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Hermeticity and Thermal Battery Lifetime

Clay D. Beevers, Daniel E. Wesolowski, Henry Peebles, Hans W. Papenguth, Steven K. Showalter

Power Sources Technology Group
Sandia National Laboratories
Albuquerque, New Mexico, 87185-0614
cbeever@sandia.gov

Abstract: *The back-pressurizing (or helium bomb) technique is a standard non-destructive technique for the evaluation of thermal battery hermeticity. Observed leak rates during the bomb technique are quite sensitive to bomb soak time, pressure, and battery free volume. A model relating the amount of sealed, air-sensitive material to the maximum leak rate and lifetime is presented for Li(Si) thermal batteries. Additionally, test articles without sealed volumes (including battery headers and cases) were analyzed using the bomb technique. He trapped in pores in glass-to-metal seals was found to confound the results, so the He bomb technique is not quantitative. Puncture gas sampling following testing indicates the leak rates were often much lower than the observations and consistent with fully sealed batteries.*

Keywords: shelf-life; leak check; bomb test

Introduction

Thermal batteries are often chosen for applications that require a one-time use and a shelf life in excess of 20 years. These batteries are hermetically sealed using case to header welds and glass-to-metal (GTM) electrical feedthroughs to prevent water and oxygen penetration. This limits the formation of Li_2O on the anode, the most reactive active cell component.

Air and water are trapped in the battery during manufacture, either from being adsorbed on surfaces such as insulation or sealed during closure welds in the dry room. These gasses will react over time with the Li(Si) anode, and as a result of exposure to water vapor during the manufacturing process, a portion of the Li(Si) has already been consumed before leaking occurs [1]. The remaining Li(Si) will then be reduced as oxygen and water penetrate imperfect seals.

Hermeticity is commonly measured by the back-pressurizing test—also referred to as the helium bomb test [2]. This paper presents a methodology for using this technique to derive a maximum leak rate for a thermal battery. We also present an experimental evaluation illustrating common pitfalls.

Determining Maximum Leak Rate

We make the assumption that battery shelf life is limited by the reaction of Li with the atmosphere. There are a number of other agents that may deteriorate in air (e.g. heat powder) but lithium is the most reducing and directly influences the electrical capacity. Determining the hermeticity requirement of a thermal battery then requires knowledge of the case volume of the battery and the total amount of lithium contained in the battery.

The equation for the maximum leak rate in terms of a volumetric flow rate at standard temperature and pressure (STP) can be derived from knowing the mass of oxygen necessary to compromise the battery. The mass of oxygen is converted into an average volumetric leak rate of oxygen (Q_{oxygen}), by knowing the mass of total oxygen (m) that is deleterious to the battery. The mass of total oxygen (m) can be estimated based on the amount of anode present. The relationship between the leak rate and total mass of oxygen is given by eqn. 1.

$$Q_{oxygen} = \frac{m}{t} * \frac{R}{MW_{O_2}} \quad (1)$$

Where:

Q_{oxygen} = Average oxygen leak rate (STP cc/sec)

m = Allowable mass of oxygen leakage (g)

t = time (sec)

R = Volumetric gas constant (22414 cc/mole)

MW_{O2} = Molecular weight of O_2 = 32 g/mole

We assume that the oxygen is the main cause of Li_2O formation. O_2 has a low rate of reaction with Li(Si) [3], but the concentration in the atmosphere is much higher than water vapor and the battery lifetime is long enough to reach equilibrium. We also assume 4 wt% of the Li(Si) anode react with oxygen before battery performance is affected; therefore, $m = 0.04\,w$, where w is the total weight of *lithium* in the battery. All O_2 that penetrates is assumed to react with the lithium.

The maximum air leak rate for any thermal battery and any desired lifetime (assuming air is 21% O_2) can be determined using eqn. 1 and the amount of lithium that can be consumed:

$$Q_{\text{air}} = 133.41 \, \frac{w}{t} \left(\frac{STP\ cc\ air}{g}\right) \quad (2)$$

Using eqn. 2 and assuming 0.85 g of lithium in a small battery, the maximum allowable leak rate of air is 1.4 x 10^{-7} standard cubic centimeter (scc) air per second for a 25 year shelf life. The maximum leak rates for shelf life of 30, 35, and 40 years have been calculated using the same techniques and are shown in Table 1. Note that the maximum allowable leak rates are about one order of magnitude higher if only H_2O (not O_2) can react with the Li(Si).

Table 1. Maximum Allowable Leak Rates

Lifetime (years)	Leak Rate (scc air/s)
25	1.43 x 10^{-7}
30	1.19 x 10^{-7}
35	1.03 x 10^{-7}
40	8.99 x 10^{-8}

Measuring Leak Rate

Howl and Mann derived a mathematical method for determining the leak size by back-pressurizing a sealed volume [2]. This has since been incorporated into the ASTM E493-06 and MIL-STD-883H method 1014.13 standards for helium bomb tests for fine leaks. Gross leaks (leaks through holes large enough for laminar flow) cannot accurately be detected with the He bomb technique. Howl and Mann derived the equation for leaks with molecular flow (fine leaks):

$$Rt = C_A P_E \left\{1 - exp\left[-\frac{TC_A}{V}\right]\right\} * exp\left[-\frac{\tau C_A}{V}\right] \quad (3)$$

Where:

$$C_A = \frac{L}{P_0}\left(\frac{M_A}{M}\right)^{1/2} \quad (4)$$

C_A = Leak conductance of the tracer gas. (L/sec)

Rt = Leak rate of the tracer gas (Torr·$L_{tracergas}$ /s)

L = Leak size: gas flow through the leak under conditions of one atmosphere of air on one side of the leak, and a vacuum on the other (Torr·L_{air} /s)

P_E = external tracer gas pressure soak (Torr)

P_0 = Atmospheric pressure (Torr)

T = Bomb time, time in bomb chamber (s)

V = Internal free volume of the specimen (L)

τ = Dwell time, time in atmosphere between backfilling and leak test (s)

M = Molecular weight of tracer gas

M_A = Molecular weight of air

The volume used in these equations is the internal free volume of the battery. Measurements performed at Sandia indicated that battery free volume varied from 30-60%, depending on the design. Insulation is low density compared to other thermal battery materials, so long-life batteries tend to have relatively large free volumes.

Figure 1 used eqn. 3 to compare the actual air leak size present in the battery to the corresponding leak rate of helium (He) tracer gas that is seen during the bomb test. A detector with a detection limit of 5.0 x 10^{-10} scc He/s was assumed. Points A and B in Figure 1 represent the maximum and minimum detectable leak sizes, respectively. The red dotted line represents the maximum allowable air leak size for a 25 year expected lifetime (1.4x10^{-7} scc air/s, as shown in Table 1). Applying equations 3 and 4 for a two hour soak in 6 atm He bomb showed that, for a particular small battery, a measured He bomb leak rate of 2.5 x 10^{-9} scc He/s corresponds to an air leak rate that is almost two orders of magnitude larger. In this case, a leak rate greater than 2.5 x 10^{-9} scc He/s would mean the battery is not recommended for a 25 year lifetime. It is prudent to have a detector that is at least one order of magnitude more sensitive than the lower limit for detection; by this criterion a He leak detector with a sensitivity of 5x10^{-10} scc He/s is inadequate. The test conditions can be adjusted to create meaningful results for such a battery. The effects of changing bomb time, dwell time, and bomb pressure are demonstrated in Figure 2a-c. Note that the soak time has the most impact on the measured leak rates and must be tightly controlled. The dwell time, on the other hand, has a negligible impact, and the bomb pressure does not have to be tightly controlled. The bomb soak time could be adjusted to create a valid “go/no go” hermeticity test for this small battery.

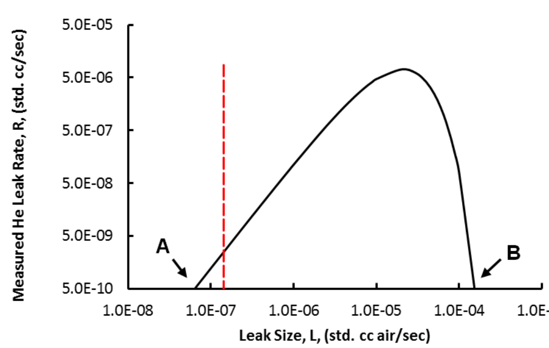

Figure 1.Measured leak rate as a function of leak size. A) Minimum leak size detectable. B) Maximum leak size detectable. Dashes) Maximum acceptable leak size for a 25 year shelf life.

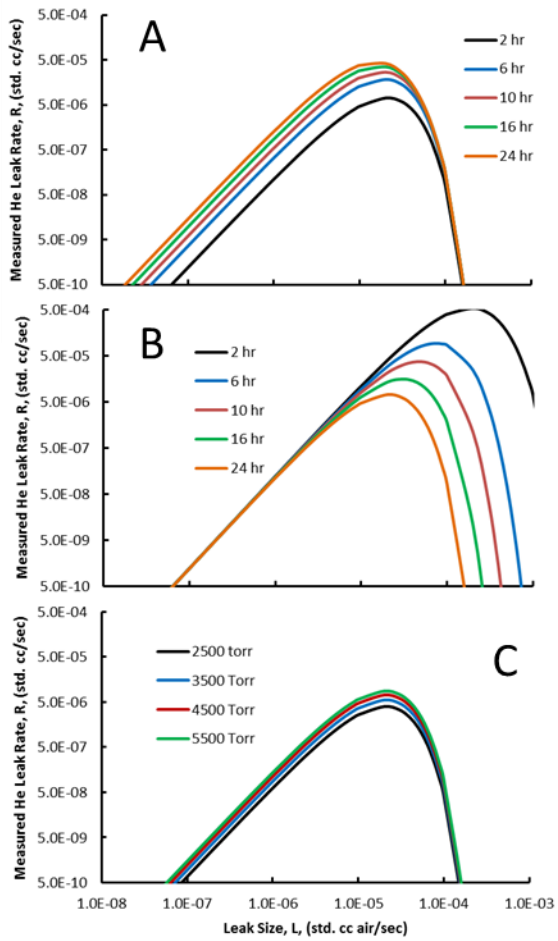

Figure 2. Effect of bomb time *T* (A), dwell time *τ* (B), and bomb pressure P_E (C) on measured He leak rate.

Experimental Analysis of Virtual Leaks

The dwell time in the He bomb technique is designed to remove adsorbed helium that otherwise would confound the measurements. A nitrogen or argon spray is often applied to the test unit to accelerate desorption. Bomb tests were performed on thermal battery cases and headers cut in half to remove any sealed volume. Testing was performed with a Varian 979 Helium Mass Spectrometer Leak Detector with a sensitivity of $5x10^{-11}$ scc He/s. The detector was calibrated and zeroed before testing. Leak checks were performed periodically during the dwell to determine if a stable leak rate could be established. All observed He in this test came from "virtual leaks" as there is no sealed volume. The leak rate declined logarithmically during the first two hours, consistent with outgassing by desorption (Figure 3). The rate of change in leak rate decreased from 120 to 180 m, indicating a change in the mechanism by which He was trapped.

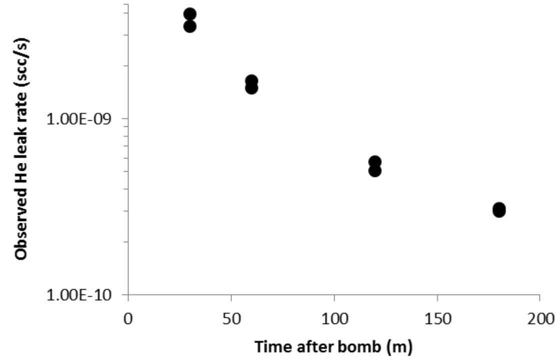

Figure 3. Observed He leak rate on thermal battery package with no sealed volume.

These slow virtual leaks make it impossible to use the He bomb test as a quantitative assessment of the rate of gas flux into a battery.

The observed leak rates are similar to the leak rates observed on complete thermal batteries, despite the lack of a sealed volume. It was suspected that the welds or the GTM seals in the header were the source of virtual leaks. Welded articles were found to have leak rates of zero. Header (no welds) leak rates varied widely depending on the number of seals and the type of sealing glass. One header with 14 seals showed a leak rate of $6x10^{-9}$ scc He/s, larger than the maximum leak rate allowed for many thermal batteries. It is believed that porosity in the GTM seals [4] is the dominant source of virtual leaks following the first two hours of dwell. This is difficult to eliminate from the background because the density of seals is process dependent and can vary from seal-to-seal.

Verification of Battery Hermeticity

Helium gas should be forced into the battery case during the bomb test, unless the battery is perfectly sealed. The data points in Figure 4 show the results of a calculation relating standardized leak rate for an example battery case to the He concentration measured in the case following a 6 atm He bomb for 2 hours. Note that standard air contains ~5.24 ppm He [5]. The red line in Figure 4 gives the corrected leak rate obtained by subtracting this background helium from the measured concentration. The presence of background helium in air sets a limit on the minimum leak rate that can be detected in the battery case using the measured He concentration. Because atmospheric helium concentrations can vary from place to place, we have set a detection limit for this method of 2.1 x 10^{-8} std cc/sec, which is equivalent to two times the standard helium background concentration.

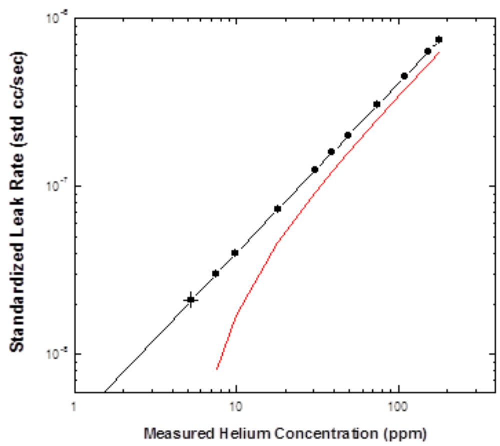

Figure 4. Leak rate for a battery case vs. helium gas measured in the case.The cross is 5.24 ppm background He level; lower red curve corrects the upper black curve rate for this background.

Table 2. Expected He in bomb test and leak rates

Measured He Concentration (ppm)	Leak Rate Calculated from the Measured He Concentration (std cc/sec)	Leak Rate Measured by the Standard Bomb Test (std cc/sec)	Expected He Concentration from Back Pressure Test (ppm)
6.87	< 2.1×10^{-8}	**2.12×10^{-7}**	**57.1**
7.40	< 2.1×10^{-8}	**1.20×10^{-7}**	**34.7**
7.13	< 2.1×10^{-8}	**6.75×10^{-8}**	**21.9**
7.22	< 2.1×10^{-8}	**4.20×10^{-8}**	**15.6**
8.15	< 2.1×10^{-8}	1.19×10^{-9}	--
8.20	< 2.1×10^{-8}	4.12×10^{-9}	--
8.60	< 2.1×10^{-8}	5.10×10^{-10}	--

Table 2 compares internal helium concentrations measured by in several batteries following the He bomb testing. The internal gas concentrations were measured by immersing the battery in a evacuated chamber with all metal seals. The battery case was then punctured to release the internal gases which were quantified by high resolution mass spectroscopy. The expected concentration calculated for leak rates determined using the He bomb test are given in Table 2 for comparison. Based on the measured helium concentrations, all the batteries should exhibit a leak rate less than 2.1 x 10^{-8} scc He/s. However, four batteries (highlighted in Table 2) showed leak rates greater than 2.1 x 10^{-8} scc He/s in the He bomb tests. In each of these cases, the He concentration measured in the battery case is significantly smaller than the concentration expected based on the higher leak rate value. This is consistent with virtual leaks dominating the observed leak rates in batteries tested by the He bomb technique.

We are currently working on verifying the hermeticity of battery seals by two parallel paths. He bombed headers have been heated in a gas sampling chamber to accelerate the removal of He from the header. We will use this data to quantify the amount of He trapped in virtual leaks in GTM seals. Additionally, batteries punctured during gas sampling will be pressurized with 1 atm of He while on a He leak detector.

Conclusion

The He bomb technique is a valuable tool for assessing the quality of battery sealing, but it must be carefully implemented. He leak rates observed in the bomb test are approximately two orders of magnitude lower than the actual air leak rates. The bomb test is highly sensitive to the soak time in the bomb, but theoretically almost insensitive to the dwell time after bombing. However, virtual leaks in GTM seals make the dwell time important and make it difficult to quantify low-level leak rates in sealed articles. Destructive tests, such as puncturing the battery, are necessary to accurately measure leak rates. The bomb test should be used as a “go/no go” test when assessing battery hermeticity.

Acknowledgements

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