ORIGINAL PAPER

Iron Disulfide Synthesis for Thermal Batteries Applications

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ABSTRACT: The necessity for ever more efficient and compact power sources drives the development of more durable and more power-intensive sources. Electrochemical sources include primary batteries that support a single discharge cycle and secondary batteries that support a defined number of charge-discharge cycles. Such sources should be suitable for the intended application, such as emergency systems, military and aerospace apparatus, where they must have long shelf life, high current density and reliability. Thermal batteries work with LiCl-KCl eutectic electrolyte anodes and FeS_2 cathodes. A pyrometallurgical synthesis route was studied for roasting reaction between Fe_2O_3 and vaporized sulfur to obtain FeS_2. The results obtained showed a conversion close to 90% and a high dispersion of agglomerates sizes, which disaggregated generate particles suitable for cathode manufacturing.

KEYWORDS: Roasting; Fluidized bed processors; Synthesis.

INTRODUCTION

Technological developments have been increasing the demand for more efficient and compact energy sources, which accelerate the development of more durable electrochemical sources that support a higher operating load. Electrochemical sources include primary batteries that support a single discharge cycle and secondary batteries that support a defined number of charge-discharge cycles.

In the case of mobile electrical or electronic devices, as well as other advanced applications, for example, mobile phones and electric vehicles, the solutions adopted are secondary electrochemical sources (batteries) (Strauss *et al.* 2000). It is important to note that the power source must be suitable for the application for which it was developed. Thus, in some special cases, such as emergency systems, military and aerospace apparatus, sources with long shelf life, high reliability and high current density are required. In this context, thermal cells that are primary sources, nonrechargeable and inactive at room temperature, are included.

Thermal cells are developed to ensure excellent thermal insulation, as well as a hermetic seal packaging, both conditions necessary for their working temperature. This design allows high operational performance under limit conditions, for example, high rotational speeds and high deceleration rates that can reach 16,000 times the Earth's gravity (Guidotti and Masset 2006).

The major concern with the packaging thermal insulation leads to the use of materials such as fiber-frax, fiberglass and alumina. For activation, two compounds of the highest importance are observed: $Zr/BaCrO_4$ and $Fe/KClO_4$. The first is known as pyrolant of high energy content and is responsible for ignition of the system, starting the termite burning ($Fe/KClO_4$).

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In the development of thermal cells, the latest generation system works with lithium alloy anodes, LiCl-KCl eutectic electrolytes and FeS_2 cathodes (Masset and Guidotti 2008a; Masset and Guidotti 2008b).

Therefore, the pyrometallurgical synthesis route from the sulfur roasting reaction of Fe_2O_3 with vaporized sulfur is suggested to obtain FeS_2. The conversion of the synthesis reaction strongly depends on the process variables: reaction temperature, vaporization temperature (gaseous sulfur partial pressure), nature of the raw materials and reaction time. Under more favorable reaction conditions (60 min and 500 °C) FeS_2 conversions above 95% was obtained, aggregate particles with size distribution in the range of 100 to 200 μm, with uniform and spheroidal morphology (Amorim 2004).

Thus, the purpose of this work was to study the synthesis route at high temperature from the Fe_2O_3 roasting reaction with vaporized sulfur to obtain FeS_2, as suggested by Amorim (2004), in a larger scale reactor. Thus, it is expected to contribute to the identification of operational conditions capable of obtaining a product of high purity and in larger amounts.

THERMODYNAMIC EVALUATION

The thermodynamic evaluation was performed by means of the HSC Chemistry 9 software, using the Equilibrium Compositions module by free energy minimization calculations of the reaction system.

The species $S_8(g)$ and $S_6(g)$ predominated at temperatures below 460 °C; while temperature increased, a gradual increase in the amount of $S_2(g)$ to the detriment of the other species. Above 560 °C, $S_2(g)$ is found to be the major carrier of sulfur, with compositions over 90% above 800 °C.

Then, a FeS_2 distribution surface was calculated as a function of the amount of $S_2(g)$ and reaction temperature, as shown in Fig. 1. It can be observed that FeS_2 is characterized as the only iron-bearing compound at temperatures below 600 °C and high amount of $S_2(g)$. The minimum amount of $S_2(g)$ required for complete conversion is around 2.75 kmol per kmol of Fe_2O_3. Therefore, it is observed that there is a favorable thermodynamic tendency to sulfur roasting reaction of iron oxide to FeS_2.

Calculation basis:
1 kmol of Fe_2O_3
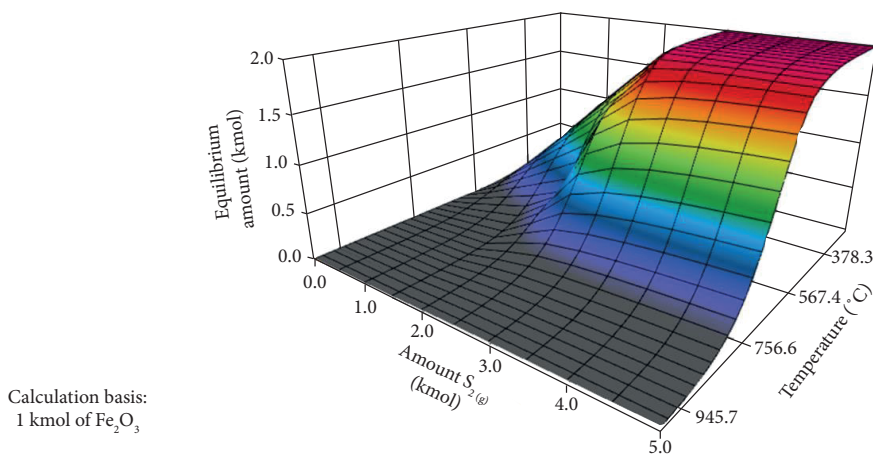
Figure 1. FeS_2 equilibrium amount surface as a function of temperature and amount of $S_2(g)$ for 1 kmol of Fe_2O_3.

METHODOLOGY

In order to obtain an efficient system, assuring a high reaction rate and a quality product, an experimental apparatus was developed to allow a sulfur roasting reaction in a fluidized bed reactor.

The reagents used are solid powder sulfur and ferric oxide (hematite, Fe_2O_3). Argon was used as carrier gas of the gaseous sulfur generated in the vaporizer system. The sulfur vaporizer system consisted of immersion heater installed in a stainless-steel container, insulated by a fiber-frax bowl (patented insulating and flexible material). The argon carrier gas passes through a porous

plate and thus transports the vaporized sulfur into the reactor, where there is another porous plate (distributor) supporting the ferric oxide powder that is fluidized by the drag force of the gas mixture and then reacts with the sulfur from the reactor atmosphere (Medeiros 2011).

RESULTS AND DISCUSSION

The conversion obtained under the different experimental conditions used in the tests, reaction temperature (T_r) and sulfur vaporization temperature (T_v), as a function of time, can be observed in Fig. 2. A minor effect of reaction temperature (T_r) on conversion can be observed. The result from the thermodynamic evaluation was already expected, as the temperature ranged from 500 to 550 °C does not suggest major changes in Fig. 1, but, kinetically, this may indicate that there are greater opportunities for gain, improving the conditions of fluidization. The strong effect of sulfur vaporization temperature (T_v) can also be observed, when increased from 250 to 350 °C, which represents a 73% increase in conversion above 1 h of reaction time.

This observation is in agreement with the behavior of sulfur vapor pressure as a function of temperature. The higher the vaporization temperature, the higher the sulfur partial pressure in the reactor and therefore the higher the reaction rate.
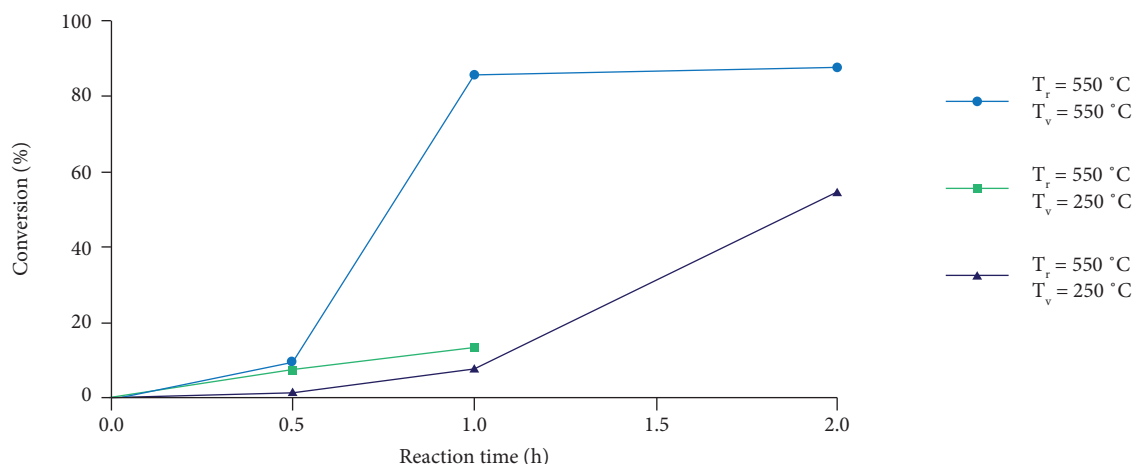
Figure 2. Conversion (%) vs. reaction time for different operating conditions, where T_r is the reaction temperature and T_v is the sulfur vaporization temperature.

CONCLUSION

The thermodynamic evaluation identified the theoretical viability of the proposed process to obtain the iron disulfide from the reaction between ferric oxide and gaseous sulfur. The evaluation of the process operational parameters showed a slight effect of the reaction temperature and a strong effect of sulfur vaporization temperature and reaction time on ferric oxide conversion.

In addition, it was identified that the vaporization temperature should be above 350 °C, as this condition provides the appropriate sulfur partial pressure to obtain FeS_2.

The maximum conversion is reached after 1 h of reaction for the vaporization temperature of 350 °C and reaction temperature of 550 °C.

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AUTHORS' CONTRIBUTION

Conceptualization, Medeiros GE and Moura FJ; Methodology, Medeiros GE and Souza RFM; Research, Medeiros GE; Writing - First version, Moura FJ and Souza RFM; Writing - Review & Editing, Moura FJ and Souza RFM; Acquisition of Funding, Moura FJ and Souza RFM; Resources, Medeiros GE and Moura FJ; Supervision, Moura FJ.

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