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Performance of thermal cells and batteries made with plasma-sprayed cathodes and anodes

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Abstract

Cathodes for thermally activated ("thermal") batteries based on CoS_2 and LiCl–LiBr–LiF electrolyte and FeS_2 (pyrite) and LiCl–KCl eutectic were prepared by thermal spraying catholyte mixtures onto graphite–paper substrates. Composite separator-cathode deposits were also prepared in the same manner by sequential thermal spraying of LiCl–KCl-based separator material onto a pyrite-cathode substrate. These materials were then tested in single cells over a temperature range of 400–600 °C and in 5-cell and 15-cell batteries. A limited number of battery tests were conducted with the separator-cathode composites and plasma-sprayed Li(Si) anodes—the first report of an all-plasma-sprayed thermal battery. Thermal-spraying offers distinct advantages over conventional pressed-powder parts for fabrication of thin electrodes for short-life thermal batteries. The plasma-sprayed electrodes have lower impedances than the corresponding pressed-powder parts due to improved particle–particle contact.

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1. Introduction and background

1.1. Characteristics of thermally activated ("thermal") batteries

A thermal battery is a pyrotechnically initiated molten-salt primary reserve battery that is used as a power source for guidance systems, radar and electronics in defense applications (e.g., missiles, torpedoes) [1,2]. The electrolyte in a thermal battery is a solid, non-conducting inorganic halide salt (typically LiCl–KCl eutectic) at ambient temperatures. However, in the molten state, the battery impedance becomes very low, allowing large amounts of power to be withdrawn. The electrolyte in the separator is immobilized by special kinds of MgO powders. The electrolyte is melted by an integral pyrotechnic heat source within the battery stack. The battery is activated by either electrical or mechanical methods. The battery stack is comprised of cells of pressed-powder components (discs) that include the anode, separator, cathode and heat pellet (pyrotechnic). The cells are stacked to obtain the desired output voltage.

The primary electrochemical system used in today's thermal batteries is the Li(Si)/FeS_2 couple that has a nominal output voltage of 1.94 V at 500 °C. The FeS_2 is derived from natural mineral pyrite, which is relative inexpensive. For special higher-power applications, the FeS_2 is replaced by CoS_2, which is synthetically made and much more expensive. There are inherent disadvantages using pelletized parts in battery construction. One is that larger presses are needed for the larger-diameter pellets. There are mechanical integrity problems when very thin (<0.5-mm thick) pellets are prepared. This necessitates using thicker (heavier) pellets than the application requires just so that the pellets can be handled. Plasma spraying offers some inherent advantages over the pressing of piece parts. Very thin films can be prepared without the constraints of mechanical presses and the process lends itself to semi-continuous processing. In addition, the electrochemical performance is enhanced.

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1.2. Plasma-sprayed, nanostructured CoS_2

The improved electrochemical performance of plasma-sprayed (PS) cathodes over pressed-powder ones was demonstrated in earlier work at US Nanocorp® (USN) [3,4]. The feasibility of using a nanostructured CoS_2-based catholyte feedstock was shown [5–7]. The physical properties of this feedstock were much different from those of the FeS_2-based material that used natural (mineral) pyrite. In the latter case, the FeS_2 particles were quite large (35–45 μm), which contrasts with the nanostructured nature of the synthetic CoS_2.

When the nanostructured CoS_2 was substituted for the coarse FeS_2 material in the feedstock, the increase in the electrolyte content of the deposit was much less. In the case of the LiCl–KCl electrolyte, as the electrolyte content of the feedstock was increased from 24 to 39%, the amount in the deposit rose above these values, from 36 to 51%. This is a much lower increase than that observed for natural pyrite, which increased by more than a factor of two under similar conditions. These data indicate that the particle size of the metal disulfide in the catholyte is crucial to minimize electrolyte buildup during plasma spraying. The fine-grained, nanostructured materials are much less likely to bounce off the substrate compared to the larger (heavier) coarser particles in the case of the natural-pyrite feedstock. This reflects the large difference in kinetic energies (viz., mv^2) involved for the two materials. Thus, these data suggest that one should use nanosized synthetic, rather than natural (mineral), pyrite in the feedstock for plasma spraying.

When catholyte feedstock was prepared with the nanostructured CoS_2, it was extremely difficult to obtain a flowable material that could be fed into the plasma-spray gun. Initially, sulfur was used as a thermal-barrier coating (to prevent thermal decomposition of CoS_2 to Co_3S_4 and S_2 vapor) and to act as a “glue” to hold the particles together during spraying. The excess sulfur that was present required its removal to avoid a large voltage transient during the initial discharge of cathodes made with this material. However, when this excess sulfur was removed, the physical integrity of the deposit was considerably weakened.

Subsequently, an electrolyte-based thermal-barrier coating was developed that avoided the problems associated with the use of the sulfur as a co-spray additive. The resulting deposit tended to be fairly porous, however, which was not desirable, as this reduces the overall energy density of the electrode and results in a structurally inferior product. This catholyte material was also much more difficult to spray than that based on coarse natural pyrite. Multiple passes were required to build up sufficiently thick layers for evaluation in single cells and batteries—much more than for the pyrite analog.

Due to the higher power capability of CoS_2 relative to FeS_2, it would be desirable to use an all-Li (e.g., LiCl–LiBr–LiF) electrolyte rather than the LiCl–KCl eutectic electrolyte that was used in these experiments. The lack of K^+ in the melt avoids the Li^+ gradients that lead to severe concentration polarization during discharge, with the resulting undesirable rapid increase in impedance. Unfortunately, it was extremely difficult to spray CoS_2 catholytes based on the all-Li electrolyte. Part of this problem may be due to the higher melting point of this electrolyte (436 °C) versus that for the LiCl–KCl eutectic (352 °C). Or, it may be due to differences in surface tension and viscosity, which impact the extent of wetting of the sulfide particles.

1.3. Multi-layered PS electrodes

A second area of interest in this work was the development of a process for plasma spraying multiple components of a thermal cell. Specifically, it was intended to plasma spray the separator layer on top of the cathode layer to make composite electrodes that could then be paired with either cold-pressed (CP) or PS Li(Si) anodes. Based on the work done at Creare (Hanover, NH) under a related U.S. Navy Small Business Innovative Research (SBIR) Phase II program [8], it should also be possible to then spray the anode directly on top of the two-layered cathode-separator composite to fabricate a complete cell by thermal spraying. Ultimately, it would be desirable to plasma spray all of the individual components to prepare a complete cell. This would greatly reduce battery construction time and costs.

This paper will document the results of single-cell tests and tests with 15-cell batteries built with the single-layer CoS_2-based PS cathodes and the all-Li electrolyte as well as similar tests with the two-layered FeS_2-based PS cathodes and the LiCl–KCl eutectic. Finally, the results of preliminary battery tests with separator-cathode composites with PS anodes will be presented. These electrolytes were selected because they are the ones most commonly used in thermal batteries. Other electrolytes could potentially be used for thermal-barrier coatings, except for those based on iodide, which would be oxidized to iodine upon passage through the plasma.

2. Experimental

2.1. Plasma spraying

The compositions of the feed materials used for the plasma-spraying tests are summarized in Table 1.

The catholyte mixtures were fused for several hours under argon at 400 °C followed by granulation to prepare the feed-

Table 1
Composition of feedstocks used for plasma-spraying tests

Active material	Content (%)	Electrolyte	Content (%)	Lithiation agent	Content (%)
CoS_2	68.0	LiCl–LiBr–LiF	29.1	Li_2O	2.9
FeS_2	68.0	LiCl–KCl	29.1	Li_2O	2.9
44% Li/56% Si (−270 + 325 mesh)	100	N.A.	0	N.A.	0

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