

## Discharge in Unactivated Thermal Batteries

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**Abstract:** *Thermal batteries are often kept in a continuous loaded condition for decades. Most modern thermal batteries have a solid-state internal resistance on the order of hundreds of megaohms. Almost any external circuit is a parasitic drain that must be accounted for in estimates of the battery shelf-life. Detailed measurements of battery internal resistance were performed in this study. Temperature was varied at relevant conditions, from room temperature to a maximum short-term storage condition temperature. Battery internal resistance (IR) was estimated from voltage measured across a 2 MOhm external resistor. Leakage current was found to have an excellent fit to an Arrhenius rate relationship for each battery considered. Activation energies ( $E_a$ ) were measured for  $\text{CoS}_2$  and  $\text{FeS}_2$  batteries with multiple types of binder (MgO formed by different processes) and multiple electrolytes (eutectic, low melting, and all-lithium). Battery self-discharge rates varied from 0.02%/year to 25%/year at 35°C, meaning for some batteries this mechanism is important for shelf-life estimation.  $E_a$  varied linearly in the range of 60 to 100 kJ/mol with the mole fraction of lithium ions in the electrolyte.  $E_a$  also varied linearly with the fraction of electrolyte added to the anode. These observations suggest that the charge transfer reaction from the anode to the electrolyte is rate limiting for discharge in the solid state.*

**Keywords:** molten salt; lithium silicon; iron disulfide and cobalt disulfide; accelerated aging

### Introduction

Thermal batteries are used as the power source in many mission-critical applications where an external switch is an unacceptable mission risk. The ignition system for the thermal battery replaces the switch in these applications, enabling the mission circuitry to be brought up as soon as the battery can source sufficient power. Modern thermal batteries (using a lithium or lithium alloy anode, salt mixture electrolyte with a MgO binder, and a metal sulfide cathode) have internal resistances that are on the order of hundreds of megaohms (MOhm) at room temperature. This resistance is so high that batteries have long been considered to be “inert” until activated [1]. Solid-state switches such as field effect transistors (FETs) have leakage currents on the order of 0.1 microamps under similar conditions [2]. 0.1  $\mu\text{A}$  at 10V is an

internal resistance of 100 MOhm, which is at best on the order of magnitude of the “switch” inside a thermal battery. The relatively low resistance of even the best isolated electrical systems compared to the battery means that any battery connected to a circuit is effectively shorted. This may be through leakage through FETs, reverse current through diodes, capacitor leakage, or the battery might literally be shorted (e.g. through a bridgewire), but any realistic electrical circuit connected to the battery will drop the voltage across the terminals to nearly zero volts. However, the electrochemical couples in the battery stack are still operational, so the battery will discharge during its entire lifetime. This leakage current must be accounted for when designing the thermal battery.

The Li(Si)/ $\text{FeS}_2$  thermal battery system was developed in the early 1980’s as a long operational life replacement for Ca/CaCrO<sub>4</sub> thermal batteries with lower intrinsic hazards [1]. The need for shelf stability is intrinsic to thermal batteries, so several accelerated aging studies were performed prior to the widespread use of this battery technology [3,4]. The studies identified the dominant aging mechanism as lithium oxidation from oxygen leaking through hermetic seals. Follow on work [5,6] has continued to focus on the aging of the chemical reagents within the battery as an isolated system.

This work examines the impact of the external circuit on the shelf-life of the batteries. Primarily, this work consisted of performing precision leakage current measurements at near-ambient conditions. Several anode, cathode, and separator compositions were considered. Electrochemical impedance spectroscopy (EIS) was used to help identify the rate-limiting step in the discharge reaction. Additionally, single-cell testing was performed on cells under accelerated aging conditions to validate that the observed leakage current has relevance to batteries in storage.

### Experimental Procedures

Leakage current measurements were performed by measuring the voltage across a 2 MOhm 1/4W resistor using a Keithley 2700 digital multimeter. The input impedance of this meter is greater than 10 GOhm at the 10V range used. The temperature was then raised from room temperature to as high as 75°C by stepping in 10°C increments and holding to equilibrium.

Thermal batteries were constructed from a range of different materials. All were based on a  $\text{Li}_{13}\text{Si}_4$  anode, but electrolyte

was mixed with the anode material in the range of 0 to 25wt%. FeS<sub>2</sub> and CoS<sub>2</sub> cathodes were both used. Three electrolytes were considered: eutectic LiCl/KCl, the “all lithium” electrolyte of LiF/LiCl/LiBr, and a low-melting temperature electrolyte with LiCl/LiBr/KBr [8]. MgO binder was used, but several different products were considered. Finally, the batteries were also manufactured at two different battery vendors.

This wide range of changes means many more combinations are possible than were explored in the experimental matrix. The combinations that are available were examined to observe trends, but it is likely other inferences can be made. Accelerated aging studies were also performed in a manner similar to previous reports [5]. Units were held at temperature without any load applied. Single-cell testing was used to determine electrochemical capacity in these units after disassembly. Tests were performed at a constant 0.125 A/cm<sup>2</sup> discharge rate with periodic pulses to assess internal resistance. The key experimental variable in these tests was the use of two different types of MgO binder.

## Results

Leakage current in every battery tested obeyed an Arrhenius dependence with temperature. Examples for live batteries are shown in Figure 1. Fit over the temperature range was extremely good, with R<sup>2</sup> values exceeding 0.99 for every test. Measurements of this activation energy were 55 to 82 kJ/mol for manufacturer #1 and about 91 to 107 kJ/mol for manufacturer #2. In addition to having a higher activation energy, the batteries from manufacturer #2 had 2-3 orders of magnitude lower absolute values of leakage current across the entire range of temperatures.

Several MgO types were considered in the study. In Figure 1 the “Traditional” MgO for Sandia batteries is compared to a representative “Alternate” MgO built into batteries by both manufacturers. The Alternate MgO batteries have an order of magnitude higher leakage current than the Traditional MgO, but the temperature dependence was very similar with an activation energy of 68 and 75 kJ/mol for manufacturer #1.

Batteries from Manufacturer #1 had the fraction of electrolyte in the anode varied from 0 to 25%. Batteries were manufactured from both MgOs for the 15% anode electrolyte concentration. Figure 2 shows that the activation energy changes linearly with fraction of electrolyte in the anode in live batteries, regardless of the absolute magnitude of the leakage current. The activation energy for D-tested batteries is also shown in Figure 2. Batteries D-tested in this experiment retain most of their active material (>50% electrochemical margin), so they will behave similarly to live batteries electrochemically. However, the electrolyte will move to its equilibrium location after activation (see Figure 5), and contaminants (such as water) will be consumed.

Batteries from Manufacturer 2 had several MgO types as well as several different electrolytes. Figure 3 shows the dependence of leakage current activation energy on the

concentration of lithium ions in the electrolyte. There is a monotonic dependence, with a linear relationship used to guide the eye, but the fit is better against a power law dependence. The MgO used does not affect this relationship.

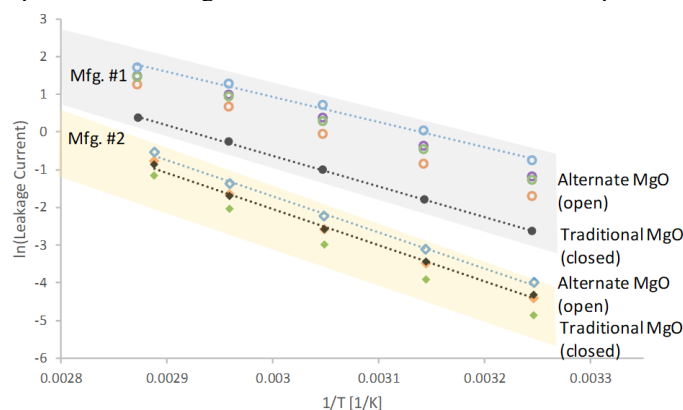


Figure 1. Arrhenius plot of leakage current vs. temperature.

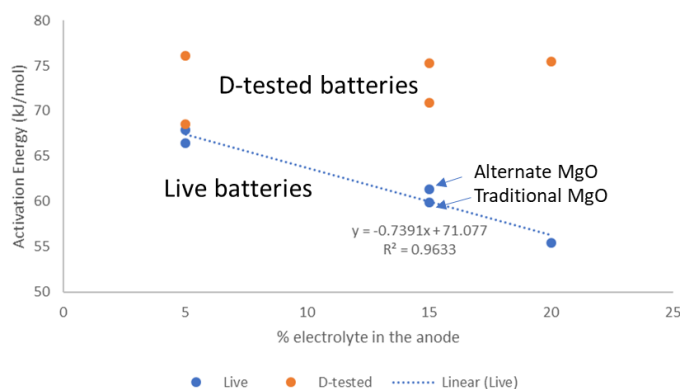


Figure 2. Activation energy vs. %electrolyte in anode (Mfg. #1, Alternate and traditional MgO).

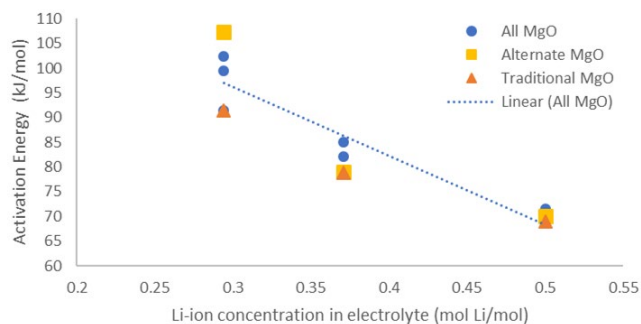


Figure 3. Activation energy vs. concentration of lithium ions in electrolyte (Mfg. 2, FeS<sub>2</sub> and CoS<sub>2</sub>)

Electrochemical impedance spectroscopy (EIS) was performed using a Solartron impedance analyzer and analyzed with Scribner ZPlot using an equivalent circuit model. A 100 mV voltage oscillation was used and swept from 1 MHz to 1 mHz after equilibration at the test temperature. The battery tested has a low voltage tap that enables the use of the 10V limited potentiostat. Results for an Alternate MgO battery are in Figure 4.

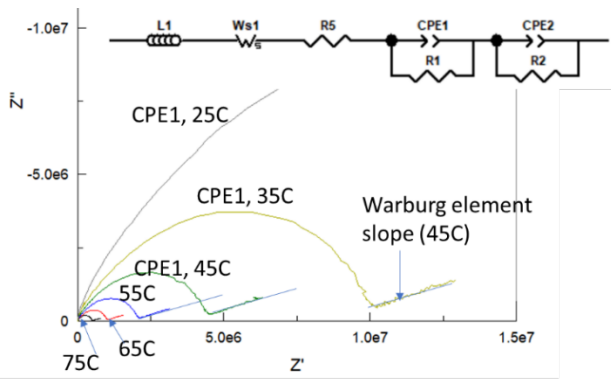


Figure 4. Nyquist plot and circuit model for EIS performed on a section of an Alternate MgO battery.

## Discussion

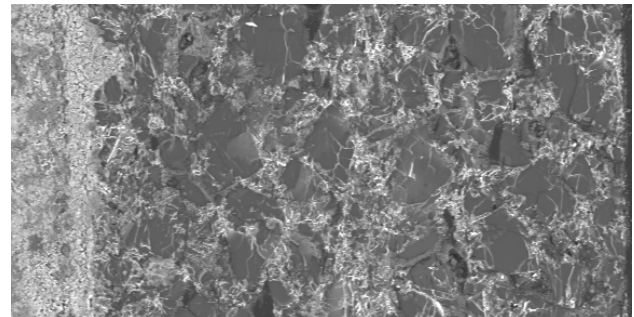
### *Rate limitation for discharge before activation*

The Arrhenius relationship for leakage current (Figure 1) indicates that there is a single activated process for this cathode formulation that controls leakage current over the entire near-ambient temperature range tested (25 to 75°C). This process is most likely the injection of lithium ions from the anode into the electrolyte. This process appears to be rate limiting because the activation energy has a linear dependence on the fraction of electrolyte in the anode (Figure 2). A higher surface area between the electrolyte and anode would only change the activation energy if this interface was related to the process that controls the overall leakage current. There is no dependence of activation energy on fraction of electrolyte in the anode after activation because the electrolyte moves to its equilibrium position, which is likely independent of the amount that is present at the start (Figure 5).

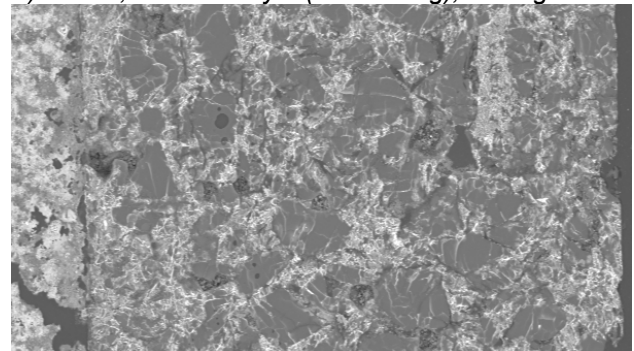
The dependence of activation energy on lithium-ion concentration in the electrolyte (Figure 3) is consistent with an anode-electrolyte interface limited reaction. Higher lithium-ion concentration will create more sites for the mobility of lithium-ions into the solid-state matrix. However, this reduction in activation energy is also consistent with a rate limitation in the separator. The EIS Nyquist plots in Figure 4 show that the electrolyte element of the circuit (the  $W_s$  Warburg element) does not have a strong dependence on temperature- it is nearly constant from 35 to 55°C as indicated by the drawn in slope lines. However, the capacitive element does have an exponential dependence on temperature. This corresponds to the electrolyte interface in either the anode or the cathode. The dependence of activation energy on electrolyte concentration in the anode was established in Figure 2. Figure 3 contains data for  $CoS_2$  and  $FeS_2$  batteries; the 37 mol%  $Li^+$  electrolyte was paired with  $CoS_2$  cathodes while the other two used  $FeS_2$  cathodes. “All MgO” includes data from two other MgO types, in addition to Traditional and Alternate. The data have been fit to a linear regression with an  $R^2$  of 0.86, despite varying the cathode. This suggests the anode / electrolyte interface limits solid-state discharge.

The activation energy is key to understanding the temperature dependence of leakage current, and therefore calculating an acceleration factor for aging. However, the absolute magnitude of leakage current will drive the total energy lost in storage. There are major differences in the magnitude of leakage current shown in Figure 1 even though the activation energies (slopes) are relatively similar. Within the batteries made by Manufacturer #1, an order of magnitude difference in leakage current exists between batteries made with our Traditional MgO and batteries made with the Alternate MgO. Manufacturer #2 has similar performance for all MgO, but the leakage current is almost two orders of magnitude lower than for Manufacturer #1.

These observations suggest that a significant processing difference exists between Manufacturer #1 and #2. It is not clear what this difference is, but a hypothesis is that it is related to the dry room conditions. Water uptake by the salts in the electrolyte will lead to increased leakage current; this phenomenon drives the use of hi-pot testing to check for leakage current in production thermal batteries [6]. The impact of dry room humidity is dramatic, with 4x greater water uptake at -34°C than at -40°C [6]. The Traditional and Alternate MgO have significant structural differences and processing differences in their manufacture that may lead to different levels of residual moisture in the MgO [9]. The processing techniques at Manufacturer #2 may dry both MgO adequately (and prevent rewetting) so the inherent differences between the MgO are less important. Manufacturer #1’s processing may not adequately dry the Alternate MgO.



A) Anode, 5% electrolyte (low melting), Alt. MgO



B) Anode, 15% electrolyte (low melting), Alt. MgO

Figure 5. SEM (BSE) showing electrolyte (white) in anode (gray) after battery activation. Equilibrium electrolyte concentration similar in A) and B)

### Estimation of capacity loss due to leakage current

The magnitude of leakage current directly impacts the expected lifetime of batteries. For comparison, we will assume a battery with 0.5 Ah capacity and 24V open circuit. Data from the test batteries was normalized to this example, and the resulting capacity loss over a 30 year storage lifetime (at 35°C) is shown in Figure 6. The capacity loss is shown on a log scale to emphasize the dramatic differences in absolute magnitude of leakage current across different manufacturers and electrolyte types. Measured leakage current is proportional to the ionic concentration of lithium in the electrolyte. Note that this is a different statement than Figure 3, which shows the activation energy is inversely proportional; Figure 3 shows the slope of Figure 1 while Figure 6 shows the intercept. High ionic concentration electrolytes both have higher leakage current and are more susceptible to increased leakage at elevated temperature.

The manufacturing differences in leakage current are even more dramatic. The batteries from Manufacturer #1 would lose 25% of their capacity under the storage conditions considered. This compares to about 4.5% capacity loss under identical conditions due to chemical deterioration alone (based on data reported in [5]).

### Internal Resistance (IR)

Leakage current can be related to IR by assuming the battery open circuit voltage (OCV) after activation applies (1.92V for Li(Si)/FeS<sub>2</sub> and 1.85V for Li(Si)/CoS<sub>2</sub>). The OCV will be different at ambient temperature than active temperature, and the OCV may be primarily driven by contaminants or overpotentials until equilibrium phases have formed. Since this is a lifetime assessment, it is assumed that equilibrium will be achieved before meaningful changes in capacity occur, so the equilibrium OCV is appropriate. The lack of correction for temperature was for convenience, but the free energy change for discharge reactions varies less than 5% from operational to ambient temperature [data from 7], compared to 6 orders of magnitude difference in leakage current depending on conditions. The IR for capacity losses shown in Figure 6 are 49 MOhm for the worst case to as high as 300 GOhm for the best performer. Most batteries were in the 1-10 GOhm range. It is only possible to accurately measure such high resistances by measuring the voltage drop across a reference resistor, since the input impedance of the meter is far lower than the battery itself.

### Conclusions

Thermal batteries are batteries even before activation. Parasitic leakage through external circuits connected to the battery may be the dominant source of capacity loss while on mission prior to activation. Leakage current is limited by ionic movement across the anode/electrolyte interface, and the high activation energy (60-100 kJ/mol) means the rate dependence is highly temperature sensitive. Leakage current depends on the electrolyte and processing conditions, not all of which were identified in this study. Expected capacity loss can be easily and quickly measured with non-destructive

techniques, such as measuring the voltage across a reference resistor connected to a battery warmed to 35 to 45°C.

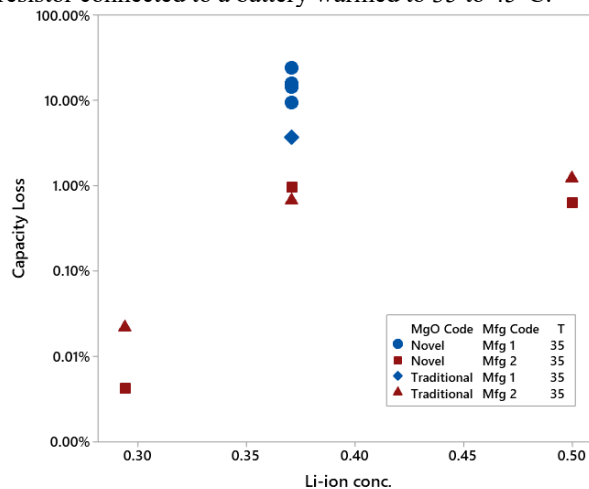


Figure 6. Estimated 30y capacity loss, assuming 24V/0.5Ah battery, vs. electrolyte ionic concentration.

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