ELECTROCHEMICAL EVALUATION OF THIN-FILM Li-Si ANODES PREPARED BY PLASMA SPRAYING

Ronald A. Guidotti, Gregory L. Scharrer, and Frederick W. Reinhardt
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0614

and

Timothy McKecknie
Plasma Processes, Inc.
4914-D Moores Mill Rd.
Huntsville, AL 35811

ABSTRACT

Thin-film electrodes of a plasma-sprayed Li-Si alloy were evaluated for use as anodes in high-temperature thermally activated (thermal) batteries. These anodes were prepared using 44% Li/56% Si (w/w) material as feed material in a special plasma-spray apparatus under helium or hydrogen, to protect this air- and moisture-sensitive material during deposition. Anodes were tested in single cells using conventional pressed-powder separators and lithiated pyrite cathodes at temperatures of 400° to 550°C at several different current densities. A limited number of 5-cell battery tests were also conducted. The data for the plasma-sprayed anodes was compared to that for conventional pressed-powder anodes. The performance of the plasma-sprayed anodes was inferior to that of conventional pressed-powder anodes, in that the cell emfs were lower (due to the lack of formation of the desired alloy phases) and the small porosity of these materials severely limited their rate capability. Consequently, plasma-sprayed Li-Si anodes would not be practical for use in thermal batteries.

INTRODUCTION

The Li-Si/FeS_2 (pyrite) couple is the primary power source used for thermally activated (thermal) batteries for nuclear weapons by the Department of Energy and for missile applications by the Department of Defense. The battery is designed to function only when the electrolyte becomes molten and can be stored over 25 years without loss of performance, as long as hermeticity is maintained. The most common electrolytes used in this system are the LiCl-KCl eutectic that melts at 352°C and the all-Li LiCl-LiBr-LiF minimum-melting electrolyte that melts at 436°C.

The anode, separator, and cathodes are prepared by cold pressing of powder mixes in dies. Typically, the separator contains MgO, which acts as a binder to hold the molten electrolyte in place by capillary action. The catholyte contains separator material and, in many cases, Li_2O, which acts as a lithiation agent to inhibit voltage transients upon

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

activation. The anodes can be used in the unflooded (dry) form or with electrolyte to aid in pelletizing. The electrolyte also improves the electrochemical performance by providing a liquid phase for transport of Li ions during discharge.

The Li-Si anode is the most difficult of the battery stack components to press into pellets, requiring the highest pressure. These anodes typically exhibit radial stress cracks and cannot normally be fabricated in thicknesses less than 0.008"-0.010". At these thicknesses, they tend to be fragile and difficult to handle. This becomes a major problem for large-diameter pellets (e.g., over 3").

For many applications, the thickness (mass) of the anode is several times greater than that necessary for the design application simply because of the poor mechanical properties of the thinner pellets. To address this issue, an investigation of the feasibility of plasma spraying thin-film Li-Si anodes was undertaken. In earlier work, it was demonstrated that this technique could be successfully applied to pyrite cathodes for use in thermal batteries (1,2).

In this work, Li-Si films approximately 0.005" thick or less were deposited onto 304 stainless steel substrates (current collectors) in a special high-vacuum chamber using the standard 44% Li/56% Si[a] anode material as a feed. The process spray parameters were varied over a range of conditions to optimize the deposit. In some cases, a thin (~0.001"-thick) film of 316L stainless steel was first deposited, to aid in adhesion. The Li-Si anodes were then tested in single cells over a temperature range of 400° to 550°C and in 5-cell batteries. Similar tests were carried out with conventional pressed-powder anodes for relative comparison. The plasma-sprayed anodes were also evaluated in 5-cell batteries. This paper will present the results of that work. The merits and problems associated with this technique will also be discussed, in the context of a thermal-battery production environment.

EXPERIMENTAL

Plasma-Spraying Setup
Li-Si thermal-battery anodes were formed utilizing totally inert processing. 44% Li-56% Si powder (-230+325 mesh particle size) was loaded into inert powder transfer containers at Sandia. The chamber was then purged with high-purity argon and stored under a positive pressure. The powder was inertly transferred into vacuum-tight powder feeders at Plasma Processes, Inc., in Huntsville, AL. The powder was fluidized and carried to a direct-current plasma gun for deposition in a 60-inch-diameter vacuum vessel, shown in Figure 1.

Inside the vacuum vessel, the plasma torch deposited the Li-Si powder with two sets of parameters listed in Table I. Argon was used as the plasma gas, with either hydrogen or helium as the secondary gas. The plasma torch was manipulated by a 4-axis CNC controlled robot to deposit Li-Si anode material on properly prepared substrates. The 1.25" x 0.005" thick 304 stainless steel substrates (current collectors) were cleaned with acetone, abraded with 325 mesh abrasive paper, and given a 25-micron 316L stainless

---

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

steel bond coating to enhance adhesion. The test matrix used in the study is shown in Table II. After vacuum plasma spraying a Li-Si deposit of 125 μm, the samples were transferred under argon cover to an argon-filled glovebox, where the samples were removed from the plasma sample holder. They were then double packaged under argon for shipment to Sandia for subsequent testing.

Materials

The LiCl-KCl eutectic electrolyte was made by fusing the required quantities of vacuum-dried Reagent-grade LiCl and KCl together in a quartz crucible at 600°C for three hours, followed by quenching and grinding. The separator mix was prepared by blending the electrolyte powder with 35% MgO (Merck Maglite 'S'), and then fusing at 400°C for 16 hours. The catholyte was prepared by blending 73.5% purified FeS_2 (American Mineral, −325+425 mesh), 25% separator, and 1.5% Li_2O. The purity of the FeS_2 pyrite was better than 98%, with the main impurities being gangue material (e.g., siliceous minerals). The control anodes were pressed from an anolyte made with 75% Li-Si anode powder (Eagle Picher, 44% Li/56% Si, −100+325 mesh) and 25% electrolyte. All preparations, processing, and handling operations with materials and parts were conducted in a dry room maintained at <3% relative humidity.

Testing of Single Cells and 5-Cell Batteries

The anode, cathode, and separator mixes were cold pressed into 1.25" (31.8-mm)-diameter discs to ~75% of theoretical density. The mass of the Li-Si control anode was 0.93 g and that of the cathode was 1.03 g. The separator masses were 1.00 g for the standard cells and 5.8 g for cells with reference-electrodes. The reference electrode was a silver wire immersed in a borosilicate-glass capillary tube filled with a 0.1m AgCl solution in the LiCl-KCl eutectic. For tests with the plasma-sprayed electrodes, individual electrodes were weighed and corrected for the substrate weights, to determine the active mass of Li-Si. Cells were discharged at temperatures of 400° to 550°C in single-cell tests. For testing of 5-cell batteries, a reusable test fixture with an "O"-ring seal was used to avoid contact of the active battery stack with ambient moisture. The pyrotechnic used was an 88% Fe/12% $KClO_4$ mixture at a heat balance of 94 cal/g of total cell mass (including the heat pellet).
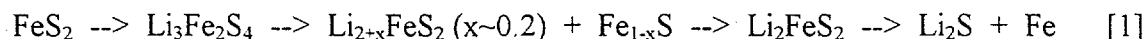
The pellets were assembled into cells that were tested under an applied pressure of 8 psig (55.2 pa) between heated platens in a glovebox under high-purity argon (<1 ppm each O_2 and H_2O). The cells were galvanostatically discharged under computer control. The majority of the tests were performed with a background current of 1 A (126 mA/cm^2) that was increased to 2 A for 1 s every 30 s or 60 s, to obtain polarization information and determine the rate capabilities of the cells. The cell discharge was terminated when the cell voltage dropped below 1.00 V. A limited number of tests at half this current density were also carried out as were high-rate tests where the pulse current was increased to 7 A.

RESULTS AND DISCUSSION

Pressed-Powder Anodes

The effect of temperature on the performance of conventional Li-Si/FeS_2 single cells made with conventional unflooded, pressed-powder anodes is summarized in Figure 2 for a steady-state current density of 126 mA/cm^2. There is a gradual loss in capacity with
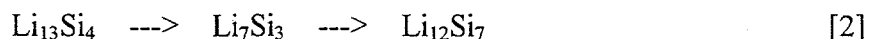
decreasing temperature. The corresponding cell polarization is shown in Figure 3. The first hump in the polarization curves at 450° and 500°C is due to the higher resistance of the first phase that forms during discharge, $Li_3Fe_2S_4$ (the so-called "Z" phase). This hump corresponds to the first phase or voltage transition evident in Figure 2. The sequence of discharge of FeS_2 in LiCl-KCl eutectic is shown in equation 1 for equilibrium conditions (3,4):

$$FeS_2 \; \text{-->} \; Li_3Fe_2S_4 \; \text{-->} \; Li_{2+x}FeS_2 \; (x\sim0.2) \; + \; Fe_{1-x}S \; \text{-->} \; Li_2FeS_2 \; \text{-->} \; Li_2S \; + \; Fe \qquad [1]$$

The electrical conductivity of the Z phase at 400°C is 0.10 S/cm, while that of Li_2FeS_2 (the "X" phase) is 4.2 S/cm—more than an order of magnitude greater (5). In comparison, the conductivity of natural pyrite can vary from 1 to 10 S/cm at room temperature (6). The second hump in the resistance curve (Figure 3) is most likely associated with the formation of the X phase. This maximum occurs at the same time as the second voltage or phase transition in Figure 2.

Plasma-Sprayed Anodes

Single-Cell Tests. The performance as a function of temperature for Li-Si/FeS_2 cells made with plasma-sprayed anodes is summarized in Figure 4. The data have been normalized to capacity per unit mass of active material. Because of the small amount of active anode material (70-150 mg), the anode was the limiting electrode in these tests. There are a number of voltage transitions evident in the data. To verify that these indeed were due to the anode, parallel tests were conducted using a Ag/AgCl reference electrode. Typical data for a discharge at 500°C are shown in Figure 5. As can been seen, the various voltage plateaus were entirely due to phase transitions in the anode. The starting Li-Si alloy exhibits the following equilibrium phase transitions during discharge (7):

$$Li_{13}Si_4 \quad \text{--->} \quad Li_7Si_3 \quad \text{--->} \quad Li_{12}Si_7 \qquad [2]$$

The relative performance of a cell with a plasma-sprayed anode and one with pressed-powder anodes is shown in Figure 6 for a temperature of 500°C. The cell with the plasma anode had a somewhat lower emf than the standard cell, although the cell polarizations were comparable. Similar results were observed at the other temperatures. The thermodynamic emf of the cell is determined by the phases present. X-ray diffraction analysis of the as-deposited plasma films indicated the presence of the starting $Li_{13}Si_4$, but with a less-ordered structure. There was evidence for small amounts of other metastable or nonequilibrium alloy phases. Complementary Auger electron spectroscopy (AES) examination confirmed that lack of a uniform composition throughout the deposit, with islands with a high Li content. The lack of a homogeneous equilibrium phase in the plasma deposit was responsible for the observed lower cell emf.

Supplemental tests were conducted where the 2 A pulse was increased to 7 A, to determine the rate capability of the plasma-sprayed anodes. The standard cells with pressed-powder (unflooded) anodes handled the pulse fine, while the cells with the plasma-sprayed anodes performed poorly. At 500°C, for example, the cell voltage in the former case dropped to only 1.2 V during the first pulse ($\Delta V=0.6$ V), compared to 0 V in the latter case. This poor performance is in large part due to the limited electrochemical surface area available in the case of the plasma-sprayed anodes, relative to that for the

pressed-powder anodes. The ready access to the rear of the pressed-powder anode dramatically increases the electrochemical area available and reduces the effective current density. When discharged at a lower rate, the cells with the plasma-sprayed anodes performed much better, as shown in Figure 7 for a temperature of 450°C. When the current density was reduced to half (63 mA/cm²), the capacity more than tripled.

5-Cell Battery Tests. A limited number of 5-cell battery tests were carried out using the plasma-sprayed anodes. The results of a typical battery discharge are shown in Figure 8 for a battery activated at 30°C, along with comparable results for similar battery built with pressed-powder anodes and activated at 74°C. The same masses of separator and catholytes were used for both tests. As with the single-cell tests, the performance of the battery with the plasma-sprayed anodes was much inferior to that with the pressed-powder anodes, for the same reasons. The temperature profile was comparable for the two tests and the overall battery polarization was similar until the battery with the plasma-sprayed anodes ran out of capacity.

Physical Properties. The adhesion of plasma-sprayed Li-Si deposit was less than ideal. There was a tendency to material to flake from the substrate in handling. Although the application of a 316L stainless steel bond coat helped considerably, the resultant adhesion would still be unacceptable from the perspective of a commercial manufacturer of thermal batteries. In addition, the lack of phase-pure material would mean additional process steps would be necessary (e.g., annealing). The high reactivity of the Li-Si alloy with atmospheric oxygen and moisture requires that the plasma spraying be conducted in a tightly controlled vacuum environment, using special expensive equipment. This makes the process impractical. Because of these limitations, plasma spraying of Li-Si anodes for use in commercial thermal batteries is not economically and technically feasible at this time.

CONCLUSIONS

Thin-film (<0.005"-thick) Li-Si anodes were prepared by plasma spraying of 44% Li/56% Si onto 1.25" dia. x 0.005"-thick 304 stainless steel current collector using a special vacuum chamber and setup. The deposits obtained are dense but nonuniform in composition and contain metastable nonequilibrium phases, which results in a lower-than-expected emf. The electrochemical performance of the anodes is inferior to that of conventional pressed-powder anodes in both single-cell tests at 400° to 550°C and in limited battery tests with the Li-Si/LiCl-KCl/FeS$_2$ system. The high-density deposit results in a lower effective surface area available for electrochemical reaction, which results in much greater polarization with the attendant voltage drop. The adhesion to the substrate is improved by the application of a 0.001"-thick 316L bonding coat but there are still handling limitations. The poor electrochemical performance and deficient physical properties of the deposits, coupled with the need for expensive specialized equipment and conditions and a limited throughput rate makes plasma-spraying of Li-Si anodes impractical for use in thermal batteries.

ACKNOWLEDGMENTS

REFERENCES

1. Ronald A. Guidotti, Frederick W. Reinhardt, Hui Ye, T. Danny Xiao, and David E. Reisner, "Evaluation of Plasma-Sprayed, Thin-Film Pyrite Cathodes for Thermal Batteries," *Proc. 34th IECEC Meeting*, Vancouver, B.C., Aug. 1-5, 1999.

2. David E. Reisner, Hui Ye, Rongde Ge, T. Danny Xiao, Ronald A. Guidotti and Frederick W. Reinhardt, "Thermal-Sprayed Thin Film Cathodes for Thermal Battery," *3rd Intern. Symp. on New Materials for Fuel Cell and Modern Battery Systems*, Montreal, Canada, July 6-10, 1999.

3. Z. Tomczuk, B. Tani, N. C. Otto, M. F. Roche, and D. R. Vissers, *J. Electrochem. Soc.*, **129** (5), 925 (1982) (and references therein).

4. S. K. Preta, Z. Tomczuk, S. von Winbush, and M. F. Roche, *J. Electrochem. Soc.*, **130**, 264 (1983).

5. S. P. S. Badwal and R. J Thorn, *J. Sol. St. Chem.* **43**, 167 (1982).

6. S. Fiechter, M. Birkholz, A. Hartmann, P. Dulski, M. Giersig, H. Tributsch, and R. J. D. Tilley, *J. Mater. Res.*, 7, 1829 (1992).

7. C. J. Wen and R. A. Huggins, *J. Sol. St. Chem.* **37**, 271 (1981).

Table I. Vacuum Plasma Parameters for Li-Si Alloy Deposition.

Parameter	#1 Process (H_2)	#2 Process (He)
Plasma Gas (flow)	Argon 260 scfh	Argon 260 scfh
Secondary Gas (flow)	Hydrogen 3 scfh	Helium 86 scfh
Plasma Power (kW)	18.5	22.1
Torch Movement	CNC Robot	CNC Robot
Standoff (in)	4	4
Deposition Environment	Vacuum	Vacuum
Powder Gas (flow)	Argon 13 scfh	Argon 13 scfh

Table II. Sample Matrix for Plasma Spraying.

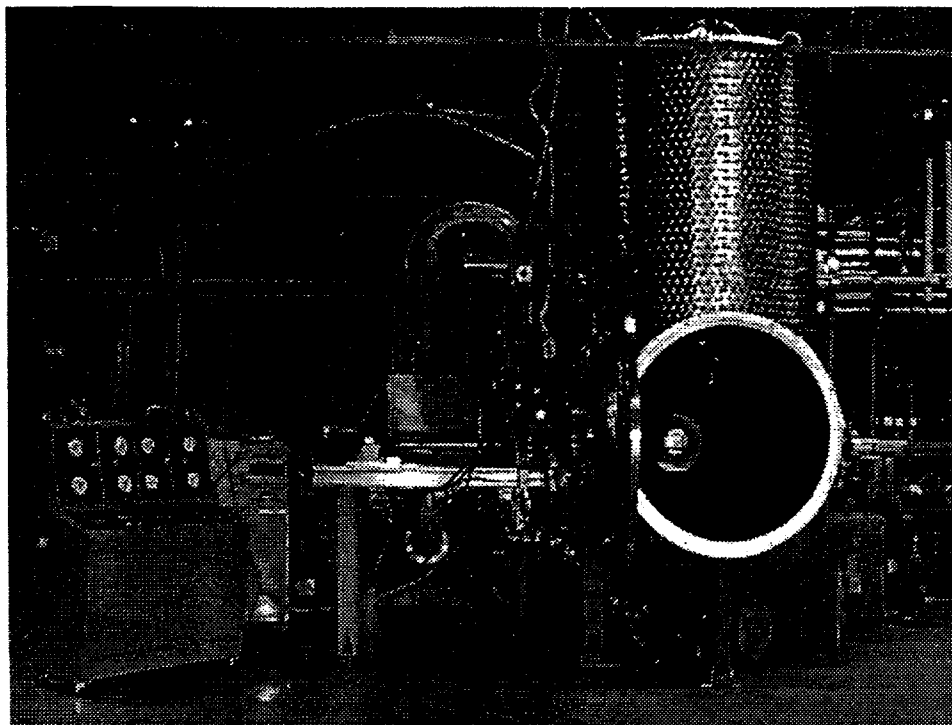| Substrate	Parameter	Number of samples
0.005" 304 SS sheet	#1 Process (H_2)	9
0.005" 304 SS sheet	#2 Process (He)	7
0.010" 304 SS sheet	#1 Process (H_2)	11
0.010" 304 SS sheet	#2 Process (He)	14
0.005" 316L SS coating on 304 SS	#1 Process (H_2)	7
0.005" 316L SS coating on 304 SS	#2 Process (He)	6

Figure 1. Vacuum Plasma Spray Chamber at Plasma Process, Inc. where Li-Si Anodes Were Prepared.
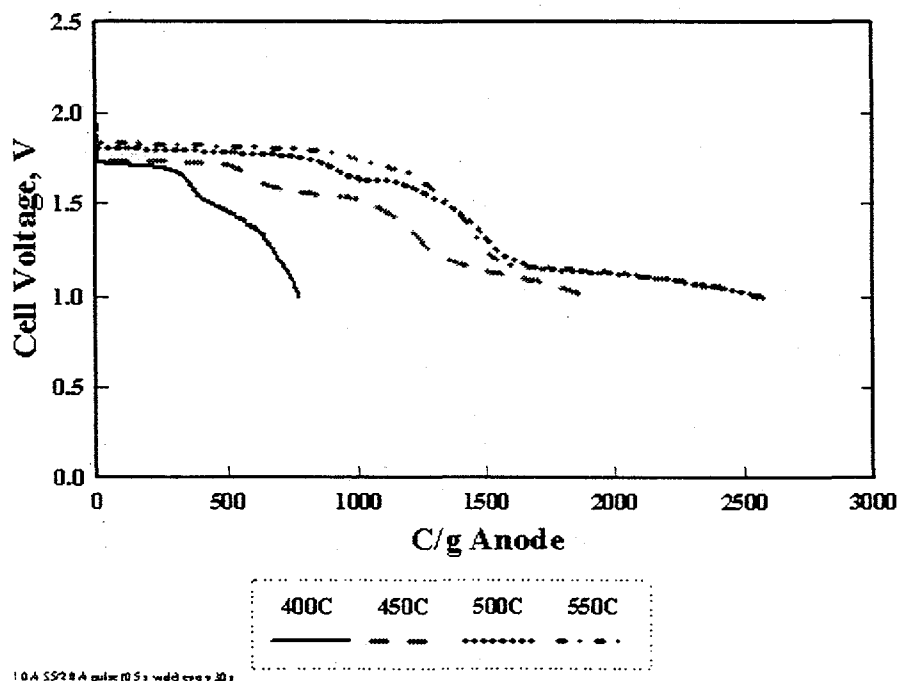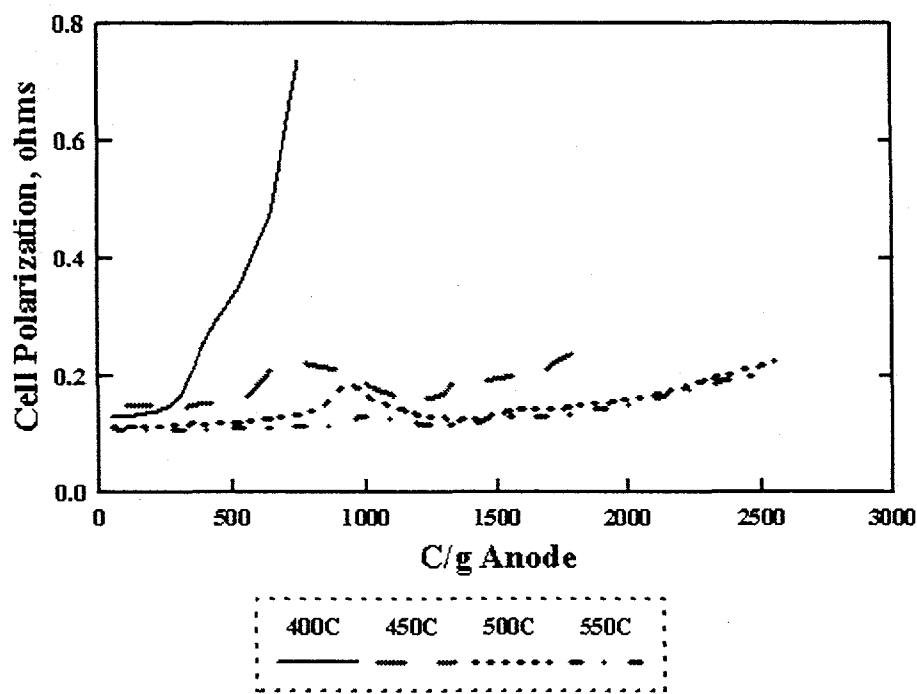

Figure 2. Capacity as a Function of Temperature of Li-Si/LiCl-KCl/FeS$_2$ Single Cells Made with Press-Powder Anodes and Discharged at 126 mA/cm^2 Steady State.

Figure 3. Polarization as a Function of Temperature of Li-Si/LiCl-KCl/FeS$_2$ Single Cells Made with Pressed-Powder Anodes and Discharged at 126 mA/cm^2 Steady State.
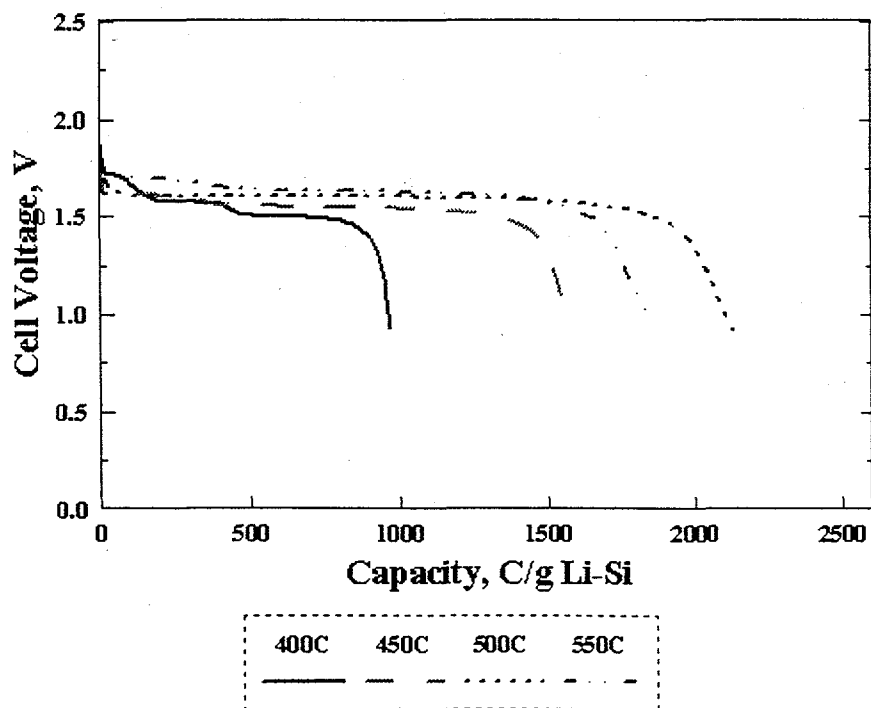

Figure 4. Capacity as a Function of Temperature of Li-Si/LiCl-KCl/FeS$_2$ Single Cells Made with Plasma-Sprayed Anodes and Discharged at 126 mA/cm^2 Steady State.
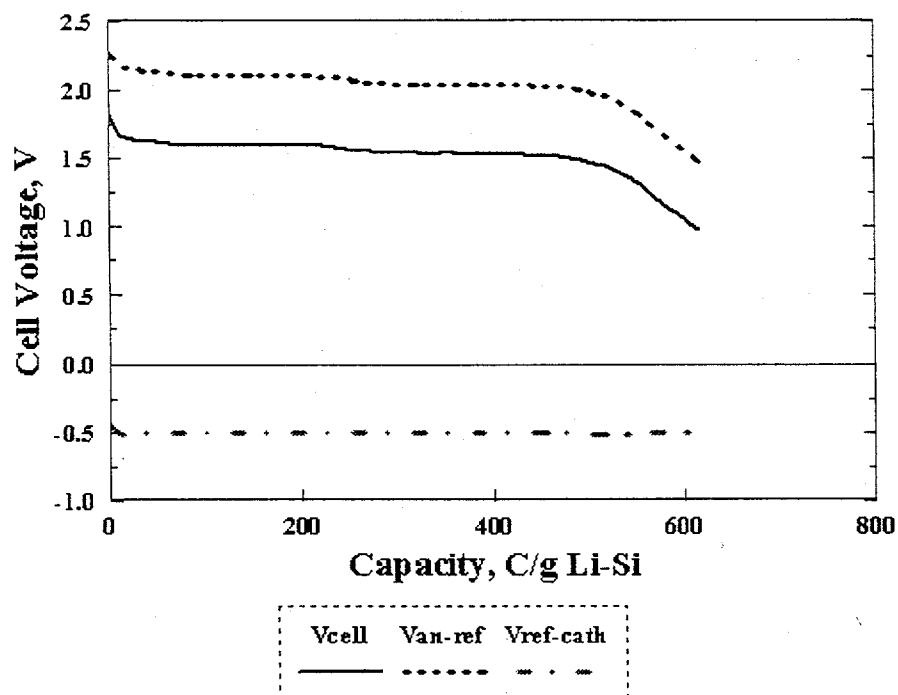
Figure 5. Performance of Li-Si/LiCl-KCl/FeS₂ Cell Made with Plasma-Sprayed Anode and Tested at 126 mA/cm² with Reference Electrode at 450°C.
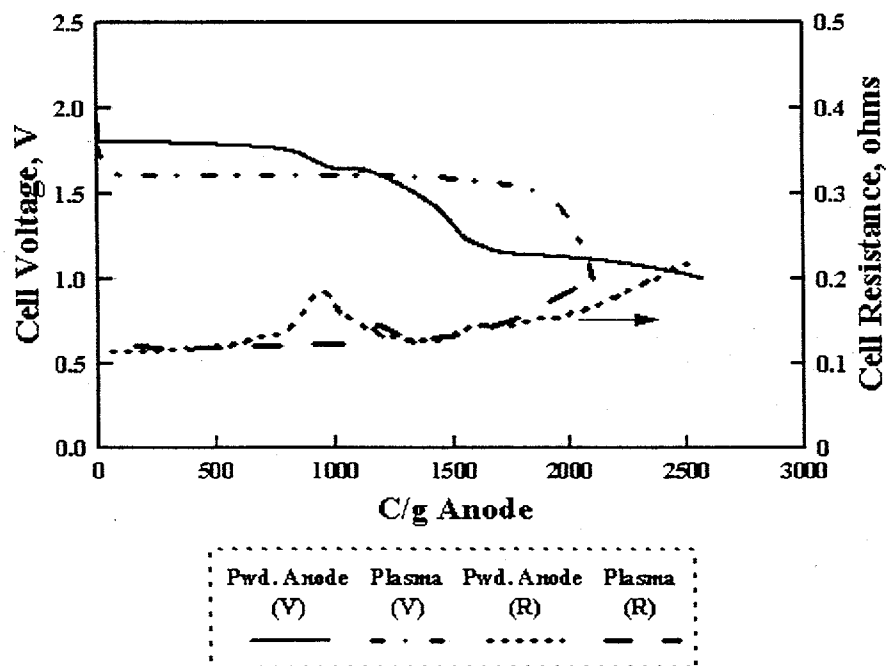

Figure 6. Comparison of Performance of Powdered Anode and Plasma-Sprayed Anode in Li-Si/LiCl-KCl/FeS₂ Cell Tested at 126 mA/cm² at 500°C.
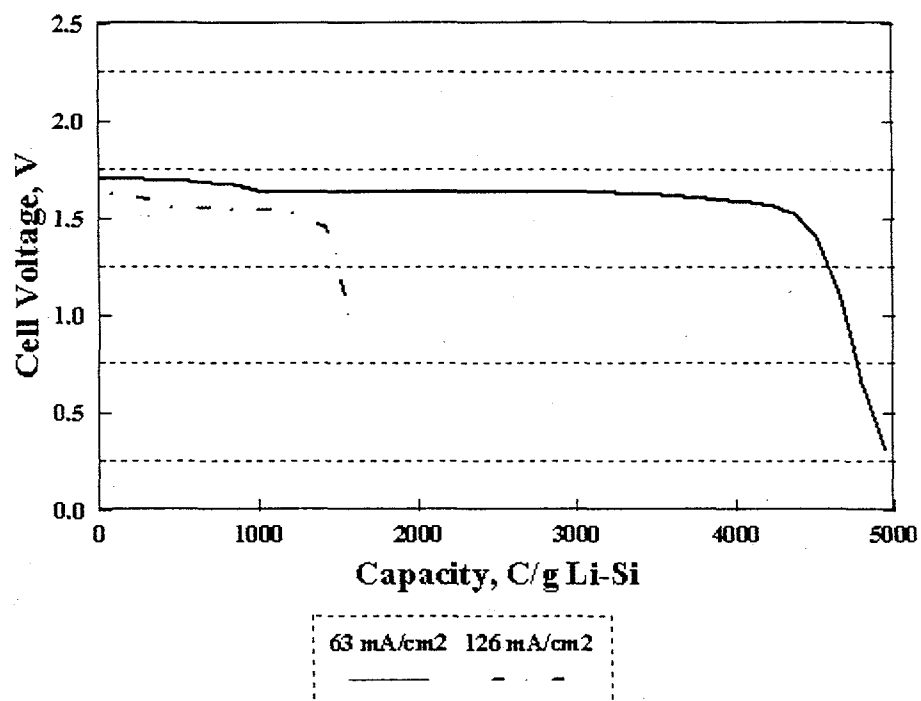
63 mA/cm2   126 mA/cm2

Figure 7. Effect of Load on Performance at 450°C of Li-Si/LiCl-KCl/FeS$_2$
Cells Made With Plasma-Sprayed Anodes.

74C   30C
Std. Anode   Plasma Anode
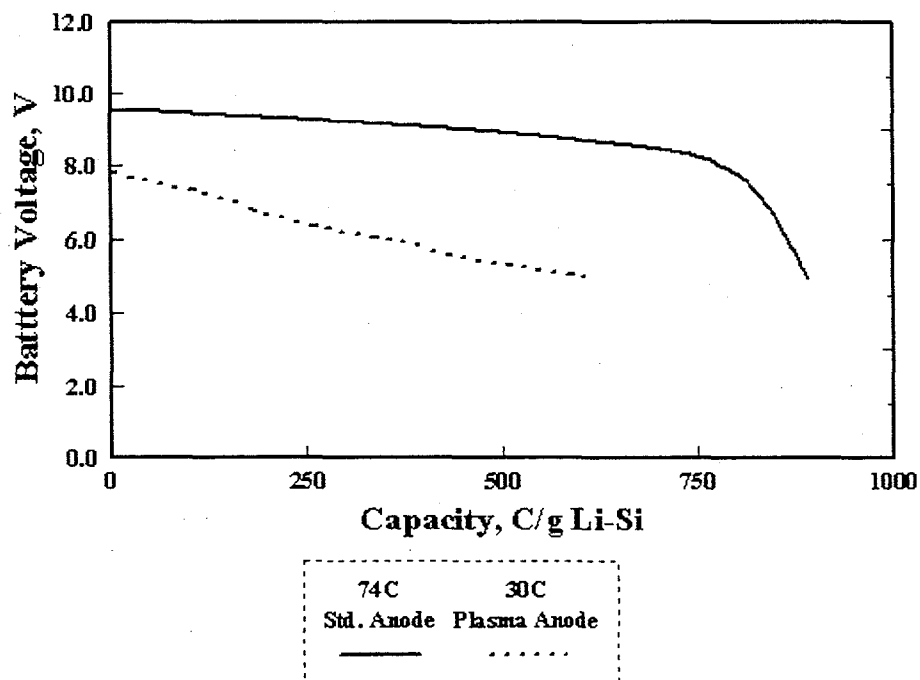
10 A SS/2 0 A pulse f0 5 s weld cvs 7 30 s

Figure 8. Comparison of Performance of 5-Cell Li-Si/LiCl-KCl/FeS$_2$ Thermal Batteries
Made with Pressed-Powder and Plasma-Sprayed Anodes and Discharged at 126 mA/cm^2.