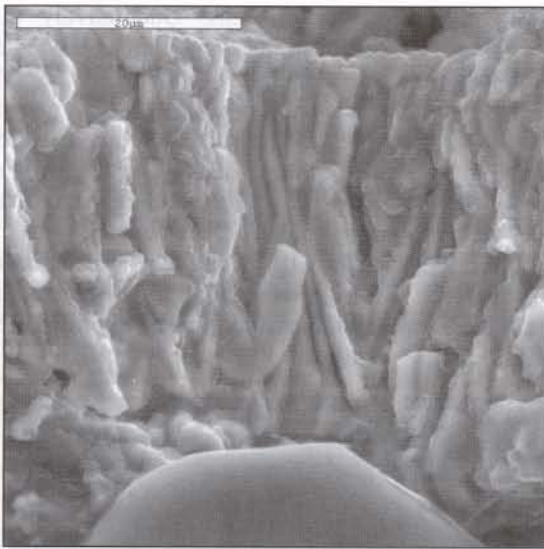Figure 3. SEM micrograph of the cathodic interface from discharged cell (2.4 kA/m^2). X 2,000.

Figure 4. SEM micrograph of the cathodic interface from discharged cell (4.5kA/m^2). X 2,000.
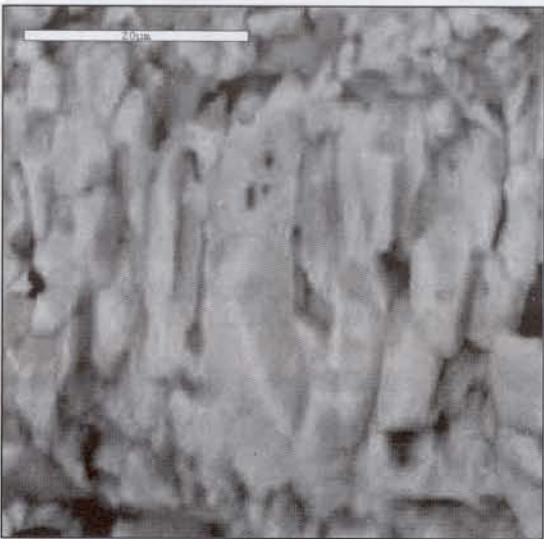

Figure 5. SEM micrograph of the cathodic interface from discharged cell (9.7 kA/m^2). Magnification of cathodic interface assigned from figure 1. X 2,000.

Conclusions

This study has shown that the discharge mechanism of the Li/FeS$_2$ battery is not as simple as previously expected. Several reactions have been identified which may contribute to increase cell resistance and loss discharge capacity. Under high current densities the primary and secondary current distributions are likely to produce stronger and oriented magnetic fields that may favour those homogeneous patterns for the main intermediate product, Li$_2$FeS$_2$. The micrographic

characterization is undeniably the main tool for the clear demonstration of this fact. Studies are underway at the present to investigate independently the cathodic mechanism in a single cell through voltammetric methods.

References

1. Amezawa, K., Yamamoto, N., Tomii,Y. and Yasuuhiko, Y. (1999). Thermodinamic properties and single-electrode peltier heats of a Li-Al alloy in a LiCl-KCl eutetic melt. Journal of the Electrochemical Society. 146(3):1069-1074.

2. Bronold, M., Pettenkofer, C., and Jaegermann, W. (1991). Surface Analysis Investigations on the Reaction of FeS$_2$ with Alkali Metals. Ber. Bunsenges. Phys. Chem. 95(11):1475-1479.

3. Guidotti, R.A. (1995). Thermal batteries: A technology review and future directions. Proc. 27th International SAMPE Technical Conference, pp. 807-817.

4. Kaun, T.D., Nelson, P.A., Redey, L., Vissers, D.R. and Henriksen, G.L. (1993). High temperature lithium/sulfide batteries. Electrochimica Acta. 38(9):1269-1287.

5. Knight, J. (1993). A voltage-time model of lithium-iron disulfide thermal batteries. Power Sources. 14:313-326.

6. Osaka, T., Komaba, S., Uchida, Y., Kitahara, M., Momma, T. and Eda, N. (1999). Performance of lithium metal anode in poly(vinylidene fluoride)-type gel electrolyte. Electrochem. Solid-State Letter. 2(5): 215-217.

7. Strauss, E., Golodnitsky, D. and Peled, E. (1999). Cathode modification for improved performance of rechargeable lithium/composite polyner electrolyte-pyrite battery. Electrochem. Solid-State Letter. 2(3): 115-117.

8. Tomczuk, Z. Tani, B. Otto, N.C. Roche, M.F. and Vissers, D.R. (1982). Phase relationships in positive electrodes of high temperature Li-Al/LiCl-KCl/FeS$_2$ cells. J. Electrochem. Soc. 129(5): 925-931.