

DECOMPOSITION KINETICS OF FeS_2 CATHODE MATERIAL FROM THERMOGRAVIMETRY DATA

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ABSTRACT

The decomposition kinetics of FeS_2 cathode material used in thermal batteries was determined by thermogravimetry (TG), using the variable heating rate method to calculate the activation energy (E_a) and pre-exponential factor (Z) of the Arrhenius equation. From the calculated kinetic parameters, the loss in discharge capacity from the decomposition of FeS_2 at various battery operating temperatures (723–973 K) can be determined.

INTRODUCTION

Thermal batteries are primary, reserve electrochemical power sources employing molten salt electrolytes that are solid and, therefore, non-conductive at normal ambient temperatures. When power is required, an integral pyrotechnic heat source is ignited which raises the internal temperature above the melting point of the electrolyte, thus making it conductive and permitting battery operation. Such batteries have specialized uses for high-power, short-term discharges in a wide range of military and aerospace applications [1]. During the last 25 years, most of these devices have employed cells consisting of a calcium anode, a calcium chromate cathode, and a lithium chloride–potassium chloride eutectic electrolyte [2,3].

Recently, thermal batteries, employing a lithium or lithium-alloy anode, a lithium chloride–potassium chloride or a lithium fluoride–lithium chloride–lithium bromide eutectic electrolyte, and an iron disulfide (FeS_2) cathode, have been developed that provide significantly improved performance [4,5]. Because of its desirable electrochemical discharge characteristics, ease of obtainability and low cost, FeS_2 is used almost exclusively in these new lithium-anode batteries. However, the thermal decomposition of FeS_2 at battery operating temperatures (723–973 K) is a major cause of performance problems. The decomposition causes an obvious loss of electrochemical discharge capacity. In addition, the sulfur vapor produced can react exothermically with various cell components such as the lithium anode or the

iron in the Fe-KClO₄ pyrotechnic mixture [6]. Furthermore, the presence of elemental sulfur in the cathode material has been associated, in part, with a voltage "spike" immediately after activation of the battery [4].

The present thermogravimetry (TG) study, employing the variable heating rate method of Flynn and Wall [7], was undertaken to determine the decomposition kinetics of FeS₂ cathode material at thermal battery operating temperatures. The discharge capacity loss from the decomposition of FeS₂ can be predicted from the calculated kinetic parameters.

EXPERIMENTAL

FeS₂ cathode material is found in nature as the mineral pyrite. Samples were obtained from a thermal battery manufacturer (Catalyst Research Corp., Baltimore, MD) and from various companies that supply the material to the thermal battery industry.

A DuPont 1090 thermal analysis system with a 951 TGA module was employed. Samples were run in platinum boats at heating rates from 1.0 to 10.0 K min⁻¹ in a flowing atmosphere (50 cm³ min⁻¹) of dry helium. The chromel-alumel sample thermocouple had to be replaced frequently because of severe corrosion by the evolved sulfur vapor. The use of high purge rates (400–500 cm³ min⁻¹) resulted in only a slight decrease in the corrosion rate.

RESULTS AND DISCUSSION

A series of TG curves of FeS₂ cathode material from various sources is shown in Fig. 1. The wide range of purity and stability of this material is apparent from these curves. The sample that appeared most stable, as indicated by the arrow in Fig. 1, was selected for this study.

The determination of the activation energy (E_a) and pre-exponential factor (Z) of the Arrhenius equation is based on the well-known methods of Flynn and Wall [7] and Zsako and Zsako [8], respectively. The E_a and Z values were calculated using the DuPont TGA decomposition kinetics program [9].

A series of typical TG curves of FeS₂ cathode material at heating rates of 1, 2, 5, and 10 K min⁻¹ is shown in Fig. 2. The FeS₂ decomposes according to



which is the main decomposition process seen in Fig. 2. The inflection in the curves at the beginning of the decomposition is caused by the vaporization of an impurity, probably elemental sulfur (b.p. 717 K), in the FeS₂ sample.

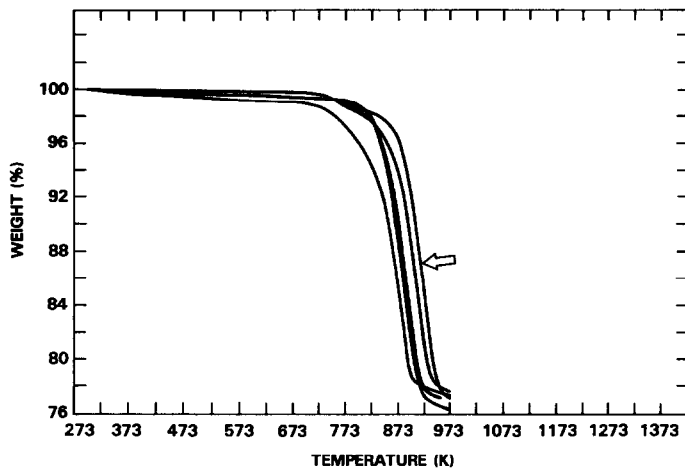


Fig. 1. TG curves of FeS_2 cathode samples; heating rate, 20 K min^{-1} ; atmosphere, helium, $50 \text{ cm}^3 \text{ min}^{-1}$.

The slow, continuing mass loss at the end of the FeS_2 decomposition is caused by the decomposition of the Fe_{1-x}S phase.

According to this method, the Arrhenius constants are calculated at a "constant conversion" level chosen for the series of runs. As seen in Fig. 2, three constant conversion levels were selected near the early stages of the decomposition, corresponding to weight losses of 25, 30, and 35%, to determine if the Arrhenius constants were the same over this region. Arrhenius plots of \log heating rate vs. $1/T$ are shown in Fig. 3 for these three decomposition levels. The slopes of the plots are virtually identical.

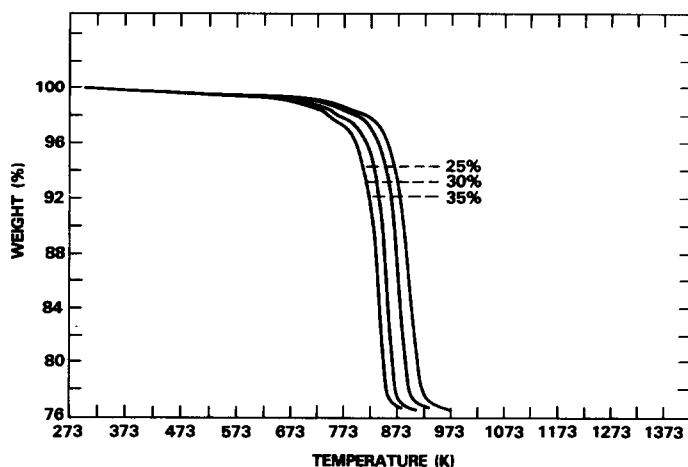


Fig. 2. TG curves of FeS_2 cathode material; heating rates, 1, 2, 5, and 10 K min^{-1} ; atmosphere, helium, $50 \text{ cm}^3 \text{ min}^{-1}$.

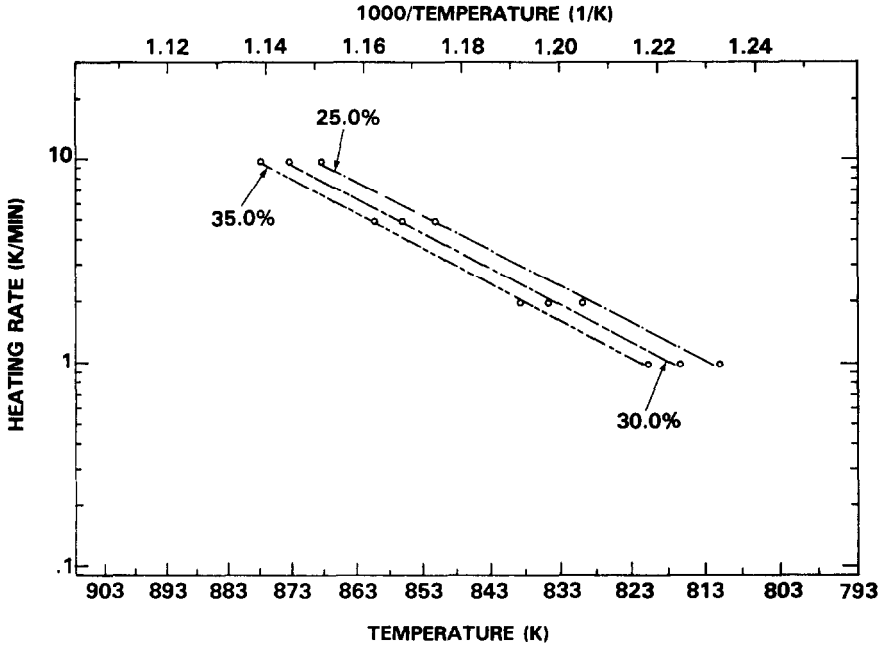


Fig. 3. Arrhenius plots of log heating rate vs. $1/T$ at 25, 30, and 35% conversion levels.

The values of E_a and Z determined from the slope of the line corresponding to 30% weight loss were 225 kJ mol^{-1} and $3.5 \times 10^{12} \text{ min}^{-1}$, respectively. This result differs considerably from the E_a values reported in other studies [10,11]. The values of the specific rate constant, $k(T)$, given in Table 1 were calculated from the E_a and Z values for temperatures in the range of thermal battery operation.

TABLE 1

Specific rate constant, $k(T)$, for decomposition of FeS_2 at battery operating temperatures

Temp. (K)	$k(T)$ (min^{-1})	Temp. (K)	$k(T)$ (min^{-1})
723.1	$2.04E-5$	813.1	0.0128
733.1	$3.39E-4$	823.1	0.0191
743.1	$5.57E-4$	833.1	0.0283
753.1	$9.04E-4$	843.1	0.0416
763.1	$1.45E-3$	853.1	0.0606
773.1	$2.29E-3$	863.1	0.0875
783.1	$3.57E-3$	873.1	0.125
793.1	$5.52E-3$	883.1	0.178
803.1	$8.43E-3$	893.1	0.250
		903.1	0.350
		913.1	0.486
		923.1	0.669

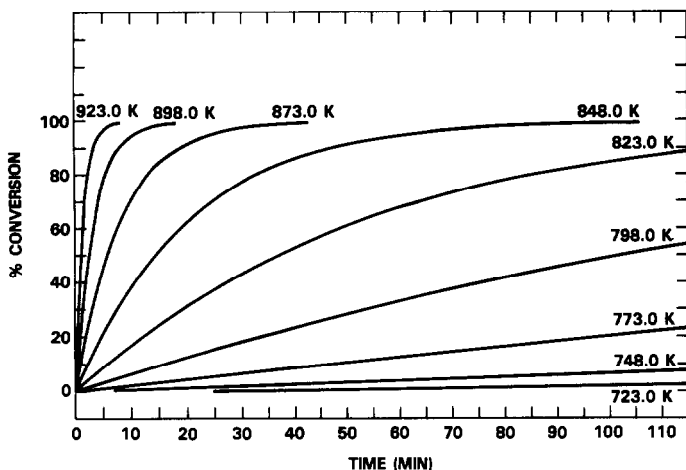


Fig. 4. Plot of percentage conversion vs. time for various battery operating temperatures.

The plots in Figs. 4 and 5 were obtained from the conversion integral for a first-order reaction

$$-\ln(1 - \alpha) = k(T)t(T, \alpha) \quad (2)$$

where α is the conversion fraction. The amount of FeS_2 decomposed as a function of time for various constant temperatures is shown in Fig. 4. Isoconversion plots at constant α of time vs. temperature to reach various decomposition levels are shown in Fig. 5. Such plots show the dramatic increase in the amount of decomposition of the FeS_2 cathode material with increasing battery operating temperatures. For a battery designed to operate 20 min at 823 K, for example, 30% of the FeS_2 would be lost parasitically via

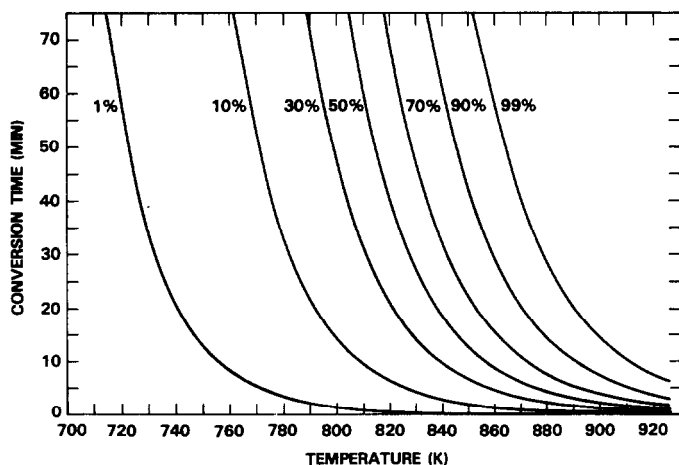


Fig. 5. Plot of conversion time vs. temperature for various decomposition levels.

thermal decomposition, as seen in Fig. 4. However, at an operating temperature of 873 K, 90% of the FeS_2 would decompose during the 20-min discharge.

In a recent study [5], lithium and lithium-alloy anode single cells employing FeS_2 cathodes were tested at current densities from 0.1 to 1.0 A cm^{-2} at temperatures from 783 to 973 K. It is seen from the results presented in Figs. 4 and 5 that serious performance degradation problems may result from the use of FeS_2 cathode material in long-life thermal batteries (discharge times up to 1 h) operating at temperatures up to 973 K.

CONCLUSION

The decomposition kinetics of FeS_2 cathode material used in thermal batteries was evaluated by TG using a variable-heating-rate method. The kinetic parameters were used to determine the extent of decomposition of the FeS_2 for typical battery discharge temperatures. The increased discharge times required for such batteries in future weapons systems may be limited by the thermal instability of the FeS_2 .

The present TG method is being used to evaluate the decomposition kinetics of both naturally occurring and synthetically prepared FeS_2 samples from various sources, in addition to other transition metal sulfides, to determine the most stable material for use in long-life thermal batteries.

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