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Study of Cell Performance in Long-Life Thermal Battery Design Space

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Abstract

A three-factor central composite design of experiments was performed on single cells of cobalt disulfide based long-life thermal batteries. Temperature, applied pressure, and discharge current density were varied and lifetime, polarization, and voltage were examined. Electrolyte retention was also studied. A three-factor linear model describes the cell polarization. Cell voltage has a quadratic dependence on temperature. Electrolyte retention is linearly dependent on temperature up to 500°C. Li_2O *and MgO both contribute to molten salt retention.*

Keywords:

thermal battery; molten salt; CoS_2; lithia; magnesia; lithium-silicon

Introduction

Cobalt disulfide (CoS_2) is the cathode of choice for long-life thermal batteries because it has a flat voltage discharge profile, a reasonably high nominal voltage (~1.8V), and a high thermal decomposition temperature of over 650°C.[1] The high decomposition temperature in particular is an advantage over FeS_2 cathodes in that it allows for a larger thermal input to the battery, extending its lifetime.

The discharge profile (voltage vs. extent discharged) provides insight into the discharge reactions. Each voltage plateau in the profile corresponds to a different reaction. The following reactions occur in cobalt disulfide cathodes near 400°C:[2]

$$3\,CoS_2 + 4\,Li^+ + 4\,e^- \rightarrow Co_3S_4 + 2\,Li_2S \qquad \textbf{(1)}$$

$$3\,Co_3S_4 + 8\,Li^+ + 8\,e^- \rightarrow Co_9S_8 + 4\,Li_2S \qquad \textbf{(2)}$$

$$Co_9S_8 + 16\,Li^+ + 16\,e^- \rightarrow 9\,Co + 8\,Li_2S \qquad \textbf{(3)}$$

These reactions can be understood as a trajectory across the Co-S phase diagram. An additional reaction occurs above 450°C:[3]

$$3\,Co_3S_4 + 24\,Li^+ + 24\,e^- \rightarrow 9\,CoS + 12\,Li_2S \qquad \textbf{(4)}$$

Only the first transition has been used in thermal batteries, but EMF only changes 200 mV until Co_9S_8 is discharged. The anode reaction sequence consistent with the equilibrium phase diagram is as follows:

$$3\,Li_{13}Si_4 \rightarrow 4\,Li_7Si_3 + 11\,Li^+ + 11\,e^- \qquad \textbf{(5)}$$

$$7\,Li_7Si_3 \rightarrow 3\,Li_{12}Si_7 + 13\,Li^+ + 13\,e^- \qquad \textbf{(6)}$$

Lithium alloys are preferred over pure lithium in thermal batteries because they are less reactive, easier to handle in industrial dry rooms, and have substantially greater melting points. The use of Li(Si) alloy results in a 44 mV penalty during the first discharge reaction.[4]

The present study uses controlled current discharge tests on single-cells of thermal batteries to determine the effect of temperature, applied stack pressure, and current on cell performance. Response surface modeling was used to analyze a central composite design of experiments (DoE) on this discharge data.[5] This technique allows for modeling of the cell performance in parameter space for battery design optimization.

Experimental Procedure

A 31.5mm diameter cell stack of pressed powder pellets was assembled between two stainless steel electrodes and two sheets of insulating mica. The electrolyte was a LiBr-LiCl-KBr mixture with a melting point of 321°C.[6] The separator contained 30wt% Maglite-S MgO to stabilize the electrolyte. The anode was $Li_{13}Si_4$ with 5wt% added electrolyte. The cathode was CoS_2 with 25wt% separator material and 1.5wt% Li_2O. This assembly was placed in an Ar glove box with a $pO_2 < 5$ ppm. The cell was heated between platens with a measured mass applied to the top platen to simulate post-activation stack pressure. The samples were allowed to equilibrate for 2 min at temperature prior to discharge. Current was pulsed during discharge to test the cell polarization.

Single-cell discharge tests were performed according to a 2^3 DoE. The three variables considered were temperature, applied stack pressure, and discharge rate. The test conditions are described graphically in Figure 1. The temperature range was 350-550°C, the applied pressure range was 38-133 kPa, and the current density range was 5-128 mA/cm^2. 15 tests were performed in this parameter space, as illustrated.

A second 2^2 DoEx was performed to evaluate the effect of catholyte composition on electrolyte leakage. Discharge tests were performed on four different CoS_2-based catholytes: compositions with and without Li_2O and compositions with and without MgO in the electrolyte. The mass of CoS_2 in all cases was fixed. Pellets were pressed to maintain a constant amount of porosity in the as-pressed state, regardless of the electrolyte.

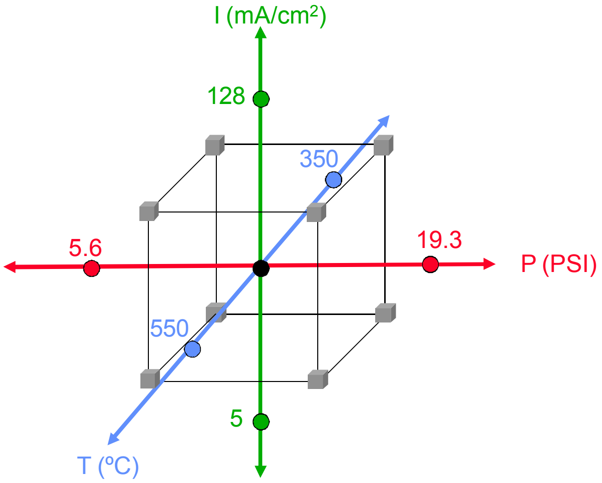

Figure 1. 2^3 design of experiments for thermal battery single-cell performance evaluation.

Electrolyte leakage tests were performed with each of these catholytes. Graphite-backed cathodes were placed between a stainless steel collector and a ~1 cm thick block of Min-K refractory insulation. The assembly was placed in the single-cell test device in the Ar glove box for 30 min at varying temperatures, without electrical load. This design exaggerates leakage beyond what would be expected in an actual thermal battery.

Results and discussion

The effect of the three variables was examined with respect to cell lifetime (defined herein as the energy discharged when the cell potential reached 1.63V), average voltage during the first transition, and cell polarization during the first transition. Significance was determined by fitting the results to the regression model described by equation 7:

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 {x_1}^2 + \beta_8 {x_2}^2 + \beta_9 {x_3}^2 \quad \textbf{(7)}$$

Significance was tested for each coefficient (β_i, x_j) at the $p < 0.05$ level. The model selected for each dependent variable included a significant constant coefficient and all significant independent variable coefficients.

Table 1. Significant effects*

Effect	Magnitude (Coefficient)	Units
I on Lifetime	–60±30 (β_1)	mAh/A
I on Voltage	–2.3±1.2 (β_1)	mV/A
T on Voltage	+1.3±0.6 (β_2)	mV/°C
T^2 on Voltage	–1.3±0.7 (β_8)	$\mu V/°C^2$
I on Polar.	–0.99±0.61 (β_1)	Ohm/A
T on Polar.	–0.96±0.35 (β_2)	$mOhm\text{-}cm^2/°C$
P on Polar.	–5.8±4.89 (β_3)	$mOhm\text{-}cm^2/PSI$

*Regression model constants omitted

and all significant independent variable coefficients.

Table 1 shows the magnitude of the significant effects and the 95% confidence interval. Lifetime and polarization reduced to simple linear models, whereas voltage is quadratic with respect to temperature.

Inspection of the discharge curves shows the expected responses. A drop in voltage with increasing current density (Figure 2) and lower temperature (Figure 3) are evident. The effect of current density on lifetime is less clear, since the terminal transition (to 1.3V) appears independent of current density. However, the discharge curves at high current density are at lower voltage and highly sloped, which contribute to shorter time to 1.63V. Current density is only weakly predictive of lifetime (2-factor linear regression $R^2 = 0.62$).

The effect of temperature is quadratic with respect to voltage but linear with respect to polarization. Cell EMF is proportional to the reaction free energy $\Delta G = \Delta H - T\Delta S$. Enthalpy and entropy, as well as heat capacity, are functions of temperature, but over the relevant temperature range these can be approximated as constants. The product of the linear Ohmic dependence of polarization and the linear dependence of equilibrium EMF may explain the quadratic cell voltage dependence with temperature. The quadratic voltage response model is illustrated in Figure 6. It has an excellent $R^2 = 0.99$.

Polarization is the sum of resistances from the rate of reaction (activation), electrical conductivity (Ohmic), and concentration gradients at interfaces (concentration).[7] A 3-factor linear model with no interaction terms (Figure 7) was used to favorably describe polarization ($R^2 = 0.80$). This implies linear dependencies of all three factors on cell polarization, including temperature. Activation and Ohmic polarization should obey Arrhenius relationships, but the activation energy is low and can be approximated as linear over the relevant temperature range for this electrolyte.[7] The activation energy for ionic migration, based on cell polarization, was 11 kJ/mol. This is similar to other halide electrolytes.[7] This has a linear $R^2=0.97$ from 350-550°C.

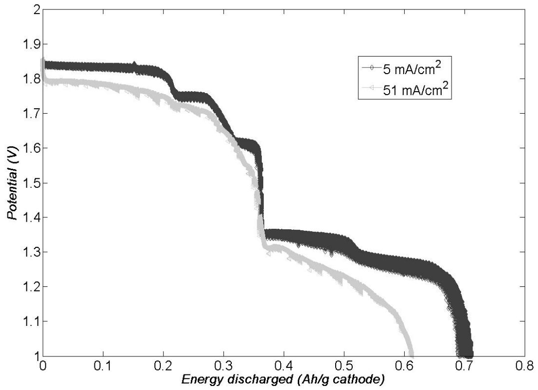

Figure 2. Discharge profiles at 5 and 51 mA/cm^2 current densities. 450°C, 12 PSI. (Dips indicate current pulses.)

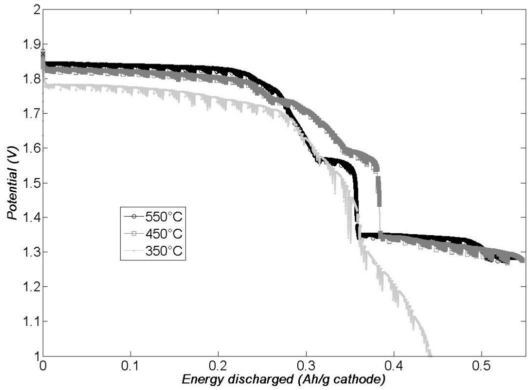

Figure 3. Discharge profiles for 350, 450, and 550°C, 25 mA/cm^2, 12 PSI. (Dips indicate current pulses.)

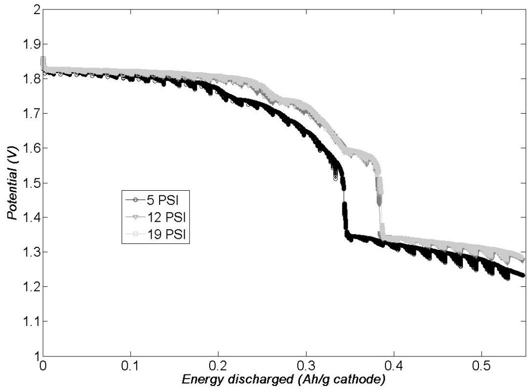

Figure 4. Discharge profiles for 5, 12, and 19 PSI. 450°C, 25 mA/cm^2. (Dips indicate current pulses.)

Applied pressure affects only the cell polarization, likely by changing the contact resistance. Inspection of discharge curves (Figure 4) suggests there may be an interaction between temperature and applied pressure, despite a weak statistical correlation (p=0.14). Cell polarization appears unaffected by applied pressure at temperatures exceeding ~450°C, but it is more significant at lower temperatures. This may be due to increased electrolyte viscosity at lower temperatures leading to poor contact resistance.

Electrolyte leakage was studied to help understand this effect and examine the impact of two additives that may help retain electrolyte. The cathode used in the cell discharge testing DoE has Li_2O (1.5wt%) and MgO (7.5wt%). Figure 5 shows this cathode retains substantially more electrolyte than cathodes that do not contain one of these components. Analysis of the DoE on the addition of Li_2O and MgO (Figure 5) shows that the effect of adding either of these components is similar, with both helping to retain about 25wt% of the electrolyte.

Electrolyte loss increases linearly in the range of 350 to 500°C (Figure 5). Viscosity decreases with increasing temperature in molten salts, likely explaining this observation. Deviation from this behavior is not expected in this temperature range, as no phase changes occur in the molten salt. The cathode without any Li_2O or MgO shows a continual decrease in retained electrolyte as temperature increases, consistent with this expectation.

Table 2. Average electrolyte loss (wt%), by cathode.

	Li_2O	**No Li_2O**	**Effect**
MgO	36%±10%	68%±7%	–21%
No MgO	75%±14%	84%±7%	
MgO effect	–28%		

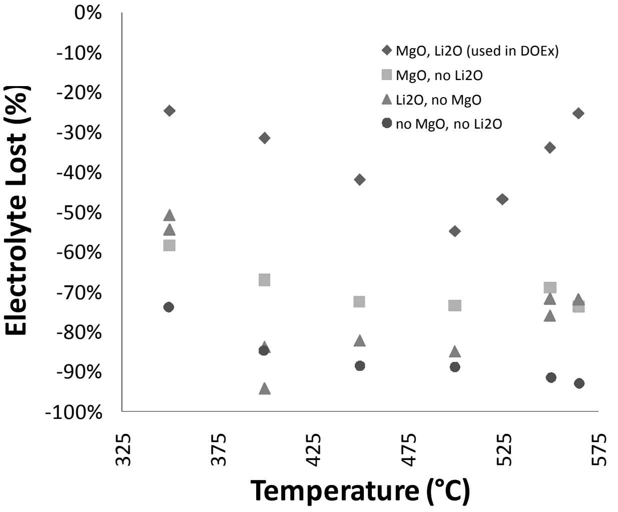

Figure 5. Electrolyte loss as a function of temperature for four catholytes.

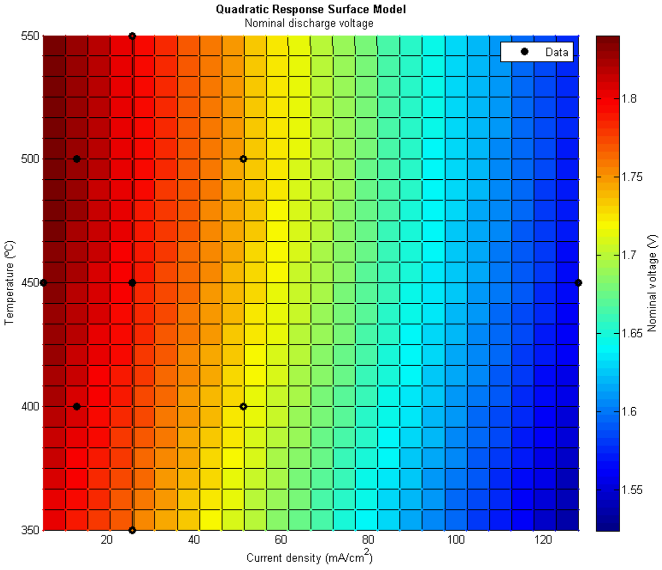

Figure 6. Quadratic model describing cell voltage as a function of temperature and current density.

The cathodes with oxides do not behave as expected. Electrolyte retention improves above 500ºC if either Li_2O or MgO is present, and particularly if both are present. This behavior is consistent with an observation that separator pellet deformation decreases in the range 500-560°C in the standard cathode containing MgO and Li_2O.[6] The mechanism by which the oxides help retain electrolyte is poorly understood. The effect may be related to molten salt surface tension, which has a much weaker temperature dependence than viscosity.[6]

Conclusion

The effect of temperature, applied pressure, and current density on CoS_2-based thermal battery cells was studied. Linear regression models were created based on the results of a central composite DoEx. Cell voltage is affected by current density and temperature. The effect is quadratic in temperature due to the combined effects of changing cell polarization with temperature and changing free energy of reaction. A 3-factor model with R^2=0.99 was developed from these results. Cell polarization is influenced by all three parameters studied. A linear model with R^2=0.80 was developed to describe the polarization as a function of test parameters. Electrolyte leakage tests in flooded cathodes indicated Li_2O and MgO both contribute to electrolyte retention. Electrolyte loss was a linear function of temperature. Further study into the mechanism of electrolyte retention is warranted.

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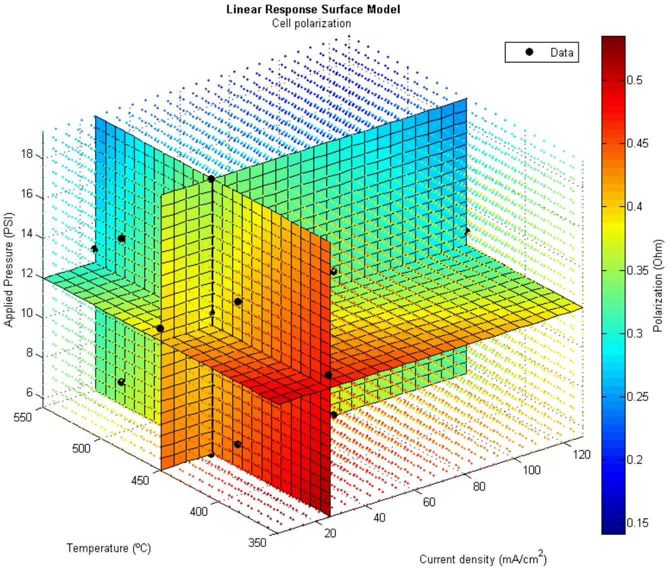

Figure 7. Linear model describing cell polarization as a function of tested variables.

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