

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 However, in the molten state, the battery impedance becomes very low, allowing large amounts of power to be withdrawn.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 CoS₂

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 CoS₂-based catholyte feedstock was shown [5–7]. The physical properties of this feedstock were much different from those of the FeS₂-based material that used natural (mineral) pyrite. In the latter case, the FeS₂ particles were quite large (35–45 μm), which contrasts with the nanostructured nature of the synthetic CoS₂.

When the nanostructured CoS₂ was substituted for the coarse FeS₂ 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 CoS₂, 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 CoS₂ to Co₃S₄ and S₂ 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 CoS₂ relative to FeS₂, 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 CoS₂ 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 CoS₂-based PS cathodes and the all-Li electrolyte as well as similar tests with the two-layered FeS₂-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 ₂ O	2.9
FeS ₂	68.0	LiCl–KCl	29.1	Li ₂ O	2.9
44% Li/56% Si (–270 + 325 mesh)	100	N.A.	0	N.A.	0

stocks. The angle of repose of the various feedstock powders was determined by measuring the height of the powder pile formed on a pedestal of known diameter when powder was poured onto it through a vibrating 60-mesh sieve.

A graphite–paper substrate (Grafoil®) (nominal 0.18-mm thick) was used for the catholyte mixes, while a 316 stainless steel substrate (0.13-mm thick) was used for the anode material. The anode discs also had a 3-mm-diameter center hole (for mounting during spraying) and were undercut at the edges by about 2 mm.

Plasma spraying was carried out with a Metco 9MB plasma spray system (Metco, Westbury, NY). A dc arc current of 188–220 A was generated in the copper nozzle. Argon passing through the dc arc was heated to >9000 °C and ionized. The feed powder was fed radially into the plasma stream near the nozzle exit at a rate of 0.7–0.9 kg h⁻¹. The plasma output was directed to a supported sheet of Grafoil® positioned 5–10 cm away. Test discs of 3.18 cm diameter were punched from the Grafoil® sheets. In the case of the CoS₂-based cells, CP separators with a composition of 35% MgO/65% LiCl–LiBr–LiF electrolyte were used with the Creare anodes and the single-layer, PS cathodes to construct 15-cell batteries for testing under both hot (+74 °C) and cold (–54 °C) conditions. In the case of the two-layered FeS₂-based PS composites, the Creare anodes [8] were also used to construct batteries for testing of the composites under the same conditions. The heat balance (i.e., heat input per cell divided by the total cell mass including the Fe/KClO₄ pyrotechnic) was adjusted for differences in total cell mass for the two sets of materials.

One of the difficulties with analyzing data for materials made by spraying of multiple layers is the need to determine the relative thickness of each component layer. In the case of a single-layer deposit, the thickness is readily determined by measurement of the thickness of the deposit relative to that of the substrate. However, due to equipment constraints at USN, it was not possible to remove the substrate after deposition of the catholyte prior to plasma spraying the separator layer. Consequently, only an overall deposit thickness could be determined. However, by taking data generated for a single-layer cathode deposit, it was possible to calculate the thickness of the separa-

tor component of the two-layer deposit. Knowing the theoretical densities of the components and the measured thicknesses, it was then possible to calculate the porosities.

2.2. Electrochemical testing

The single cells were 3.18 cm in diameter and were tested galvanostatically between heated platens under computer control in a glovebox in high-purity argon that contained <1 ppm each water and oxygen. A background load of 125 mA cm⁻² was used with 250 mA cm⁻² pulses (500 ms to 1 s wide) being applied every 30 s to obtain a measure of cell polarization (i.e., dV/dI). The cells were tested at a temperature of 400 and 500 °C (to bracket the normal operating range of a thermal battery) to a cutoff voltage of 1.0 V.

The batteries were built using a reusable test fixture in which the stack temperature was monitored during activation and discharge. A thermocouple was inserted between two Grafoil® discs adjacent to the cathode in the end cell (furthest away from the header) to record the battery stack temperature. In some cases, it was necessary to adjust the heat balance after testing a cold battery, to avoid a possible thermal runaway in one tested under hot conditions. It was not possible to replicate these tests due to the limited number of PS anodes available. Where possible, data for the PS batteries were compared to similar data for batteries made with CP parts. When that was not possible, voltage and polarization data for five-cell batteries were used and the two sets of data were compared on a per-cell basis.

3. Results and discussion

3.1. Feedstock characterization

To be able to spray separator mixes required some effort to define the proper grinding parameters to produce material that was much coarser than the separators used for cold pressing of pellets. The angle of repose is a good metric for defining the flowability of a material and proved very useful in this work. Typical data for the angle of repose of a number of typical thermal-battery powders are summarized in Table 2. (All compositions in this paper are reported as weight percent.)

Table 2
Average angles of repose for thermal-battery powder mixes

Material	Active material	Particle size (mesh)	Electrolyte	Lithiation agent	Angle of repose (°)	Remarks
Catholyte	Mineral FeS ₂	–325 + 425	LiCl–KCl eut.	3% Li ₂ O	54.0 (0.62) ^a	Fused, sieved
	Mineral FeS ₂	–325 + 425	LiCl–KCl eut.	3% Li ₂ O	37.6 (0.32)	
	Mineral FeS ₂	–325	LiCl–KCl eut.	3% Li ₂ O	50.6 (0.72)	Fused and ground in mill
	USN FeS ₂	Nanostructured	LiCl–KCl eut.	3% Li ₂ S	65.0 (0.09)	As prepared
	USN FeS ₂	Nanostructured	LiCl–KCl eut.	3% Li ₂ S	52.7 (0.33)	Pelletized and then ground
	USN FeS ₂	Nanostructured	LiCl–KCl eut.	3% Li ₂ S	26.3 (0.42)	5 wt% poly(methylmethacrylate) in methyl ethyl ketone
Separator	35% MgO	–80	LiCl–KCl eut.	N.A.	45.9 (0.74)	Std. grind
	35% MgO	–20	LiCl–KCl eut.	N.A.	38.9 (1.12)	Coarse grind
	35% MgO	–100	LiCl–KCl eut.	N.A.	53.1 (0.19)	LN ₂ blend
	35% MgO	–60 + 100	LiCl–KCl eut.	N.A.	25.6 (0.42)	LN ₂ blend

N.A., not applicable.

^a Standard deviations for the average of three measurements are shown in parentheses.

Table 3
Properties of plasma-sprayed samples used to construct 15-cell batteries

Sample ID	Sample thickness (mm)	Active material	Content (%)	Active material mass (mg)	Deposit density (% TD ^a)
71	0.147	CoS ₂	56.7	90	40–62
72	0.127		56.8	70	
74	0.460–0.485	FeS ₂	22.8	78	45–73
75	0.331–0.345		25.1	77	
Creare	0.087–0.136	44% Li/56% Si	100	50–80	65–75
Creare	0.087–0.136	44% Li/56% Si	100	70–80	

^a TD, theoretical density.

Empirically, it has been found that good flowability can be expected if the angle of repose of a material is under 35°. However, the angles of repose for the bulk of the thermal-battery mixes are well above that, mostly above 50°. The electrolytes have the highest angles of repose, while the catholytes made with coarse mineral pyrite have the lowest. By developing a coarse grind, however, it was possible to reduce the angle of repose of the separator based on LiCl–KCl eutectic from ~46° to ~39°. (In general, the standard deviation for three measurements was quite low, usually <1%.) Similar results were achieved with the all-Li-based separator made by a liquid-nitrogen-blending process and modified to be coarser than the typical mix. The angle of repose for this material was 25.6°, which resulted in good flowability. However, the yield will be reduced when processing the coarser mixes due to the loss of fines.

Also, note that with the use of nanostructured synthetic pyrite the average angle of repose for the as-prepared materials was quite high, 65°. By changing processing and by use of (poly)methylmethacrylate (Plexiglas®) as a binder, it was possible to reduce this considerably to produce a material with reasonably good flow properties. In the case of CoS₂-based catholytes, the flowability was much worse than the corresponding catholytes made with synthetic FeS₂. A considerable effort was made to develop a suitable binder that would result in improved flowability. A number of common organic binders used in the ceramics industry were evaluated with all-Li-based mixes. These included polyethylene glycol, polyvinyl alcohol, paraffin, Durez® resin and (poly)methylmethacrylate. The best overall results were obtained with the (poly)methylmethacrylate binder.

While the physical properties of these mixes were improved by the use of the binders, there were adverse impacts on the performance in electrochemical cells due to pyrolysis that generated moisture and other undesirable gases that reacted with the CoS₂ directly or with the Li(Si) anode. The compromise in the electrochemical performance was unacceptable. Attempts to use a suitable binder that did not pyrolyze but evaporated cleanly were not successful, in that the desired physical properties of the powders could not be attained. In the end, it was necessary to use a catholyte made solely with electrolyte and no binders. This material was processed to give the best possible flow properties for plasma spraying.

3.2. Deposit characterization

The characteristics of the PS deposits are summarized in Table 3. Note that the active mass of the sulfide cathodes is

quite small relative to that typically used for pressed-powder cathodes of 365–735 mg. The cathode thickness is correspondingly greater in the latter case. The anode masses used for the CP powder cathodes are typically 700 mg, or an order of magnitude greater than the active masses of the PS anodes. This gives rise to the increased possibility of loss of material through self-discharge caused by dissolution of the pyrite in the molten salt during activation of PS thermal batteries, relative to standard thermal batteries. This leads to loss of capacity by reaction with the Li(Si) anode [9–11]. For the size of samples used in this work, the bulk of the batteries were cathode limited.

The densities of the PS cathodes were generally lower than those for CP powder electrodes in conventional thermal cells, typically 72.5–75% TD. The low density of the CoS₂-based deposits is readily evident in the scanning electron microscope (SEM) photomicrograph of Fig. 1. Similar morphological results were obtained when using the LiCl–KCl eutectic electrolyte as a co-spraying additive. In comparison, the density of the pyrite-based PS cathode deposit is much higher, as can be seen in the photomicrograph of Fig. 2.

One concern about thermal spraying of the separator material was the potential for a change in composition while passing through the plasma. To evaluate this potential, a sample of the separator based on LiCl–KCl eutectic and 35% MgO were plasma sprayed onto a graphite–paper substrate for sub-

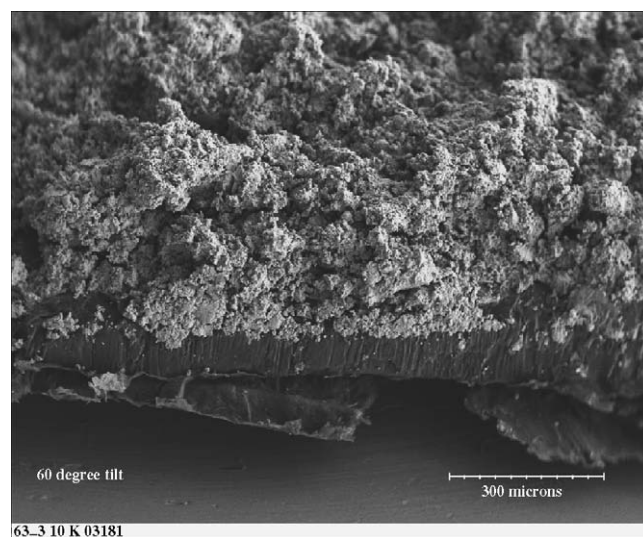


Fig. 1. SEM photomicrograph at 60° tilt of cross-section of PS CoS₂–LiCl–LiBr–LiF deposit (300 μm marker).

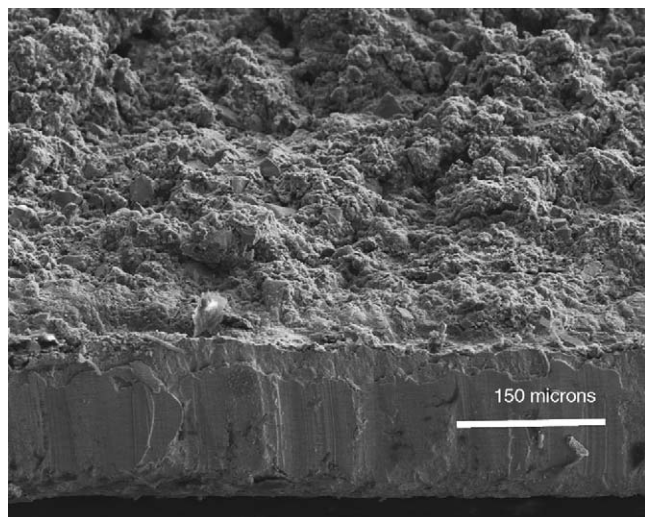


Fig. 2. Cross-sectional view at a 60° tilt of a PS FeS_2 –LiCl–KCl deposit (150 μm marker).

sequent analysis. Compositional changes were minimal (<7%) for plasma spraying of this material. The fine particle size of the MgO very likely is responsible for this behavior (much as for the nanostructured CoS_2 material). The density of the resulting separator deposit was 67.3% of theoretical, which is close to the nominal value of 75% TD used for CP pellets of this material.

The PS anodes deposits had densities greater than the nominal 72.5% TD normally used in CP anodes. These Li(Si) samples were made without any co-spray material and do not experience the thermal decomposition inherent with the disulfide cathode materials at elevated temperatures— FeS_2 begins to decompose at 550 °C, while CoS_2 decomposes at 650 °C.

Accurate characterization of the two-layered cathode-separator composites made with pyrite-based feedstock was not possible due to lack of information on each discrete layer. Therefore, properties data were calculated with certain reasonable assumptions being made. One is that the properties of the separator layer would be comparable to those prepared on a graphite–paper substrate. Another is that the earlier deposit-composition data could be extrapolated to include samples with the somewhat higher electrolyte content of 29.1% used in the present work. Based on these assumptions and the measured FeS_2 content of the deposits, it was found that the separator layer constitutes about a fourth of the total deposit weight and makes up about half of the total sample thickness. In earlier two-layered PS deposits, the separator layer was too thin, so that cells made with these materials showed breaching of the separator shortly after initiation of discharge. This was not a problem with the current samples, as the separator layer was considerably thicker.

3.3. PS CoS_2 cathodes

3.3.1. Single-cell tests

The relative performance of the PS CoS_2 cathode samples with CP counterparts made with the same USN CoS_2 was determined in single cells prior to final battery tests. Pressed-powder, flooded (25% electrolyte) anodes were used for these tests, in

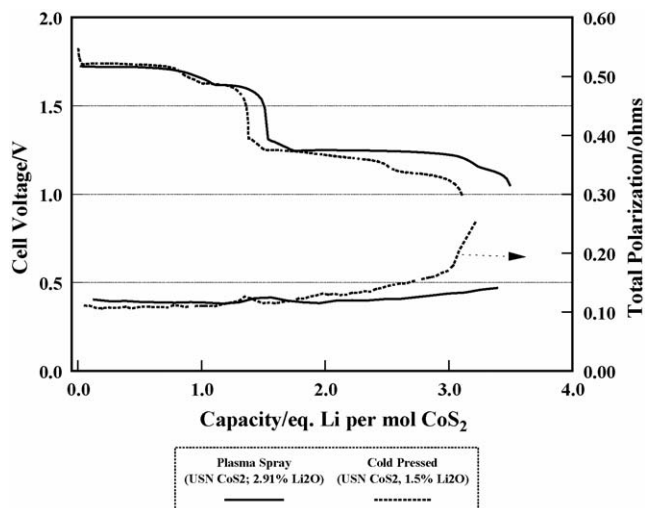


Fig. 3. Discharge at 500 °C and 125 mA cm^{-2} of Li(Si) (flooded)/LiCl–LiBr–LiF (MgO)/ CoS_2 cells made with PS and CP CoS_2 cathodes.

order to reserve the requisite PS anodes for battery tests. The results at a temperature of 500 °C and a discharge current density of 125 mA cm^{-2} are shown in Fig. 3.

The performance of the PS cathode was quite similar to that of the CP counterpart under these conditions, with complete elimination of the initial voltage spike at the start of discharge with the higher level of Li_2O . The cells with the PS cathodes ran longer with reduced polarization later in discharge than the cells with the CP cathodes. In preliminary tests at twice the current density of these tests, the improvements in performance of the cells with the PS cathodes over those with pressed-powder cathodes was even greater than at the lower current density.

The effects of temperature on the discharge characteristics of the Li(Si)/LiCl–LiBr–LiF/ CoS_2 single cells made with PS cathodes are summarized in Fig. 4. The best performance was obtained at 500 °C. At higher temperatures, the cell lifetime was reduced most likely to self-discharge reactions resulting from the

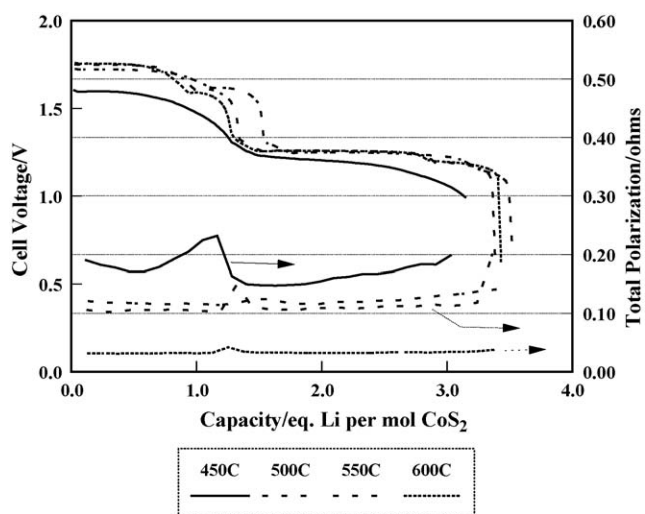


Fig. 4. The effect of temperature on the discharge at 125 mA cm^{-2} of Li(Si) (flooded)/LiCl–LiBr–LiF (MgO)/ CoS_2 cells made with PS cathodes (2.91% Li_2O ; 260- μm thick).

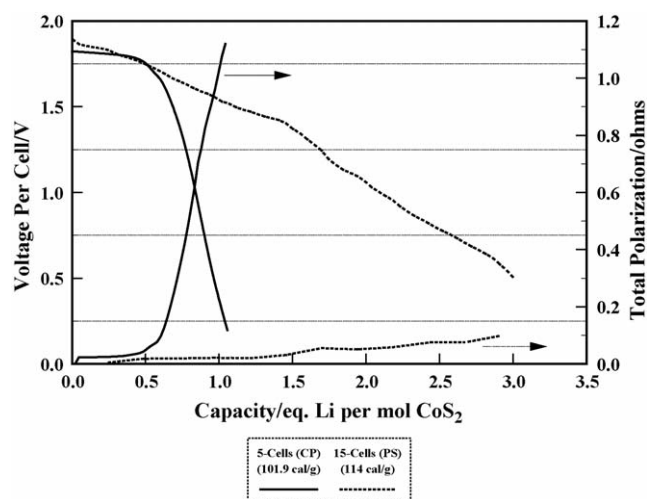


Fig. 5. Comparison of the performance for an activation temperature of -54°C of a 15-cell $\text{Li}(\text{Si})/\text{LiCl-LiBr-LiF}/\text{CoS}_2$ battery made with PS anodes and cathodes to that of a five-cell analog made with CP parts.

solubility of the CoS_2 in the all-Li electrolyte. (Self-discharge of conventional $\text{Li}(\text{Si})/\text{FeS}_2$ cells was found to be more pronounced under similar conditions when using the all-Li electrolyte [12].) The poor performance at 450°C is probably related to wetting issues with the nanostructured CoS_2 ; similar effects have also been observed for nanostructured FeS_2 with the LiCl-KCl eutectic electrolyte. By appropriate pretreatment of the sulfides using a proprietary process, the low-temperature performance can be dramatically improved [13].

3.3.2. Battery tests

Data were not available for the 15-cell battery made with CP parts, but were for the 5-cell analogs. However, those batteries used flooded anodes, whereas the anodes for the 15-cell batteries were plasma sprayed without electrolyte. For a more-meaningful comparison, the two sets of data have been normalized on a per-cell basis. The results of tests for batteries activated at -54°C are shown in Fig. 5.

The 15-cell battery with the PS electrodes showed a deeper discharge (capacity extracted) relative to the 5-cell unit with CP parts. It showed exhaustion of the limited amount of CoS_2 present (90 mg), as the temperature was well above the freezing point of the electrolyte of 436°C at the end of discharge. In contrast, the amount of active cathode material for the five-cell battery was almost 10 times greater. The end of life for this battery was totally thermally related, resulting from electrolyte freezing, and is reflected in the rapid rise in total polarization (impedance) near 0.6 eq. Li per mole CoS_2 .

The peak temperature for the PS battery was almost 100°C greater than that for the CP battery, due to an excessively high heat balance. This skews the data considerably and leads to enhanced performance of the PS unit relative to the CP one. Consequently, the heat balance was reduced from 114 to 100 cal g^{-1} for the PS battery when tested hot ($+74^{\circ}\text{C}$). The results of the tests under hot conditions paralleled those for the cold batteries in the relative trends in performance. The maximum capacity that was realized for the PS battery was twice that for the CP

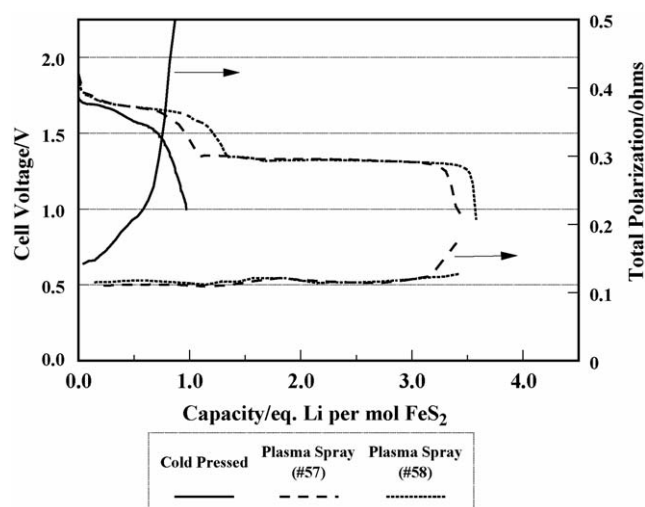


Fig. 6. Discharge at 400°C and 125 mA cm^{-2} of $\text{Li}(\text{Si})$ (flooded)/ LiCl-KCl (MgO)/ FeS_2 cells made with PS, two-layered, cathode-separator composites and CP anodes and cells made with all CP parts.

unit, which contained 6.5 times more active cathode material. At the lower heat balance used for the PS battery, the peak temperature was only 38°C higher than that for the CP battery, and the temperature profiles became quite similar after 100 s. This agreement is as good as can be expected, given the large differences in thermal mass for the two battery stacks.

While these data are somewhat limited, they serve to show the performance enhancements that are possible through the use of PS electrodes. In this case, both the anode and cathode were plasma sprayed, with only the separator being prepared by cold pressing of powders. It is possible to plasma spray separator material, as will be discussed in the next section of this report. Ultimately, one can envision an entire cell being prepared by the plasma spraying of multiple layers of the requisite materials.

3.4. Plasma spraying of cathode-separator composites

3.4.1. Single-cell tests

The successful plasma deposition of FeS_2 -based cathodes led to attempts to also plasma spray a separator layer onto the cathode to form a composite electrode. For these tests, a lithiated pyrite-based catholyte containing LiCl-KCl eutectic was used. In earlier tests with a similar material, good performance was obtained in single-cell tests [3,4]. Fig. 6 shows the performance at 400°C compared to that for single cells made with discrete, CP parts. The catholyte feedstock for these tests contained 20% electrolyte and 2.91% Li_2O , with composite thicknesses varying from 0.350 to 0.625 mm.

The cells with the PS composite parts ran much longer than the one with discrete CP parts. They showed a considerably reduced polarization (impedance) throughout the entire discharge. The cell made with the composite with the thicker separator (#58) ran somewhat better. At 500°C , however, the initial upper-voltage plateau was somewhat less for the cells with the PS composite parts, relative to the cell with discrete CP parts. Again, the composite having the thicker separator performed

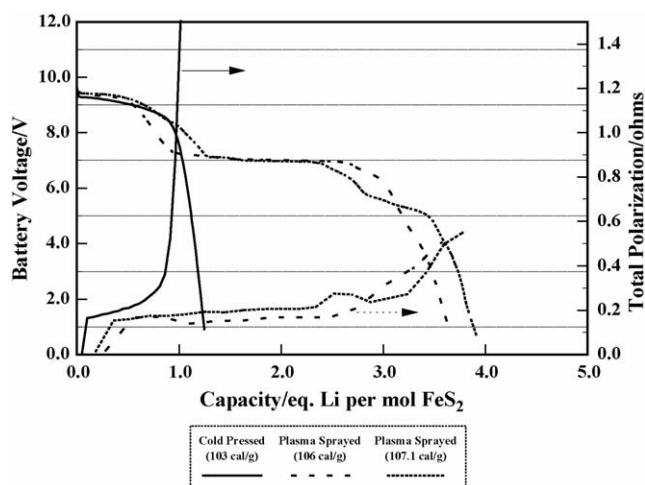


Fig. 7. Discharge at -54°C and 125 mA cm^{-2} of Li(Si) (flooded)/LiCl–KCl (MgO)/ FeS_2 five-cell batteries made with PS two-layered cathode-separator composites and CP anodes and batteries made with all CP parts.

better than the one with the thinner separator layer. The lower-voltage plateau was much longer and at a higher potential in the last case compared to the cell with the CP parts. Both cells with PS composite parts exhibited very low polarization throughout discharge, without the hump that was exhibited by the cell with discrete CP parts. This is attributed to better interfacial contact for the composite part and better particle–particle contact among the pyrite particles for the PS material. (This behavior has been noted previously for PS, single-layer, pyrite-based cathodes.) The loss in capacity for the upper-voltage plateau may be a result of increased self-discharge that would be greatly accentuated because of the low mass of the active FeS_2 in the deposit ($<100\text{ mg}$) relative to the mass in the CP cathode. This would translate into a dramatic loss in capacity for the PS cell because of a larger fraction of FeS_2 being lost.

3.4.2. Battery tests

A limited number of five-cell battery tests were conducted with the PS two-layered composite materials. The results for batteries discharged at -54°C are summarized in Fig. 7 along with data for a battery made with CP parts. (The latter battery used a cathode weight of 0.50 g instead of the typical 1.05 g , to better approximate the weight of the PS cathode.) A heat balance of $106\text{--}107.1\text{ cal g}^{-1}$ was used for the batteries with PS parts, while 103 cal g^{-1} was used for the standard battery. The capacities for the batteries made with the PS composite parts were almost 3.5 times greater than those with discrete pressed-powder parts. Part of this is due to the slightly higher battery-stack temperatures, but the bulk of the improvement was a direct result of a lower overall impedance in the former case.

In the case of five-cell batteries activated at $+74^{\circ}\text{C}$, the battery stack temperature was somewhat higher for the batteries with the PS composites. At the higher temperatures, the relative trend in performance mirrored that for the single cells at 500°C , in that the upper-voltage plateau was somewhat shorter for the cells with the PS parts, with the sample having the thicker separator (107.1 cal g^{-1}) performing better. Again, this very likely

reflects increased self-discharge under hot conditions with a limited amount of active FeS_2 present in the PS composites. (The self-discharge is accelerated at higher temperatures [5,6].) In the case of the composite with the thicker separator, the lower-voltage plateau was initially comparable to that for the battery with discrete pressed-powder parts up to about 2.2 eq. Li per mole FeS_2 , at which point the latter battery showed a dramatic increase in impedance. The battery with PS composite with the thicker separator exhibited a final capacity of $\sim 3.24\text{ eq. Li}$ per mole FeS_2 to a 1.0 V cutoff versus 2.45 Li per mole Fe for the battery with the CP parts. Part of this improvement was due to the somewhat higher stack temperatures of the PS batteries during discharge as a result of a slightly higher heat balance.

These results are extremely encouraging, given that the overall plasma-spraying process has not been optimized for preparation of two-layered composites. The actual densities of the individual layers of the composite are not known at this time, but it should be possible prepare materials with the desired porosities and compositions to improve their performance even more. The composites were tested under conditions one would use for a battery designed to run for minutes or tens of minutes. Thus, such a battery with CP parts contains a substantial mass of active pyrite. In contrast, the very thin composites contain a very limited amount of active pyrite and would be better suited for use in small, high-current-density pulse batteries designed to run for milliseconds or hundreds of milliseconds. Under those conditions, the self-discharge issues would be minimized. Replacement of the natural pyrite with synthetic, nanostructured pyrite could lead to even greater improvements in performance.

The results of the testing of more-recent, comparable two-layered pyrite-based composite materials at -54°C in 15-cell batteries with PS anodes are compared in Fig. 8 to those for the earlier 5-cell batteries made with similar two-layered composites but with pressed-powder anodes. Again, the data have been normalized to a per-cell basis. (The weight of the CP cathode

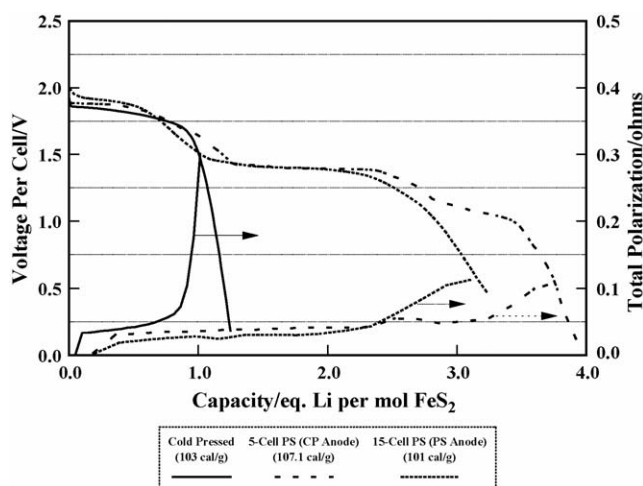


Fig. 8. Comparison of relative performance of five-cell Li(Si)/LiCl–KCl/ FeS_2 battery made with CP parts, a five-cell battery made with PS two-layered, cathode-separator composites and CP anodes and a 15-cell all-PS battery (with two-layered cathode-separator composites), all at an activation temperature of -54°C .

was 0.50 g for these tests. The stack-temperature data were not available for the 15-cell battery due to loss of the thermocouple during activation.) The data for the 15-cell all-PS battery tracked that of the 5-cell counterpart with CP anodes. These data indicate that the performance of batteries with PS parts essentially scales linearly with the number of cells, which facilitates battery design.

A similar 15-cell battery tested at +74 °C showed a rapid degradation in performance during discharge, in marked contrast to that for the sister 5-cell unit. A sustained high stack temperature indicates that a thermal runaway may have occurred, most likely as a result of breaching of the thin PS separator early in the discharge. Unfortunately, there were insufficient anodes available for repeating this test.

The breaching problem was noted earlier during the initial attempts to plasma spray a separator layer onto a PS cathode. It may be easy to resolve this issue by simply increasing the number of passes during separator spraying to form a thicker layer. It should be noted the results of these tests with the 15-cell batteries are quite promising, given the limited number of samples that were prepared. The overall composite samples were very likely prepared under less-than-ideal conditions. Additional experiments could optimize the properties of these materials to avoid problems encountered with some of the present samples.

Given the limited effort in these experiments, the overall project is still considered a success. This is especially true when one compares several sets of data in which both flooded and unflooded (PS) anodes were used and where it was difficult to heat balance the batteries due to differences in intrinsic heat capacities and thermal requirements due to compositional differences. (For example, additional heat may be required for flooded anodes due to the requirement for the heat of fusion of the electrolyte.) In addition, there were gross differences between the active masses of materials for the CP batteries versus those using PS electrodes.

3.5. Advantages of plasma spraying

Plasma-spray technology as it relates to thermal batteries is best suited for the production of short-lived, pulse batteries, since it is relatively easy to deposit thin anode and cathode films. The longer-lived thermal batteries require much heavier (thicker) anodes and cathodes, and it may be difficult to plasma-spray deposits with the necessary thickness. The advantage of thin films is doubly important for pulse batteries in that only the actual amount of material needed for the pulse-battery application need be deposited. The production of such batteries using conventional pressed-powder parts necessitates the use of anode and cathode parts that are much thicker than necessary, due to the fragility of thin parts. Actual capacities can be as much as ten times greater than the required capacities. Thin parts are difficult to press uniformly in reasonable yields and are hard to handle during battery assembly without breakage.

In contrast, PS anodes and cathodes can be readily prepared and are robust. The thinner (lighter) parts translate into a reduced pyrotechnic (heat-pellet) weight for the same pulse application. The end result is a much lighter and smaller battery, which is

very advantageous in many cases. The performance of the PS materials is superior to that of the cold-pressed analogs, due to improved particle-to-particle contact that results from the high kinetic energies and improved bonding to the substrate. It should be possible to develop a semi-continuous or possibly a continuous process for the production of sheets of materials under robotic control. This automation should also result in improved control over the properties of the PS deposits.

Cutting electrode discs from such sheets is straightforward and avoids the need for large numbers of expensive pressing dies. Inexpensive cutting dies can be used, much like cookie cutters, to cut whatever sized part is necessary. Using conventional dies, extreme pressures are required to press pellets greater than 8 cm in diameter. Consequently, this requires increasingly larger and larger presses (over 1.8 MN, in some cases). In addition, the dies have to be designed to withstand such pressures during the pelletizing operation. Such pressure difficulties are eliminated with PS sheets by simply using a larger die cutter with the PS sheets.

In this work, we have demonstrated that electrolytes other than the LiCl–KCl eutectic can be successfully used as thermal-barrier coatings for the plasma spraying of thermally sensitive metal disulfides. Thus, plasma spraying of the cathodes and anodes can be modified as necessary to satisfy the requisite chemistries for the various thermal batteries.

4. Conclusions

The use of PS materials for thermal batteries was evaluated using both single-layer and composite electrodes. Cathodes based on synthetic, nanostructured CoS₂ prepared at USN and blended into plasma-spray feedstock with the all-Li, LiCl–LiBr–LiF electrolyte were tested in single cells over a range of temperatures. A variety of binders and process treatments were examined to improve the flowability of this material, which intrinsically has a high angle of repose. Organic binders that work well generate reactive gases during pyrolysis that make their use impractical. Improved flowability is attained by adjusting the catholyte fusion conditions and granulation.

The composition of PS cathodes is close to that of the feedstock, with only a moderate increase in the final electrolyte content. This contrasts markedly with what is observed when one uses coarse natural (mineral) pyrite under similar conditions, where the electrolyte content of the deposit can more than double during plasma spraying. Single cells were tested using the CoS₂-based PS cathodes and flooded CP Li(Si) anodes. The performance of these cells is superior to that for cells made with CP parts, even though the overall cathode-deposit density is lower than that of the normal CP cathodes (40–60% versus 72.5%, respectively). The PS cells have increased lives with reduced overall polarization. Some loss in capacity occurs at 550 °C due to increased self-discharge related to dissolution in the molten electrolyte of the small amount of active cathode present.

Follow-on 15-cell battery tests were conducted at –54 and +74 °C using the PS CoS₂ cathodes from USN and PS Li(Si) anodes from Creare. The batteries built with the PS electrodes showed a deeper discharge (capacity extracted) relative to five-

cell units made with CP parts. End of life was due to exhaustion of the limited amount of CoS_2 present (90 mg) and not from electrolyte freezing, which is normally the case.

The plasma spraying of separator mixes was also successfully demonstrated. Two-layered composites of a FeS_2 -based cathode and typical separators were prepared with the LiCl – KCl eutectic. There is no significant change in the composition of the separator during plasma spraying. Separator densities of 67% TD are readily attained, which is close to the nominal value of 75% for CP separators. The performance of the composite tested in single cells with flooded $\text{Li}(\text{Si})$ anodes is superior at the lower temperatures (400°C), but shows some loss in capacity at the higher temperatures (500°C). This is attributed to the loss of active material in the PS cathode by dissolution in the molten electrolyte at the elevated temperatures while heating to temperature under open circuit. Follow-on 15-cell battery tests were conducted at -54 and $+74^\circ\text{C}$ with the composite electrode and PS $\text{Li}(\text{Si})$ anodes from Creare. *This is the first report of an all-plasma-sprayed thermal battery.* Excellent results were obtained with the cold battery, where the capacity extracted was three times that for the unit with CP parts. However, breaching of the thin separator probably occurred in the hot battery that resulted in a severe degradation in performance. Given the limited number of tests that were conducted in this work, the success that was demonstrated is significant in showing that an all-PS battery is feasible. More work is needed to better define the spraying conditions for optimum thickness of the separator to prevent breaching. The optimum spray conditions would have to be adjusted with changes in the composition of the catholyte and separator feedstocks.

Plasma-spray technology is best suited for the production of short-lived, pulse batteries, since it is relatively easy to deposit thin anode and cathode films. Such technology would result in thinner electrodes with a concomitant reduction in battery volume and mass. This technology also lends itself to a semi-continuous production process that has the potential to produce batteries more economically due to the use of robotic equipment. PS electrodes avoid the need for expensive pressing dies and costly high-pressure presses. Electrodes can be readily cut from sheets of PS materials using inexpensive cutting dies. Fabrication of an all-PS thermal cell would also greatly facilitate battery construction, since there would be fewer piece parts. This would also reduce the chance for assembly errors.

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Acknowledgments

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