Review of US Nanocorp® - SNL Joint Development of Thermal-Sprayed Thin-Film Cathodes for Thermal Batteries

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ABSTRACT

The use of plasma spray to deposit thin metal-sulfide cathode films is described in this paper. Conventional electroactive stack components in thermal batteries are constructed from pressed-powder parts that are difficult to fabricate in large diameters in thicknesses <0.010". Plasma-sprayed electrodes do not suffer from this difficulty, allowing greater energy densities and specific energies to be realized. Various co-spraying agents have been found suitable for improving the mechanical as well as electrochemical properties of plasma-sprayed cathodes for thermal batteries. These electrodes generally show equal or improved performance over conventional pressed-powder electrodes. A number of areas for future growth and development of plasma-spray technology will be discussed.

Introduction

We have been extensively involved in the development of thermal-spray technology for preparation of metal-sulfide electrodes for use in thermally activated ("thermal") batteries, since November, 1997. The principal couple used in these batteries is Li(Si)/FeS\textsubscript{2}. For high-power applications, the Li(Si)/CoS\textsubscript{2} couple is also used. These batteries are the primary power source for nuclear weapons and missile applications. The ionically conductive molten-salt electrolytes used in this technology are extremely conductive (several orders of magnitude greater than for sulfuric acid or KOH solutions at room temperature). This high conductivity is responsible for the high power levels that are possible with such batteries.

In earlier work, we were able to demonstrate the first use of thermal spray for the preparation of pyrite-based cathodes for thermal batteries based on the LiCl-KCl eutectic that melts at 352 °C (1-5). We were also able to extend this initial effort to include CoS\textsubscript{2} cathodes(6). It was necessary to add sulfur as a thermal-barrier agent to prevent decomposition of the pyrite in the plasma.

In this paper, we report on the results of recent characterization tests of pyrite that was co-sprayed with electrolyte. Efforts to control the intrinsic voltage transient that caused problems with past plasma-sprayed cathodes are also addressed. In addition, we outline the direction in which plasma spraying can go with other battery technologies. The promises of future efforts will allow a quantum leap in the thermal battery technology. In addition, there can be corresponding improvement realized upon successful transfer of this technology to lithium-ion batteries and fuel cells.

Experimental

Plasma Spraying

The pyrite used for the plasma-spraying tests was ~325 mesh in size. This was blended with 20% LiCl-KCl eutectic electrolyte and fused under argon at 400 °C for several hours. After ballmilling, the powder was fed to the plasma gun. (Details concerning the plasma-spraying conditions can be found in reference 6.) Electrode substrates of 304 stainless steel 1.25" in diameter by 0.005" thick were used for single-cell tests.

Materials

Single cells 1.25" in diameter were built with the plasma-sprayed cathodes and standard anodes and separators. The anode composition was 75% of 44% Li/56% 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').

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 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 1.00 V. Steady-state currents of 1 A (125 mA/cm\textsuperscript{2}) or 2 A (250 mA/cm\textsuperscript{2}) were used with a 0.5-s, 2-A (250 mA/cm\textsuperscript{2}) or 4-A (500 mA/cm\textsuperscript{2})

\textsuperscript{a} All compositions are reported in weight percent.
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mA/cm²) 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.

Results

One of the main driving forces for development of a viable plasma-spray process for electrode fabrication is that very thin films can be deposited in this fashion. For some thermal-battery applications, active electrodes are many times greater than the theoretical capacities required for an application. This excess unutilized material reduces the overall energy density and specific energy of the batteries. There are serious problems with the fabrication of very thin (<0.010" thick) electrodes that are over 5" in diameter. In many cases, it is not possible to spread the small amount of powder into the die cavity used to make the pellets without risking low-density or soft spots in the pellets. Handling of such parts during battery construction—if they can be fabricated at all—is difficult if not impossible. This results in low parts yield and increased production costs. Plasma spraying also has appeal since it is versatile and is carried out under strict computer control. This allows a wide range of thickness of electrodes to be readily fabricated once the spray parameters have been clearly defined.

Co-Spray with Sulfur

In earlier tests, it was necessary to co-spray the pyrite with 15% to 30% elemental sulfur to prevent complete thermal decomposition to FeS during spraying. Pyrite becomes thermal unstable above 550 °C, as shown by equation 1:

$$\text{FeS}_2 \rightarrow \text{FeS} + 0.5 \text{S}_2 \text{(g)}$$  \[1\]

Addition of sulfur prevents this reaction by taking place to any significant extent while the pyrite travels through the plasma. However, some residual sulfur remains in the deposit and must be removed prior to cell testing. Any free sulfur gives rise to an elevated voltage due to its higher potential relative to FeS²⁻. The sulfur also served to bind the pyrite particles together, so that its removal tended to weaken the deposit and make it somewhat fragile. Flexing of the substrate could result in flaking of the pyrite deposit. This is undesirable from a handling perspective during battery construction.

Even with these limitations, the viability of this technology was demonstrated over a range of temperatures at a reasonable current density (125 mA/cm²) in earlier tests (1-5). Representative data are shown in Figure 1, which compares the discharge of CS₂-leached plasma-sprayed pyrite to that of a standard pressed-powder lithiated cathode. (The capacities are corrected to the active content of pyrite.)

Several features are evident in these data. The cell with the plasma-sprayed cathode ran considerably longer and showed much lower overall polarization. This is attributed to the better particle-particle contact that results as a result of the plasma treatment. The good interfacial contact that results from the plasma spraying also contributes to a lower polarization. The maximum in polarization evident in the standard cell is virtually absent with the cell with the plasma-sprayed cathode.

Even with the removal of residual sulfur, there is still a problem with an undesirable voltage transient at the initiation of discharge. This is not a problem with conventional lithiated cathodes that contain Li₂O additive. The Li₂O acts to eliminate the transient by fixing the Li activity in the cathode (7,8):

Thermal batteries are designed to utilize the upper voltage plateau during discharge. The discharge process is illustrated by equation 2:

$$\text{FeS}_2 + 1.5\text{Li}^+ + 1.5\text{e}^- \rightarrow 0.5\text{Li}_3\text{Fe}_2\text{S}_4$$  \[2\]

This further discharges according to equation 3, during the next short voltage plateau:

$$0.5\text{Li}_3\text{Fe}_2\text{S}_4 + 0.5\text{Li}^+ + 0.5\text{e}^- \rightarrow \text{Li}_2\text{FeS}_2$$  \[3\]

This phase, in turn, undergoes a two-electron reduction to Fe, according to equation 4:

$$\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Fe} + 2\text{Li}_2\text{S}$$  \[4\]

It is this later discharge that is responsible for the lower-voltage plateau. Under high-rate discharge, a mixed potential can result, where simultaneous discharge of the...
various phases occurs, without well defined voltage plateaus for each phase.

**Li$_2$O Treatment**

One approach that was explored to address the voltage-spike problem was coating of the plasma-sprayed electrode with Li$_2$O powder after wetting slightly with water. The voltage profile at 450 °C and a background load of 125 mA/cm$^2$ is shown in Figure 2 for a Li(Si)/FeS$_2$ cell that used a vacuum-dried, CS$_2$-leached, plasma-sprayed sample coated with 130 mg of Li$_2$O. Comparable data for an uncoated plasma-sprayed cathode are included for comparison. The presence of Li$_2$O dramatically reduced the initial voltage transient but at the expense of increased polarization (impedance).

![Figure 2](image)

**Figure 2.** Comparison of the Performance of Li(Si)/LiCl-KCl/FeS$_2$ Cells with as-Leached Plasma-Sprayed Cathode and a Li$_2$O-Coated (0.13 g) Plasma-Sprayed Cathode at 450 °C and 125 mA/cm$^2$ Background with 0.5 s, 250 mA/cm$^2$ Pulses every 30 s.

The differences were even more pronounced at double the load, as shown in Figure 3. (Data for a pressed-powder cathode are also shown.)

![Figure 3](image)

**Figure 3.** Comparison of the Performance of Li(Si)/LiCl-KCl/FeS$_2$ Cells with as-Leached Plasma-Sprayed Cathode, a Li$_2$O-Coated (0.15 g) Plasma-Sprayed Cathode, and a Standard Pressed-Powder Cathode at 450 °C and 250 mA/cm$^2$ Background with 0.5 s, 500 mA/cm$^2$ Pulses every 30 s.

Coating of the electrode with a 5% solution of Li$_2$O, followed by vacuum drying, was much more effective. There was no measurable effect on the voltage spike at <1% Li$_2$O (relative to FeS$_2$ mass). However, at levels of 7% Li$_2$O or more, substantial improvements were obtained. The results for a single-cell test at a level of 15.7% Li$_2$O are shown in Figure 4 for a temperature of 450 °C and a load of 125 mA/cm$^2$, along with data for an untreated plasma sprayed cathode for comparison.

The initial voltage spike was completely eliminated for the cell with the Li$_2$O coating on the cathode. The overall polarization for this cell was comparable to the cell without the coating. Application of the Li$_2$O coating by an aqueous process allows much better control of the overall final film noted for the cells with heavier powdered Li$_2$O coatings.

An alternative method of applying the Li$_2$O is to add it to the electrolyte, during co-spraying with electrolyte (discussed in the next section of this report). This is the preferred approach, as it minimizes the number of processing steps. Initial results are promising and more work is currently underway to optimize the process.
Co-Spraying with Electrolyte

The use of KCl-LiCl eutectic electrolyte for co-spraying instead of sulfur was studied. This avoids the need for removal of residual sulfur from the deposit, which can result in damage to the structural integrity of the deposit. The heat required for melting of the electrolyte serves to allow the electrolyte coating to function as a thermal barrier for the pyrite particles as they traverse the high-temperature plasma, thus preventing thermal decomposition (eqn. 1).

This LiCl-KCl electrolyte is an integral part of the separator in a thermal cell. It must penetrate the pyrite deposit to be able to electrochemically access as much of the deposit as possible. By adding the electrolyte to the pyrite feedstock, it is directly incorporated into the deposit, which should enhance the electrochemical performance.

In initial tests, the electrolyte was blended with the pyrite and the mixture was fused at 400 °C to allow good coating of the pyrite particles by the molten electrolyte. The electrolyte concentration of the feedstock was typically 15% to 20%. After spraying, the electrolyte concentration had increased to ~45%. A scanning electron photomicrograph of a representative deposit is shown in Figure 5. A cross-sectional view of the same deposit is shown in Figure 6. The deposit was about 150 µm thick and was dense and uniform in thickness. X-ray diffraction (XRD) analysis showed the presence of pyrohite (Fe_{1-x}S) as well as pyrite.

Figure 5. Surface Topography of Electrolyte-FeS_{2} Plasma-Sprayed Deposit (300 µm Marker).

The relative performance of the CS_{2}-leached plasma-sprayed pyrite and water-leached electrolyte-coated deposit is compared in Figure 7. The voltage and polarization behavior was almost the same for the two cells. As expected, the voltage transient still remained. Similar performance was obtained when the electrolyte was not leached from the deposit.

Besides the good electrochemical performance that was realized with this approach, a secondary mechanical benefit also was obtained. The adhesion of the deposit to the substrate was exceptional, allowing the electrode to be bent 180° without spalling of the deposit. This was not possible for deposits co-sprayed with sulfur.

Follow-up tests were also conducted using graphite paper (Grafoil®) as a substrate. This material is normally used as a reinforcing substrate as well as a current collector when making pressed-powder cathodes. Spraying directly onto

Figure 6. Cross-sectional View of Plasma-Sprayed Deposit shown in Figure 5 (150 µm Marker).

Figure 7. Comparison of the Performance of Li(Si)/LiCl-KCl/FeS_{2} Single Cells at 450 °C Made with Sulfur-Coated and Electrolyte Coated-Plasma-Sprayed Pyrite. (Background Load of 125 mA/cm^{2} was Increased to 250 mA/cm^{2} for 0.5 s every 30 s.)
sheets of the graphite paper greatly facilitates battery construction. Instead of using expensive dies for pressing powders, one can now simply use inexpensive cutters to cut the discs of the desired diameter directly from the sheet electrode. Thus, fabrication of 7"-diameter electrodes becomes as easy as 2"-diameter electrodes. The force needed to make the corresponding pressed-powder electrodes will increase as the square of the diameter, requiring the use of enormous and expensive presses. The use of sprayed graphite-paper sheets translates into reduced labor and materials costs that will ultimately result in less expensive batteries. It should be possible to establish a commercial process that runs continuously rather than in the batch mode now used for pelletizing.

**Future Work** — Currently, other electrolytes are being examined for co-spraying with pyrite and other metal sulfides. Both halide-based as well as no-halide salts are under investigation. An all-Li, minimum-melting electrolyte containing LiCl-LiBr-LiF which melts at 436°C will be examined, for comparison to the results obtained with the LiCl-KCl eutectic which melts at 352 °C. This electrolyte is the one of choice for high-power applications.

The effect of melting point and heat of fusion are an integral part of the study. Both mechanical and electrochemical properties of the deposits are important for successful implementation of this technology. Initial tests indicate adhesion of the electrolyte-pyrite deposit on graphite paper as good as that obtained on 304 stainless steel. Once single-cell screening tests have been complete, follow-up battery tests are planned to study electrode performance under dynamic conditions.

**Plasma Spraying of CoS₂**

The initial promising results with FeS₂ were extended to include another metal disulfide, CoS₂, which is used in high-power batteries. This material does not occur as a natural mineral as does pyrite but must be synthesized. It is available in a finely divided form with an average particle size of 7 μm. This is much smaller than the size of the pyrite particles of <40 μm. Consequently, an extensive effort was necessary to make this finer material suitable for spraying. By agglomeration using a polyvinyl alcohol (PVA) solution, it was possible to obtain sprayable material.

The initial tests were conducted using a feedstock with 20% to 30% sulfur. The results of single-cell test using CS₂-leached plasma-sprayed deposit are compared in Figure 8 with a cell using a lithiated pressed-powder cathode. The biggest difference is the higher initial voltage and corresponding capacity of the cell with the plasma-sprayed cathode. This reflects the presence of electroactive free sulfur even after leaching with CS₂. XRD analysis confirmed the presence of sulfur, Co₉₆S, as well as CoS₂ (catterite). The free sulfur is probably responsible for the higher polarization for the cell with the plasma-sprayed electrode. Globules of sulfur are visible in the SEM photomicrograph of the deposit in Figure 9. This deposit had higher porosity and lower strength than did the corresponding pyrite film.

![Figure 8. Comparison of Voltage and Polarization for Cells Discharged at 400 °C with Plasma-Sprayed CoS₂ Cathode and Standard Cathode. (Background Load of 125 mA/cm² was Increased to 250 mA/cm² for 0.5 s every 30 s.]

![Figure 9. Surface Topography of CoS₂–S Plasma-Sprayed Deposit (300 μm Marker).]

The deposit composition differed greatly from the feed composition. Thermogravimetric analysis (TGA) showed that the as-deposited electrode contained almost 63% S—over twice that in the feedstock. After leaching with CS₂, the observed weight loss was reduced to slightly under 17%. The remaining sulfur was not removed for several possible
reasons. First, the solution was not agitated during stirring, to prevent loss of active material, since adhesion was not as good as observed with FeS$_2$-S precursors. A second possibility is that some sulfur was trapped in the sample, perhaps in closed pores, and was not accessible to the CS$_2$. This residual sulfur is readily removed, however, by thermal treatment; removal of sulfur is complete by 300°C.

The upper voltage plateau involved the following discharge:

$$\text{CoS}_2 + \frac{4}{3}e^- \rightarrow \text{Co}_9 \text{S}_4 + \frac{2}{3} \text{S}^{2-} \quad [5]$$

This phase can further discharge as indicated in equation 6:

$$3\text{Co}_9 \text{S}_4 + 8e^- \rightarrow \text{Co}_9 \text{S}_8 + 4\text{S}^{2-} \quad [6]$$

The excessive sulfur present causes unacceptable voltage transients from a battery-design perspective, as well as taking up valuable space in the electrode.

**Future Work – Plasma-spray**

Tests are scheduled with CoS$_2$ using various electrolytes (e.g., LiCl-KCl eutectic) instead of sulfur as a co-spraying agent. The use of electrolyte is expected to result in better flow properties as well as more adherent deposits with high density and superior electrochemical properties. Single-cell tests as well as full-sized battery tests are planned with the best plasma-sprayed electrodes that result from this work.

Some work has already been carried out plasma spraying of Li-anode materials (9-11). The results in some cases have been encouraging, suggesting that it should be possible to extend plasma-spraying work to anodes as well as cathodes. In addition to the plasma spraying of cathodes and anodes, complementary studies are also planned with the thermal-battery separator. This is normally prepared by blending MgO with the electrolyte, which is held in place when molten (during battery operation) by capillary action. The ultimate goal is to be able to plasma spray multilayer electrodes—cathode, separator, and anode—in multiple passes, to form a three-layer composite cell. If successful, this would result in dramatic savings in production costs for thermal batteries. The good interfacial bonding that would be expected under these conditions would translate into lower interfacial resistance, resulting in higher power densities. By using thinner separators, further increases in overall energy densities and specific energies would be realized.

**Other Battery Technologies**

Lithium-ion batteries are typically fabricated by application of active anode and cathode materials onto metal substrates. Copper foil is used for the carbon anodes and aluminum foil is used for the cathode which is generally Mn-based (e.g., LiMn$_2$O$_4$) or Co-based (e.g., LiCoO$_2$ or LiNi$_x$Co$_{1-x}$O$_2$). This is an area where plasma-spray technology has applicability.

It should be possible to plasma spray the oxide material directly only the aluminum substrate in a continuous process. The high kinetic energy of the particles can result in lower interfacial resistance than conventional electrodes. The tight control available using plasma spray can result in potentially much thinner electrodes. For many applications, only a small amount of electroactive material is needed. A similar approach may be possible with the anode, as well. We recently demonstrated that it is possible to plasma spray graphite powder after proper agglomeration. Plasma-spray technology may have equal suitability for other battery electrodes, such as for Ni/Cd cells and fuel cells. This is an area that merits serious consideration.

**Conclusions**

Thermal spray has been demonstrated to be a viable method for fabrication of thermal-battery cathodes based on pyrite. The use of sulfur as a co-spraying agent is effective in prevention of FeS$_2$ decomposition during spraying. However, improved results are obtained when sulfur is replaced by LiCl-KCl eutectic. The initial voltage transient caused by free sulfur in the deposit is mitigated and a much stronger bond to the substrate is possible.

Post-addition of Li$_2$O to the pyrite deposit to remove the residual voltage transient (by fixing the Li activity) at the start of discharge is most effective when applied as a solution, followed by vacuum drying. Coating the electrode with powdered Li$_2$O results in high impedance during discharge. Incorporation of the Li$_2$O directly into the electrolyte promises to offer the best means of addressing this issue.

The use of graphite paper to replace stainless steel provides additional advantages by making it much easier to punch a variety of sizes for electrodes using inexpensive dies. This avoids the need for large expensive presses now required for pressed-powder electrodes.

Initial results with CoS$_2$ co-sprayed with sulfur show excessive sulfur reports to the deposit, resulting in poor adhesion and an unacceptable voltage transient during discharge. Future work co-spraying with electrolyte is expected to resolve this problem.

The successful development of thinner cathodes, anodes, and separators in thermal batteries by use of plasma-spray technology will dramatically reduce the costs of battery fabrication while greatly enhancing the energy density and specific energy. Plasma spraying also offers the potential to reduce electrode fabrication costs and to speed throughput of other electrodes beside those for thermal batteries (e.g., Li ion cells, Ni/Cd, fuel cells, etc.). This is an area that needs more attention.
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