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Evaluation of Plasma-Sprayed CoS_2 Cathodes for Thermal Batteries

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ABSTRACT

Conventional electroactive stack components in thermal batteries are constructed from pressed-powder parts. These include the anode, separator, and cathode pellets (discs). Pressing parts that are less than 0.010" thick is difficult. The use of plasma spray to deposit thin CoS_2 cathode films onto a stainless steel substrate was examined as an alternative to pressed-powder cathodes. The plasma-sprayed electrodes were tested in single cells under isothermal conditions and constant-current discharge over a temperature range of 400 °C to 550 °C using standard LiSi anodes and separators based on the LiCl-KCl eutectic. Similar tests were conducted with cells built with conventional pressed-powder cathodes, which were tested under the same conditions for comparative purposes. This paper presents the results of those tests.

INTRODUCTION

The primary electrochemical system used in thermally activated ("thermal") batteries is the LiSi/FeS_2 (pyrite) couple. These batteries are the primary power source for nuclear weapons and missile applications. The immobilized electrolytes used for these applications include the LiCl-KCl eutectic that melts at 352 °C and the all-lithium LiCl-LiBr-LiF minimum-melting electrolyte that melts at 436 °C. Thermal batteries are inert until an internal heat source raises the temperature of the battery stack above the melting point of the electrolyte. Until the internal pyrotechnic heat source is ignited, the batteries are inert and have an almost unlimited shelf life.

The cathode, separator, anode, and pyrotechnic source are prepared by cold pressing of powders in dies. This is a slow and labor-intensive process. The deposition of a cathode coating onto a current-collector substrate could dramatically reduce battery costs while still maintaining the desired functionality. In earlier work, we were able to demonstrate this concept by plasma spraying thin pyrite films onto 304 stainless-steel current collectors *(1-4)*. After optimization of the spray conditions, deposits with good adhesion were obtained that performed well under low-rate to moderate-rate conditions.

In this work, we report on the results of characterization tests of CoS_2 plasma-sprayed cathodes in single cells over a temperature range of 400° to 550 °C. Standard flooded LiSi anodes and separators based on the LiCl-KCl eutectic and MgO binder were used. For comparison purposes, conventional single cells built with pressed-powder pellets were also tested under the same conditions.

EXPERIMENTAL

Plasma Spraying

The average particle size of the as-received CoS_2 powder was nominally ~6-7 μm. The CoS_2 was obtained from Cerac (Butler, WI) and was vacuum dried at 120 °C for 16 h before use. The dried CoS_2 powder was mixed with cornstarch or sulfur powder and then ball milled, to improve the flowability.

Plasma spraying was carried out with a Metco 9MB plasma spray system (Metco, Westbury, NY). A dc arc current of 200 A to 400 A was generated in the copper nozzle. Argon passing through the dc-arc was heated to >9,000 °C and ionized. The CoS_2 powder was fed radially into the plasma stream near the nozzle exit at a rate of 1 kg/h to 5 kg/h. The plasma output was directed to the supported 1.25"-dia. by 0.005" thick 304 stainless steel substrates, positioned 5 mm to 10 mm away.

Since CoS_2 is susceptible to oxidation at elevated temperatures, the plasma spraying was carried out using an inert-gas shroud around the sample

Materials

Single cells 1.25" in diameter were built with the plasma-sprayed CoS_2 cathodes and standard anodes and separators. The anode composition was 75% of 44% Li/56%[a] Si alloy (Eagle Picher) and 25% LiCl-KCl eutectic electrolyte (melting point of 352 °C). The separator composition was 65% LiCl-KCl eutectic and 35% MgO (Merck Maglite 'S').

[a] Unless noted otherwise, all compositions are reported in weight percent.

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The mass of active CoS_2 in each cathode sample was measured before each test to allow calculation of the gravimetric efficiency during discharge. Prior to use, the plasma-sprayed cathode coupons were leached with CS_2 to remove excess sulfur. The thickness of the plasma-sprayed electrodes ranged from 0.010" to 0.015". Standard cells were also tested using conventional pressed-power cathodes containing 73.5% CoS_2/25% separator/1.5% Li_2O. All cell assembly and handling operations were conducted in a dry room maintained at <3% relative humidity.

Electrochemical Testing

The cells were placed between heated stainless-steel platens at the desired temperature using an applied pressure of 8.0 psig. They were discharged galvanostatically between heated platens at 400 °C to 550 °C. All tests were carried out under computer control in a glovebox under an atmosphere of high-purity argon. The cells were discharged to a cutoff voltage of 1.25 V. A steady-state current of 1 A (~125 mA/cm^2) was used with a 0.5-s, 2-A (~250 mA/cm^2) pulse applied every 30 s. High-speed digital voltmeters were used for digitizing the cell voltage and current during the pulse, to allow calculation of the overall cell polarization.

The cells were placed on open circuit for 60 s prior to discharge, to allow them to thermally equilibrate before applying the load. Each test condition was replicated at least once.

RESULTS AND DISCUSSION

Standard Pressed-Powder Cathodes

The effects of temperature on the discharge voltage of standard cells and the corresponding polarization behavior are summarized in Fig. 1. The cell lifetime was greatly extended at the higher temperatures, relative to 400 °C. There was little difference in performance of the cells at temperatures of 450 °C and 550 °C. The drop-off in voltage at 400 °C was accompanied by a corresponding rise in the cell polarization. This is a result of severe concentration gradients of Li^+ at the anode-separator interface. At this temperature, the cell is only 48 °C above the melting point of the eutectic. As the Li^+ gradient builds up during discharge, there is a localized shift in the melting point of the electrolyte to higher temperatures with the accompanied precipitation of LiCl. This shift off eutectic causes a rapid increase in the cell resistance. This is not a problem at the higher temperatures at this discharge rate.

Plasma-Sprayed CoS_2 Cells

A typical discharge trace at 400 °C and the corresponding polarization of a cell made with a plasma-sprayed cathode are shown in Fig. 2. The large elevated voltage at the beginning of discharge is due to the presence of free sulfur, which has a higher voltage than the CoS_2 phase. X-ray diffraction analysis of the cathode after leaching with CS_2 showed the major phases to be S and CoS_2. This suggests that the residual sulfur was more tightly bound with the small particle size of CoS_2 used for plasma spraying. In the case of FeS_2, CS_2 leaching readily removed the bulk of the sulfur because of the much larger size—by a factor of five or more—of the FeS_2 particles. About 5.5% to 9.0% loss of sulfur was noted with the plasma-sprayed cathodes in this initial study. The data of Fig. 2 indicate that a substantial amount of sulfur still remained in the electrode after CS_2 leaching. Minor amounts of lower sulfides of cobalt were noted in the plasma-sprayed deposit, as well. The emf of an electrochemical couple is directly related to the phases that are present. There is a slight inflection in the voltage evident near 600 coulombs/g (C/g).

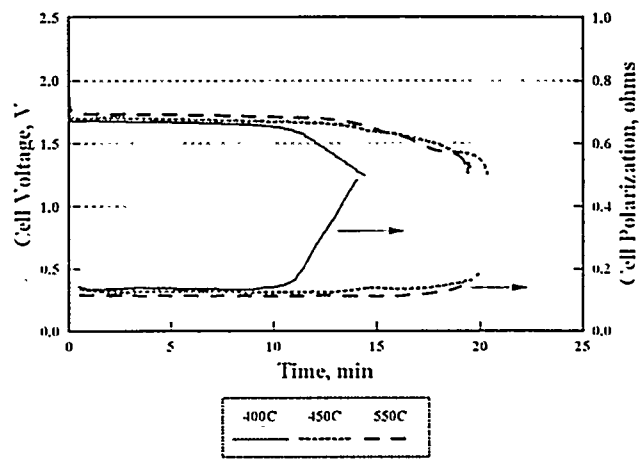

Fig. 1. Cell Voltage and Polarization as a Function of Temperature for Standard LiSi/LiCl-KCl/CoS_2 Cells Discharged at 1 A Background with 0.5-s/2-A Pulse every 30 s.

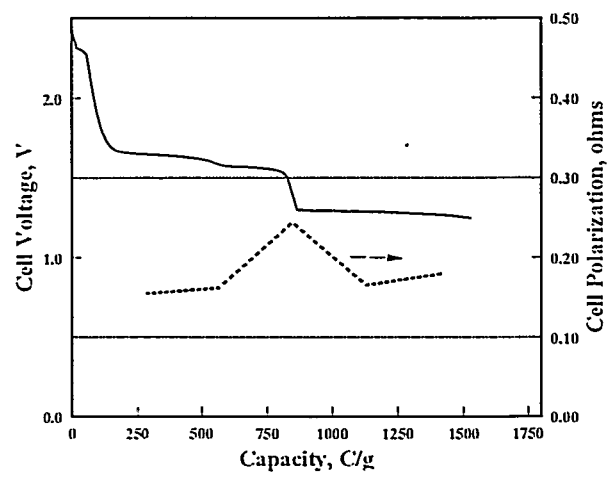

Fig. 2. Discharge at 400 °C of LiSi/LiCl-KCl/Plasma-Sprayed CoS_2 Cell at 1 A Background with 0.5-s/2-A Pulse every 30 s.

This indicates the onset of discharge of a new phase. possibly a metastable sulfide of cobalt. The major voltage transition near ~840 C/g is due to the following reaction:

$$CoS_2 + 4/3\ e^- \text{ -----> } Co_3S_4 + 2/3S^{-2} \qquad [1]$$

This transition occurred at about 80% of theoretical. This indicates that, at this discharge rate, the first discharge phase, Co_3S_4, is discharging before all of the CoS_2 is consumed. This voltage transition is not evident in the data for the standard cells (Fig. 1) because the mass of material used in the standard cell was 7 to 10 times greater.

The polarization in the $LiSi/CoS_2$ cells is primarily cathode related at the start and middle of discharge. It reflects voltage losses due to the internal cell resistance plus those associated with Li^+ concentration gradients in the separator. The maxima in cell polarization (Fig. 2) is attributed to the increase in resistance of the first discharge phase that forms. Co_3S_4. This phase probably has a higher resistance than the CoS_2 starting phase. (This is analogous to what is observed during the discharge of FeS_2.) The Co_3S_4 then discharges to a lower sulfide phase.

$$3Co_3S_4 + 8\ e^- \text{ -----> } Co_9S_8 + 4S^{-2} \qquad [2]$$

The voltage and polarization of a cell built with plasma-sprayed CoS_2 is compared in Fig. 3 to those of a standard cell for a discharge temperature of 400 °C. The data have been normalized on a C/g basis. for ease of comparison.

The biggest difference is the higher initial voltage and corresponding capacity of the cell with the plasma-sprayed cathode. As mentioned above, this reflects the presence of free sulfur. The minor voltage transition noted for this cell is totally absent in the voltage response of the standard cell. Also, the initial increase in resistance observed at the major voltage transition near 840 C/g for the cell with the plasma-sprayed cathode was much less and showed only a weak maximum. In contrast, the polarization continued to increase for the standard cell. This may be a result of the much thicker cathode pellet in the latter case.

The relative performance of the standard and plasma-sprayed cathodes at the highest temperature of 550 °C are compared in Fig. 4. The cell with the plasma-sprayed cathode showed a voltage transition near 300 C/g which occurred much sooner than that for the standard cell of ~1,000 C/g. This indicates that there was less active mass of CoS_2 available in the plasma-sprayed cathode. The initial voltage excursion at the start of discharge was reduced due to loss of sulfur while the cell was on open circuit for 60 s prior to discharge. The front end of the discharge now looked more like that of the standard cell. This behavior was not evident during the 400 °C test (Fig. 3) due to discharge limitations imposed by concentration gradients that resulted in a much lower depth of discharge.

The cell with the plasma-sprayed cathode also showed a very long second voltage transition which had not yet appeared in the case of the standard cell. This again could reflect the presence of a metastable lower sulfide of cobalt with a slightly higher emf than the equilibrium Co_8S_9 phase. The polarization (cell resistance) was also slightly higher for the cell with the plasma-sprayed electrode. This could be due to reduced particle-particle contact imparted by the excess sulfur initially present. This contrasts to what was observed in the case of pyrite. where a reduction in cell polarization was noted. as a result of reduced interfacial resistance. *(1)*

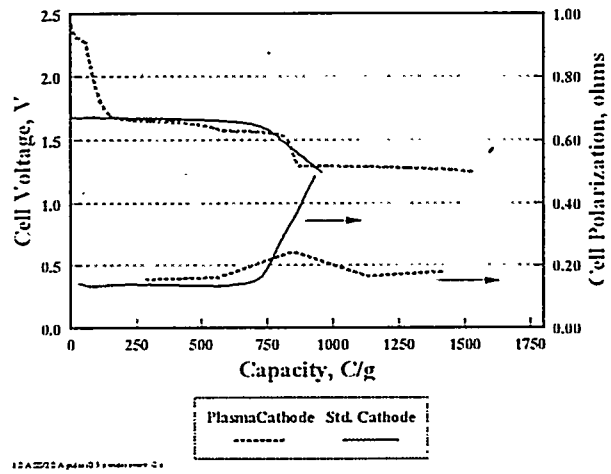

Fig. 3. Comparison of Voltage and Polarization for Cells Discharged at 400 °C with Plasma-Sprayed CoS_2 Cathode and Standard Cathode.

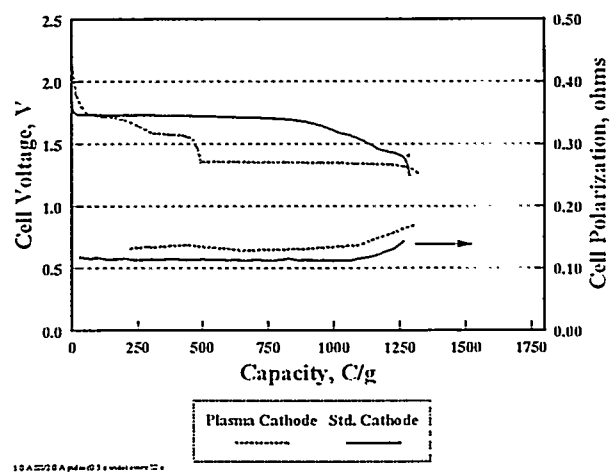

Fig. 4. Comparison of Voltage and Polarization for Cells Discharged at 550 °C with Plasma-Sprayed CoS_2 Cathode and Standard Cathode.

Future Work

While these preliminary results are encouraging, there are several areas that require further work. The amount of free sulfur must be reduced in the plasma-sprayed deposit. This will require adjustment of the spraying conditions or the use of alternative additives to repress thermal decomposition of the CoS_2 during spraying. To increase the power capability of these cathodes, the introduction of controlled porosity will be examined, to allow electrolyte to penetrate to the rear of the cathode during discharge, thus effectively increasing the electroactive surface area. Once those objectives have been attained, five-cell batteries will be tested to properly evaluate these thin-film deposits under the dynamic conditions of a thermal-battery environment.

CONCLUSIONS

Preliminary tests with plasma-sprayed CoS_2 cathodes show that plasma spraying can be applied to this material as well as the less-thermally-stable pyrite material. The performance of plasma-sprayed cathodes in single cells at 400 °C is comparable to that of the standard press-powder cathodes, in terms of capacity and overall cell polarization.

At 550 °C, however, the performance of cells with plasma-sprayed cathodes was inferior to that of the standard cells. The upper-voltage plateau is much less due to a low content of CoS_2 in the deposit. This is a result of excessive amount of free sulfur being present. There is also evidence for a metastable phase that has a slightly higher emf than that expected for the equilibrium Co_8S_9 phase. Better control of the plasma-spraying conditions should mitigate this problem to a large extent.

The presence of excessive free sulfur in the thin-film deposits must be eliminated. Fugitive sulfur in a thermal-battery environment will lead to chemical reaction with the LiSi anode and cause a thermal runaway condition that can destroy the battery. Other sulfur removal techniques need to be explored to minimize the amount of free sulfur or alternative agents for inhibiting thermal decomposition during plasma spraying need to be considered.

It is possible to thermal spray thin films (0.010" thick) of CoS_2 that are suitable for use in a thermal battery. Once the sulfur and phase purity issues had been adequately addressed, it should be possible to substantially improve the energy density of thermal batteries by using thin-film cathodes of CoS_2, FeS_2, or other suitable sulfides prepared by plasma spraying.

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